Development of Novel Instrumentation and Methodologies for Particulate Bound Phthalate Measurements

by

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B.Sc., Vancouver Island University, 2011

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Chemistry Faculty of Science

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Abstract

Presented is the development of a method to generate reproducible gaseous phthalate standards, a setup for generating airborne particulate matter and a membrane introduction mass spectrometry system suitable for the online measurement of gaseous phthalates. Upon development of appropriate standards and instrumentation, particulate-phthalate adsorption/desorption experiments were performed using dimethyl phthalate and two particulate species. Initial adsorption/desorption experiments were conducted using C18 coated silica particles, followed by further experimentation with house dust particles. Results from the development stages of the gas phase standards, the membrane introduction mass spectrometry system and phthalate adsorption/desorption experiments are presented.

Keywords: Phthalates; Gaseous Standards; Membrane Introduction Mass Spectrometry; Adsorption; Desorption; Particulate matter
“To my friends and family for all of their encouragement and support and especially to my little yam who was with me through thick and thin.”

It’s not what’s filled your hand,
But what hasn’t filled the other.
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I would like to express my gratitude and appreciation for all of the support my two supervisors, George and Chris, have given me over the years. I would like to thank Dr. George Agnes for sharing his knowledge and for his incredible patience as well as his willingness to let me experiment and work out problems for myself. I would like to thank Dr. Chris Gill for all of his motivation and much needed support and guidance both in and outside of the lab. Thank you for showing me the hoop and holding it for me. I would like to thank Dr. Erik Krogh, co-director of the Applied Environmental Research Labs (AERL), who always provided an ear, a question and an answer to what seemed like some of the trickiest chemical problems. I would also like to thank my committee member Dr. Vance Williams for providing a different perspective on my research which helped forge new ideas.

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List of Acronyms

% Percent
' Foot
" Inches
® Registered trademark
µg Microgram
µL Microliter
µm Micrometer
3D QIT Three dimensional quadrupole ion trap mass spectrometer
APPI Atmospheric pressure photo ionization
a_z Mathieu equation parameter for DC field component
b.p. Boiling point
BBzP Benzyl butyl phthalate
BTEX Benzene, Toluene, Ethylbenzene and Xylene
b_X Rate of adsorption to desorption
C Carbon
C_1 Concentration in system 1
C18 Octadecyl
C_2 Concentration in system 2
CAS Chemical abstracts service
C_g Gas phase concentration of a compound
CI Chemical ionization
CI Confidence interval (typically 95%)
C_{ig} Concentration of analyte in gas phase
C_{ig,ppmv} Concentration of analyte in gas phase in parts per million by volume
C_{ppm} Concentration of gas in parts per million
cm Centimeter
CW_{sat} Water solubility at saturation
D Density
D Substance diffusivity
DC Direct Current
DEHP Bis(2-ethylhexyl) phthalate
DEP Diethyl phthalate
DMP Dimethyl phthalate
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>Molecular charge</td>
</tr>
<tr>
<td>e−</td>
<td>Electron</td>
</tr>
<tr>
<td>EI</td>
<td>Electron (impact) ionization</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray (ionization)</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>F</td>
<td>Particle phase concentration of a compound</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated ethylene propylene</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatogram</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>I.D</td>
<td>Internal diameter</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ICR</td>
<td>Ion cyclotron resonance mass spectrometer</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>K</td>
<td>Proportionality constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>K\textsubscript{aw}</td>
<td>Air-water partition coefficient</td>
</tr>
<tr>
<td>k\textsubscript{LM}</td>
<td>Rate loss from membrane and housing</td>
</tr>
<tr>
<td>k\textsubscript{LS}</td>
<td>Rate loss from particle surfaces</td>
</tr>
<tr>
<td>K\textsubscript{oa}</td>
<td>Octanol-air partition coefficient</td>
</tr>
<tr>
<td>K\textsubscript{oc}</td>
<td>Organic carbon-water partition coefficient</td>
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<tr>
<td>K\textsubscript{P}</td>
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<td>K\textsubscript{P}</td>
<td>Particle-air adsorption/desorption coefficient</td>
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<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>ln</td>
<td>Natural logarithm</td>
</tr>
<tr>
<td>LPM</td>
<td>Litres per minute</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>M</td>
<td>Molecule</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>M\textsuperscript{+}</td>
<td>Parent ion</td>
</tr>
<tr>
<td>m\textsuperscript{3}</td>
<td>Cubic meter</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix assisted laser desorption ionization</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
</tbody>
</table>
m_i Mass of ion
MIMS Membrane introduction mass spectrometry
mm Millimeter
mmHg Millimeters of mercury
mol Mole
MS Magnetic sector mass spectrometer
MTBE Methyl tert-butyl ether
MW Molecular weight
n Moles
N Noise
ng Nanogram
NIST National institute of science and technology
nm Nanometer
° Degree
O.D Outer diameter
°C Degrees Celsius
P Pressure
P Experimental pressure
P_1 Pressure in system 1
P_2 Pressure in system 2
PDMS Polydimethylsiloxane
pm Afternoon
PM_{10} Particulate matter with a diameter less than 10µm
PM_{2.5} Particulate matter with a diameter less than 2.5µm
P^o Vapor pressure
P^o_X Vapor pressure of contaminant X
ppbv Parts per billion by volume
ppmv Parts per million by volume
psi Pounds per square inch
PTFE Polytetrafluoroethylene
P_{tot} Total pressure
PVC Polyvinyl chloride
q_d Permeation rate
q_D Flow rate of diluent gas
q_z Mathieu equation parameter for RF field component
R Ideal gas constant
r Outer radii
R Radial axis

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<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient of determination</td>
</tr>
<tr>
<td>$r_o$</td>
<td>Inner radii</td>
</tr>
<tr>
<td>S</td>
<td>Signal</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>STP</td>
<td>Standard conditions for temperature and pressure</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi volatile organic compound</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_{10-90%}$</td>
<td>Rise time between 10 and 90% signal intensities</td>
</tr>
<tr>
<td>TAPT</td>
<td>Thermally assisted permeation tube</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight mass spectrometer</td>
</tr>
<tr>
<td>TSP</td>
<td>Total suspended particulate matter</td>
</tr>
<tr>
<td>U</td>
<td>Direct current</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>V</td>
<td>Alternating current</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_1$</td>
<td>Volume in system 1</td>
</tr>
<tr>
<td>$V_2$</td>
<td>Volume in system 2</td>
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<tr>
<td>$V_i$</td>
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<tr>
<td>$V_{tot}$</td>
<td>Total volume</td>
</tr>
<tr>
<td>W</td>
<td>Width</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Ratio of particulate surface covered</td>
</tr>
<tr>
<td>$X$</td>
<td>Contaminant</td>
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<td>$\bar{x}$</td>
<td>Mean</td>
</tr>
<tr>
<td>$X_g$</td>
<td>Contaminant in gas phase</td>
</tr>
<tr>
<td>$X_p$</td>
<td>Concentration of $X$ on particle phase</td>
</tr>
<tr>
<td>z</td>
<td>Equatorial axis</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Resistivity (Ohm)</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1. Air Quality and Pollution

On a daily basis, the air in which we breathe is a mixture of both gases and suspended particulate matter. The gaseous portion is comprised primarily of nitrogen and oxygen, which makes up the bulk portion of the gas (approximately 78% and 21% respectively). Argon is the next most abundant species at nearly 1% abundance, and trace components make up the remainder of gas at substantially less than 1% abundance. If one were to plot the scientific interest in the different gaseous species against their abundance they would observe an inverse relationship where the most abundant species are of minimal interest and the least abundant species are of the most scientific interest. Of course the idea of this fictitious plot would not provide any information on the specific species of interest and it would be false to assume that all trace species are of equal importance.

In addition to the gaseous portion of the atmosphere are the airborne solid or liquid phase particulates. Environmental particulates are rarely comprised of a single chemical species, rather, they are heterogeneous, being composed of multiple different molecules and/or elements. Along with the species that make up the particulate core, is the surface of the particle that is a site available to adsorption/desorption processes of various other chemical species. Of particular importance is the availability of these surfaces to sequester large, semi-volatile chemical species. Although particulates tend to settle from the atmosphere with time, they can also be re-suspended and transported in the air when disturbed. Disturbance sources can be both abiotic and biotic, where either a gust of wind or dusting a house will both contribute to the abundance of airborne particulate matter in their respective local environments.
1.1.1. Indoor Air Quality

Interest in the indoor environment has arisen in part due to the historic interest generated by contaminants present in the outdoor environment. According to a study performed in 1995 the average Canadian spends as much as 88.6% of their time in the indoor environment. The substantial amount of time spent indoors is easy to understand when considering the amount of time which an individual can spend at work, school and home. Since such a large amount of our daily lives is spent indoors, it is easy to appreciate that the indoor environment constitutes a significant source for human exposure to contaminants. Different indoor environments have different contaminants and each of these can have varying human health effects. Determining the different sources and health effects of each of these contaminants is particularly important as they directly affect our lives.

Each indoor environment is different, with different factors affecting their air quality. Things such as human habits, building type and age as well as the materials used during building all have an impact on the chemicals which may eventually be present in the indoor air. An example of this is the known carcinogen, formaldehyde, which is gradually released from wood products such as particle board and furniture. Another indoor contaminant, carbon monoxide, arises from combustion processes such as smoking, natural gas heating and biomass burning. Biomass burning also leads to other indoor contaminants such as soot based particulate matter and highly carcinogenic polyaromatic hydrocarbons.

Human habits can have a large effect on the concentrations of these indoor contaminants. Providing proper air circulation by opening windows or incorporating suitable filters can lower indoor contaminant concentrations by establishing contaminant sinks. Other habits such as the frequency of dusting, cleaning and vacuuming will lead to a reduced amount of settled particulate matter, eliminating it before it becomes airborne. Human choice in terms of consumer products will also affect the range of chemical species brought into the home. An example of this is the increasing trend for incorporating plastic materials into everyday products. Plastics products, especially those made from polyvinyl chloride (PVC), are of particular interest, since many studies
have shown the potential for plasticizers to leach from the plastic and into the surrounding environment (Chapter 1.2). Although the gaseous concentrations of PVC plasticizers are typically at trace levels, the continual incorporation of plasticized plastic products into households ensures that, at least in North America, household residents will continually be exposed to plasticizers for the duration of their lives.\textsuperscript{10}

\section*{1.2. Phthalates: Physical Properties, Exposure Sources, Health Effects}

Plasticizers are an interesting group of chemicals that are used to modify the structure of plastics. With the discovery of the first plasticizer, it was quickly demonstrated that plasticized plastic products could be both easily and cheaply made. Interest in plasticizers has stemmed not only from the remarkable properties they can induce into plastics but also, from an environmental and health science point of view, from the potential problems they can induce in the local environment.

\subsection*{1.2.1. Plasticizers}

The synthesis of the first plastic is attributed to the London chemist Alexander Parkes in 1856.\textsuperscript{11} This first plastic, Parkesine, was synthesized using cellulose nitrate, camphor and alcohol and demonstrated the desirable ability to be shaped using heat, pressure and dies.\textsuperscript{12} In 1870 an American researcher, J.W. Hyatt, obtained the US Patent \#105338, for adding large amounts of camphor oil to cellulose nitrate to generate a product he named celluloid.\textsuperscript{12} The additions of increased amounts of camphor oil (the plasticizer in this case) to cellulose nitrate resulted in a more favorable product than Parkesine, which in turn signaled a starting point for the addition of plasticizers to plastics.\textsuperscript{12}

Although the incorporation of camphor improved the usability of cellulose nitrate, this plasticizer was not suitable for many end applications.\textsuperscript{13} In 1912 synthetic triphenyl phosphate replaced camphor oil, initiating the development of synthetic plasticizers.\textsuperscript{13} By the 1920’s, plasticizers called phthalates had made their way into the plastics industry.\textsuperscript{13}
In 1994, global production of one of the most common phthalates, Bis(2-ethyl)hexyl phthalate, was estimated to be 258 million pounds/year.\textsuperscript{14} Current estimates on phthalate production are not available because the information is considered proprietary by chemical manufacturing companies.\textsuperscript{15}

As mentioned previously, plasticizers are a group of chemical species which are added to a plastic material to modify the properties of that material. In order for a plasticizer to properly function over the lifetime of the plastic, it needs to interact with the plastic in the same manner that the polymer chains interact among themselves.\textsuperscript{16} Different plastic polymers can accommodate different plasticizers, depending on both the properties of the polymer and plasticizer. PVC, one of the most commonly produced plastics, for example contains a polarized carbon-chlorine bond, allowing the polymer to interact with plasticizers via both van der Waals and dipole-dipole interactions.\textsuperscript{16} Phthalates are commonly used as plasticizers for PVC because the aromatic and ester groups of the phthalate interact effectively with the carbon-chlorine bonds.\textsuperscript{16}

There are several theories and models which have attempted to describe the mechanism by which a plasticizer affects a polymer. These include; the lubricity theory, the gel theory, the free volume theory,\textsuperscript{17} and the kinetic or mechanistic theory.\textsuperscript{16, 18} A concise overview of these theories is as follows; the lubricity theory describes the plasticizer as acting as a solvent and lubricant between polymer chains. The gel theory extends the lubricity theory and describes the polymer-plasticizer interaction as a dynamic system where non-covalent bonds between polymer and plasticizer are continually being broken and reformed. The free volume theory migrates away from directly focusing on chemical bonds and describes the addition of a plasticizer to a polymer as increasing the free volume of the polymer. An increase in free volume results in an increased ability for individual polymer chains to move freely, which is believed to be why the addition of plasticizers decreases the rigidity of a plastic. The final theory, the kinetic theory or mechanistic theory, describes the interactions between polymer and plasticizer as a system of continual change. It is likely that none of these theories is entirely correct in describing the plasticizer-polymer system, and that the sum of these theories provides the greatest understanding for their interaction.
Regardless of which theory is most correct in describing how plasticizers interact with polymers, the addition of an appropriate plasticizer to a polymer results in a reduction of the temperature of the polymers glass transition state ($T_g$). The glass transition state is a boundary state between two sets of temperatures, where the polymer behaves as a ridged polymer on the low end of this gradient, and a soft pliable rubber-like material at the higher end. Using DEHP with PVC, it has been demonstrated that increasing the quantity of the phthalate from 0-45 percent by weight, reduces the $T_g$ of the PVC product by about 130K (or about 35%). A decrease in the glass transition temperature of PVC results in a polymer which contains a less ridged structure than the non-plasticized form. Being able to induce different properties for PVC by using different quantities or types of plasticizers, particularly phthalates, is one of the main reasons PVC products are so popular today.

1.2.2. Phthalates – Physical Properties, $K_{ow}$, $K_{aw}$, $K_{oa}$ and $K_p$

As previously mentioned, the most common group of plasticizers today are the group known as phthalates. The unifying structure for phthalates is a six membered aromatic ring with which two ester groups are present at the 1,2 positions (Figure 1.1). Typically the ester R groups are aliphatic [i.e. Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Di-octyl phthalate and Bis-(2-ethylhexyl) phthalate (DEHP) etc.] with rare exceptions containing an aromatic ring [i.e. Benzyl butyl phthalate (BBzP)]. The R groups attached to the phthalate esters are what define both their physical as well as toxicological properties.
1.2.2.1 Phthalate Physical Properties

The physical properties of phthalates not only govern how strongly they associate with a plastic, but also effect where in the environment they will be found once outside the plastic. For example, properties such as the boiling point (b.p.) and vapor pressure (P°) reflect the volatility of a phthalate at a given temperature, and the water saturation (CW_{sat}) term relates to the phthalates hydrophilicity. The quotient of the physical properties P° divided by CW_{sat} provides an approximation for the Henrys constant or K_{aw} which can be used to determine concentrations of phthalate in both air and water for a system at equilibrium (Equation 1). Several other equilibrium constants exist, some of which include the K_{ow} (octanol-water), K_{oa} (octanol-air), K_{oc} (organic carbon-water) and K_p (particle-air). Along with K_{aw}, these other constants are useful in determining the environmental distribution of phthalates.
Equation 1:

\[ K_{aw} = \frac{P^0}{C_{W_{sat}}} \]

Unlike \( K_{aw} \), the octanol-water partition coefficient \( K_{ow} \) is typically obtained through experimentation. A simple example of how \( K_{ow} \) can be determined is to agitate a mixture of octanol, water and compound then measure the resulting concentration in the phases at equilibrium.\(^2\) Another example of how \( K_{ow} \) values for low molecular weight phthalates have been determined is through chromatography, specifically high performance liquid chromatography (HPLC).\(^3\) Here, \( K_{ow} \) values are estimated using the compounds retention time in a reverse phase (C\(_{18}\)) column. To calibrate \( K_{ow} \) with retention time, compounds with known \( K_{ow} \) values must also be separated on the same column, allowing the prediction of unknown \( K_{ow} \) values.\(^4\) Although octanol is not found at a particularly high concentration in nature, the information \( K_{ow} \) values provide is still valuable since octanol contains a similar carbon:oxygen ratio (8:1) as lipids.\(^5\)

Like the \( K_{aw} \) and \( K_{ow} \) partition coefficients, the octanol-air partition coefficient \( K_{oa} \) can also be obtained by an indirect means by dividing the compounds \( K_{aw} \) by its \( K_{ow} \).\(^6\) In fact, if any two of the three constants (\( K_{aw}, K_{ow}, K_{oa} \)) are known then the third one can be determined (Figure 1.2).
Figure 1.2. $K_{ow}$, $K_{aw}$ and $K_{ao}$ equilibrium triangle showing the inter-relationship between $K_{oa}$, $K_{aw}$ and $K_{ow}$.

The final coefficient which will be discussed is the particle-air coefficient, $K_p$. As before, this coefficient can be determined either directly through measurement or indirectly if other information about the compound is known. An example of an indirect means of determining phthalate $K_p$ values has been demonstrated by multiplying the phthalates $K_{oa}$ value by $1.88 \times 10^{-12}$ (Equation 2).  

$$\text{Equation 2:}$$

$$K_p \left( \frac{m^3}{\mu g} \right) = \frac{[\text{Particle}]}{[\text{Air}]} = (1.88 \times 10^{-12}) (K_{oa})$$

Directly determining phthalate $K_p$ values has also been accomplished provided the following are known; the equilibrium particle phase concentration of the compound ($F$) (ng/m$^3$), the gas phase concentration of the compound ($C_g$) (ng/m$^3$), and the total mass of particulates (TSP) (µg/m$^3$) (Equation 3).  

$$\text{Equation 3:}$$

$$K_p \left( \frac{m^3}{\mu g} \right) = \frac{F}{TSP} \frac{1}{C_g}$$
Using polyaromatic hydrocarbons, it has been determined that the relationship between particle and gas phase concentrations ($K_p$) follows Langmuir isothermal adsorption. The Langmuir isotherm concept describes the equilibrium ($K_{eq}$) established by a gaseous species ($X_g$) adsorbing onto the surface of another species ($S^*$) creating a monolayer ($S$-$X$) (Equation 4 and Equation 5).

**Equation 4:**

$$X_g + S^* \rightleftharpoons S-X$$

**Equation 5:**

$$K_{eq} = \frac{[S-X]}{[X_g][S^*]}$$

In the Langmuir model, the number of occupied sites is given the term $\theta$ which is represented in Equation 5 as $S-X$. By definition number of unoccupied sites is 1 minus the number of occupied sites (i.e. 1-$\theta$), represented by $S^*$ in Equation 5. Finally the concentration of the gas $X_g$ can be obtained from its partial pressure ($P$). Substituting these terms into Equation 5 yields a new equation for the equilibrium constant (represented by $b$) (Equation 6). Re-arrangement of this new equation provides the familiar way of expressing the Langmuir isotherm where the number of occupied sites on a surface is represented by both the equilibrium constant ($b$) and the compounds partial pressure ($P$) (Equation 7).

**Equation 6:**

$$b = \frac{\theta}{P(1-\theta)}$$

**Equation 7:**

$$\theta = \frac{bP}{1+bP}$$
For low fractional particulate coverage, as would be expected in ambient air, the Langmuir equation can be reduced. Here the ratio of the particulate surface covered (θ_X) by the contaminant (X) equals the rate of adsorption to desorption (b_X) of X multiplied by the vapor pressure (P^o_X) of X (Equation 8). The ratio of particulate surface covered (θ_X) can also be expressed by multiplying a proportionality constant (K_{OX}) by the concentration of X associated with the particulate phase (X_p) and dividing the product of these two by the total suspended particulate matter (TPS) present (Equation 9). If the temperature of the system covers a relatively narrow range then the vapor pressure of X (P^o_X) is equal to a proportionality constant (K_{PX}) multiplied by the concentration of X in the gas phase (X_g) (Equation 10). Finally these three equations can be combined to provide the ratio of the rate of adsorption to desorption (θ_X) as a function of the concentration of contaminant (X) in the vapor (X_g) and particle phase (X_p) (Equation 11).

Equation 8:

\[ \theta_X = b_X P^o_X \]

Equation 9:

\[ \theta_X = \frac{K_{OX} (X_p)}{TSP} \]

Equation 10:

\[ P^o_X = K_{PX} X_g \]

Equation 11:

\[ \frac{1}{b_X} = \frac{K_X (X_g)}{X_p \left\{ \frac{X_p}{TSP} \right\}} \]
Where: $K_X = \frac{K_{PX}}{K_{OX}}$

Since many PAHs and phthalates have similar molecular weights and vapor pressures it is assumed that phthalates should also abide by Langmuir adsorption.

To obtain a better understanding of the relative environmental distribution of phthalates it is important to examine their physical properties. Table 1.1 provides pertinent physical properties for five of the most commonly used phthalate plasticizers.

**Table 1.1. Physical properties of the five most common phthalates**

<table>
<thead>
<tr>
<th></th>
<th>DMP</th>
<th>DEP</th>
<th>DnBP</th>
<th>BBzP</th>
<th>DEHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW (g/mol)</td>
<td>194.19</td>
<td>222.24</td>
<td>278.35</td>
<td>312.37</td>
<td>390.57</td>
</tr>
<tr>
<td>b.p. (°C)</td>
<td>283.7</td>
<td>295</td>
<td>340</td>
<td>370</td>
<td>384</td>
</tr>
<tr>
<td>$P^o$ (atm)</td>
<td>4.05x10^{-6}</td>
<td>2.76x10^{-6}</td>
<td>2.64x10^{-8}</td>
<td>1.09x10^{-8}</td>
<td>1.87x10^{-10}</td>
</tr>
<tr>
<td>CW sat (mg/L)</td>
<td>4000</td>
<td>1080</td>
<td>11.2</td>
<td>2.69</td>
<td>0.27</td>
</tr>
<tr>
<td>Log $K_{ow}$</td>
<td>1.60</td>
<td>2.42</td>
<td>4.50</td>
<td>4.73</td>
<td>7.60</td>
</tr>
<tr>
<td>$^a$Log $K_{aw}$</td>
<td>-5.09</td>
<td>-4.60</td>
<td>-4.13</td>
<td>-4.29</td>
<td>-4.96</td>
</tr>
<tr>
<td>$^b$Log $K_{oa}$</td>
<td>6.69</td>
<td>7.02</td>
<td>8.63</td>
<td>9.02</td>
<td>12.56</td>
</tr>
<tr>
<td>$^c$Log $K_p$</td>
<td>-5.03</td>
<td>-4.70</td>
<td>-3.09</td>
<td>-2.70</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Values obtained from the SRC PHYSPROP Database

$^a$Log $K_{aw} = P^o/CW_{sat}$

$^b$Log $K_{oa} = \log (K_{ow}/K_{aw})$

$^c$Log $K_p = \log (1.88x10^{-12} \cdot K_{oa})^{27}$

Upon examination of the different physical constants associated with each of the phthalates (e.g. $K_{ow}$, $K_{oa}$) it is obvious that all phthalates are most favorably associated with the octanol phase. DEHP is the only phthalate shown to be more favorably associated with the particulate phase than the gas phase ($K_p$). The trend which displays that phthalates with longer than 6C ester chains are more associated with particles and phthalates with shorter than 6C ester chains are more associated with the gas phase has been reported elsewhere.$^{29, 30}$

### 1.2.3. Phthalate Exposure Sources

The non-covalent forces that retain phthalates within a polymer are associative by nature, leading to the inevitable release of at least some of the phthalate into the environment. Continual leaching of phthalate from plastics will occur as long as there is
phthalate present in the source plastic reservoir. The physical properties of a specific phthalate will determine where in the environment it will be most strongly associated (Section 1.2.2.1). Phthalates which have a low molecular weight such as DMP are much more volatile than the high molecular weight phthalates, therefore at equilibrium they will be found at higher concentrations in the air. Phthalates such as DEHP, which have a low vapor pressure, will be mostly associated with hydrophobic components such as surfaces and dust. During the 50’s there was a trend to move away from the lower molecular weight phthalates such as DBP to higher molecular weight phthalates such as DEHP to increase the lifetime of the phthalate in the polymer matrix (typically PVC).\textsuperscript{31} To date, a substantial amount of information exists which demonstrates that high molecular weight phthalates, such as DEHP, are steadily leaching out of plastics and into their local environments.\textsuperscript{32, 33, 34, 35}

Due to the broad use of plastic appliances containing phthalates, there are multiple routes for human exposure within the indoor environment. Some of the common exposure sources for phthalates includes; cosmetics, appliances, foods, drinks, medicines, dusts and PVC materials such as flooring, toys and gloves (Figure 1.3).\textsuperscript{36} These sources lead to three major human exposure routes; dermal absorption, oral ingestion and inhalation.\textsuperscript{37}
Among the three exposure routes, ingestion of dust and food is currently believed to be the major source for human phthalate exposure. Different food items also appear to be correlated with the consumption of different phthalates. For instance, the consumption of meats and fats appears to be a major dietary source for DEHP, whereas the consumption of vegetables such as potatoes and tomatoes appears to be a major dietary source for DEP.

Another major source for phthalate exposure is by the inhalation of gaseous phthalates or phthalates associated with PM$_{10}$ and PM$_{2.5}$. Dust and particles are capable of concentrating phthalates to substantially higher concentrations than the gas phase, which is particularly important for the higher molecular weight phthalates such as DEHP. In a study examining the concentrations of phthalates in a Berlin apartment building, the ratio for the average concentration of DEHP in the gas phase versus particle phase was found to be 126/659 (ng/m$^3$)/(µg/g) respectively. The only other
phthalate detected which also contained a higher average concentration in the dust, versus the gas phase, was BBzP 19/29 (ng/m³)/(µg/g). All other phthalates including; DMP, DEP, DnBP and DiBP were detected at a higher concentration in the gas phase. Another study examining the concentration of phthalates in USA and China demonstrated a similar trend, with the higher molecular weight phthalates present in dust at greater concentrations. Human exposure to the higher molecular weight phthalates can occur when contaminated dust is disturbed and made airborne then subsequently inhaled. Concentrations of phthalates on particulate matter also appears to be seasonally variable, with higher concentrations present during the summer months.

1.2.4. Health Effects

Because phthalates are continually leached into the environment where they are available for human exposure, there is substantial interest regarding the potential health effects of phthalates. In the scientific community, phthalate related research has steadily increased since their initial use in plastics industry (Section 1.2.1), and specific interest in their health effects has more recently gained momentum (Figure 1.4).
The initial publication establishing interest in phthalates as environmental contaminants was published in the 1970’s by Mayers, reporting phthalate residues in fish obtained from different parts of North America. The results from this work showed that phthalate residues were not only making their way into the environment at detectable levels but were also making their way into the local food chains. Interest was raised from this paper regarding the potential ecosystem effects of phthalates upon the environment, particularly upon aquatic invertebrates. Further studies at the time, focused on DEHP, indicated both the ability of DEHP to bioconcentrate to particularly high levels (up to 13,600x the water concentration), as well as demonstrated the ability of DEHP to impair the reproductive function of the aquatic invertebrate, Daphnia magna, at 3µg/L. Since the initial discovery of phthalates in the environment, many papers have focused on the potential health effects of phthalates on humans.

To date, research has indicated the possibility of phthalates to serve as human endocrine disruptors, carcinogens, teratogens and the ability to interfere with male
fertility.\textsuperscript{45} Many of these studies have focused on the effect of different phthalates on animals, with the assumption that similar effects would be observed for humans. Correlations between asthma and DEHP concentrations in the household environment were also shown by a study examining children in Swedish households.\textsuperscript{46} Their study also correlated higher concentrations of BBzP with rhinitis and eczema.\textsuperscript{46} In a follow up study 10 years later, a new correlation was drawn between PVC flooring in the parent’s room and the eventual development of asthma for the child.\textsuperscript{47} Here, it was predicted that the presence of PVC flooring could be indicative of the mothers’ exposure to phthalates during her pregnancy, believed to be a critical period in the child’s development of delayed asthma.\textsuperscript{47}

1.3. Gaseous Chemistry

The ability to accurately and reproducibly generate gas phase standards is of critical importance when examining gas phase chemistry. Without a reproducible standard, neither replica nor comparison experiments can be made. Laws describing the effect with which pressure, volume and temperature (such as Boyles Law and Charles Law) have on gases can typically be found in any standard first year chemistry textbook, therefore this section will focus on the analytical formulas and techniques used to both generate as well as place a unit of quantity on gas phase concentrations.

1.3.1. Gas Phase Standards

Gas phase standards can be generated in both static and dynamic manners with the end use determining which is most suitable.\textsuperscript{48} Standards made in a static manner typically involve placing a known quantity of analyte into a vessel of a known fixed volume, allowing the analyte to reach equilibrium with gas within the container. If the compound is volatile and completely volatilizes, then the concentration within the container can be determined since the amount added and the final volume are known. If the analyte added is either added in excess, or is semi-volatile, then the concentration can still be determined using the vapor pressure of the analyte after an equilibrium between the gaseous and condensed phase is achieved. Although relatively straight
forward, standards made in a static manner can have their drawbacks. For instance the concentration in the gas phase is effected not only by the amount of substance added, but is also reduced if a substantial amount of substance becomes adsorbed onto the inner surfaces of the container. Delivering concentrations made in a static manner can also be problematic because a dilution is performed if using gas to push the standard from its vessel. Fortunately, the dynamic method for generating gas phase standards overcomes many of the problems associated with the static method.

Dynamic gas standard preparation is achieved by continually flowing a known volume of gas over an apparatus which is continually emitting a known amount of analyte into the gas stream. These standards are advantageous over static standards, in that the adsorption of the compound from the gas phase onto the vessel surface does not affect the resulting concentration when all surfaces are coated and at equilibrium. The application of these standards to various experiments is also relatively straightforward since they are already calibrated with a known amount of continually flowing gas. Some examples of previously used dynamic standards include; continually mixing two gas streams of known flow rates, the nebulization of liquids and finally the use of permeation tubes filled with the analyte of interest. Permeation tubes have become one of the standard techniques in generating reliable low level gas phase concentrations because of the many advantages they provide.

1.3.2.1 Permeation Tubes

Permeation tubes are a particularly important means of generating dynamic gas phase standards. The permeation tube design is relatively simple and involves a tubular polymeric membrane that has been filled with the compound of interest then sealed at both ends (Figure 1.5). Fluoropolymers such as PTFE (Polytetrafluoroethylene) and FEP (Fluorinated ethylene propylene) are a commonly used material due to their elasticity and chemical resistivity. Typical applications for fluorinated polymers have historically been for highly volatile, low molecular weight species. Such species include gases (e.g. \( \text{SO}_2 \) and \( \text{NO}_2 \)) and low molecular weight VOC’s (e.g. \( \text{CF}_3\text{Br} \), \( \text{CH}_2\text{CH}_2\text{O} \) and \( \text{C}_6\text{H}_6 \)).
Since permeation tubes are typically made of thermally resistive materials they can be heated to relatively high temperatures (>100°C), which allows different emission rates to be achieved as a function of temperature.\textsuperscript{50, 51} Subsequent dilution of the volatilized analyte is achieved by the controlled gas flow, which is external to the permeation tube. Aside from temperature, there are other factors that affect the permeation tube emission rate. These are governed by Fick’s First Law, which is discussed in Section 1.6.1.2.

Calibrating a permeation tube is accomplished by monitoring its emission rate. Determining the emission rate is typically performed by exposing the permeation tube to specific conditions (e.g. controlled temperature and gas flow) and monitoring the mass loss (of the analyte) from the tube over time. If the volume of air flowing over the permeation tube is controlled and regulated to be litres per minute (LPM), the concentration of analyte in the gas phase ($C_{ig}$) downstream from the permeation tube can be obtained by dividing the permeation tube emission rate by the diluent air flow (Equation 12).

Equation 12:

\[
C_{ig} = \frac{\text{Perm. Tube emission rate}}{\text{Flow rate}} = \left( \frac{g}{\text{min}} \right) = \text{Concentration in} \left( \frac{g}{L} \right)
\]

When the mass per unit volume concentration of analyte in the gas phase is known, it can be used to determine the concentration of gas in terms of ppmv and ppbv (parts per million and billion by volume, respectively) which are more typical units for reporting gaseous concentrations (Equations 13 and 14, respectively).\textsuperscript{48}
Equation 13:

\[
\text{ppmv} = \frac{mg}{m^3} \times \left( \frac{0.08205 \times T}{\text{MW}} \right)
\]

Where \(T\) is in kelvins (K) and \(\text{MW}\) is in g/mol

Equation 14:

\[
\text{ppbv} = \frac{\mu g}{m^3} \times \left( \frac{0.08205 \times T}{\text{MW}} \right)
\]

Where \(T\) is in kelvins (K) and \(\text{MW}\) is in g/mol

The following formula can also be used to calculate the gaseous concentration generated by a permeation tube and is useful if the experiment is not performed under standard temperature and pressure conditions (Equation 15).\(^{48}\)

Equation 15:

\[
C_{\text{ig ppmv}} = 22.4 \times 10^6 \times \left( \frac{T}{273} \right) \times \left( \frac{760}{P} \right) \times \frac{q_d}{(q_d \times \text{MW})}
\]

Where \(C_{\text{ig}}\) is the average gas phase concentration (in ppmv), \(T\) is the temperature (in K), \(P\) is the experimental pressure (in mmHg), \(q_d\) is the permeation rate (g/min), \(q_0\) is the flow rate of diluent gas (L/min) and \(\text{MW}\) is the molecular weight (g/mol).
1.4. Mass Spectrometry

Since the initial developments of the mass spectrometer in the 1900s by F.W. Aston and J.J Thompson, a large focus of research has been devoted to the improvement, diversification and optimization of the now modern day instrument. Many different mass spectrometers are available on the market today, each optimized or suited to obtain varying degrees of information from various sample types. Whether the instrument is high resolution and capable of separating two different species with the same nominal mass or is a low resolution instrument used for the sensitive detection of analyte species, the mass spectrometer is a key instrument in the modern day chemistry laboratory. The following section outlines several of the components of the modern mass spectrometer (sample introduction, ionization, and detection) with an emphasis on the types of components which are suited for monitoring gaseous phthalates.

1.4.1. Sample Introduction: Membrane Introduction Mass Spectrometry

One of the goals for any instrument is to be able to selectively isolate and remove the compounds of interest from the bulk matrix. The inlet to the mass spectrometer can be thought of as the first stage for this process where it can be variously adapted for this purpose. Of the many different inlet designs, membrane introduction mass spectrometry (MIMS) has presented itself as an elegant way to both effectively and continually extract specific compounds from sometimes complex samples.

Membrane introduction mass spectrometry (MIMS) is a technique which involves the use of a membrane placed directly on the inlet of a mass spectrometer (Figure 1.6). The birth of MIMS occurred in 1963 when two researchers, Hoch and Kok, desired an instrument capable of monitoring gaseous products from biological reactions.52 Due to the nature of their sample, the authors required a barrier which could selectively isolate compounds directly from the liquid phase of a reaction vessel.52 During that time manometers had previously been used for these types of experiments however problems with the manometer setup were inherently present. Since the reaction to be
measured was in the liquid phase, manometers would be unable to measure product formation since no substantial gas was expected to form above the solution. The other problem with using manometers was that they would be incapable of measuring the concentrations of the specific chemical species formed. With the drawbacks of the manometer the authors explored another option for detection which involved using a semipermeable membrane placed directly onto the inlet of a mass spectrometer. Application of the membrane allowed the authors to submerse the MS inlet into the liquid of the reaction vessel, detecting specific analyte concentrations over time. Once a mass spectrometer with a suitable membrane inlet was developed, it was quickly used to demonstrate the advantages of MIMS when it was used to measure the photosynthesis/respiration products O₂ and CO₂ from algae. Since the initial development of MIMS it has been applied to a variety of different samples including complex mixtures of gases, liquids and solids. The acceptor phase of the MIMS system is also variable and can either be a gas phase acceptor (as seen with the Hoch and Kok experiment) or a liquid phase, enabling both hard (electron ionization) and soft (electrospray ionization) ionization sources to be used.

**Figure 1.6.** Basic MIMS concept involving a sheet type membrane as the semi permeable barrier.
1.4.1.1 Sample Introduction

The major advantage to MIMS revolves around the ability to continuously flow sample over the membrane, providing rapid data acquisition and real time monitoring of concentration changes with minimal to no sample preparation.\textsuperscript{58} Many different configurations exist for the membrane housing or how sample is exposed to the membrane and most of these are summarized in the following reviews.\textsuperscript{58, 59, 60, 61} One typical MIMS interface configuration, the “flow cell” geometry, consists of an inlet and an outlet through which sample flows through while concurrently passing over the membrane (Figure 1.7). When sample is exposed to the membrane, analytes soluble in the membrane adsorb, permeate through then desorb from the membrane on the opposite side where they are then transported by a counter current flow of acceptor phase (\textit{e.g.} He\textsubscript{(g)}) towards the detector. The geometry of the membrane affects the shape of the housing with the two types being either hollow fibre or a sheet style membrane (Figure 1.8 and Figure 1.6 respectively).
1.4.1.2 Permeation

The sensitivity of MIMS measurements is dependent upon the ability for the molecule of interest to permeate through the semi-permeable membrane, become ionized then detected. In order for a molecule to reach the mass spectrometer it must first undergo selective partitioning into the membrane (relative to concomitant compounds), diffuse through the membrane then desorb into either a gaseous acceptor flow or the vacuum of the mass spectrometer.\textsuperscript{62} For a hollow fiber membrane, steady state permeation is governed by several factors which are described by Fick’s First Law (Equation 16).\textsuperscript{62} In general the permeation rate is related to the membranes dimensions, the membrane/analyte permeability and the analyte concentration (Equation 17).\textsuperscript{62}
Equation 16:

\[
F = \frac{2\pi L D (C_1 - C_2)}{\ln\left(\frac{r}{r_o}\right)}
\]

Where \( F \) is the permeation rate of the analyte in the extract stream, \( D \) is the substances diffusivity, \( L \) is the length of the hollow fiber, \( C_1 \) and \( C_2 \) are the analyte concentrations in the high and low pressure surfaces of the membrane respectively and \( r \) and \( r_o \) are the outer and inner radii of the hollow fiber membrane respectively.

Equation 17:

\[
\text{Permeation rate} = (\text{Dimension factor})(\text{Permeability })(\text{Concentration})
\]

### 1.4.1.3 Membranes

The most commonly used membrane material for MIMS based instruments is polydimethylsiloxane (PDMS) which can be seen by its prevalence in the literature.\(^{58, 59, 60, 61, 63, 64, 65}\) PDMS is advantageous because it is commercially available in many different configurations; it is thermally and chemically stable and is highly permeable.\(^{66}\) Typically PDMS is used when the analyte of interest is a small relatively non-polar VOC or SVOC.\(^{58}\) Some examples of the analytes PDMS-membrane MIMS has been used to examine include; benzene, toluene and xylene (BTEX),\(^{67}\) gasoline markers such as methyl tert-butyl ether (MTBE),\(^{68}\) and isoprene from damaged plants.\(^{69}\) With the more recent development of thinner membranes, PDMS MIMS has been successfully employed to monitor SVOCs in the aqueous phase such as estrone, nonylphenol and naphthenic acids.\(^{70}\) Heated membranes have also shown promise in improving the applicability of PDMS for expanded applicability toward other SVOC compound analysis. For instance a heated resistive wire placed within the MIMS membrane has been used to monitor PAHs such as Naphthalene and Fluorene.\(^{71}\) One major advantage to the incorporation of a heating stage is that it allows for trap and release experiments to be performed. Trap and release experiments increase the sensitivity of the instrument by pre-concentrating hydrophobic compounds in the sample then rapidly releasing them.
with heat. Other methods of heating such as directly inserting the membrane into the heated inlet of the mass spectrometer\textsuperscript{72} or using a heated rod with which the membrane was wrapped around have also been investigated.\textsuperscript{73}

Aside from PDMS, other membrane materials have also been used in attempts to extend the range of analytes detectable by MIMS. As previously discussed, PDMS is suitable for analyzing hydrophobic compounds. The application of different membrane types to MIMS enables different analyte types to be examined. For instance different membranes can increase in the analytes affinity for the membrane and they can also enhance the substances diffusivity through the membrane. Many different membrane types have been used to these effects and several brief examples are as follows. Microporous Teflon, for instance, has been used to analyze VOCs and anthropogenic halocarbons in seawater where a greater sensitivity relative to PDMS was observed, as well as a faster response time for polar compounds such as chlorobenzene.\textsuperscript{74} An allyl alcohol membrane was shown to have a greater sensitivity to methanol than PDMS in both air and water samples.\textsuperscript{75} An alkylamine-modified cellulose membrane was successfully used to monitor the concentration of benzaldehyde in a liquid sample.\textsuperscript{76} More recently Nafion, a cation exchange membrane, has been used to monitor solutions containing both polar and non-polar VOCs and SVOCs such as methanol, benzene and chlorophenols.\textsuperscript{77} Modifications to the basic PDMS membrane have also been demonstrated. For instance an enzyme derivatized PDMS membrane was used to both catalyze the decomposition of hydrophilic esters and monitor their products by MIMS.\textsuperscript{78} Outside of MIMS applications, the effect of incorporating different polymers into PDMS has on membrane permeability have also been examined. For instance incorporating styrene into the PDMS chain as a block copolymer, poly(DMS-styrene), elevated the membrane partition coefficient, or the membrane affinity for a contaminant, by as much as 10-30x when analyzing hydrophobic aromatic compounds.\textsuperscript{79} With the continual development of new polymers and materials it is evident that the extension of MIMS applications will only continue to increase.
1.4.2. Ionization

After analyte molecules are transferred through the inlet of the mass spectrometer, the next major step is their ionization. The requirement for placing a charge on the incoming analyte is actually so important that it can be thought of as at least one of the unifying features of all mass spectrometers. The reason charge is so important is that without charge, the trajectory of the analyte within the mass spectrometer cannot be controlled using electric and/or magnetic fields, and therefore the original neutral analyte would not be detected.

The methods for generating ions are quite variable, but in general terms can be divided into two main categories, either hard or soft ionization. Differentiation between the two categories is based upon the amount of energy being transferred to the molecule during ionization. Ionization techniques which transfer sufficient energy to induce substantial fragmentation of the parent molecular ion are termed hard ionization sources. Defining whether an ionization mode is either soft or hard is typically performed by comparing it to another ionization technique. For example electron impact ionization (EI), a gas phase ionization technique, is considered to be a harder ionization technique than chemical ionization (CI) and chemical ionization is considered to be a harder ionization technique than atmospheric pressure photoionization (APPI). Extension of ionization away from the gas phase and into the condensed phase has resulted in utilization of even softer ionization techniques. Two examples of very soft, condensed phase ion formation techniques include matrix assisted laser desorption ionization (MALDI) and electrospray ‘ionization’ (ESI). Both ESI and MALDI are advantageous in that they are able to ionize molecules with little to no fragmentation. Electrospray has successfully been used to ionize biomolecules with charge ratios of up to 30 000 000m/z.

Many ionization techniques exist and there are clear advantages and disadvantages of each. Although electrospray is an incredibly soft technique it actually does not form ions in the traditional sense but leaves a charge on molecules after the other components of the solution have been removed and is accomplished at ambient temperature and pressure. Electron ionization on the other hand, typically performed at 70eV, forms ions by colliding energetic electrons with molecules in a high vacuum. This
imparts substantial energy, some of which partitions into the molecule leading to its fragmentation.\textsuperscript{83}

### 1.4.2.1 Electron Ionization

Among the initial techniques, and still commonly used, is the generation of ions through electron-molecule collisions. It has been shown that if an electron carrying sufficient energy (eV) collides with a gaseous molecule, it can eject an electron from that molecule, resulting in a molecular ion.\textsuperscript{83} The ionization energy required by most molecules is between 7-15eV.\textsuperscript{84} The variation in ionization energies (IE) is based upon the presence of different functional groups as well as the bonding within the molecule. Using ethane (IE: 11.52eV), ethyl chloride (IE: 10.98eV) and ethanol (IE: 10.48eV) it can be seen that alkanes have higher ionization energies than halocarbons, which have higher ionization energies than alcohols.\textsuperscript{84} Electron ionization instruments typically operate using 70eV electrons, well above the 7-15eV range. Reasons for the choice of 70eV are twofold, being defined both by the ionization efficiency of this energy\textsuperscript{83} as well as the establishment of a universal standard for performing reproducible fragmentation experiments.

The formation of energetic electrons in the ion source of the mass spectrometer is accomplished by passing current through a resistive filament, which begins to sputter electrons. Through the use of a series of lenses and voltage differences, the generated electrons are accelerated from the filament and into an ion source where they collide with gaseous neutral molecules. If the force of the collision is sufficient to eject an electron from that molecule then the molecule becomes a radical cation (Equation 18).

\begin{equation}
M + e^- \rightarrow M^+ + 2e^-
\end{equation}

Given the high energy of the accelerated electrons (70eV), a substantial amount of energy can be transferred from the electron to the molecule during collision events. The molecule accommodates for this excess energy in its different vibrational modes.\textsuperscript{83} If
sufficient excess energy is transferred during this collision, the ionized molecule undergoes subsequent fragmentation (Equation 19).

Equation 19:

M^{**} \rightarrow m^+_i + n^*

Fragmentation is advantageous in that each molecule fragments reproducibly, depending on its functional groups, leading to a unique molecular ‘fingerprint’ in the resulting mass spectrum. The major advantage of this ‘fingerprint’ is that it can be used to generate, or be compared against, a library of known mass spectra which can be used to identify molecules in a sample. Under these ion source conditions that lead to extensive fragmentation, the molecular ion is often not observed in the mass spectrum and as such, direct information regarding the molecules in a sample is not feasible.

Phthalates are a group of compounds that (unfortunately) are easily fragmented, and typically result in an EI spectrum containing little to no parent molecular ion peak. The fragmentation pathways for most phthalates follow a similar trend with the 149m/z peak being the most abundant ion (Figure 1.9). Dimethyl phthalate (DMP) is an exception to the 149m/z peak trend due to the inability for the DMP ion to form either the C_2H_2R: or CH_3 leaving group. In place of the 149m/z ion, 163m/z is the most abundant ion in the DMP EI spectrum (Figure 1.10 and 1.11).
Figure 1.9. General electron impact fragmentation process for phthalates. Here, cycl. represents a cyclization process and On. represents the formation of an onium ion.\textsuperscript{85}
Figure 1.10. EI spectrum for DMP. Reproduced and adapted from the NIST database with permission.\textsuperscript{84}

Figure 1.11. EI spectrum for DBP. Reproduced and adapted from the NIST database with permission.\textsuperscript{84}
1.4.3. Detection: Quadrupole Ion Trap

Once a molecule has entered the inlet of the mass spectrometer and has become ionized, it is then transported using ion optics to the mass analyzer where it can then be 'sorted' based upon its mass to charge ratio. Many mass analyzers exist today utilizing different techniques for ion sorting. Historically, mass analyzers have incorporated large magnets to perform such sorting; these instruments include the Magnetic Sector (MS) and the more modern Ion Cyclotron Resonance (ICR) spectrometer. Other types of sorting mass analyzers operate either upon field free drift regions (e.g. the Time of Flight analyzer (TOF)), time variable electric fields (e.g. radiofrequency instruments), and time invariable electric fields (e.g., orbitrap). Radiofrequency instruments, particularly the 3D quadrupole ion trap (3D QIT) have presented themselves as relatively inexpensive, fast scanning and robust analyzers. The design of the 3D QIT is relatively simple and consists of two end cap electrodes and a ring electrode (Figure 1.12). The 3D QIT stores and analyzes ions, as its names implies, through the use of a three dimensional quadrupole field, most commonly achieved by applying a radiofrequency signal to the central ring electrode, and a DC potential to the endcap electrodes.
As previously mentioned, all mass analyzers require an ionization step to place a charge on molecular analytes, allowing them to be sorted in some manner by the instrument. With the 3D QIT, ionization can either occur within the trap, called internal ionization, or ions can be formed externally then injected into the trap called external ionization. Regardless of whether the ions are formed internally or externally, the trajectories of ions within the 3D QIT can be described by Mathieu equations (Equations 20 and 21). An ion of a specific mass to charge ratio will remain within the trap depending on whether it falls within the stability region of the trap, or the portions where solving the Mathieu equations overlap (Figure 1.13).
Equation 20:

\[ a_z = -2a_r = \frac{16eU}{m_i(r_0^2 + 2z_0^2)\Omega^2} \]

Equation 21:

\[ q_z = -2q_r = \frac{8eV}{m_i(r_0^2 + 2z_0^2)\Omega^2} \]

Figure 1.13. Stability region defined by the Mathieu equation. A and B denote regions of both r and z stability. Reproduced from QITMS with permission.86

From these formulas it can be seen that the motion of the ion is based upon the amplitude of the applied DC voltage (U), the amplitude of the alternating current voltage (V), the molecular charge (e), the mass of the ion (m_i), the dimensions of the trap (r_0 and z_0) and finally the frequency of the applied alternating current waveform (Ω). In addition to the mentioned parameters, helium gas is introduced supplementally into the 3D trap to provide ion-He(g) collisional cooling which aids in focusing the ions!towards the center
of the trap.\textsuperscript{87} The sum of all of these forces results in a filtering process, leaving ions which are stable within the trap adopting a Lissajous trajectory.\textsuperscript{88}

In order for ions to be detected they must be ejected from the trap then collide with a detector. Stable ions can be ejected from the trap by altering these parameters so that the ions trajectory is no longer stable. One of the key innovations in the 3D QIT world was the development of the mass-selective axial instability scan.\textsuperscript{84} The key advantage that this scan offered over the other methods at the time was that it allowed for the storage of all incoming ions into the trap then their sequential ejection from the trap based on their m/z values.\textsuperscript{86} In brief, a mass-selective instability scan is performed by grounding the two end cap electrodes then only applying an RF-voltage scan (V) to the ring electrode. The application of this voltage causes the ejection of ions in their order of m/z values along the q_z axis.\textsuperscript{82} Applying a low amplitude AC waveform to the endcap electrodes, corresponding to the secular frequency of a given m/z, usually at the a=0, q=0.908 edge of stability/instability in a-q space (Figure 1.13), improves the overall performance of the ion trap in terms of mass resolution and sensitivity.\textsuperscript{91}

The 3D QIT is advantageous in that is has the capability of performing tandem MS\textsuperscript{n} experiments within the confined area of the trap. Tandem experiments are typically performed by applying a supplementary oscillating potential (or AC voltage) across the end cap electrodes resulting in the resonant excitation of a specific group of ions.\textsuperscript{90} Upon application of this waveform, termed the secular frequency (or resonant frequency) for a specific mass-to-charge, causes the trapped ions to absorb energy of the external waveform, causing the ion’s trajectories to increase in amplitude (and therefore velocity as the ion secular frequency isn’t affected at low amplitudes).\textsuperscript{90} The application of this resonant excitation voltage is advantageous in MS\textsuperscript{n} experiments since it can be used to mass-scan a packet of ions, isolate ions of a specific m/z ratio, as well as be used to selectively induce collision induced dissociation (CID).\textsuperscript{90} Collision induced dissociation occurs within the trap upon application of this frequency since it increases the ions amplitude of motion resulting in more energetic collisions with the helium buffer gas. Under the normal operating conditions of a 3D ion trap, the rate of energy deposition into the ion through the collisions with He is greater than the rate of de-excitation of internal
energy, thus effecting net increase in the internal energy of the ion, eventually leading to its dissociation.\textsuperscript{90} Resonant excitation for one purpose or another is utilized in nearly all modern 3D QIT mass spectrometers.\textsuperscript{91} The described general mechanism of ion internal energy increase leading to its dissociation is generic in tandem mass spectrometry, and it is termed collision activated dissociation (CAD) or collision induced dissociation (CID).

Another property of the 3D QIT is that it can store ions, integrating ions from low concentration samples which can greatly increase the sensitivity of the instrument. Considerations need to be made when storing high concentrations of ions however since coulombic repulsion of ions with the same charge results in a space charge which, perturbs the ion secular frequencies.\textsuperscript{92} Typically, the maximum number of ions which can be stored within a trap is $10^6$-$10^7$ where space charge would be present. Normally, the number of ions able to be trapped whilst maintaining normal operating performance of the 3D ion trap (e.g., unit mass resolution) is approximately $10^3$.\textsuperscript{85} Increasing the number of ions within the trap while keeping stable trajectories can be accomplished through axial modulation which is a subtype of resonant excitation/ejection. During axial modulation a secondary frequency is applied to the end cap electrodes at about half the fundamental frequency ($\Omega$), which removes ions of lower m/z ratios during a scan.\textsuperscript{90} Axial modulation increases the number of ions which can be stored within the trap by about an order of magnitude.\textsuperscript{93}

1.5. Research Objectives

The aim of this thesis was to develop instrumentation and methods that can be used to investigate and address the ongoing concern for the relationship between gas phase phthalates and particulate matter (aka house dust). Here, it is hypothesized that the amount of phthalate adsorbed onto the particle surfaces will be substantially higher than the gas phase concentration at equilibrium. Furthermore it is hypothesized that the rate of phthalate desorption from particle surface will be directly proportional to the amount of surfaces, or particles, present.
In order to address these hypotheses, this thesis has three distinct sections. First, the reproducible generation of gas phase phthalate standards at known concentrations was required in order to calibrate the response of an instrument. Second, determining a suitable species of particulate matter was required to perform reproducible phthalate-particle adsorption/desorption experiments. Third, was the development and application of a specialized membrane introduction mass spectrometry (MIMS) system suitable for the analysis of gaseous versus particle bound phthalates in an online manner.

The developed components of this thesis provided the means for addressing the proposed hypotheses and preliminary results regarding the quantification of gas phase-particulate matter interactions are presented. Further applications for the developed MIMS system specifically are discussed in the ‘future directions’ section of this thesis.
Chapter 2. Polydimethylsiloxane Permeation Tubes

2.1. Introduction

An essential component for monitoring the concentration of any analyte is to develop reproducible standards of known concentration to allow quantitative calibrations. Unlike aqueous solutions, where a known concentration can be obtained through adding a specified mass of analyte to a liquid, gas phase standards must be generated using air as the diluent. Multiple papers and books have been devoted to the subject of generating gas phase standards, and the information which follows focuses only on one method for generating gas phase standards, the permeation tube method. Interested readers should refer to Section 1.3.2 or consult the following reference for a more complete overview of the subject.48

2.1.1. Permeation Tubes

The use of permeation tubes and a gaseous dilution manifold is one of the more common techniques used for generating gas phase standards. A permeation tube consists of a polymer tube filled with one or more compounds, then sealed at both ends. Compounds undergo steady-state diffusion through the walls of the tube to the gas phase environment outside the tube, under constant conditions including temperature and external pressure. Subsequent dilution of analyte outside the tube can be achieved using a housing manifold through which a steady stream of gas flows. Permeation tubes are advantageous when generating gas phase standards since the presence of a semipermeable membrane controls the rate of analyte addition to a gas flow, enabling the production of reproducible, low concentration, gas phase standards. In theory any
A semipermeable membrane can be used to generate permeation tubes, however a few materials are particularly suitable for these devices.

The most common material used to construct permeation tubes are fluorinated polymers polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP). A major advantage to PTFE lies with its resistance to degradation under the influence of solvents and heat (mp. >300°C). Other advantages to PTFE and FEP include the fact that they are flexible polymers when thin, and that the final product polymer does not contain any plasticizers.

Although PTFE and FEP are commonly used permeation tube materials, the compounds that can permeated through these polymers are generally restricted to VOCs. Application of these permeation tubes to higher MW compounds is limited, with the driving force behind their emission being increasingly high temperatures and internal pressures. In order to overcome the limitations imposed by these fluorinated polymers for SVOCs, other materials which are more permeable are required. One highly permeable material which also contains many of the favorable features of PTFE is polydimethylsiloxane (PDMS). One such study which compared the permeability of a fluorinated polymer (Tetrafluoroethylene–hexafluoropropylene copolymer) against PDMS, showed that the later permeation tube material had a 100 fold greater permeability for water vapor than the former. Since minimal work has been performed using PDMS as a permeation tube material, experimentation regarding its feasibility was examined.

2.2. Experimental

2.2.1. Reagents

All phthalates Dimethyl phthalate (CAS # 131-11-3), Diethyl phthalate (CAS # 84-66-2), Diisobutyl phthalate (CAS # 84-69-5), Di-ethyl phthalate (CAS # 84-74-2) and Bis(2-ethylhexyl)phthalate (CAS # 117-81-7)) used for this study were purchased from Sigma Aldrich and were of 99% purity or higher. Solvents used for cleaning the
permeation tubes and their hardware consisted of methanol, hexane and dichloromethane (HPLC grade, Fisher Scientific).

2.2.2. Polydimethylsiloxane Permeation Tubes

Silastic brand (Dow Corning, Midland, MI) polydimethylsiloxane (PDMS) tubing was used for developing all PDMS permeation tubes. The most experimented with tube material was a 1.47mm I.D x 1.96mm O.D x 7.0cm (length) with a few experiments performed using a 3.35mm I.D x 4.65mm O.D membrane. All membranes were 'washed' with HPLC grade hexane three times prior to being used as a permeation tube. Upon addition of hexane, the PDMS swells significantly (about 1.5x) and short, non-covalently bound siloxane species are presumably removed. After exposure to hexane, the permeation tubes were allowed to dry overnight in a loosely covered Erlenmeyer flask. Calibration was accomplished by housing the permeation tube in a custom made heating manifold, and monitoring its mass loss over time. The heating manifold consisted of a water bath heated to 30°C within which a custom glass U-Tube holding the permeation tube was immersed (Figure 2.1). Gas flow over the permeation tube remained constant at 1.0 liter per minute (LPM) throughout all experiments and was heated to the water bath temperature as it traversed through 3mm glass beads within the U-tube. An air pump (Rena Air® Model 300) connected to a variable rotameter (Porter Instrument, Model B-436) was used to accomplish this regulated flow. In the event that a new permeation tube was to be used within this setup, the old tube was removed and clean air, at 30°C, was allowed to flow through the interface for a minimum of 3 days (generally 1 week). During this time, it was expected that any traces of previous phthalate were removed.
Figure 2.1. Schematic apparatus for heating permeation tubes using a water bath.
2.3. Results and Discussion

2.3.1. Polydimethylsiloxane Permeation Tubes

Three different PDMS permeation tube designs of different dimensions were developed and tested over the course of this work, each providing different gas phase phthalate concentrations under unified conditions (30°C and 1.0LPM respectively). A previously discussed, custom made heating manifold provided an accurate and consistent means of controlling the conditions the permeation tubes were exposed to during their calibration (Section 2.2.2, Figure 2.1). Dimethyl phthalate (DMP) was initially tested as a model phthalate compound, with other phthalates examined later during the more refined stages of permeation tube development.

The initial permeation tube design experimented with was a 7.0cm section of 1.47mm I.D x 1.96mm O.D PDMS tubing. This tube was filled with DMP then sealed at each end using a plug, a bent 1/16” stainless steel support rod (Figure 2.2). The portions of the snug fitting PDMS membrane extending over the rod were further secured to the rod using GC brand wrapping wire. Data was obtained by housing the permeation tube within the heated manifold then removing it and weighing it on a four decimal balance (Denver Instrument, Model M-220) at select time intervals (typically several days). The emission results obtained from this type of tube showed initial linearity over a period of about eleven days (Figure 2.3). Plotting the linear portion of the mass loss curve yielded a concentration of 460ppbv (in 1.0 LPM Air) (Figure 1.15) (also see Section 1.3.2.1). During the linear portion of the emission plot, the tube could be reproducibly used for experimentation. After the eleven day period, the rate of mass loss was no longer linear, and the amount of mass lost between measurements began to decrease, defining the useful lifetime of the device as eleven days or less.
Figure 2.2. Stainless steel rod supported polydimethylsiloxane permeation tube.

Figure 2.3. Mass loss curve generated from stainless steel supported PDMS permeation tube (Left). Linear portion of mass loss curve used for performing analyses (Right).

The reduced permeation rate, or mass loss, over time was believed to be the result of the continually decreasing membrane area to which phthalate was exposed to. This is an interesting result since typically permeation tubes are believed to function in a linear manner as long as there is liquid analyte in the reservoir. A couple factors which could be contributing to this problem include both the aging of the membrane as well as the fact that dimethyl phthalate has a low vapor pressure (~10^{-6}atm). In an attempt to overcome this problem, an extended reservoir type permeation tube was developed. This permeation tube used a 7.0cm membrane of the same I.D. x O.D. as the previous device, however contained a 5.0cm (L) x 1/16in (W) stainless steel tube at one end (Figure 2.4). This new device was mounted to the cap of the glass U-tube using copper wire, then suspended in an upright position during calibration.
The calibration mass loss curve for this permeation tube demonstrated an extended linear range, increasing the usable time for this permeation tube from eleven to twenty days (Figure 2.5). The overall concentration from this linear range was determined to be 429ppbv which is marginally lower than the previous permeation tube (460ppbv). This decrease in concentration is attributed to the slightly different membrane areas exposed to phthalate in the different devices.

The third type of permeation tube experimented with was an altered version of the previously discussed extended permeation tube. In this device the membrane length was reduced to 2.0cm and the stainless steel tube was increased in length to 10.0cm (Figure 2.6). The goal of this permeation tube was to obtain a permeation device which contained an extended linear portion as well as deliver a lower gas phase concentration.
A lower gas phase concentration became desirable at later stages in this project for the particle loading experiments (Section 5.3.3).

![Diagram of a permeation device](image)

**Figure 2.6.** Reduced PDMS membrane permeation tube with an elongated membrane used for generating long term, low concentrations of gaseous phthalate.

The results from this device followed the trend previously observed and demonstrated an increased linear portion within the calibration mass loss graph (Figure 2.7). The changes made to this permeation device extended its usable lifetime to at least 131 days. After converting mass loss into concentration, it was determined that the gaseous dimethyl phthalate concentration obtained here was 109 ppbv. This concentration was lower than previously observed and was primarily due to the reduced membrane length.
Figure 2.7. Mass loss curve of dimethyl phthalate generated from the third design of the PDMS permeation tube (Left). One of two linear portions of mass loss curve used for performing analyses (Right).

A potential problem which was observed with this final permeation tube which was not observed with the previous permeation tubes was the periodic ‘collapse’ of the PDMS membrane. It was noted that about every ten days during calibration, the membrane portion of the permeation tube was collapsed (observed during weighing). To solve this problem, the nut on the Swagelok™ fitting was loosened then re-finger tightened. This seemed to resolve the problem (at least temporarily) although slight deviations from linearity in mass loss were observed (Figure 2.7, Left Panel).

2.4. Summary

The results of this section demonstrate that PDMS based membrane permeation tubes can be used to generate reproducible concentrations of gaseous DMP. Three permeation tube structures were developed and it was determined that increasing the permeation tube reservoir increased the useful lifetime of the device from 11 to 20 days. Depending on the length of the membrane, the resulting concentration of DMP being emitted from the tube was either 429-460ppbv or 109ppbv (from a 7.0cm and 4.0cm membrane respectively). Limitations of the experimental setup primarily revolved around
the heating manifold which was restricted to relatively low temperatures (less than 40°C) due to the use of water in the constant temperature bath. Future experiments involving other phthalates, particularly the heavier ones, will likely require a manifold which can go to higher temperatures or some other sort of mechanism for increasing the temperature of the permeation tube resulting in quantifiable emission rates.
Chapter 3. **Modified Polydimethylsiloxane Permeation Tubes**

### 3.1. Introduction

A major factor which contributes to the permeability of an analyte in a permeation tube constructed from a specific material type and overall dimension is temperature. Standard commercially available permeation tubes, along with those previously described (Section 2.1.1), often rely on altering the temperature of the gas which surrounds and heats the permeation tube in order to yield different permeation rates. Externally heating a permeation tube is sufficient for generating gas phase standards, but can also be problematic. One problem which arises from externally heated permeation tubes is that the bulk gas flow which exits the heated chamber is typically at a substantially higher temperature than may be desirable for an experiment. A second disadvantage to externally heated permeation tubes is that they are unable to rapidly alternate between different permeation rates since changing the temperature of the manifold is typically slow, as is the re-equilibration of the permeation tube to the changed condition.

With the two setbacks of the externally heated permeation tubes in mind, a permeation tube modification was designed and tested that incorporated a resistive heating wire within the tube. The goal of the resistive wire was to provide an alternate means of rapidly heating the liquid analyte within the permeation tube, using an applied DC potential. Upon application of this potential, rapid heating of the membrane occurred resulting in an elevated permeation rate. The desirable outcome from such an approach was to obtain a permeation device which could quickly deliver multiple different permeation rates by simply altering the applied DC potential.
3.2. Experimental

3.2.1. Reagents

Refer to Section 2.2.1

3.2.2. Thermally Assisted Permeation Tubes

The Thermally Assisted Permeation Tubes (TAPT) consisted of two different sizes of PDMS membranes. One size used was 1.47mm I.D x 1.96mm O.D x 7.0cm (length). The other size used was 3.35mm I.D x 4.65mm O.D. x 7.0 cm. Within each of the permeation tube types a 30 gauge, 80:20 (Ni:Cr) coiled Nichrome® wire (Omega® NIC80-010-125-200) was placed. The ends of this wire extended onto the tubular plugs of the permeation tube at each end, such that a DC potential could be applied using a variable power supply (Circuit Test: Model PSB-3030). The housing for each of the permeation tubes was either a thermally stable fume hood (Figure 3.2, Section 3.3.1.1) or the water bath setup as previously described (Figure 2.1, Section 2.2.2). In the water bath setup, each of the permeation tubes were suspended from the cap of the glass U-Tube to ensure that portions of the nichrome coils were not touching, preventing any short circuits. When recording mass loss, the device was removed from the glass U-Tube and mounted upright on an analytical balance (Denver Instrument Model M-220) using an elongated vial. Three variations of thermally assisted permeation tubes were developed, and the following lists define each. Schematic diagrams for each device can be found in the corresponding results sections.
TAPT Type I (Figure 3.1, Section 3.3.1.1)

Membrane: 1.47mm I.D x 1.96mm O.D x 7.0cm (length) (Silastic brand; Dow Corning, Midland, MI) (Cat. No. 508-006)

Nichrome®: Stretched to a final length of 5.0cm with ~1mm spacing between coils. (Omega® Part No. NIC80-010-125-200)

Ferrules: 1/16" graphite/vespel (40%/60% respectively) ferrules drilled by hand to snugly fit the stainless steel tubing (Chromatographic specialties Part No. C75004)

Swagelok (Supelco, Bellefonte, PA): 1/16" Swagelok straight through fittings (Cat. No. SS-100-6)

TAPT Type II (Figure 3.12, Section 3.3.1.2)

Membrane: 3.35mm I.D x 4.65mm O.D x 7.0cm (length) (Silastic brand; Dow Corning, Midland, MI) (Cat No. 508-011)

Nichrome®: Stretched to a final length of 6.5cm with ~1mm spacing between coils. (Omega® Part No. NIC80-010-125-200)

End Plugs: Plugs were hand made from 18 gage copper wire with glass beads annealed on them.

TAPT Type III (Figure 3.15, Section 3.3.1.3)

Membrane: Silastic brand (Dow Corning, Midland, MI) PDMS 3.35mm I.D x 4.65mm O.D x 5.0cm (length) or Cole-Parmer PTFE 6.00mm I.D x 7.00mm O.D x 5.0cm (length) (Cat No. 06363-10)

Nichrome®: Stretched to a final length of 5.0cm with ~1mm spacing between coils. (Omega® Part No. NIC80-010-125-200)
Ferrules: 1/16” and 1/4” hand drilled graphite/vespel ferrules (Chromatographic specialties)

Swagelok (Supelco, Bellefonte, PA): 1/4” SS Straight Tube Fitting (Cat. No. SS-400-6CP), 1/16” Swagelok Straight Tube Fitting (Cat. No. SS-100-6)

3.3. Results and Discussion

Thermally Assisted Permeation Tubes

The proposal to generate gas phase standards at high concentrations by methods other than using heated bulk gas flows, led to the development of the thermally assisted permeation tubes (TAPT). This development put the heating element inside the permeation tube, neatly containing the heating element within the permeation tube. In the development phase of making and testing TAPT, it was hypothesized these tubes may elicit useful permeation rates for higher molecular weight phthalates. As has been the case thus far, dimethyl phthalate was used during development stages, with successful designs tested further using other phthalates.

3.3.1.1 Thermally Assisted Permeation Tube Type I

The Type I thermally assisted permeation tube was the first design experimented with. Its design was based upon the previously described extended permeation tube (Figure 2.4, Section 2.3.1). The Type I permeation tube consists of a 7.0cm (L) section of 1.47mm I.D x 1.96mm O.D PDMS membrane (Figure 3.1). Within the hollow portion of the membrane is a coiled resistive wire (nichrome) of 6.5cm (L) that was spot welded to two 3.0cm sections of 1/16” stainless steel tubes. The ends of the tubes were capped using two ‘straight through’ 1/16” Swagelok fittings then sealed with 1/16” stainless steel compression tube fitting plugs (plugs were made by compressing the supplied 1/16” SS ferrules onto a 1/16” stainless steel rod (of about 1/4” in length)).
To ensure the membrane was tightly sealed onto the tubes it was fixed in place using GC brand wire wrapping wire (the coating of which was removed, providing a ‘naked’ wire for a better seal). In order to apply a voltage to the device, alligator clips were connected onto the stainless steel tubes on each side of the resistive wire. Later in development it was determined that soldering the electrically conductive wire to the tube rather than using alligator clips provided better conductivity. Typical DC potentials applied to the Type I permeation device were in the range of 0-5 volts with the corresponding current being variable based on the resistivity (length) of the nichrome wire (typically ~1/10th of the applied voltage).

![Schematic for the Type I thermally assisted permeation tube.](image)

The first test for the Type I permeation device was to simply mount it within an ambient temperature fume hood (19°C) (Figure 3.2). To ensure temperatures within this fume hood remained consistent during the analysis, a thermometer was placed beside the permeation tube and a time lapse camera recorded its temperature at 10min intervals. The advantage to the fume hood setup during the development phase was to provide both a means for diluting the emitted phthalates as well as easy accessibility to the permeation device. Since most phthalates have relatively low vapor pressures, the fume hood setup eliminated the close proximity of surfaces which phthalates could be adsorbed upon. Excess adsorption during calibration could be problematic if the permeation tube and its enclosed housing were both being weighed. Since the goals of these initial experiments were to determine permeation rate, this simple fume hood housing proved satisfactory.
Figure 3.2. Type I thermally assisted permeation tube mounted in a temperature controlled fume hood during device calibration.

In order to obtain the permeation rate from the TAPT Type I device at the specified applied potentials, mass determinations were required before and after the analysis. Through trial and error, a time frame providing masses of >10mg were obtained. This minimum mass loss provided three significant figures from a four decimal place analytical balance. The power supply used provided both voltage and current readbacks that were recorded during the analyses. Using dimethyl phthalate, it was determined that as the applied power increased, the mass loss from the TAPT increased exponentially (Figure 3.3). This exponential increase can be accounted for using the Arrhenius equation, which describes permeation rate (P) as a function of the initial permeation rate (P_i) the activation energy for the permeation process (Ea) the ideal gas constant (R) and finally the temperature (T) (Equation 22).\(^\text{94}\)

Equation 22:

\[ P = P_i \cdot e^{\left(\frac{E_a}{RT}\right)} \]
Figure 3.3. Relationship between mass loss and applied power for the Type I thermally assisted permeation tube.

To study the reproducibility of the Type I TAPT, multiple devices were constructed and tested (Figure 3.4). It can be seen that although the devices were developed in a similar manner, there is a notable difference in the gas phase concentrations they emit. This suggests that assembling multiple devices to obtain similar concentrations is not currently feasible due to the inability to perfectly duplicate the construction of the membrane assemblies. Furthermore this suggests that individually calibrating each device is a necessity.
To test the extent of the linear mass loss range of the TAPT, a single device was mounted on a balance and measurements were taken at 10 minute intervals (Figure 3.5). Previous knowledge of PDMS permeation tubes (Chapter 2) provided evidence that the emission rate from the TAPT would contain a large linear portion. For this study, 2.5V (0.55 watts) were applied to a single device and a time lapse camera was used to record the resulting mass loss. To compensate for any drift in the balance, photos of the permeation tube mass were taken for about 90min both before and after the analysis to record balance stability. The results from this experiment provided evidence that a long linear emission period was achieved and that no recordable drift in the balance readings was observed (Figure 3.6).

**Figure 3.4.** Evaluation of emission reproducibility for 6 different Type I thermally assisted permeation tubes.
Figure 3.5. Type I thermally assisted permeation tube mounted on a balance for continual monitoring of mass loss during calibration.

Figure 3.6. Representative mass loss curve from balance mounted Type I thermally assisted permeation tube (Left). Linear calibration portion of the mass loss curve (Right). Applied Voltage: 2.5V (11.4Ω). Calculated dimethyl phthalate emission rate: 65.2µg/min.

By examining the representative mass loss curve, for the Type I TAPT (Figure 3.6), it is observed that the nonlinear portion of the emission curve is reduced when compared to the previously described, externally heated devices (Chapter 2). One explanation for this ‘extended’ linearity is to consider the phthalate volatilization process
occurring at the points where liquid phthalate are in contact with the resistively heated wire. Through the process of volatilization and condensation the membrane is likely being continuously coated with liquid phthalate, resulting in the observed decreased nonlinear mass loss portion.

Another explanation for the reduced nonlinear mass loss portion is to consider the ability for the wire to allow the liquid phthalate to ‘creep’ to other sections of the TAPT from capillary action, uniformly exposing the interior portion of the membrane to phthalate. To determine which of these processes is the dominant factor affecting the shape of the mass loss curve; a TAPT was placed within the 30°C water bath setup (Figure 2.1, Section 2.2.2) and was analyzed without applying any voltage (Figure 3.7).

**Figure 3.7.** Mass loss calibration curve for a heated (30°C) thermally assisted permeation tube with no voltage applied (Left) and the linear portion used for calibrating during analysis (Right). Calculated dimethyl phthalate emission rate: 2.28ug/min.

From examination of the mass loss curve obtained from the zero voltage experiment (Figure 3.7), evidence is provided which suggests that the presence of the internal wire, resistively heated or not, helps extend the linear emission region of the permeation tube when comparing it to the previously described ‘basic’ permeation tubes (Chapter 2). The direct result of this increased linearity, is a permeation tube which can
be used reproducibly for a longer period of time. When comparing the mass loss curve of the zero voltage TAPT to the similar dimensioned PDMS permeation tube (Figure 2.4, Section 2.3.1), it appears that the presence of the 3.0cm sections of 1/16” stainless steel tubes at both ends of the PDMS membrane, acting as reservoirs, also aids in extending the lifetime of the TAPT.

After determining the effects by which the physical properties of the TAPT has on permeation rate and how this was affected by the application of voltage, the next set of experiments was to determine whether the TAPT could be calibrated then refilled and reused over an indefinite period of time. To perform this experiment, a voltage of 2.5V (0.55watts) was selected and the entire mass loss curve was recorded as before (Figure 3.8, Table 3.1).

![Figure 3.8](image)

**Figure 3.8.** Drift in permeation rate after depleting, refilling with DMP and re-analyzing a single thermally assisted permeation tube multiple times. Applied voltage: 2.5V (0.55watts) (Resistivity: 11.2Ω)
Table 3.1: Compiled data from multiple DMP TAPT runs at 2.5V (0.55watts)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Average Permeation rate (ug/min)</th>
<th>% Difference from Initial*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.2</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>67.6</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>65.5</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>79.1</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>80.7</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>89.8</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>94.0</td>
<td>44</td>
</tr>
</tbody>
</table>

* %Difference = ((X - X_i)/X)*100%

Each data point was obtained by depleting, refilling then re-analyzing a single TAPT multiple times.

The result of this experiment demonstrated that the permeation rate remained relatively consistent for the first three trials (maximum of 4 % Difference), but by the final trial, the permeation rate had increased by 44% of the original rate (from 65.2ug/min to 94.0ug/min respectively). The results of this experiment demonstrated that the Type I TAPT could be used and refilled a maximum of three times reproducibly when operated at 2.5V, and that further analyses with the same tube would experience a change in performance. The likely explanation for this change in permeation rate is from PDMS thermal degradation, however other contributing factors may also exist. Future modification on the basic design of the TAPT may provide a device which is capable of being used for extended analysis times with multiple refills.

Although the idea of calibrating the TAPT Type I device and indefinitely using it is currently not possible, the TAPT can still be used as a device to obtain gas phase concentrations if the mass both before and after any given application is known. The current form of the device is still useful because it allows the user to heat the permeation tube as a function of applied electrical power, enabling high internal temperatures and therefore high permeation rates. Analysis of Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP) was performed to determine the applicability of the TAPT to other phthalate species (Figure 3.9, Table 3.2).
Figure 3.9. Permeation rates obtained from several thermally assisted membrane permeation tube using four different phthalates (DMP (10.8Ω), DEP (11.9Ω), DBP (10.9Ω), and DEHP (10.9Ω)).

Table 3.2: Watts and resulting emission rates obtained from applying the TAPT Type I to four phthalate species (DMP, DEP, DBP and DEHP)

<table>
<thead>
<tr>
<th></th>
<th>Dimethyl phthalate</th>
<th> </th>
<th>Diethyl phthalate</th>
<th> </th>
<th>Dibutyl phthalate</th>
<th> </th>
<th>Bis(2-ethylhexyl) phthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watts</td>
<td>0.37</td>
<td>0.825</td>
<td>0.575</td>
<td>0.84</td>
<td>1.12</td>
<td>1.5</td>
<td>0.575</td>
</tr>
<tr>
<td>Emission rate (ug/min)</td>
<td>26.7</td>
<td>1.155</td>
<td>2.78</td>
<td>1.085</td>
<td>0.495</td>
<td>10.6</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>0.5875</td>
<td>1.52</td>
<td>0.78</td>
<td>1.4</td>
<td>0.20</td>
<td>33.3</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>0.825</td>
<td>1.9575</td>
<td>0.78</td>
<td>1.755</td>
<td>93.3</td>
<td>1165</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>1.155</td>
<td>2.45</td>
<td>0.78</td>
<td>2.2</td>
<td>93.3</td>
<td>1085</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>1.52</td>
<td>2.97</td>
<td>1.12</td>
<td></td>
<td>0.113</td>
<td></td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>1.9575</td>
<td>4500</td>
<td>1.12</td>
<td></td>
<td>113</td>
<td></td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>2.45</td>
<td>6200</td>
<td>1.12</td>
<td></td>
<td>520</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All TAPT trials were performed at an ambient temperature of 30°C
A separate device was used for each analysis due to membrane failure at the higher voltages.
The resulting emission rates for each of the phthalates follow an expected trend where an increase in phthalate molecular weight results in a decreased phthalate emission.

Although the TAPT Type I device in its current form provides an inconsistent permeation rate over multiple refilling experiments (Figure 3.8), future developments of this device should be considered since it has demonstrated itself as being capable of rapidly generating different, stable phthalate concentrations by simply applying different DC potentials when hooked up to an online detector (MIMS, Chapter 5) (Figure 3.10 and 3.11 and Table 3.3).

![Graph](image)

**Figure 3.10.** Resulting MIMS signal trace obtained for the TAPT Type I device mounted in a gas dilution apparatus. (Resistivity: 11.2Ω).
Figure 3.11. Plot of averaged DMP permeation rates obtained from the MIMS/TAPT experiment. ( Resistivity: 11.2Ω)

Table 3.3: Data for Figures 3.10 and 3.11 showing the relationship between applied voltage (or power) and signal intensity (counts)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Voltage (Watts)</th>
<th>Resistivity (Ω)</th>
<th>Watts</th>
<th>Averaged Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>423-665</td>
<td>0.0</td>
<td>11.2</td>
<td>0.00</td>
<td>9029</td>
</tr>
<tr>
<td>877-1028</td>
<td>0.6</td>
<td>11.2</td>
<td>0.03</td>
<td>14952</td>
</tr>
<tr>
<td>1482-1603</td>
<td>0.8</td>
<td>11.2</td>
<td>0.06</td>
<td>29093</td>
</tr>
<tr>
<td>2026-2147</td>
<td>1.0</td>
<td>11.2</td>
<td>0.09</td>
<td>57961</td>
</tr>
<tr>
<td>2662-2783</td>
<td>1.2</td>
<td>11.2</td>
<td>0.13</td>
<td>124689</td>
</tr>
<tr>
<td>3448-3569</td>
<td>1.4</td>
<td>11.2</td>
<td>0.18</td>
<td>261989</td>
</tr>
</tbody>
</table>

TAPT device was mounted in the previously described water bath setup (30°C, 1.0LPM air, Section 2.2.2)

3.3.1.2 Thermally Assisted Permeation Tube Type II

After determining that the lifetime of the TAPT Type I device was somewhat limited (Section 2.3.2.1), an attempt to increase the analyte reservoir volume by changing membrane dimensions was evaluated. For the TAPT Type I, a 7.0cm (L) section of 1.47mm I.D. x 1.96mm O.D. PDMS membrane was used. To increase the
reservoir of the membrane, the Type II TAPT contained a 7.0cm section of 3.35mm I.D x 4.65mm O.D PDMS membrane. Other alterations from the Type I TAPT included the use of copper wire rather than stainless steel tubes, a solder-union to join the Nichrome resistive wire to the copper wire and finally glass “beads” melted around the copper, in a glass to metal seal, to act as electrically conductive sealing plugs (Figure 3.12). As with the previous device, the direct temperature of the permeation tube was not measured, and only the temperature of the fume hood was recorded (19°C).

![Diagram](image)

**Figure 3.12. Schematic of the Type II thermally assisted permeation tube.**

The goal for the Type II permeation tube was to have a device that would contain a large enough reservoir, that it could be calibrated, stored, and then used for multiple experiments thereafter. To obtain the mass loss curve generated by a Type II device, an experiment was conducted where 2.5V (1.2W) was continually applied to a device while it was mounted on a balance (Figure 3.13). The same device was then refilled and reanalyzed providing a similar shaped curve as the first (Figure 3.13).
3.1.3 Thermally Assisted Permeation Tube Type III

The third and final type of TAPT was developed and tested in an attempt to overcome the issues outlined with both the TAPT Type I and II devices. The TAPT Type III permeation device was developed as a scaled up version of the Type I device. Here 1/4" stainless steel tubing as well as 1/4" Swagelok fittings were used, permitting a drastically increased reservoir (Figure 3.14). Within this 1/4" reservoir ran the interior component of the Type I TAPT (the nichrome wire spot welded onto two stainless steel tubes with soldered electrical feeds) which served as the heating component for this device. Plugs for this device was also reused from the TAPT Type I device and consisted of 1/16" straight through Swagelok fittings with compression fitting plugs.
Having the 1/16” tubing feeding directly into the device through the 1/4” components was utilized for refilling the phthalate reservoir. Two membrane types were used with the Type III device, including both PDMS and PTFE.

![Diagram of Type III thermally assisted permeation tube.](image)

**Figure 3.14. Schematic for the Type III thermally assisted permeation tube.**

The initial experimentation with the Type III device involved the use of a 6.00mm I.D. x 7.00mm O.D. 5.0cm (length) PTFE membrane. Since PTFE is commonly regarded as both a thermally and chemically stable polymer it was believed that its incorporation into the TAPT series would potentially reduce any membrane degradation, which we speculate was occurring in the previous experimental work based on observation. Upon placement of the PTFE Type III device into the heated water bath setup (Figure 2.1, Section 2.2.2), it was quickly determined that the resulting emission rate from PTFE was notably lower than PDMS (~10 fold, 555ng/min) (Figure 3.15). This result was expected since PDMS is commonly considered to be a much more permeable polymer than PTFE.
Although PTFE appeared to be a desirable material, several problems arose when it was incorporated into the Type III design. The first problem was the difficulty in the original fabrication of the device, and specifically coaxing the membrane over the 1/4” stainless steel tubing of the device. This difficulty led to an incomplete seal which resulted in phthalate droplet formation on the bottom of device, leading to a mass loss curve not representative of the amount of phthalate actually being emitted. The second problem which arose was the unexpected pressure increase upon voltage application which resulted in leaking at the sealed Swagelok fittings. In an attempt to overcome this problem, a small glass capillary was placed in the upright fitting of the Type III device to allow for both a pressure release as well as a zone for increased phthalate emission. Unfortunately, this modification only led to problems of its own; the primary one being the rapid expulsion of phthalate through the capillary upon application of a voltage. With several problems quickly discovered with using PTFE as the Type III membrane material, re-examination of the PDMS membrane was performed.

Upon replacement of the PTFE membrane with PDMS, a higher permeation rate was obtained. Since previous experimentation with the Type I device showed irreproducibility at 2.5V, the Type III device was only tested with at voltages up to 2.0 (or 0.417W) (Figure 3.16).
Figure 3.16. Relationship between emission rate and applied power for the Type III thermally assisted permeation tube filled with dimethyl phthalate.

The emission rate from the Type III device appears to provide similar concentrations per applied power to the TAPT Type I device. These similar concentrations were predictable since the heating components of the Type III device were salvaged from the ones used in the Type I device. Although multiple replicate analyses were not performed with the Type III device, the amount of phthalate in its reservoir greatly exceeds that of the Type I device and therefore it is hopeful that the device could be calibrated then reused for extended periods without having to refill the phthalate reservoir.

3.4. Summary

In conclusion it was demonstrated that the modification of PDMS permeation tubes to incorporate a nichrome resistive wire provided a means for generating different concentrations of gaseous phthalates. Different configurations of these new devices, the thermally assisted permeation tube (TAPT) (Types I, II and III), were examined with the Type I being most capable based solely on the preliminary experimental work described herein.
The Type I device contained a smaller, thinner membrane than the other devices allowing it to be rapidly heated to higher temperatures (inferred by the elevated voltages applied). This advantage led to its further application to several other phthalates (DEP, DBP and DEHP), where it demonstrated the ability to elicit suitable emission rates for each (ug/min). Connecting the device to an online detector (MIMS, Chapter 5), showed the ability of this device to rapidly produce a broad range of stable DMP concentrations upon applying different DC potentials. Unfortunately, the major drawback to the Type I device, which led to the development of the Type II and III devices, was its inability to be used reproducibly for more than three replicate analyses.

Both the Type II and III devices were designed to have a larger inner diameter PDMS membrane than the Type I device. The theory behind the incorporation of the larger internal diameter of the membrane was to provide additional space between the heated nichrome wire and the membrane, removing any membrane-wire contact points. Another hypothesized advantage to having a wider membrane was that it would allow an individual permeation tube to contain a larger phthalate reservoir, extending the lifetime of the permeation tube. Unfortunately, the Type II device did not contain the same emission linearity as the Type I device and the Type III device became prone to leaking at higher applied potentials.

Regardless of the current problems with the TAPT devices, they, along with the previously described PDMS permeation tubes (Chapter 3), were suitable for generating different concentrations of gas phase phthalates. Permeation rates of DMP from the Type I and III PDMS devices ranged from 2.11-6200ug/min and 3.19-36.7ug/min respectively (voltage dependant).
Chapter 4. Particulate Matter

4.1. Introduction

Interest in phthalates in the scientific community not only revolves around gaseous phthalates but also the surfaces on which phthalates are adsorbed. Particulate matter is a major component of the air we breathe. An interesting research topic regarding particulate matter is the development of a technique that will reproducibly generate particulate matter of a known composition, surface morphology and size. Having such a set of particles could then be used to generate information such as heterogeneous and multi-phase particle chemistry, sequestration efficiency for compounds by particles, to particle-induced responses from lung cells. This chapter describes techniques used to obtain different particulate matter species, which were used along with the previously described gaseous phthalate standards to examine phthalate-particle interactions in the subsequent chapter.

4.2. Experimental

4.2.1. Carbon Particles

A continuous stream of gaseous carbon particles was generated using a custom built interface (Figure 4.1). Particles entering this interface were generated using a Meinhard ICP pneumatic nebulizer (part no. TR-50-AI). The nebulized solution was generated by diluting 100µL of India ink solution (Speedball Super Black) into 10mL of DI water then subsequently diluting 1mL of this solution into 10mL of DI water (1000X dilution total). The working solution was transferred into a 1000µL syringe then fed through the nebulizer at 1mL/hr using a syringe pump (Cole Parmer 74900 series). The gas flow feeding through the nebulizer was supplied by a compressed air cylinder.
(Praxair, Nanaimo, Medical Grade) and was delivered at 1.0LPM and 60psi. A rotameter (0-2.4LPM Air, Porter Instruments) was used to monitor/regulate the gas flow. Further details on the designing of this apparatus can be found in the results section of this Chapter (Section 4.3.1)

![Diagram](image)

**Figure 4.1.** Experimental setup for generating phthalate doped carbon particles from an India ink solution using a pneumatic nebulizer.

### 4.2.2. HPLC Column Particles

Particles used for MIMS adsorption/desorption experiments were obtained from an HPLC column (Supelcosil®) which contained 10µm diameter C18 coated silica particles. Particles were rinsed three times with about 20mL of deionized water, then 20mL of methanol and finally 20mL of hexane. After the final wash with hexane the
particles were then dried in air at room temperature in a loosely covered beaker prior to use. The washing stages were utilized to remove any aqueous or hydrophobic contaminants which may have been associated with the C18 coated silica particles prior to use (i.e. it was a previously used HPLC column).

4.2.3. House Dust

House dust was obtained by vacuuming the researcher’s house using a Dyson (Model DC40) bagless vacuum. The bulk component trapped within the canister was disposed of and only the finer portion which remained attached to the canister walls was gathered into a glass vial. No further refinement or filtering processes were used for this dust sample prior to subsequent experiments.

4.3. Results and Discussion

The ultimate goal from each of the outlined methods for obtaining particulate matter was to use these particles for experiments to investigate phthalate adsorption/desorption phenomenon (Section 5.3.3). The development of the carbon particle nebulizer setup is discussed below (Figure 4.1, Section 4.2.1). The HPLC particles and House Dust particles were used as described above. Results obtained for HPLC particle and the house dust phthalate adsorption/desorption experiments can be found in Chapter 5 (Section 5.3.3).

4.3.1. Carbon Particles

The goal for the development of the inline carbon particle generator was to create a setup which could reproducibly deliver carbon particles with adsorbed phthalates. In achieving such a goal it became apparent that the generation of particles needed to occur upstream and separately from the emission of gaseous phthalate. Since surface adsorption/desorption experiments was the goal, a setup which delivered both particles and phthalates in one step would result in particles which are internally mixed.
A two-step approach was therefore developed where carbon particles were generated, then passed through a second gaseous stream that contained the phthalate.

The initial formation of the carbon particles was accomplished using a Meinhard ICP nebulizer. An India Ink solution, in water, was nebulized to provide the carbon for the resulting carbon particles. Upon exiting the tip of the nebulizer the resulting aerosol was expanded into an ICP spray chamber where particularly large droplets settled and partial removal of water from the remaining particles occurred. Particles exited the spray chamber into a 3/8” stainless steel tube that was heated to 150°C. The additional heat provided during this stage was used in an attempt to remove water from the particles, ideally resulting in dry ‘carbon’ particles. As the now hot aerosol exited the 3/8” tubing it entered a long section of 1/4” tubing which was held at room temperature. Cooling the sample stream resulted in the condensation of the water vapour from the gas flow onto the inner surfaces of the tubing leaving a relatively dry particle stream. At the bottom of this long tube, a T-fitting was present which allowed the separation of the dry particles from the surface condensed water. As the surface condensed water built up it formed droplets which were removed when they fell through the partially submerged tube and into a beaker filled with water. The water filled beaker permitted back pressure to inhibit the escape of dry particles while permitting water to be removed. The resulting airborne particulates were subsequently exposed to gaseous phthalate in the remaining portion of the manifold before exiting it.

The application of gaseous phthalate onto the surface of the particles was accomplished using the TAPT Type I device. As previously discussed (Chapter 3, Section 3.3.1) this device seemed advantageous over a commercially available permeation tube since it was capable of providing high phthalate emission rates at room temperature (upto 6200ug/min for DMP at 3.0W). Two experimental setups could be used for adsorbing phthalates onto the particles while using this permeation device. First, the particles could be directly passed over the permeation tube, subjecting themselves to the emitting phthalates. Secondly, the particles could be mixed into a secondary gaseous flow which arose from the permeation tube. The second option was chosen for the adsorption experiment since it provided the user the option to calculate
an emission rate from the permeation tube without incorporating a possible bias from particles adhering to or contacting the permeation tube. Once both particle and phthalate streams were merged, the resulting combined flow exited the setup where it could then be further studied. Figure 4.2 shows a photograph of laser light scattering of the exiting particles from the aerosol generation device.

![Figure 4.2. Photo of 532nm light scattering off of particle stream exiting the particle generating/phthalate adsorbing setup.](image)

Although initial testing with the inline carbon particle generating device appeared promising, its ultimate application to adsorption-desorption experiments was limited. By suctioning the exiting particle stream over a 1.2µm glass microfiber filter (Whatman™) it was determined that little size fractioning of particle size was achieved. Visual inspection of the particles on the filter under a microscope, provided an estimate that the size distribution of particles exiting the device was over several orders of magnitude. Problems with the wide variation in particle size quickly became apparent when the goal was to relate a specific size fraction of particles to the concentration of phthalate it could either adsorb or desorb. Eventually an easier particulate matter surrogate of known dimensions and composition was chosen (the discussed 10µm HPLC column particles) and experimentation involving the carbon particulate matter generator setup was discontinued.
4.4. Summary

The results of this section provided three different particulate matter surrogates or mimics (Carbon particles, C18 coated silica particles and house dust) that can be used to examine phthalate-particle interactions. The majority of development went into generating the carbon particles, as the C18 coated silica particles were simply obtained from an HPLC column and the house dust was obtained from a bag less vacuum cleaner. The problem associated with the carbon based particles was the inability to control the range in particle size, which led to the utilization of the 10µm C18 coated silica particles during the majority of the phthalate-particle experiments (Chapter 5).
Chapter 5. Membrane Introduction Mass Spectrometry

5.1. Introduction

The use of a semipermeable membrane as a sample introduction inlet of a mass spectrometer is advantageous in that it semi selectively removes components from the bulk gas or liquid phase prior to measurement by the mass spectrometer. By serving as a barrier to the bulk sample flow, high vacuum conditions can be maintained within the mass spectrometer, which increases analyte sensitivity and is essential to the functioning of the instrument. MIMS has previously been proved to be a useful detection system for rapidly obtaining information in an online manner. The on-line measurements provided by MIMS are particularly advantageous for examining changing concentrations and chemical kinetics, including reaction monitoring or adsorption/desorption behavior. An overview of MIMS and the processes which are involved in analyte detection have previously been discussed (Chapter 1, Section 1.4.1).

5.2. Experimental

5.2.1. Membrane

A single PDMS membrane (Silastic brand; Dow Corning, Midland, MI, 1.47mm I.D x 1.96mm x 10.0cm (length)) was used for all studies presented. Both the bulk of information as well as duration that an individual membrane can be used for is in itself a testament to the durability and versatility of PDMS membrane MIMS.
5.2.2. Membrane Housing Interface

A flow cell style MIMS interface was used as the housing for the hollow fiber membrane. This housing consisted of 1/4" tubes, two 1/4" Swagelok tee fittings and two~1/16" hypodermic stainless steel (SS) tubes with which the PDMS hollow fiber membrane was wire wrapped on to (Figure 5.1).

The ends of the hypodermic tubes were either connected to a helium line or to a line feeding into the mass spectrometer using 1/16" SS Swagelok fittings and Graphite/Vespel Ferrules (to ensure a gas tight seal) (Restek Chromatographic Specialties, Brockville, ON, Canada). Ferrules were hand drilled to snugly fit the small SS tubes. The entire MIMS housing was contained within a GC oven (GC-Q; Thermo- Electron, San Jose, CA) which both controlled the temperature of the housing (30-150°C) as well as the countercurrent acceptor phase helium flow (~1mL/min) supplied through the MIMS membrane and into the mass spectrometer.

5.2.3. Gas Phase Phthalates

The standards used for generating gas phase phthalates consisted of PDMS permeation tubes (Chapter 2 and Chapter 3). Typically the unmodified (non ‘thermally assisted’), extended reservoir, PDMS permeation tubes were used (Chapter 2) and different concentrations were achieved depending on the length of the PDMS membrane (all permeation tube temperatures were 30°C). All adsorption and desorption studies were performed using the exact same permeation tube that consisted of a short PDMS
membrane with an extended phthalate reservoir (Figure 2.6, Section 2.3.1). Dimethyl phthalate was used for all MIMS experiments involving method development. Details of the method used for generating gaseous phthalate and its subsequent dilution are described in Chapter 2, Section 2.3.

5.2.4. **Mass Spectrometer**

A Saturn II quadrupole ion trap (Varian, Walnut Creek, CA) equipped with internal ionization (*e.g.* directly within the ion storage volume) was used as the mass spectrometer. The mass scan parameters used for the analyses are as follows:

- **Mass Range:** 50-300m/z
- **Scan Time:** 1.210s (average of 6 µScans)
- **Ion mode:** EI
- **Ion control:** Auto
- **Max Ionization Time:** 25msec
- **EM Voltage:** 1150V
- **Helium:** 1.0mL/min at 25PSI
- **Base Pressure:** ~1x10⁻⁵Torr
- **Rough Pump Pressure:** ~1x10⁻²Torr
- **Manifold Temperature:** 80°C
- **Transfer Line Temperature:** 150°C

5.3. **Results and Discussion**

Dimethyl phthalate was used in order to evaluate suitable Membrane Introduction Mass Spectrometry (MIMS) interface conditions for the analysis of gaseous phthalates. The following results explain the development of the MIMS conditions and the modifications necessary to permit the successful online analysis of DMP. The ultimate goal was to construct an experimental system that was sensitive for the detection of gaseous phthalates and also suitable for monitoring the interactions between gas phase phthalates and particulate matter (Section 5.3.3.2).
5.3.1. MIMS Development

Previous studies involving the analysis of semi volatile organic compounds (SVOCs) using MIMS with a gaseous acceptor phase demonstrated the requirement of heating the membrane in order to obtain a signal (See Chapter 1 Section 1.4.1). In anticipation of a heating requirement, the entire MIMS interface was assembled and mounted in a GC oven (Figure 5.2). Through experimentation, it was determined that heating the MIMS interface to 150°C was suitable to obtain a measureable DMP signal (Figure 5.3). Throughout the following experiments, gaseous phthalates were supplied through the previously described PDMS permeation tube setup (Figure 2.1, Section 2.2.2).

![Figure 5.2. Initial housing of the MIMS assembly directly within a gas chromatography oven. A: Sample inlet, B: Sample outlet, C: MIMS interface, D: Helium gas flow, E: Flow of helium and permeable analytes towards the mass spectrometer.](image-url)
Figure 5.3. Demonstration of the increased sensitivity for the MIMS system after heating the MIMS membrane from 30°C to 150°C. The gaseous flow feeding into the MIMS interface was maintained at 30°C throughout all portions of the experiment.

Upon determining that 150°C was a suitable MIMS interface temperature for conducting experiments to continuously obtain DMP signals, the next experiment was to determine the rise time and resulting signal intensity that this setup generated (Figure 5.4). It was determined that a steady state signal was obtained after 170 seconds which provided a signal of about 110,000 a.u. at 460 ppbv DMP. The rise time to go between T_{10-90%} was approximately 100 seconds. This experiment demonstrated that the overall experimental apparatus demonstrated a reasonable response time and a good sensitivity to DMP.
As is the goal with most analytical approaches, high sensitivity coupled with a quick response time is desirable. Since one of the end uses of this approach was to monitor the rate of adsorption and desorption of low concentrations of phthalates from particles, both of these requirements were particularly important. Furthermore determining the detection limits of this setup would also prove valuable should this technique be applied to a mobile MIMS system which could be used to monitor both low and high concentrations of phthalates in households and other indoor environments.

After successfully measuring a single concentration of DMP, a calibration curve was generated in which several concentrations of DMP were examined (Figure 5.5). The process used for this experiment included an additional, secondary, rotameter which could be adjusted to deliver different amounts of diluent air (0-1.4LPM) (Figure 5.6). With the addition of the secondary gas flow, a calibration curve was formed by altering the flow of the secondary gas in increments of 0.2LPM. The resulting flows into the mass spectrometer were 2.0, 1.8, 1.6, 1.4, 1.2 and 1.0LPM total respectively (Table 5.1). Since the emission rate from the permeation tube was known, signal intensities could be averaged at each step and then plotted against their concentration resulting in a linear calibration curve (Figure 5.7).
Figure 5.5. Signal response for different concentrations of gaseous phthalate used to calibrate the MIMS instrument. Concentrations represent 0.2LPM decreases in total diluent air flow starting at 2.0LPM (230ppbv) and ending at 1.0LPM (460ppbv).

Table 5.1: Flow rates, concentrations and times used for generating Figures 5.5 and 5.7

<table>
<thead>
<tr>
<th>Dilution flow</th>
<th>Sample flow</th>
<th>Final concentration (ppbv)</th>
<th>Average Counts</th>
<th>Time (s)</th>
</tr>
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<td>4.6</td>
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<td>1.0</td>
<td>1.0</td>
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<td>24922</td>
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<td>33901</td>
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<td>289.01</td>
<td>48965</td>
<td>1189 - 1370</td>
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<td>1.0</td>
<td>330.29</td>
<td>69520</td>
<td>1451 - 1696</td>
</tr>
<tr>
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<td>1.0</td>
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</table>

Concentration of gaseous DMP delivered from the PDMS permeation tube (aka Sample flow) was 460ppbv at 30°C.
Figure 5.6. Schematic diagram of the apparatus used to supply two gas flows (primary and diluent) required to prepare different concentrations of gaseous phthalate for calibrating the MIMS system.

Figure 5.7. Calibration curve generated by diluting 460ppbv DMP with air.

\[ y = 525.27x - 100462 \]
\[ R^2 = 0.9964 \]
5.3.2. Application of a Heat Exchanger

Although the MIMS system presented above achieves relatively linear calibration for DMP at low flow rates, problems with linearity at high gas flow rates were considered to be potentially problematic. Since the path between where the sample first enters the GC oven to where it flows over the MIMS membrane is relatively short there is the potential for inadequate heating of the incoming air stream. This would result in membrane cooling, becoming problematic when analyzing SVOCs since it would reduce the dynamic range of the calibration curve, and also result in a poor response time and reduced analyte sensitivity. High flow rates (up to 10LPM), are anticipated when applying this interface to the analysis of particle bound phthalates, since higher concentrations of phthalates are expected to be associated with surfaces over the gas phase (Chapter 1, Section 1.2.2).

Problems associated with inconsistent gas flow temperatures and membrane cooling can be overcome by using a heat exchanger upstream of the MIMS interface. A preliminary heat exchanger design was constructed that incorporated a 3.0’ (L) coiled 1/4” (O.D) stainless steel tube between the inlet to the GC oven and the MIMS membrane (Figure 5.8). Results from this preliminary heat exchanger were initially poor, and demonstrated a very slow signal response ($T_{10-90\%} > 2000$ seconds) at a flow rate of 2.0LPM (Figure 5.9).
Figure 5.8. Modified MIMS setup. A: MIMS membrane housing, B: a 3.0’ (L) 1/4” (O.D) coiled heat exchanger.
Figure 5.9. Slow MIMS signal response for the initial modified heat exchanger device.

The undesirable effect which occurred upon addition of the three feet of stainless steel tubing was either a result of the increase in dead volume within the system or an increase in surfaces present for the phthalates to adsorb onto. To determine if a reduction in dead volume would solve the issue, the heat exchanger was filled with 3mm stainless steel ball bearings. Filling the 1/4" tube reduced the rise time, providing a rise time similar to what was previously seen without the heat exchange loop (Figure 5.10).
After incorporating the improved heat exchanger, the resulting rise time $T_{10-90\%}$ was determined to be 110s which is similar to that of the setup which did not contain the heat exchange loop (100s, Figure 5.4). With this new design, a calibration curve was generated and the resulting curve showed good linearity (Table 5.2 and Figures 5.11 and 5.12 respectively).
Figure 5.11. Analytical signals for DMP at different concentrations used for generating a calibration curve for the MIMS setup with the modified heat exchanger.

Table 5.2: Flow rates, concentrations and times used for generating Figures 5.11 and 5.12

<table>
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<th>Time (s)</th>
</tr>
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<td>18666</td>
<td>919-988</td>
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<tr>
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<td>460.00</td>
<td>30759</td>
<td>1127-1211</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0</td>
<td>0.00</td>
<td>/</td>
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</tr>
</tbody>
</table>

Concentration of gaseous DMP delivered from the PDMS permeation tube (aka Sample flow) was 460ppbv at 30°C.
After generating a calibration curve, the detection limit of the overall system was evaluated. Determining the instrument sensitivity is important since the goal of the instrument is to monitor kinetic rate losses of phthalates from surfaces and therefore the sensitivity in part will determine how much data is supplied in the rate loss curve. The sensitivity of the developed instrumentation was assessed by passing a 3.0LPM gaseous flow of 23.7ppbv DMP through the setup and into the mass spectrometer (Figure 5.13). To minimize the noise, a five point moving boxcar was applied to the resulting data set which provided a chromatogram with a well-defined signal above the baseline. The resulting signal (S) to noise (N) ratio ($\bar{x}/\sigma$) for the modified plot was 11, well above what is typically accepted as a detected signal (S/N = 3). From these results, an estimated detection limit of 6.5ppbv (S/N = 3) is expected.
5.3.3. Particle-Phthalate Interactions

Once an instrument was developed which could monitor trace level gaseous concentrations of DMP with reasonable sensitivity and response time, the next step was to use this instrument for particle-phthalate interaction experiments. The initial goal of these experiments was to determine a suitable method that could be used to quantify the concentration of phthalate associated with particles. Once the amount of phthalate adsorbed onto particles could be quantified, desorption experiments were performed to measure the rate of phthalate loss from the particles in a continuous, online manner.
5.3.3.1 Phthalate Adsorption/Desorption Instrumentation

The previously described MIMS interface allowed for the detection of a wide range of gaseous phthalate concentrations (Section 5.3.2). Only slight modifications to this interface were required to enable the application of this interface for particle adsorption/desorption experiments. Modifications such as the placement of a particle support filter inline in the sample stream as well as a pump, post GC oven, to pull rather than push air were added (Figure 5.14). Pulling the air through the setup allowed for the dilution flow rotameter upstream of the filter to be maintained at ambient pressures. Since these rotameters were calibrated at 1.0atm, it was important to maintain a pressure similar to this during their use. Several filters were evaluated, and eventually a 1/4” diameter sintered 5µm stainless steel in-line filter (Parker Cat. No. 4A-F4L-5-SS) was found to be the most suitable for the adsorption/desorption experiments. This conclusion was made after observing that this filter housing adsorbed the least amount of phthalates onto its surfaces which is likely the result of this filter and associated housing having the least surface area for phthalate adsorption (Figure 5.14 for an example comparison between the LS25 Filter Holder (Advantec, Dublin, CA) equipped with a 2.5µm silver membrane filter and the 1/4” 5µm stainless steel Parker A-lok sintered filter (Parker, North Jacksonville, AL).
Figure 5.14. Schematic diagram of the experimental apparatus for DMP measurement and particle adsorption/desorption experiments.
5.3.3.2 Phthalate Adsorption/Desorption C18 Particles

After implementing the modified experimental setup, phthalate-particle adsorption/desorption experiments were performed. Initial experiments were conducted by flowing a known concentration of gaseous phthalate through a three way valve and into the MIMS system. The initial flow of gaseous phthalates into the system provided a steady state signal of known concentration which could be used to monitor the progress of phthalate adsorption when loading the filter and associated particulate matter. This process was also useful in that it pre-coated the inner surfaces of the tubing leading into the MIMS system, eliminating their contribution to the particle adsorption process upon switching the three way valve to the filter. Once the signal for the gaseous phthalate reached a steady state, the three way valve was activated so that gaseous phthalate would flow over and adsorb onto the filter. The resulting signal from this entire process was the formation of a steady state signal for gas phase DMP and then the re-
establishment of the steady state signal at the same level when all surfaces on the filter were occupied (Figure 5.16).

Figure 5.16. Resulting signal for gaseous dimethyl phthalate entering the MIMS setup before, during and after filter adsorption. The adsorption profile for DMP onto the filter surfaces can be seen by the dip in signal at 915s and the re-establishment of the steady state signal at max adsorption (~1800s).

After the re-establishment of this state signal, the filter was then heated using a heat rope (Omega FGR-030) to thermally desorb the phthalate from the filter, providing a desorption peak. Since the filter setup was connected to the MIMS, the time at which surface saturation occurred was easily determined since the signal plateaued at this point. Results from the initial experiments demonstrated that phthalate desorption by heating the filter was possible, and after several attempts and filter types, a relatively narrow desorption peak was obtained (Figure 5.17).
Figure 5.17. Results of thermal desorption experiment where the filter housing was heated after becoming saturated with gaseous dimethyl phthalate. Concentration: 97.4 ppbv DMP @ 2.0 LPM total flow. Filter: Advantec 25mm with 2.5 µm silver membrane.

Although thermally desorbing phthalates from the filter housing was successful, several problems with this experiment were inherently present. One major problem, which can be observed from the thermal desorption signal, is the particularly large phthalate peak which was obtained after heating the filter housing. To minimize this large desorption peak, several filter housings were experimented with. Eventually it was determined that regardless of which filter housing was used, the large surface area provided by the filter and housing would continually produce a large phthalate desorption peak. Problems with quantifying the amount of adsorption attributed to the particles versus the filter were anticipated, since the resulting signal ‘peak’ would be large for the filter and only marginally larger for the filter+phthalate, and therefore it was determined that a different approach to quantifying phthalate adsorption was required.

Through the initial filter loading experiment, it was predicted that the amount of time it took for the phthalate signal to re-reach a steady state concentration after beginning to load the filter would be proportional to the amount of phthalate adsorbed onto the surfaces of the filter. Using this knowledge, a second experiment was designed. Instead of heating the filter to desorb the phthalates, the ‘loading time’ of the phthalates
was examined (Figure 5.18). From this experiment, an equation was derived where the amount of phthalate adsorbed could be determined by multiplying the concentration of phthalate supplied over unit time by the ratio of the signal intensity at a given point. The total mass at each of these points was then added together providing the total mass of phthalate adsorbed (Equation 23).

Equation 23:

$$\text{Mass Adsorbed} = \left( \frac{\text{Total Time Loading} \times 7.1 \text{ ng/sec}}{\text{sec}} \right) \sum \left( \frac{\text{Signal}_i}{\text{Signal}_{\text{max avg}}} \times 7.1 \text{ ng/sec} \times (\text{Time}_{x+} - \text{Time}_x) \right)$$

Where; $\text{Signal}_{\text{avg}}/\text{Signal}_{\text{max avg}}$ refers to the ratio of the signal at any given time interval (Signal$_i$) versus its hypothetical maximum (if adsorption were not occurring) (Signal$_{\text{max avg}}$), $\text{Time}_{x+} - \text{Time}_x$ refers to the discrete time at Signal$_i$ and finally 7.1ng/sec was obtained by converting the phthalate loading flow from the permeation device and manifold into units of mass per second.

Figure 5.18. Phthalate-particle loading experiment showing the portion quantified as the shaded area within the box.
After obtaining a suitable method for quantifying the mass of phthalate adsorbed by the filter, experiments involving particles deposited on the filter were performed. Replicate analyses were obtained for three phthalate adsorption experiments, the filter blank, 1.67mg of 10μm C18 HPLC particles, and 3.74mg of 10μm C18 HPLC particles (Figure 5.19). Since the instrument began to lose relative sensitivity from a failing electron multiplier, the data were normalized so they could be plotted on the same y-axes.
After determining the amount of phthalate adsorbed for each of the masses of C18 particles, a relatively linear relationship was observed between the particle mass on the filter and quantity of phthalate adsorbed (Figure 5.20, $R^2 = 0.9688$).

**Figure 5.19.** Normalized data resulting from filter loading experiments using 10µm C18 coated silica particles.
5.3.3.3 Phthalate Adsorption/Desorption from House Dust

After demonstrating that the designed MIMS interface could be applied to measurements of phthalate adsorption on particles of known size and composition, the next goal was to determine whether the technique would be suitable for “real world particle” samples. House dust was chosen as a “real world” sample since it has previously been shown to concentrate phthalates (Chapter 1, Section 1.2.3). House dust was obtained for this experiment by vacuuming in a private residence, then selecting a ‘fine fraction’ of dust from the vacuum canister (Chapter 4, Section 4.2.3). The desired amount of dust was then added onto the filter by drawing air through the filter using a diaphragm pump (GAST Manufacturing Inc., Benton Harbor, Michigan, U.S.A. Model: DOA-P704-AA), resulting in a dust fraction of >5µm being retained. Following the experimental procedure as developed using C18 particles, adsorption/desorption experiments were performed using different masses of house dust (0, 1.86mg, 5.23mg) (Figure 5.21). After determining the mass of phthalate adsorbed per mass unit dust, a similar linear relationship ($R^2 = 0.9996$) was observed where the mass of phthalate adsorbed increased with the increasing amount of dust (Figure 5.22).
Figure 5.21. Normalized data from filter loading experiments using house dust.
Figure 5.22. Results of three adsorption experiments using different masses of house dust.

Although the house dust followed a similar linear trend as the C18 particles, the relationship between the mass of the dust present and the amount of phthalate adsorbed was notably lower than observed with the model C18 particles. A notable side discovery was that the corresponding blank adsorbed a lower amount of phthalate than had been observed using the C18 particles (1.24µg and 1.54µg respectively). This change in filter blank loading corresponded primarily to the higher temperature the filter was maintained at (30-31°C) during the dust analysis versus the C18 filter analysis (27°C). The effect of different temperatures upon the adsorption process can be described by the Arrhenius equation. This equation (see Equation 22), in simple terms, describes temperature effecting adsorption in an exponential manner. Since all analyses involving the filter housing and dust were performed on the same day under the same conditions, the associated error between individual experiments was minimal.

5.3.3.4 Phthalate/Particle Constants and Coefficients

Once the quantity of phthalates adsorbed onto either particles or house dust was known, constants or partition coefficients involving the relationship between phthalate
and particle interactions could be determined. This section outlines the examination of two of these terms; the rate constant governing loss of phthalate from particle \( (k_{LS}) \) and the phthalate/particle adsorption partition coefficient \( (K_p) \).

The rate of loss of phthalate from particles \( (k_{LS}) \) can be determined by examining the amount of time in which it takes for the concentration of phthalate associated with the particle to go from fully saturated to fully desorbed (Figure 5.23).

![Figure 5.23. Adsorption/desorption experiment highlighting the boxed region used to calculate the rate loss constant \( k_{LS} \).](image)

Converting the signal of phthalate into mass (ng), then taking the natural logarithm of this mass and plotting it against time, the pseudo first order rate constant \( (k_{LS}) \) for loss of phthalate from surfaces can be determined (Figure 5.24). The rate loss constant \( (k_{LM}) \) of phthalate from the housing surfaces/membrane can also be roughly determined from these signals by examining the degree in signal loss immediately following the switching of the three way valve to the filter (Figure 5.25 and Figure 5.26). Here it is assumed that all incoming gaseous phthalates are adsorbed onto the unoccupied surfaces of the filter resulting in a ‘zero’ gaseous phthalate concentration being exposed to the membrane.
Figure 5.24. Natural logarithm plot for determining the first order rate loss constant for DMP desorption from the filter. Data covers signal over $T_{90-10\%}$ (Where the slope = $k_{LS}$)

\[ y = -0.00427x + 15.08451 \]
\[ R^2 = 0.9604 \]

Figure 5.25. Adsorption/desorption experiment highlighting the section used to calculate the rate loss constant $k_{LM}$. 

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Figure 5.26. Natural logarithm plot for determining the first order rate loss constant for DMP from the membrane and housing. Data covers signal over T_{90-10%}. (Where the slope = k_{LM})

Using this method, the rate of mass loss of phthalate from the filter, the C18 coated particles and the house dust was determined (Table 5.1). As can be seen from the data, as the amount of surface increases (e.g.: the quantity of dust or C18 coated particles) the rate of desorption decreases.

Table 5.3: Desorption rate constants (k_{LS} and k_{LM}) of DMP from surfaces

<table>
<thead>
<tr>
<th>Surface Description</th>
<th>k_{LS} (s^{-1})</th>
<th>σ</th>
<th>k_{LM} (s^{-1})</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter (27°C)^a</td>
<td>0.0048</td>
<td>0.0005</td>
<td>0.035</td>
<td>0.001</td>
</tr>
<tr>
<td>1.67mg C18^a</td>
<td>0.0037</td>
<td>0.0004</td>
<td>0.030</td>
<td>0.002</td>
</tr>
<tr>
<td>3.77mg C18^a</td>
<td>0.0024</td>
<td>0.0002</td>
<td>0.027</td>
<td>0.001</td>
</tr>
<tr>
<td>Filter (30°C)^b</td>
<td>0.0084</td>
<td>NA</td>
<td>0.029</td>
<td>NA</td>
</tr>
<tr>
<td>1.86mg House dust^b</td>
<td>0.0077</td>
<td>NA</td>
<td>0.031</td>
<td>NA</td>
</tr>
<tr>
<td>5.23mg House dust^b</td>
<td>0.0068</td>
<td>NA</td>
<td>0.024</td>
<td>NA</td>
</tr>
</tbody>
</table>

^a Series of experiments conducted at 27°C
^b Series of experiments conducted at 30°C

After determining the rate constant for phthalate loss from the mentioned surfaces and particles another environmentally relevant term, the phthalate-particle partition coefficient (K_{p}), was examined (Chapter 1, Section 1.2.2.1). The Phthalate-
particle partition coefficient can be determined in this case since the equilibrium particle phase concentration of the compound (F) (ng/m$^3$), the gas phase concentration of the compound (c$^g$) (ng/m$^3$), and the total mass of particulates (TSP) (ug/m$^3$) were known (Equation 3). As can be expected from comparing the mass of phthalate adsorbed per particle type, the C18 coated particles contained a higher K$^p$ than the house dust per unit mass (Table 5.4).

Table 5.4: Determining the DMP K$^p$ for different masses of particles

<table>
<thead>
<tr>
<th></th>
<th>F (ng/m$^3$)</th>
<th>c$^g$ (ng/m$^3$)</th>
<th>TSP (ug/m$^3$)</th>
<th>K$^p$ (m$^3$/ug)</th>
<th>Average K$^p$ (m$^3$/ug)$^c$</th>
<th>K$^p$ (m$^3$/ug)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter$^a$</td>
<td>1550</td>
<td>1.38x10$^6$</td>
<td>0</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.67mg C18$^a$</td>
<td>940</td>
<td>1.38x10$^6$</td>
<td>1640</td>
<td>4.15x10$^7$</td>
<td><strong>5.3x10$^7</strong>**</td>
<td>6.0x10$^{-5}$</td>
</tr>
<tr>
<td>3.74mg C18$^a$</td>
<td>3340</td>
<td>1.38x10$^6$</td>
<td>3740</td>
<td>6.47x10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter$^b$</td>
<td>1240</td>
<td>1.38x10$^6$</td>
<td>0</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.96mg House dust$^b$</td>
<td>290</td>
<td>1.38x10$^6$</td>
<td>1960</td>
<td>1.07x10$^7$</td>
<td><strong>1.1x10$^7</strong>**</td>
<td>6.0x10$^{-5}$</td>
</tr>
<tr>
<td>5.33mg House dust$^b$</td>
<td>830</td>
<td>1.38x10$^6$</td>
<td>5330</td>
<td>1.13x10$^7$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Series of experiments conducted under 27°C
$^b$ Series of experiments conducted under 30°C
$^c$ Value = (Filter + particle value) - Filter value
$^d$ Literature value for Dimethyl phthalate based on K$_{OA}$ (25°C)$^{27}$

Comparing the values obtained here against predetermined literature approximations (based on saturated vapor pressure and K$_{OA}$ values), shows an apparent discrepancy (Table 5.2). The K$^p$ values determined here show a consistency within an order of magnitude, differing by about 2 orders of magnitude from the literature.$^{27}$ Most of the literature uses these two estimations for determining K$^p$ values$^{27, 96, 97}$ which are primarily based off of equations derived for PAHs.$^{98, 99}$ Furthermore the literature values were calculated for 25°C while the experiments here were performed at 30°C. Because of these factors, comparisons between the values obtained here to experimentally derived DMP K$^p$ values were difficult.
5.3.3.5 Thermal Desorption of Species from House Dust

A final experiment which was performed, was to determine whether a collected house dust sample could be directly analyzed for phthalates using the MIMS system developed for this thesis. In this experiment, a subsample of the already collected house dust (Chapter 4, Section 4.2.3) was loaded onto the filter as previously described. After placing the dust onto the filter, the filter was then connected upstream of the MIMS membrane and wrapped in heating rope (following the design of the thermal desorption experiments Section 5.3.3.2).

To thermally desorb associated compounds from the house dust, the dust was rapidly heated to 240°C (Figure 5.27). Any compounds which were desorbed by this process were subsequently carried towards the MIMS system at a flow rate of 2.0LPM. The resulting information obtained from this experiment provided evidence that phthalates were likely associated with the dust, since the characteristic 149m/z and 163m/z fragmentations were observed in the resulting mass chromatograms (Figure 5.27, Figure 5.28) (for the fragmentation pathway see Chapter 1, Section 1.6.2.1). Further examination of these mass chromatograms provides evidence consistent with that of the physical properties of phthalates where the smaller, lighter DMP (represented by 163m/z) peaked first while the peak consistent with all heavier phthalates (149m/z) occurred later. Further verification of the compounds leaving the dust and potential contamination from the vacuum cleaner and other sources was not accounted for and therefore these observations are only speculation.

Unfortunately many compounds were desorbed simultaneously from the dust and therefore the resulting mass spectra were complex (Figure 5.29 and Figure 5.30 at example times 550s and 750s respectively). The simplified interpretation of the spectra is that there are alkyl hydrocarbon fingerprints present in the sample (repeating mass loss peaks of 14).\textsuperscript{85}
Figure 5.27. Total ion current (TIC) signal observed from rapidly heating the filter loaded with house dust to 240°C at 2.0LPM air flow.

Figure 5.28. SIM of 149 and 163m/z obtained from rapidly heating the filter loaded with house dust to 240°C. 163m/z is characteristic of DMP, 149m/z is characteristic of all other phthalates.
Figure 5.29.  Mass spectrum at 550s showing a prominent 163m/z peak among the noise.

Figure 5.30.  Mass spectrum at 750s showing the complex spectrum suggesting alkyl hydrocarbons.
5.3.4. Summary

The results of this section conclude that a MIMS system suitable for monitoring dimethyl phthalate was developed. This system was not tested with other phthalates directly but is assumed to be suitable for their analysis as well (should an appropriate gas phase standard be available). Further application of the developed MIMS system was applied to the monitoring of phthalate-particle interactions for C18 coated 10µm silica particles and house dust allowing the phthalate/particle adsorption coefficient \( (K_p) \) to be determined \((5.31 \times 10^{-7} \text{ and } 1.10 \times 10^{-7} \text{ respectively})\). During these same experiments, the rate of phthalate loss from the membrane housing \((k_{LM})\) and particles/surfaces \((k_{LS})\) were also monitored showing a 10 fold faster desorption rate from the membrane than the particles/surfaces.

The final experiment which was examined using the developed MIMS system was to thermally desorb compounds from a subsample of house dust. Here, the MIMS system proved capable of monitoring peaks which are characteristic of phthalates \((163m/z \text{ and } 149m/z)\), however many compounds were desorbed simultaneously and therefore the resulting mass spectra were complex.
Chapter 6. Conclusions

The results of this research indicate that a suitable technique has been developed for generating gaseous dimethyl phthalate, measuring gaseous dimethyl phthalate using MIMS and creating airborne particulate matter. The ultimate goal for this research was to develop a method which could be used to monitor the relationship between gaseous phthalates and airborne particulate matter. The success of this research was demonstrated by the ability to; quantify the mass of dimethyl phthalate which could be adsorbed onto two different particle surfaces (C18 coated particles and house dust), determine the desorption constant ($k_{LS}$) of dimethyl phthalate from the particle surfaces and finally to quantify the air-particle partition coefficient $K_p$ for this system.

6.1. Future Directions

6.1.1. Generation of Gaseous Phthalates

The development of reliable gaseous phthalate standards will continue to be of importance for as long as phthalates are considered problematic. Through this research the development of two classes of permeation tubes were experimented with, externally heated permeation tubes and internally heated permeation tubes. A reliable method was developed for generating externally heated permeation tubes and with these devices, multiple gaseous concentrations of dimethyl phthalate were achieved. Problems with the externally heated permeation tubes only occurred with phthalates of higher molecular weight than dimethyl phthalate were examined. The internally heated permeation tubes (aka the Thermally Assisted Permeation Tubes, TAPT), overcame this problem, and using these devices, concentrations of gaseous phthalates were obtained for the higher molecular weight phthalates. Unfortunately with the TAPT permeation
tubes, membrane degradation appeared to inhibit the long-term reproducible generation of gaseous phthalates, and therefore the devices could only be used and reused for a maximum of three phthalate refills before their reproducibility was compromised. Future research in this area could include; examining membrane polymers other than PDMS which are more temperature resistant, different designs of the permeation tube which may provide less thermal strain on the tube membrane and finally the possibility of generating gas phase standards using techniques other than permeation tubes such as diffusion vials, flash vaporizers or nebulizer systems. Non-permeation tube based techniques may overcome the problems observed here, particularly problems which were associated with the membrane material.

Future research in this area could also be to apply both these permeation tube types to chemicals other than phthalates. For example, if compounds other than SVOCs were used within the internally heated permeation tube, high temperatures would be avoided, possibly solving the current problems with the device.

6.1.2. Particulate Matter Generation

Minimal research was performed on generating airborne particulate matter which was in part due to the inability to properly characterize the formed particulate stream. Future research in this section could be to characterize the airborne particles generated as well as quantify the amount of phthalate which is actually being adsorbed onto the particles. If the interface proved to be efficient at reproducibly generating phthalate coated particles then it could be applied to numerous studies, both involving phthalates or other compound/particle systems (such as diesel exhaust, wood smoke etc.).

6.1.3. Membrane Introduction Mass Spectrometry

The developed MIMS system and sampling interface proved to be suitable for monitoring different concentrations of gaseous dimethyl phthalate as well as for monitoring phthalate interactions with particulate matter. Future experiments involving MIMS could be to use the developed interface for other phthalates, as well as to extend the application of this interface outside of the phthalate realm and look at other SVOC-
particle systems (such as polyaromatic hydrocarbons and soot). Modifications to the basic MIMS system, such as the ones described here, may also be useful in mobilizing a mass spectrometer system so that it could be taken outside the lab and into the field, where it could provide valuable information, such as contaminant concentrations directly in the household environment.
References


23. Paschke, A.; Neitzel, P. L.; Walther, W.; Schüürmann, G., Octanol/water partition coefficient of selected herbicides: Determination using shake-flask method and


