

UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES  
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9 JUNE 2004

APPROVAL SHEET

Title of Thesis: Chemical Agent Identification Using Field-Based Attenuated Total Reflectance Infrared Detection and Solid Phase Microextraction

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# Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

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1. REPORT DATE <b>2005</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-2005 to 00-00-2005</b>		
4. TITLE AND SUBTITLE <b>Chemical Vapor Identification Using Field-Based Attenuated Total Reflectance Fourier Transform Infrared Detection and Solid Phase Microextraction</b>		5a. CONTRACT NUMBER		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)		5d. PROJECT NUMBER		
		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Uniformed Services University of the Health Sciences, F. Edward Hebert School of Medicine, 4301 Jones Bridge Road, Bethesda, MD, 20814-4799</b>		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>				
13. SUPPLEMENTARY NOTES <b>The original document contains color images.</b>				
14. ABSTRACT <b>see report</b>				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	18. NUMBER OF PAGES <b>110</b>	19a. NAME OF RESPONSIBLE PERSON

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## ABSTRACT

Title: Chemical Agent Identification Using Field-Based Attenuated Total Reflectance Infrared Detection and Solid Phase Microextraction

Chet Kaiser Bryant, Master of Science in Public Health, 2005

Directed By: Peter T. LaPuma, LtCol, USAF, BSC  
Assistant Professor, Department of Prev Med and Biometrics

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) technology is used to identify chemicals in a liquid or solid phase but not in a vapor phase. This research identified vapor phase chemicals using a field-portable ATR-FTIR spectrometer combined with a solid phase microextraction (SPME) film. Two nerve agent simulants, diisopropyl methylphosphonate (DIMP) and dimethyl methylphosphonate (DMMP), and three polycarbosiloxane polymers were evaluated using a TravelIR™ ATR-FTIR instrument. A SPME film was adhered to the TravelIR™ sampling interface to extract and concentrate vapors to be identified by the TravelIR™. The lowest air concentration identified was 50 ppb DIMP and 250 ppb DMMP. A remote sampling technique where SPME films were exposed to vapors and then transferred to the TravelIR™ was only able to identify DMMP down to 10 ppm. This research demonstrates it is feasible to use ATR-FTIR to detect vapor phase chemicals when combined with SPME film concentration techniques.

CHEMICAL VAPOR IDENTIFICATION USING FIELD-BASED ATTENUATED  
TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED DETECTION AND  
SOLID PHASE MICROEXTRACTION

By

Chet Kaiser Bryant

Thesis submitted to the Faculty of the Graduate School of the  
Uniformed Services University of the Health Sciences in partial fulfillment  
of the requirements for the degree of

Master of Science in Public Health

2005

Advisory Committee:  
LtCol Peter T. LaPuma, Chair  
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## **Dedication**

- To God for his many blessings and love.
- To my wife, Elaine, who supported me throughout this two year journey.
- To my parents who taught me the many reasons to strive for a good education (such as being able to buy all the carnival ride tickets I want when I grow up).

## Acknowledgements

I could not have accomplished this work without the help of many people and organizations. I gratefully acknowledge the support I received from:

- Dr. Eric Houser and the Naval Research Laboratory for providing the polymers used in this study along with numerous useful discussions on their structures and properties.
- Dr. Mark Norman, Patrick Dempsey, Dr. David Schiering, and Smiths Detection (Danbury, CT) for providing the TravelIR<sup>TM</sup> used in this study along with invaluable information on infrared spectroscopy practices, theory, and spectral interpretation.
- Ms. Cara Olsen of the Uniformed Services University of the Health Sciences for her assistance with statistical analysis.
- My advisory committee, LtCol Pete LaPuma, CDR Gary Hook, and LCDR Gary Morris, for their never-ending flow of comments and suggestions along with a spectacularly unselfish donation of red ink.

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## List of Symbols and Abbreviations

ANOVA	Analysis of Variance
ATR	Attenuated Total Reflectance
AU	Absorbance Units
CAS	Chemical Abstracts Service
CW	Carbowax
CWA	Chemical Warfare Agent
DIMP	Diisopropyl Methylphosphonate
DMMP	Dimethyl Methylphosphonate
DVB	Divinylbenzene
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
HQI	Hit Quality Index
IMS	Ion Mobility Spectrometry
IR	Infrared
IRE	Internal Reflection Element
KBr	Potassium Bromide
LOD	Limit of Detection
MS	Mass Spectrometer
NB	Nitrobenzene
PA	Polyacrylate
PDMS	Polydimethylsiloxane
PIB	Polyisobutylene
Q-Q	Quantile-Quantile
SAW	Surface Acoustic Wave
SPE	Solid Phase Extraction
SPME	Solid Phase Microextraction
TGS	Triglycine Sulfate
UTH	Universal Tube Holder
ZnSe	Zinc Selenide

# **1 Introduction**

## **1.1 Background**

There are huge challenges facing today's civilian and military first-response personnel. September 11<sup>th</sup>, 2001 ushered in a new era where acts of intentional vandalism or terrorism must be considered in any hazardous material incident. Also, increased technology and communication has empowered individuals and State actors to produce weapons of mass destruction as evidenced by the 1995 Tokyo subway sarin attack and the 2001 anthrax mailings in the United States. The need to quickly detect and identify unknown substances is of the utmost importance to the safety of first responders and the general public. While laboratory analysis continues to be the gold standard for confirmatory testing, advancing field sampling and direct reading instruments are needed to provide vital and timely information that can be used for decision making by incident commanders.

The ideal direct reading instrument would be fast, portable, reusable, and simple to operate. It would provide both qualitative and quantitative results and have a low limit of detection (LOD). It would be able to sample materials of any chemical composition and any sample matrix (solids, liquids, or vapors). Although this instrument does not exist, first-response teams may get close to these capabilities through a variety of field sampling and analysis tools.

One chemical analysis tool that has received broad acceptance by the DoD, Civil Support Teams, and civilian fire departments is the HazMatID<sup>TM</sup>. The HazMatID<sup>TM</sup> is a ruggedized, man-portable, infrared detector that is capable of identifying a wide range of

chemical compounds. The HazMatID™ relies on attenuated total reflectance Fourier transform infrared (ATR-FTIR) detection to identify solids, powders, pastes, gels, or liquids. Samples can be placed directly on the HazMatID™ without preparation and analyzed within 2 minutes.

Even with such versatility, the HazMatID™ has limitations. Results are qualitative in nature and only attempt to indicate the presence or absence of a chemical. Water will interfere with any infrared detector so in order to identify a chemical mixed in water, the chemical needs to be at least 5-10% of the mixture. Since the HazMatID™ will not detect chemicals at trace concentrations, the absence of a chemical in water cannot be confirmed (Fricker, 2003; Ong, 2003). The system also cannot separate a mixture of different chemicals. It may detect the dominant chemical in a mixture but it will often miss other chemicals that are present at lower concentrations. Finally, the HazMatID™ is not designed to detect gases or vapors due to the poor contact with the instrument's sample interface.

This research is intended to broaden the capability of field portable ATR-FTIR spectrometers to identify chemicals in the vapor phase without extensive sample preparations. Solid phase microextraction (SPME) films will be used to concentrate a vapor phase chemical on the instrument's sample interface. If enough chemical can be concentrated in the SPME film, then ATR-FTIR spectrometers may be able to identify chemicals from the air, which would greatly enhance chemical detection capabilities for first responders.

### **1.1.1 Attenuated Total Reflectance Infrared Detection**

ATR infrared (IR) detection is an analytical technique used to obtain the IR spectra of solids, liquids, and semisolids. ATR instruments pass an IR beam through an IR transparent crystal with a high refractive index. This crystal is known as the internal reflectance element (IRE). Because of the IRE's high refractive index, the IR does not leave the crystal but instead it undergoes total internal reflection and is directed back into the instrument. The IR radiation beam is continuously reflected by the crystal and a standing wave of radiation called an evanescent wave is created at the crystal's surface. This evanescent wave extends just slightly beyond the surface of the crystal where it can interact with a sample. Any compound able to absorb IR radiation will provide a reproducible IR absorption spectrum that can be used like a fingerprint to identify the chemical by comparing the sample spectrum to a spectral library of known chemicals (Smith, 1996).

### **1.1.2 Solid Phase Microextraction**

The concept of using adsorbent materials to extract trace compounds from liquid mixtures has been extensively studied (Dressler, 1979, Poole and Schuette, 1983). These studies led to a partitioning technique called solid phase extraction (SPE). SPE has been used to extract compounds directly from water and air and indirectly from soils. In addition, SPE offers several improvements over traditional solvent extraction because it is simple, inexpensive, quick, and it uses relatively little solvent. Some drawbacks that have been noted with SPE include poor reproducibility due to batch-to-batch variation, high carryover between samples, and interaction between the extracting phase and the sample, which may result in low recovery of analytes. Fortunately, these drawbacks can

be overcome by using a minute quantity (usually less than 1 $\mu$ L) of the extracting phase on a rod made of fused silica in a technique called SPME (Pawliszyn, 1997).

## 1.2 Research Question And Specific Aims

**Research Question 1:** Can a SPME film added directly to the IRE of an ATR-FTIR spectrometer be used to identify and quantify vapor phase analytes?

### Specific Aims:

1. Test three different polymeric SPME films on an ATR-FTIR system (TravelIR™) to identify two nerve agent simulants at high vapor concentrations.
2. Progressively decrease analyte concentrations to establish a lower limit of detection.
3. Determine if variables such as exposure time and film thickness cause a statistically significant difference in instrument response.
4. Apply Beer's Law to determine if the analyte concentration can be quantified.
5. Determine how quickly the analytes desorb from the SPME films over time.

**Research Question 2:** Can a SPME film be used to remotely collect a vapor phase analyte and introduce it to the ATR-FTIR system for detection?

### Specific Aims:

1. Develop a collection method to expose SPME films to analytes remotely.
2. Determine lower detection limits using remote collection techniques.

## **2 Literature Review**

This research brings together ATR-FTIR and SPME technologies to enhance a field sampling and analysis methodology. ATR spectroscopy has been well established but with the recent introduction of more rugged and portable ATR instrumentation, its use in emergency response and field sampling has become more prevalent. SPME is a sampling technique that was pioneered in the 1990s and research to improve the technique continues today. SPME materials continue to evolve along with new applications and the material development is heavily influenced by the need for rapid field analysis. Research is ongoing to develop better materials with desirable physical properties like inertness and durability as well as desirable chemical properties like stability, broad chemical absorption and hydrophobicity. The sections below provide insight into recent developments in areas related to ATR-FTIR and SPME that were the motivation for combining them in this research to sample and analyze airborne chemical agents.

### **2.1 Attenuated Total Reflectance Fourier Transform Infrared Instrumentation**

As described above, ATR-FTIR detection is an analytical technique used to obtain the IR spectrum of a sample. The instrument generates an evanescent wave at the surface of the IRE where the IR radiation is attenuated by chemical bonds that absorb IR energy. These bonds include any covalently bonded chemical compounds with two or more different atoms. The IR absorption spectrum that results is like a fingerprint that can uniquely identify the chemical. However, the absorption spectrum can be affected by several factors related to the instrument or the sample. These factors must be controlled to attain reproducible results.

The depth of penetration of the evanescent wave into the sample, defined as the depth where the electric field intensity of the radiation decays to  $1/e$  of its initial value, is given by the following equation (Smith, 1996):

$$\text{Depth of Penetration(cm)} = \frac{1}{2\pi W N_c \left( \sin^2 \Theta - \left( \frac{N_s}{N_c} \right)^2 \right)^{1/2}} \quad \text{Equation 2-1}$$

where:

- W = wavenumber ( $\text{cm}^{-1}$ )
- $N_c$  = crystal refractive index (unitless)
- $N_s$  = sample refractive index (unitless)
- $\Theta$  = angle of incidence (degrees)

As the wavenumber decreases, the depth of penetration increases so that the radiation is exposed to more of the sample. As a result, ATR spectra contain peaks that are more intense at low wavenumbers than at high wavenumbers. Because of this, ATR spectral results should only be compared against ATR spectral libraries unless the spectrum is manipulated to remove the depth of penetration factor.

The depth of penetration for most instruments is usually less than 5  $\mu\text{m}$ . Because the penetration depth is so small, sample thickness is not a factor that has to be considered in most cases. Also, depth of penetration represents the pathlength through the sample. Therefore, ATR is not as sensitive as some IR detectors with a longer pathlength. For most ATR systems to detect an analyte, the concentration of an analyte typically must be greater than 0.1% for non-aqueous solutions and at least 5-10% for water based solutions (Smith, 1996).

Qualitative identification of samples is made by comparing the sample's IR spectrum to spectral libraries containing the IR spectra of known chemicals. Computer algorithms are used to match points on the sample's spectrum to points on the library

spectra. Although many different algorithms can be used, the results typically use a measure of data correlation called a hit quality index (HQI). After searching the entire library, the most highly correlated matches are listed and the sample is identified as the chemical with the highest HQI.

ATR can be used for quantitative work through the principles of the Beer-Lambert Law which relates radiation absorbance to sample concentration (Smith, 1996). The Beer-Lambert Law is stated as:

$$A = \epsilon l c \quad \text{Equation 2-2}$$

where:

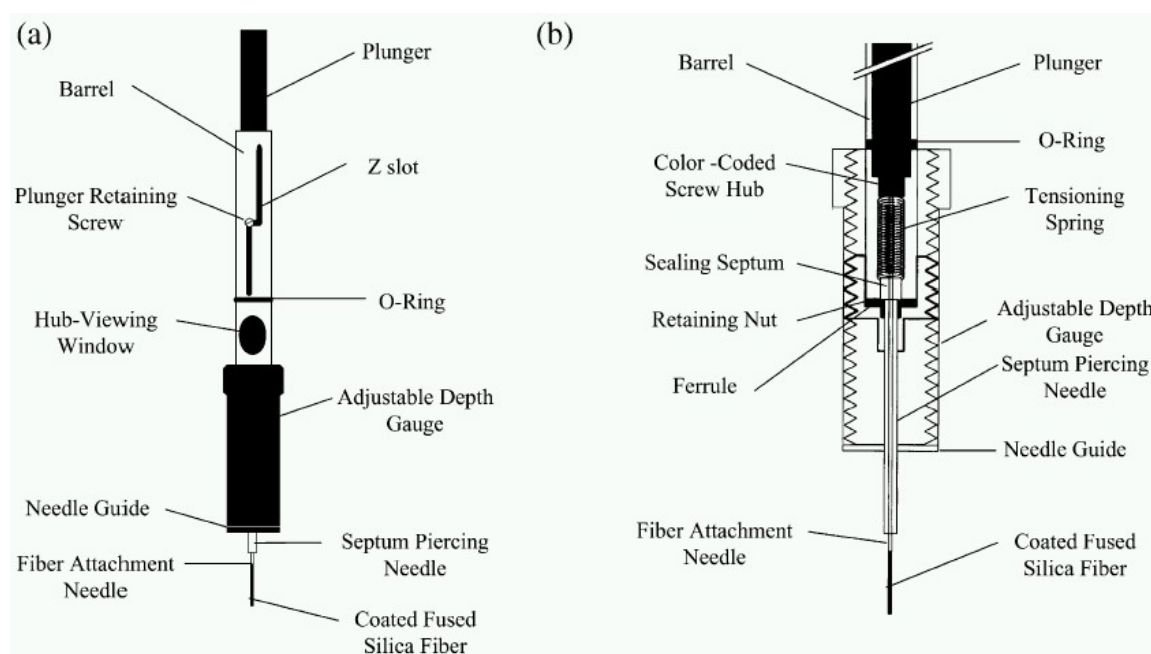
- A = absorbance (AU)
- $\epsilon$  = absorptivity (L/mol $\cdot\mu\text{m}$ )
- l = pathlength ( $\mu\text{m}$ )
- c = concentration (mol/L)

The pathlength (depth of penetration) can be calculated by Equation 2-1 for a specific wavelength and the absorptivity constant is a repeatable characteristic of the sample material at specific wavelengths. With pathlength and absorptivity held constant at each wavelength, the absorbance from the sample spectrum is directly influenced by the chemical concentration. Therefore, the concentration may be estimated using a calibration curve. It should be noted however that the pathlength remains constant only if the IRE/sample contact and pressure is reproducible. Also, the exact same crystal, not just crystals of the same material, must be used to generate the calibration curve when doing quantitative analysis (Smith, 1996).

## 2.2 Solid Phase Microextraction Fiber Sampling

SPME fiber sampling is a two-step sampling process that utilizes a small amount of extraction material (usually less than 1 $\mu\text{L}$ ) on a fused silica rod to partition and

concentrate analytes from the sample matrix. This is followed by desorbing the analytes from the SPME material into an analytical instrument. This technique was developed to create a rapid, solvent-free, and simple sampling method for gas chromatography (GC) analysis. In the GC application, a fused silica fiber (Figure 2-1) is coated with a polymeric phase such as polydimethylsiloxane (PDMS), polyacrylate (PA), or Carbowax (CW), or a combination of these liquid phases with a solid phase such as divinylbenzene (DVB) or Carboxen (Pawliszyn, 1999). The fiber is exposed to a sample so that the SPME material can extract analytes and then placed into a heated GC injection port where the analytes are desorbed.



**Figure 2-1: Commercial SPME Fiber Holder and Fiber Assembly (Mester, 2001)**

Although dynamic SPME fiber sampling is possible, it is usually considered a passive sampling technique since it only needs to be placed into the sample matrix to extract chemicals. For passive liquid sampling, the fiber can be immersed directly into the liquid or it can be placed in the headspace to collect volatile or semivolatile

compounds. However, as the partitioning begins, a zone of depletion (boundary layer) forms around the SPME fiber. For gaseous samples, the natural convection of air is usually sufficient to facilitate rapid partitioning but for liquid samples, a high stirring rate may be required (Pawliszyn, 1999).

Because the SPME fiber is often very small in comparison to the sample, it reaches equilibrium with the surrounding media as opposed to performing an exhaustive analyte extraction. Equation 2-3 describes the amount of analyte extracted by the SPME fiber after equilibrium has been reached by the system.

$$n = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \quad \text{Equation 2-3}$$

where:

- $n$  = analyte extracted by the polymeric phase ( $\mu\text{g}$ )
- $K_{fs}$  = fiber coating/sample distribution constant
- $V_f$  = fiber coating volume ( $\text{m}^3$ )
- $V_s$  = sample volume ( $\text{m}^3$ )
- $C_o$  = concentration of analyte in the sample ( $\mu\text{g}/\text{m}^3$ )

As long as the sample volume is very large ( $V_s \gg K_{fs} V_f$ ), Equation 2-3 becomes:

$$n = K_{fs} V_f C_o \quad \text{Equation 2-4}$$

This equation emphasizes the usefulness of SPME fibers for field sampling applications. The amount of analyte extracted is independent of the sample volume so there is no need to collect a defined sample prior to analysis. The SPME fiber can be exposed directly to ambient air or water and the amount of extracted analyte will correspond directly to the concentration in the matrix (Pawliszyn, 1997).

The chemical properties of the target analyte ultimately determine what SPME material should be used. The rule of thumb that “like dissolves like” applies very well to

these liquid polymeric coatings and selection is based primarily on the polarity and volatility of the analyte. The types of SPME fiber coatings that are currently commercially available can be classified as polar, semipolar and nonpolar (Pawliszyn, 1999). Selective partitioning caused by the polarity of the fiber coating in relation to the analyte gives some degree of selectivity to the SPME method. This can be beneficial when using analytical instruments that are not designed to separate and identify chemicals.

The SPME fiber sampling technique has been studied to show that it is a viable sampling method for the detection of chemical warfare agents (CWA). Lasko and Ng (1997) compared SPME fiber sampling with liquid/liquid extraction for the detection of nerve agents and found that SPME was a comparable sampling method for detecting the nerve agents sarin, soman, tabun, and VX at 60 ppb in river water, seawater, and sewage water. Sng and Ng (1999) developed a SPME fiber procedure for detection of CWA degradation products in water with detection limits of 1 ppb benzoic acid, 10 ppb methylphosphonic acid and n-propylphosphonic acid, and 100 ppb ethyl methylphosphonic acid. Schneider *et al.* (2001) developed a method to analyze air and water for the nerve agent sarin through SPME fiber sampling and laboratory GC-mass spectrometry (MS). Results showed a LOD of 100 ng/L of sarin in headspace sampling and 12 µg/L during direct immersion of the SPME fiber into a sarin/water solution. Hook *et al.* (2003) showed that the nerve agent VX could be detected through SPME fiber sampling and GC-MS analysis. Studies such as these show that SPME fibers are a viable collection media for CWAs and similar chemicals.

### 2.3 Solid Phase Microextraction Film Sampling

The physical design of SPME fiber sampling devices makes them suitable for use with chromatographs but is incompatible with some other analytical instruments. A form that could be used with both transmission and ATR-IR instruments would be a SPME film. As long as the total volume of the film is small (less than 1  $\mu\text{L}$ ), all aspects of SPME theory that have been demonstrated through SPME fiber sampling should apply to SPME film sampling. The SPME film could be applied directly to the analytical instrument or used independently as a sampling device.

Few studies have combined SPME film sampling techniques and ATR-FTIR spectrometry. Acha *et al.* (2000) coated the IRE of an ATR-FTIR with a 5.8  $\mu\text{m}$  layer of polyisobutylene (PIB) to measure trichloroethylene, tetrachloroethylene, and carbon tetrachloride in the water effluent of a fixed-bed dechlorinating bioreactor. Water absorbs across much of the diagnostic range of the IR spectra, which can mask the analyte of interest. In fact, IR is not normally used to detect analytes in water for this reason. However, the SPME film was able to concentrate the analytes from the water resulting in LODs of 2-2.5 ppm. These LODs are much lower than LODs of 500 ppm achieved by the same ATR-FTIR instrument without the polymer film (Acha, 2000).

In 2001, surface acoustic wave (SAW) devices were used to test the sensitivity of newly synthesized polymers. As part of the study, ATR-FTIR spectroscopy was used with SPME film sampling to determine the nature of the polymer/analyte interaction. A  $>1 \mu\text{m}$  layer of hexafluoroisopropanol functionalized polycarbosilanes was applied to the ATR IRE seen in Figure 2-2, a new background to account for the polymer was

established, and the test cell was flooded with a saturated vapor concentration of dimethyl methylphosphonate (DMMP) (1,265 ppm) and nitrobenzene (NB) (355 ppm).

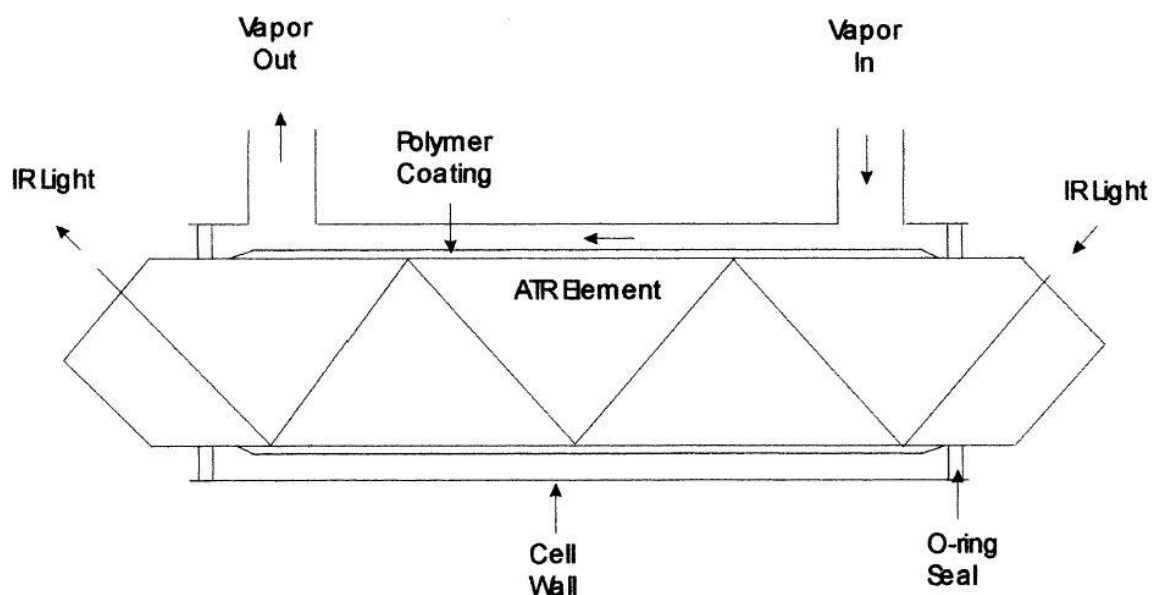


Figure 2-2: ATR-FTIR Test Cell With SPME Film (Houser, 2001)

In samples from both DMMP and NB, there was a shift of IR absorbance from 3600 wavenumbers to lower wavenumbers which is consistent with the analyte molecules forming hydrogen bonds with the O-H sites in the polymer and demonstrates how the polymer and analyte interact (Houser, 2001). Figure 2-3 shows the spectral results from both DMMP and NB samples. The spectral shifting is identified by the negative absorbance at 3600 wavenumbers (Point A) and the increased absorbance at 3150 wavenumbers for DMMP (Point B) and 3475 wavenumbers for NB (Point C).

This analysis showed that the SPME film sampling technique and ATR-FTIR analysis is capable of showing IR spectral changes in polymer/analyte combinations. However, it did not explore whether or not the analyte could be identified qualitatively or quantitatively or if the LOD would be low enough to make SPME combined with ATR-FTIR a viable field sampling technique.

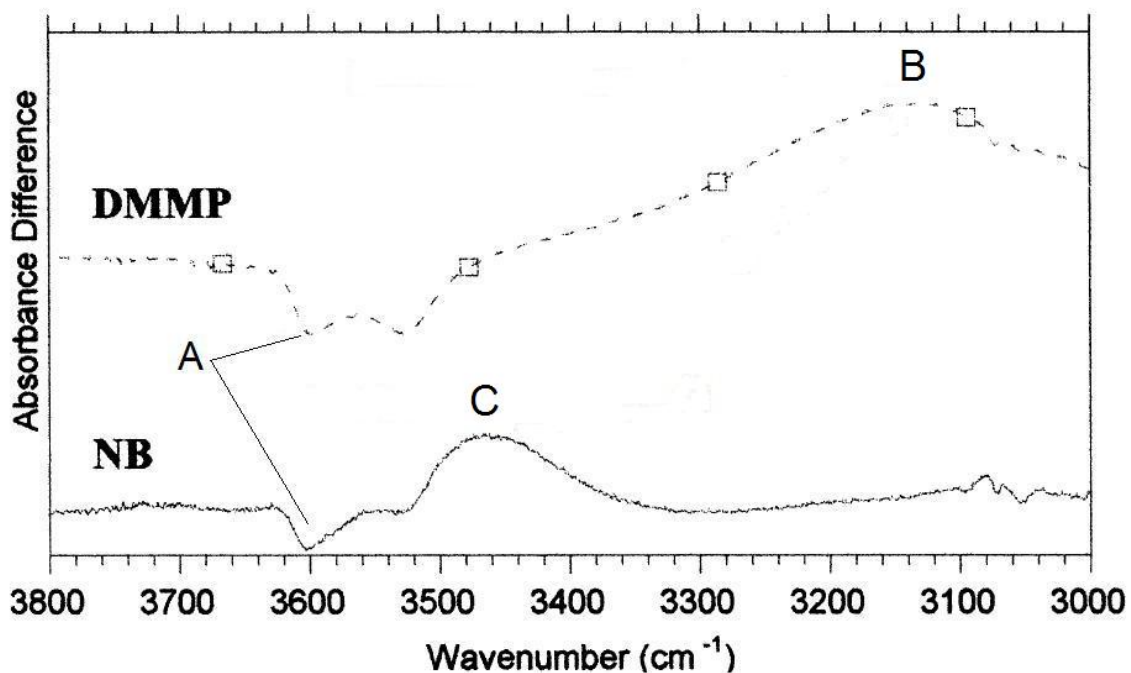
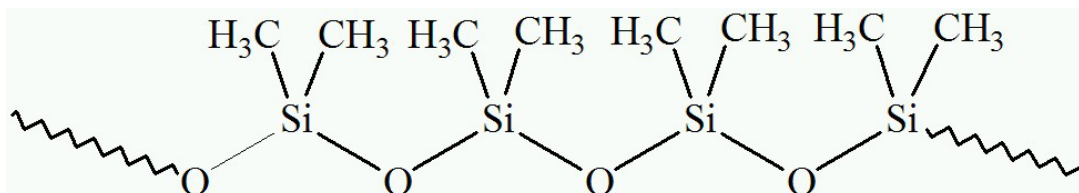


Figure 2-3: Spectral Results of Increased Polymer/Analyte Hydrogen Bonding (Houser, 2001)

## 2.4 Polymeric Phases

To date, the SPME polymeric phases commercially available are limited to PDMS, PA, and CW or a combination of these with DVB or Carboxen. However, polymer designs continue to evolve. PDMS, the most widely used and most durable SPME coating (Pawliszyn, 1999), is a highly viscous liquid, linear chained polysiloxane as seen in Figure 2-4. The extraction of analytes by PDMS is based on the non-competitive process of absorption. PDMS is a nonpolar compound so it will absorb most other nonpolar substances. It does not have properties, such as hydrogen bond acidic (an electron deficient hydrogen) functional groups, to preferentially extract target analytes. When looking specifically at organophosphonates and other hydrogen bond basic analytes, it is well established that hydrogen bond acidic polymers will provide superior

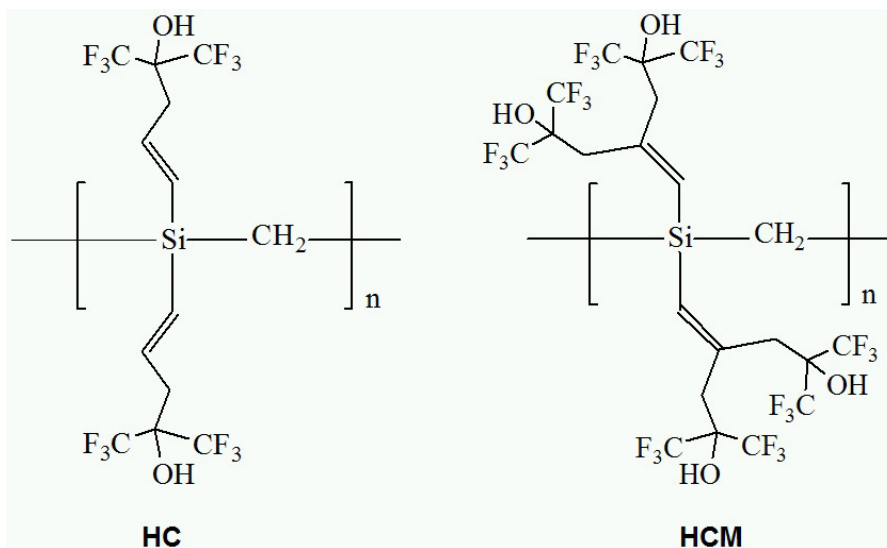
sensitivity to general absorptive polymers (Grate, 1999). The addition of these functional groups would allow the polymer to extract analytes by chemisorption rather than absorption and should improve sensitivities, lengthen desorption times, and selectively target specific analytes.



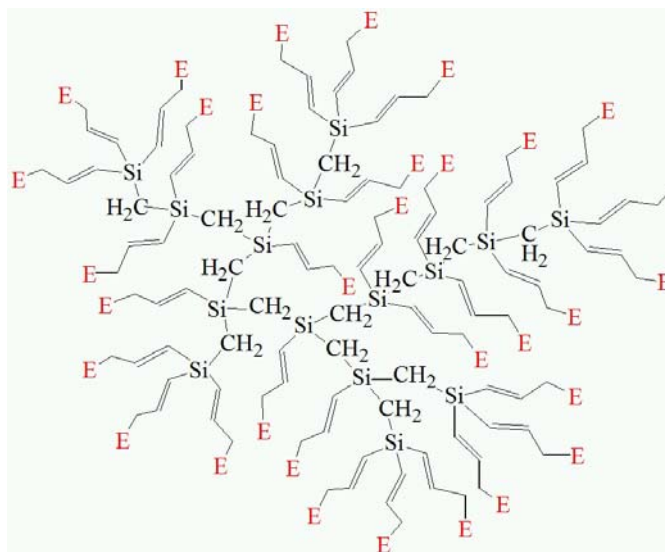
**Figure 2-4: Chemical Structure of the Linear Polymer PDMS**

Polymers with hydrogen bond acidic functional groups are currently available. Until recently, these polymers were fluoroalcohol-substituted polycarbosiloxanes. However, Houser *et al.* (2004) prepared the fluoroalcohol substituted polycarbosilane hydrogen bond acidic polymers, seen in Figure 2-5, with the goal of improving their chemical and thermal stabilities and their sensitivity to hydrogen bond basic analytes over the more commonly available polycarbosiloxanes.

The fluoroalcohol groups are hydrogen bond acidic due to the electron withdrawing effects of the fluorocarbons on the oxygen of the O-H group. These new polycarbosilanes have chemical structures that contain a mix of linear, dendritic, and branched units that provide a high density of functional groups as seen in Figure 2-6. In addition, the lack of hydrogen bond basic sites in the polymer backbone (such as the oxygen atoms contained in polycarbosiloxanes) reduces hydrogen bonding internal to the molecule, which increases the number of available functional groups. This optimizes the number of fluoroalcohol groups available for reversible hydrogen bonding with hydrogen bond basic



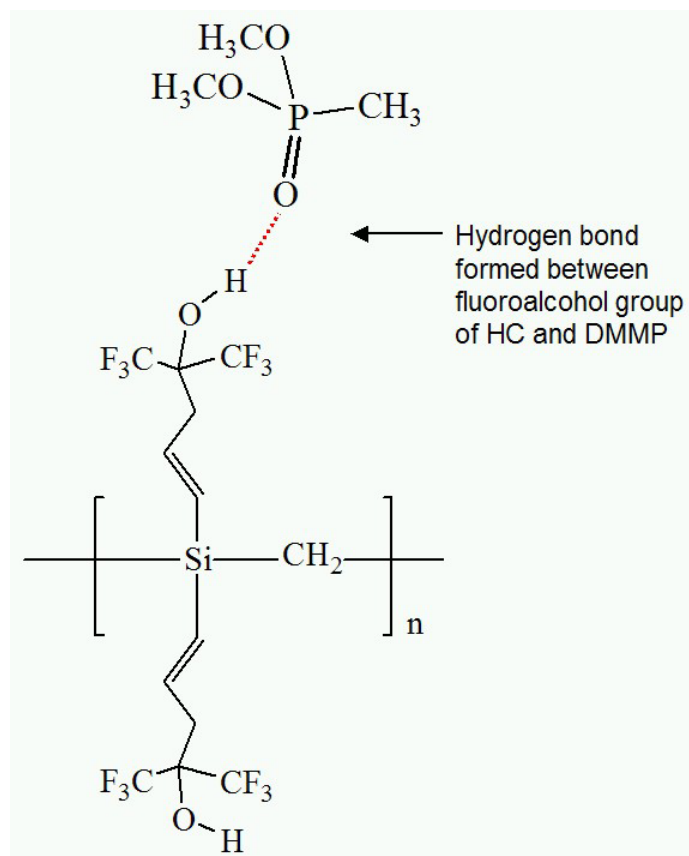
**Figure 2-5: Basic Structural Units of Two Hyperbranched Polycarbosilanes**



**Figure 2-6: Molecular View of the Hyperbranched Polymer HC**

analytes. Figure 2-7 shows the bonding mechanism between HC polymer and DMMP, a chemical that is hydrogen bond basic at the terminal oxygen of the P=O bond.

The sensitivities of the hydrogen bond acidic polycarbosilanes were compared to those of the more common hydrogen bond acidic polycarbosiloxanes by coating SAW devices with the polymers and exposing them to the hydrogen bond basic analyte



**Figure 2-7: Hydrogen Bonding Between a Hydrogen bond Acidic Polymer and a Hydrogen bond Basic Analyte**

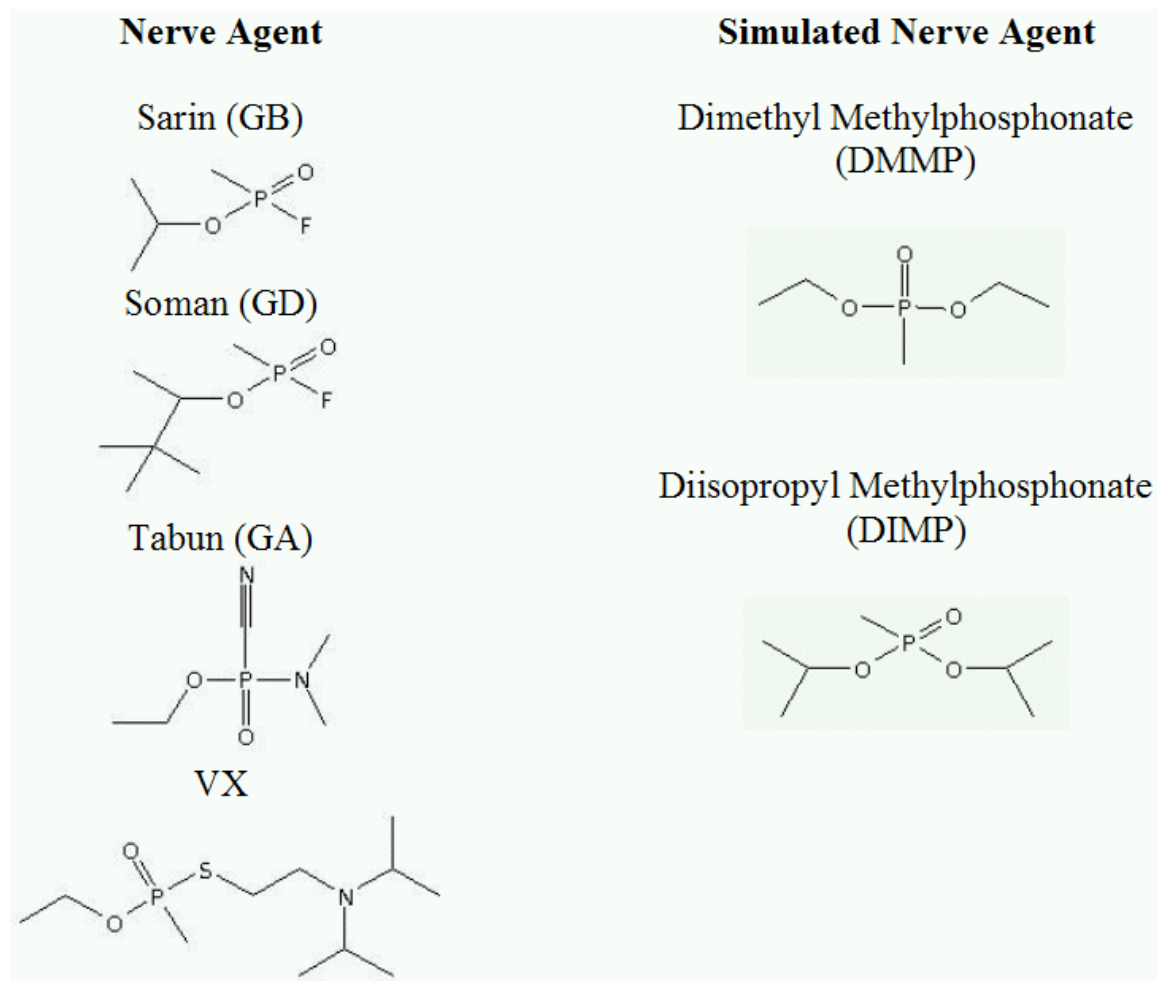
DMMP. The polycarbosilanes showed a significant enhancement in sensitivity toward the hydrogen bond basic analyte relative to analogous polycarbosiloxanes (Houser, 2004, Hartmann-Thompson, 2004). This enhancement is tentatively attributed to the absence of hydrogen bond basic sites within the polymer (Houser, 2004).

### 3 Methodology

This chapter describes the methods used to answer the research questions discussed in Chapter 1. The primary objective of this research was to determine if SPME films could be used with an ATR-FTIR spectrometer to identify vapor phase chemicals. The SPME films were added directly to the IRE of the ATR-FTIR spectrometer or they were used to collect samples remotely and then placed on the IRE. Each SPME film was exposed to known vapor concentrations of a CWA simulant and the resulting IR spectrum was compared to the TravelIR™ spectral library. Variables such as exposure time of the film to the sample (aka extraction time), flow rate of the air over the film, and film thickness were evaluated.

The analytes used in this study were chosen based upon military, environmental and industrial relevance to first responders. Diisopropyl methylphosphonate or DIMP (96% Alfa Aesar, CAS# 1445-75-6), and dimethyl methylphosphonate or DMMP (97% Aldrich Chemical Co., CAS# 756-79-6) were selected due to their structural (Figure 3-1) and spectral (Figure 3-2) similarities to military nerve agents and the many organophosphonate based chemicals used in industry and as pesticides.

The polymers used in this study were selected based on their ability to concentrate the analytes of interest, IR spectra, selectivity, physical properties, and availability. The polycarbosilanes HC, HCM, and HCMAM were selected because, as mentioned in Chapter 2, their hyperbranched structure should result in a higher molecular density of available functional groups than their linear structured counterparts. Also, the dominant IR absorbance peaks of the three polymers are outside the range of 1100-800 wavenumbers where the dominant peaks of the selected analytes occur. This creates a



**Figure 3-1: Structural Comparison of Nerve Agents and Selected Chemicals**

transparent absorbance “window”, as seen in Figure 3-3, which is desirable because the polymer’s spectrum will not mask the analyte’s spectrum.

The hydrogen bond acidic nature of the polymers adds some selectivity for hydrogen bond basic analytes and should diminish the impact from any non-hydrogen bond basic contaminants during field sampling. This is a helpful feature since separating the spectra of multiple analytes is not a strong point of ATR-FTIR spectrometers. Finally, the polycarbosilane polymers can be dissolved in organic solvents, which can then be applied to the IRE with a microliter syringe. Once the solvent evaporates, a very thin polymer film remains on the IRE.

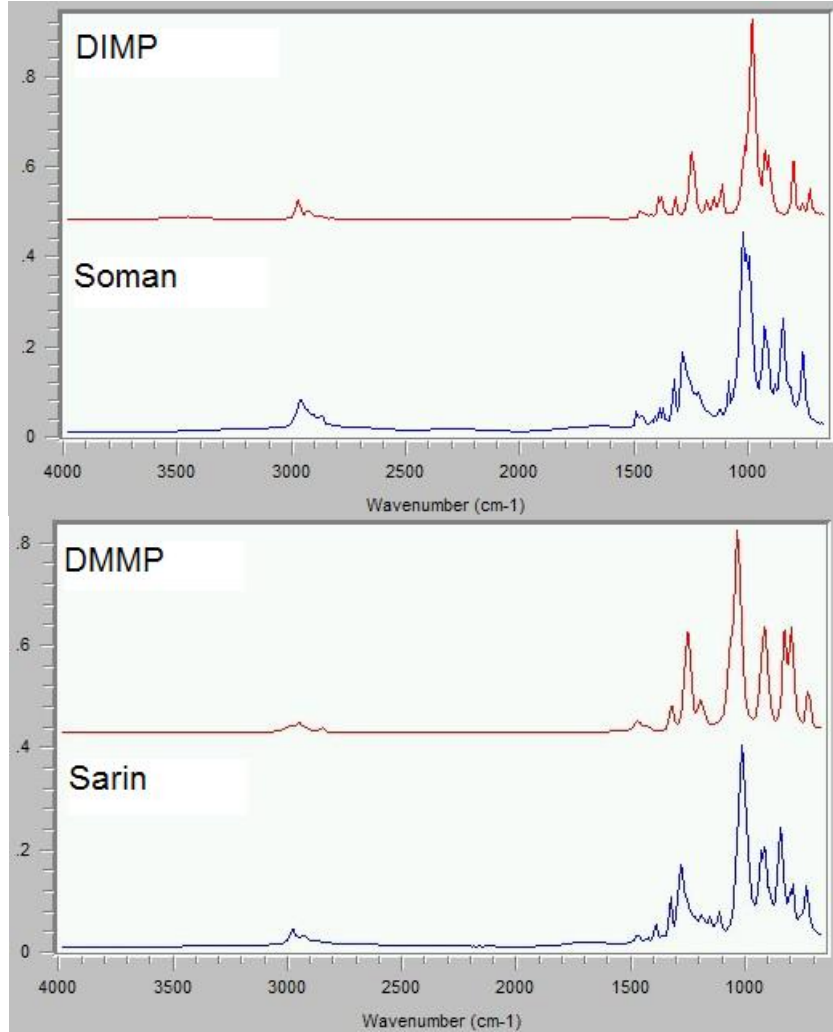


Figure 3-2: Spectral Comparison of DIMP/Soman and DMMP/Sarin

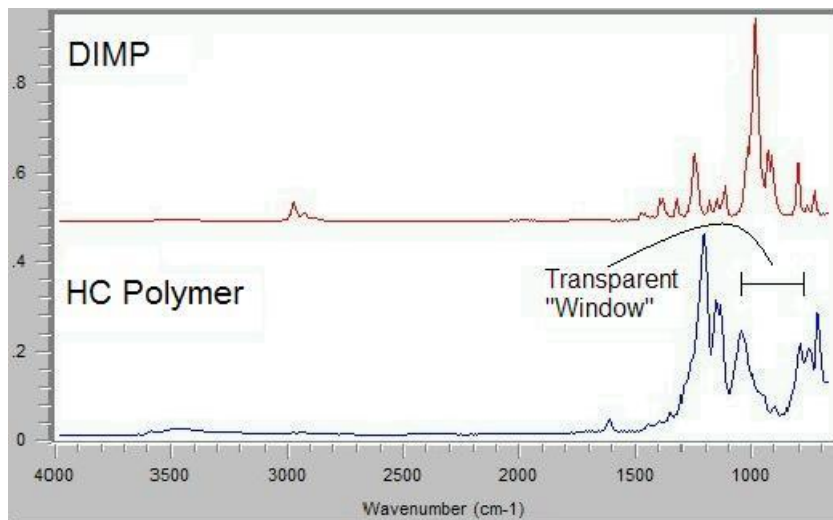


Figure 3-3: DIMP and DMMP Compared to HC Polymer

### 3.1 ATR Instrument

The ATR-FTIR instrument used in this study was a TravelIR™ spectrometer (Smiths Detection, Danbury, CT). In 2000, the TravelIR™ was introduced for laboratory and field-based identification of a wide range of organic and inorganic liquid and solid chemicals. The sample time of the TravelIR™ is between 30-120 seconds, depending on the number of scans performed during the sample analysis. Despite the utility of the TravelIR™, the design did not meet the rigorous needs of a hazardous material response. To meet these needs, a second-generation system called the HazMatID™ was developed. The physical design of the HazMatID™ makes it more rugged, compact, easier to use in personal protective equipment, and allows it to be decontaminated with bleach solutions. However, the main internal components and underlying principle of operation for the HazMatID™ are essentially identical to the TravelIR™.



**Figure 3-4: HazMatID™ (left) and TravelIR™ (right)**

The TravelIR™ uses a miniaturized Michelson interferometer, a Zinc Selenide (ZnSe) focusing crystal, and an integrated 1.5 mm diameter by 0.5 mm thick diamond IRE illustrated in Figure 3-5. The ZnSe crystal and the diamond IRE both have a refractive index of 2.42 so there is no reflection loss at the ZnSe/diamond interface. This refractive index and an angle of incidence of 45° produce an evanescent wave that

extends beyond the diamond surface a distance of 0.5-3.1  $\mu\text{m}$ . The beamsplitter is made with a thin ZnSe substrate that is not susceptible to humidity damage like the potassium bromide (KBr) beamsplitters used for most laboratory FTIR systems.

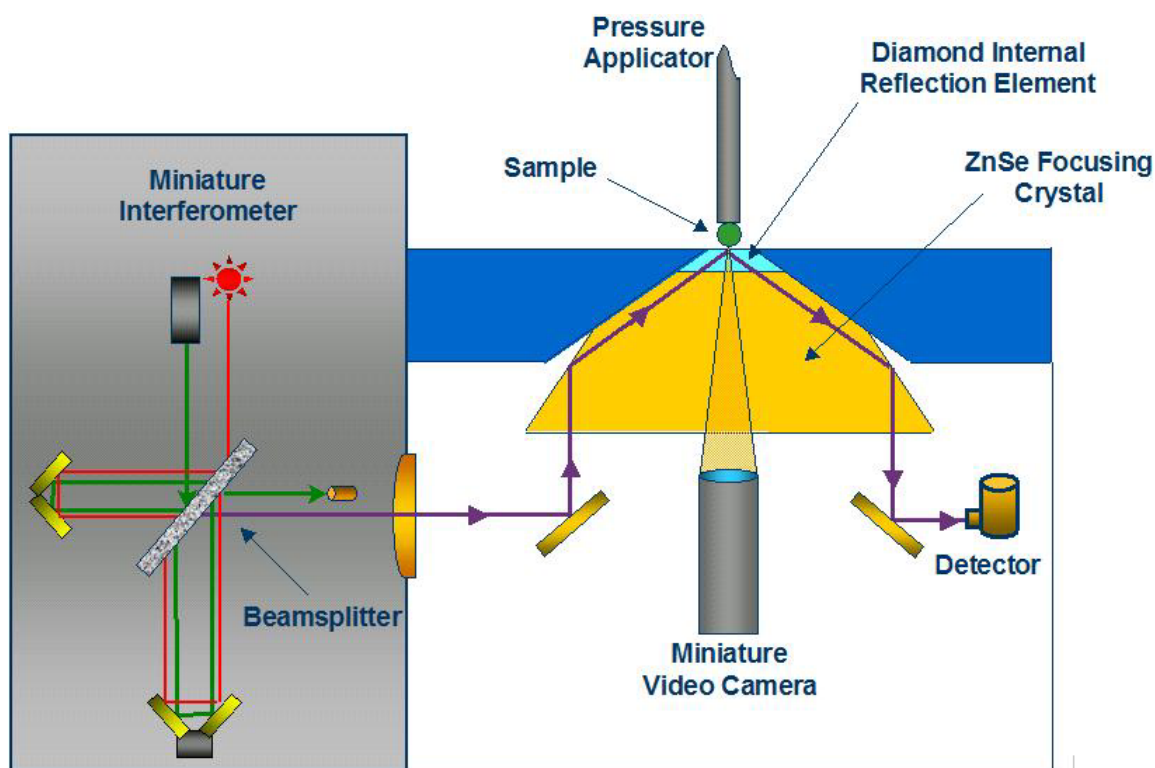


Figure 3-5: TravelIR™ Instrument/Sample Interface (Courtesy of Smiths Detection)

Other TravelIR™ hardware features include a helium-neon gas laser, which is used to track the position of the moving mirrors and as an internal standard for wavenumbers. The radiation source is a resistively heated ceramic blackbody emitter. The radiation detector is a room temperature operated deuterated triglycine sulfate (TGS) pyroelectric bolometer. The entire infrared optical path within the TravelIR™ is approximately 24 cm and the optical system allows mid-IR beam coverage in the range of 4000-650 wavenumbers. To ensure good physical contact between the sample and the IRE, a variable pressure applicator rod can be lowered. The force on the IRE is displayed in calibrated increments (1-10) corresponding to approximately 5-25 ft-lbs of applied force.

Characteristics unique to the HazMatID™ are smaller optical elements, a smaller Michelson interferometer, a low power diode laser, and a low power wire wound infrared source, all of which provide a smaller, more rugged interferometer design. The pressure applicator rod is fixed at 25 ft-lbs for the HazMatID™. Even with these differences, the HazMatID™ and TravelIR™ produce identical spectra and use the same spectral libraries for comparison.

### 3.2 ATR Instrument Setup

The TravelIR™ used in this study was assembled according to the instrument's user manual. The instrument's throughput and alignment were verified using the "System Check" function in the QualID™ software. The data acquisition parameters used for all samples in this study were as follows:

- Resolution                      4 cm<sup>-1</sup>
- Analysis Scans                64
- Background Scans            64
- Spectral Range                Full (4000-650 cm<sup>-1</sup>)
- Background Handling        Overwrite filename
- Y Axis Units                    Absorbance
- Detector Type                 TGS
- Search Quality Format        Similarity Value (0-1)
- Minimum Hit Quality        0

### 3.3 Sample Preparation

#### 3.3.1 Chemical Vapor Concentrations

To expose a sample to a constant concentration of analyte vapor, known concentrations of DIMP and DMMP were created in 5 Liter SKC Tedlar bags. The liquid volume required to reach a specific vapor concentration was determined using the ideal gas law (Equation 3-1) and the chemical properties shown in Table 3-1 to find the

number of moles required. The number of moles was then converted to a liquid volume using the chemical's molecular weight and density.

$$V = \frac{nRT}{P} \quad \text{Equation 3-1}$$

where:

- V = volume of gas
- n = number of moles
- R = 0.082057 L atm/mol K
- T = 298 K (assumed)
- P = 1 atm (assumed)

	DIMP	DMMP
Molecular Weight	180.18 g/mol	124.08 g/mol
Density	0.976 g/mL	1.145 g/mL
Vapor Pressure	0.277 mmHg @ 298 K	0.962 mmHg @ 298 K
Saturation Concentration	364 ppm	1265 ppm

**Table 3-1: Values Used in the Ideal Gas Law Equation**

As an example, Table 3-2 lists the liquid volumes that were injected into Tedlar bags to achieve the desired concentrations at 4 liter air volumes. After the liquid injection, the bags were held for at least 12 hours and visually inspected to ensure all liquid had evaporated.

Chemical	Desired Concentration (ppm)	Container Volume (L)	Liquid Volume Required (ul)
DIMP	364	4	11.0
	100	4	3.0
	10	4	0.3
DMMP	1265	4	22.4
	100	4	1.8
	10	4	0.2

**Table 3-2: Liquid Volumes Used to Generate Known Concentrations**

The Tedlar bags were filled to the desired volume of ambient air using a 0.5 L macro-volume syringe (SGE Inc.). A 10  $\mu$ L syringe (Hamilton, #701) was used to inject

the appropriate liquid volume of DIMP or DMMP. A double air plug injection method (drawing 1  $\mu\text{L}$  of air before and after drawing the liquid) was used to ensure measurement accuracy.

A different mixing technique was used to create vapor concentrations below 10 ppm. One Tedlar bag was filled with 4 L of air and 30  $\mu\text{L}$  of DIMP and a second Tedlar bag was filled with 4L of air and 60  $\mu\text{L}$  of DMMP. After 24 hours there was still visible liquid remaining and it was assumed that the concentrations inside the Tedlar bags had reached equilibrium at the saturation concentrations listed in Table 3-1.

Another Tedlar bag was filled to the desired volume of ambient air using a 0.5 L air pump as before. Instead of injecting liquid chemical, a 2.0 mL gas syringe (Precision Sampling Corp. Pressure-Lok®) was used to draw the required volume of air from one of the two saturated Tedlar bags to inject into the clean Tedlar bag. Before each injection, the syringe was purged with the saturated air 3 times to minimize vapor losses to the syringe wall. The required volume of saturated air was determined by the ratio in Equation 3-2. As an example, the values used in this study to mix 4 L bags are given in Table 3-3. To ensure uniform mixing, the Tedlar bags were not used for sampling until an equilibration time of at least 30 minutes had passed since the air injection.

$$V_s = \frac{C_D V_D}{C_S}$$

**Equation 3-2**

where:

- $V_s$  = saturated volume
- $C_s$  = saturated concentration
- $V_D$  = total desired volume
- $C_D$  = desired concentration

Chemical	$C_D$ Desired Concentration (ppm)	$V_D$ Total Volume (mL)	$C_S$ Saturation Concentration (ppm)	$V_S$ Saturated Volume Required (mL)
DIMP	1	4000	364	11.0
DIMP	0.1	4000	364	1.1
DIMP	0.05	4000	364	0.6
DIMP	0.01	4000	364	0.1
DMMP	1	4000	1265	3.2
DMMP	0.25	4000	1265	0.8
DMMP	0.1	4000	1265	0.3

**Table 3-3: Saturated Volumes Used to Generate Known Concentrations**

Each Tedlar bag was used to create the same vapor concentration multiple times for as long as it stayed in serviceable condition. The bag and septum were checked before each sample to ensure there were no signs of leaking. After sampling, the bag was evacuated using a high-flow pump (Gilian, 800485) until the fault indicator signaled that a vacuum was created. The bag was then filled with 1 L of ambient air and evacuated once again with the high-flow pump. After the second evacuation, the bag was filled for sample preparation and brought to the desired concentration.

### 3.3.2 General Sampling Protocol

Prior to any sampling, the TravelIR™ was allowed to warm up for at least 30 minutes. Acetone and chemical wipes were used to thoroughly clean the IRE and adjacent areas before each sample. Once the sampling area was clean and dry, a background sample was collected. To minimize any internal or external changes, the time between background collection and the start of sampling was less than 3 minutes.

All parts of the sampling train, including Tedlar bags, Tygon tubing, and universal tube holders (UTH) (Gilian, THH-S-225), were marked and used for sampling at only one concentration. Before the first daily sample was collected, 4 L of the vapor

concentration to be sampled were pumped through the sample train to minimize the effect of chemical losses to any of the components.

During exposure to analyte vapors, all samples and the TravelIR™ were placed inside a lab hood with an average face velocity of 100 fpm. During background or sample spectrum collection, the lab hood was turned off to reduce vibration, which can affect the path of the IR beam and add variability to the output. A minimum of three replicates was run for each sample set used in this study.

### **3.4 Direct Sampling**

Direct sampling is a technique used in this research to collect analyte samples directly on the instrument's IRE. During direct sampling, a SPME film is placed directly on the instrument's IRE and a background is recorded. Recording a new background with the SPME film on the IRE accounts for the IR absorbance from the polymer and reestablishes a baseline of zero absorbance across the spectral range. This effectively "subtracts" the IR absorbance due to the SPME film. The SPME film is then exposed to the analyte and the polymer/analyte spectrum is recorded.

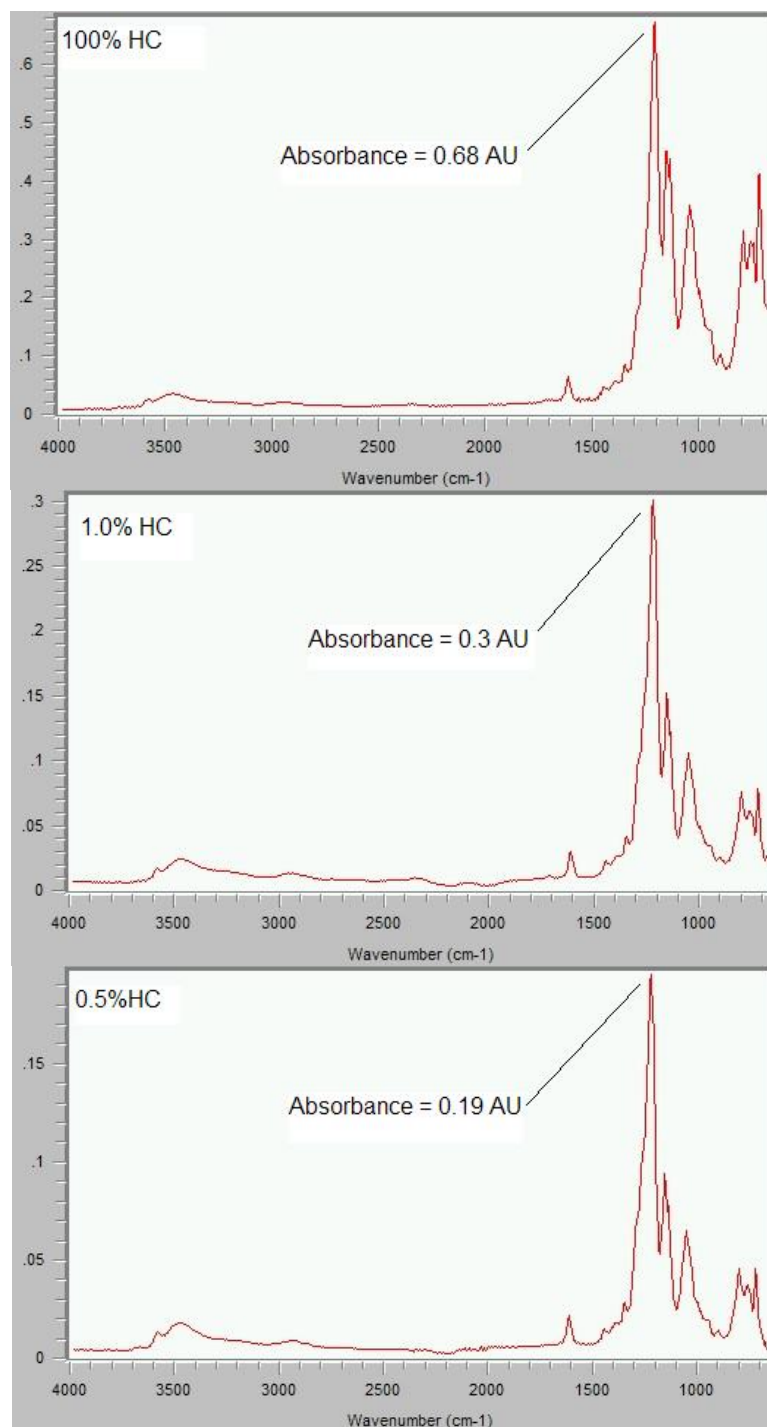
#### **3.4.1 Internal Reflectance Element SPME Film Coatings**

To answer the first research question regarding the use of a SPME film with an ATR-FTIR spectrometer to identify vapor phase analytes, the diamond IRE was covered with a polymeric SPME film. To achieve this, each polycarbosilane polymer was dissolved in chloroform (99% Aldrich Chemical Co., CAS# 67-66-3) where the polymer concentration ranged from 0.5-7% on a mass basis. Due to the thick viscosity of the polymers, a portion of polymer was separated, added to a vial and weighed on a microbalance (Sartorius, BP615). To achieve the desired percentage, chloroform was

then added based on the weight of the polymer. Three to five drops of tetrahydrofuran (99.9% Aldrich Chemical Co., CAS# 109-99-9) were added per 100 g of polymer/chloroform solution to ensure complete dissolution of the polymer. Next, a 1  $\mu$ L syringe (Precision Sampling Corp. Pressure-Lok®) was used to place a 1  $\mu$ L drop of solution on the IRE. After the chloroform completely evaporated, a polymer SPME film was left on the surface of the IRE.

The thickness of the SPME film left on the IRE varied with each application even when the same polymer concentration was used. The actual film thickness was not measured and its thickness may have been uneven due to the manner in which the chloroform evaporated. To mitigate the effects of changes in thickness, a spectrum of each SPME film was generated to show the polymer's IR absorbance value at its main peak. Since the entire IRE was coated with the SPME film and assuming the thickness was less than the IR penetration depth, any increase or decrease in absorbance can be attributed to an increase or decrease in film thickness. Therefore, absorbance was used as an indirect measure to approximate the SPME film thickness. When a thick (>1mm) film of pure, highly viscous HC is placed on the IRE, the penetration depth of the IR beam does not exceed the boundary of the sample and the resulting absorbance at the 1200 wavenumber C-F stretch is 0.68 absorbance units (AU). To achieve absorbencies less than 0.68 AU, the SPME film must be less than the IR penetration depth. The absorbencies due to SPME films from 0.5% and 1% solutions of HC, although they would vary from one application to the next, were typically less than the absorbance due to a thick film from pure HC as can be seen in Figure 3-6. Figure 3-6 illustrates that the 0.5% and 1% solutions leave a SPME film that is thinner than this instrument's typical IR

pathlength of 3  $\mu\text{m}$  and is approximately proportional to the percentage of polymer in the solution.



**Figure 3-6: IR Absorbance from 100%, 1%, and 0.5% HC Polymer Solutions**

### 3.4.2 Polymer Comparison

To compare the sensitivity of the HC, HCM, and HCMAM polymers, a SPME film of each polymer was exposed to 2 L of DIMP or DMMP at 10 ppm. The amount of IR absorbance at the analyte's main peak was used to provide a relative measure of sensitivity. After establishing a clean background, a SPME film was placed on the TravelIR™ as described in Section 3.4.1, IRE SPME Film Coatings. To ensure the SPME film thickness remained constant, a spectrum was recorded to ensure the absorbance of the C-F stretch peak (1200 wavenumbers) was at  $0.25 \pm 0.05$  AU. If the SPME film thickness was out of tolerance, the IRE was cleaned and the procedure was repeated. Once the film thickness was within tolerance, a new background was recorded with the SPME film still on the IRE.

The SPME film was then exposed to the analyte. An 18 inch long, 3 mm inner diameter Tygon tube was attached to the Tedlar bag valve and the end of the tube was placed over the SPME film at a distance of approximately 0.5 cm as seen in Figure 3-7.



Figure 3-7: Sample Procedure for Direct Sampling

Over a 2 minute exposure time, the Tedlar bag's volume of 2 L was forced out of the bag and over the SPME film by applying hand pressure to the bag: this resulted in an average flow rate of approximately 1.0 lpm and an exit velocity of about 465 fpm.

Various air sampling pumps were tested in an attempt to achieve more precise flowrates but significant amounts of analyte were lost to the system when the pumps were inserted between the Tedlar bag and the SPME film.

After the 2 minute exposure time, a sample spectrum was recorded. If peaks of the sample spectrum could be attributed to IR absorption from the chemical bonds of the analyte and they were more than 3 times the surrounding noise, the spectral change was considered to be from the analyte extracted by the SPME film. HC provided the greatest sensitivity (highest absorbance) and was therefore selected for all remaining sampling.

### **3.4.3 Limit of Detection**

To find the LOD for the analytes when sampling with HC polymer, a HC SPME film was placed on the IRE and the sample procedures were followed as described in Section 3.4.2, Polymer Comparison. The exposure time and volume were increased to 8 minutes and 8 L at the same average exit velocity of 465 fpm. Exposure concentrations started at 100 ppm and were decreased by one order of magnitude if the instrument was able to positively identify the chemical. For each sample, the result was considered a positive identification if all of the following criteria were met:

1. The sample spectrum is visually similar to the analyte's library spectrum
2. Peaks in the sample spectrum can be attributed to IR absorption from the chemical bonds of the analyte through spectral interpretation
3. The peaks of the sample spectrum are more than 3 times the surrounding noise
4. The correct library spectrum is identified as the best match (highest HQI) by the QualID<sup>TM</sup> software

5. The difference between the HQI of the correct library match and the HQI of the first incorrect library match are statistically different ( $\alpha = 0.05$ )

### 3.4.4 Extraction Time

As discussed earlier, SPME involves an equilibrium extraction rather than exhaustive extraction. Thus, the optimal approach to SPME sampling is to allow the analyte concentration in the polymer to reach equilibrium with the sample concentration. However, to be a desirable field detection method, sampling must be accomplished in a timely manner. The required extraction time (exposure time) must be short enough to be of beneficial use in the field. To explore the effects of changes in sample extraction time, HC polymer was placed on the IRE and the sample procedures were followed as described in Section 3.4.2, Polymer Comparison. The concentration for this experiment was held to 1 ppm for DIMP and DMMP with the same air velocity of 465 fpm. The exposure times varied from 2, 4, 8, and 12 minutes with 2, 4, 8, and 12 liter volumes, respectively. Differences in the IR absorbance at the main peak of the analyte were recorded and compared.

### 3.4.5 Sample Velocity

Fluid dynamic theory dictates that when a fluid (air in this case) moves past a stationary object (the polymer), a boundary layer forms between the fluid and the object. Theoretically, the air is always stationary at the object's surface and the velocity increases with distance from the object. As the polymer extracts analytes from the sample, the concentration of analyte in the boundary layer will decrease faster than the concentration of the sample resulting in a concentration gradient. If the velocity of the sample is increased, the boundary layer will become thinner which would allow for faster analyte extraction. To explore the effects of air velocity on the extraction of analytes by

HC polymer, a HC SPME film was placed on the IRE and the sample procedures were followed as described in Section 3.4.2, Polymer Comparison. The SPME film was exposed to 2 L of 1 ppm concentrations of DIMP and DMMP during exposure times of 2 and 4 minutes resulting in exit velocities of 465 and 232 fpm. A second set of samples was collected using 4 L of analyte for 2 and 4 minutes resulting in velocities of 930 and 465 fpm. Differences in the IR absorbance at the main peak of the analyte were recorded and compared.

### **3.4.6 SPME Film Thickness**

In SPME sampling, increasing the polymer volume will increase the total amount of analyte extracted at equilibrium conditions, and it will increase the time required to reach equilibrium. When combined with ATR analysis, if the SPME film thickness is less than the IR penetration depth, increasing the thickness will increase the pathlength of interaction between the IR beam and the sample. To study the effect of the SPME film thickness on the IR absorbance from a sample, the relative thickness of the film was varied while all other parameters remained constant. A HC SPME film was placed on the IRE and the sample procedures were followed as described in Section 3.4.2, Polymer Comparison. The SPME films were created using 0.5%, 1.0% and 7.0% polymer/chloroform solutions. Since thickness could not be measured directly, it was indirectly measured by the absorbance of the main C-F peak. The thickness was evaluated at 0.1 ( $\pm 0.008$ ), 0.3 ( $\pm 0.025$ ), and 0.5 ( $\pm 0.042$ ) AU. Samples were exposed to 4 L of analyte over 4 minutes at a concentration of 10 ppm. Differences in the IR absorbance at the main peak of the analyte were recorded and compared.

### 3.4.7 Quantitative Analysis

When applying quantitative infrared analysis, if the Beer-Lambert Law applies, a calibration curve of peak height or peak area vs. concentration should be linear. However, when using SPME sampling and ATR analysis, factors from both the Beer-Lambert Law and SPME theory must be addressed. Pathlength, IR absorptivity, analyte/polymer distribution coefficient, and equilibrium times are some of the factors that would have to be addressed to find an equation for quantification of ATR analysis of SPME samples. To explore whether or not this method can quantify analyte concentrations, the samples used to generate the LOD results were analyzed to create a calibration curve based on the peak heights of the analyte. The calibration curve was evaluated to determine if there was a relationship between the peak heights and the analyte concentrations.

### 3.4.8 Desorption Time

In many analytical processes such as GC, rapid desorption of the analyte from a SPME fiber is desirable. For ATR analysis, where the polymer and analyte are likely to be analyzed together, the analyte must remain in the SPME film long enough to acquire and coadd spectra to sufficiently reduce signal to noise ratios. To measure the desorption of the analyte from the SPME film over time, a HC SPME film was placed on the IRE and the sample procedures were followed as described in Section 3.4.2, Polymer Comparison. The exposure time and volume were 8 minutes and 8 L respectively. Exposure concentrations were set at 10, 1, and 0.1 ppm for DIMP and 100, 10, and 1 ppm for DMMP due to differences in the sensitivity to each analyte. The samples were reanalyzed at 5 minute intervals for a period of 30 minutes. No new background readings

were gathered during this sampling. Degradation of the IR absorbance at the main peak of the analyte was recorded and compared.

### **3.5 Remote Sampling**

Remote sampling is a technique used in this research to collect analyte samples on a sampling device and then bring the sample to the instrument for analysis. During remote sampling, a SPME film is used to collect a sample separate from the ATR instrument. The instrument records a background with a clean IRE and then the SPME film sample is placed on the IRE, the pressure applicator rod is lowered, and the sample spectrum is recorded.

To explore whether or not chemical vapors can be extracted with a SPME film in a remote location and brought to an ATR-FTIR instrument for analysis, a transportable sampling device was assembled. This was accomplished by applying a HC SPME film to a rigid, inert surface. Sheets of clear acrylic overhead transparencies (Skilcraft, A-A-2958, Type1) were cut into strips. As described in Section 3.4.1, IRE SPME Film Coatings, a 1  $\mu\text{L}$  drop of 0.5% HC polymer/chloroform solution was placed on the acrylic strip. As before, the chloroform would evaporate leaving a SPME film of polymer on the acrylic strip. There was no way to verify the thickness of the SPME film on the acrylic strip since analyzing the strip required the use of the pressure applicator rod to ensure even contact between the film and the IRE. The contact between the SPME film and the IRE destroyed the original physical properties of the film. However, the methodology used in Section 3.4.1, IRE SPME Film Coatings provides some sense for the thickness resulting from the 0.5% HC solution.

The SPME film was then placed inside a UTH and connected by two 10 inch long, 3 mm inner diameter Tygon tubes to the exhaust valve of a Tedlar bag and the inlet valve of a low-flow pump (SKC, 222-3). An example of this sample train can be seen in Figure 3-8. Analyte vapors were drawn from the Tedlar bag and across the SPME film at a flow rate of 0.195 ( $\pm 0.005$ ) lpm. With the diameter of the UTH being 1.1 cm, the corresponding velocity in the tube was 6.9 fpm. Concentrations of 1200, 100, and 10 ppm were each sampled for periods of 15, 10, and 5 minutes. After exposure to the analyte the SPME film was removed from the UTH and placed on the IRE (approximately 30 seconds elapsed from the end of exposure to placement on the IRE). The pressure applicator rod was set to a load of 8 (approximately 20 ft-lbs) and the sample spectrum was generated. Each sample was considered a positive identification if the criteria listed in Section 3.4.3, Limit of Detection, were met.



**Figure 3-8: Sample Procedure for Remote Sampling**

### 3.6 Library Generation

Spectra of the analytes, polymers, SPME film coated acrylic strips, and analyte/polymer combinations were all added to the computer library. During the spectrum generation, all of the sampling protocol listed in Section 3.3.2, General Sampling Protocol, were followed. For pure analytes and polymers, a 1mL liquid sample was placed on the IRE to ensure complete coverage and a thickness greater than the IR penetration depth. The resulting spectrum was added as a new library entry. Two replicate samples were analyzed and compared to the library entry to ensure the original spectrum could be reproduced with a HQI not less than 0.99. For SPME film coated acrylic strips, the required HQI of the replicates was reduced to 0.95 due to the variability of the film thickness.

The library generation for combinations of analyte and polymer was accomplished during the LOD sampling. The spectra that were chosen had to meet the following criteria:

1. The sample spectrum is visually similar to the analyte's library spectrum
2. Peaks in the sample spectrum can be attributed to IR absorption from the chemical bonds of the analyte through spectral interpretation
3. The peaks of the sample spectrum are more than 3 times the surrounding noise

In addition, the spectra chosen for the library had to be capable of correctly identifying the analyte/polymer combination at every concentration from the LOD up to 100 ppm. During the LOD sampling, each time the analytes were positively identified at a lower concentration a representative spectrum was added to the spectral library and compared against all higher concentrations. The final choice for a polymer/analyte library spectrum

was a representative spectrum from the lowest concentration that could still correctly identify all samples at higher concentrations.

### 3.7 Data Analysis

All visual spectral interpretations made in this study were conducted using *Interpretation of Infrared Spectra, A Practical Approach* by John Coates and *Infrared Spectral Interpretation: A Systematic Approach* by Brian Smith. Additional information on these sources can be found in the Bibliography.

QualID™ version 2.21 was used for spectral library searching and comparison. Sample spectra were compared to library spectra created during this study as well as to spectra contained in the ATR libraries, provided by Smiths Detection, listed in Table 3-4.

Library	Number of Spectra
Common Chemicals	3303
Drug Precursors	43
Forensic Drugs	454
NIOSH Toxic Chemicals	226
White Powders	41
Explosives	31
Chemical WMD	7

**Table 3-4: Commercial Libraries Used for Spectral Comparisons**

QualID™ employs a full spectrum correlation search that is similar to a Euclidean Distance algorithm except that both the unknown and library data points are centered about their respective means. The mean centering step allows the HQI to be independent of the normalization of the spectra. The algorithm treats spectra as vectors and uses a normalized dot product correlation algorithm to output a HQI scaled between 0 and 1. This puts equal emphasis on both intensity and position of a spectrum's data points (Thermo, 2005). A unity correlation value would be a theoretical perfect match but this is

never achieved due to differences in noise levels between the sample and library spectra. Maximum absorbance unit values and peak median wavenumbers were generated using GRAMS/AI™ version 7.02 software.

## **4 Experimental Results**

### **4.1 Direct Sampling**

During direct sampling, a SPME film was placed directly on the instrument's IRE and a background was recorded. Recording a new background with the SPME film on the IRE accounted for the IR absorbance from the polymer and reestablished a baseline of zero absorbance across the spectral range. This effectively "subtracts" the IR absorbance due to the SPME film. The SPME film was then exposed to the analyte and the polymer/analyte spectrum was recorded.

#### **4.1.1 Polymer Comparison**

Each polymer (HC, HCM, and HCMAM) was tested against a 10 ppm concentration of DIMP or DMMP. A SPME film ( $0.25 \pm 0.05$  AU) was placed on the IRE. The film was then exposed to the analyte which was extracted from the air into the polymer. To demonstrate that the SPME film was extracting the vapor analyte in quantities large enough for detection by the instrument, the sample spectra had to meet one of two criteria:

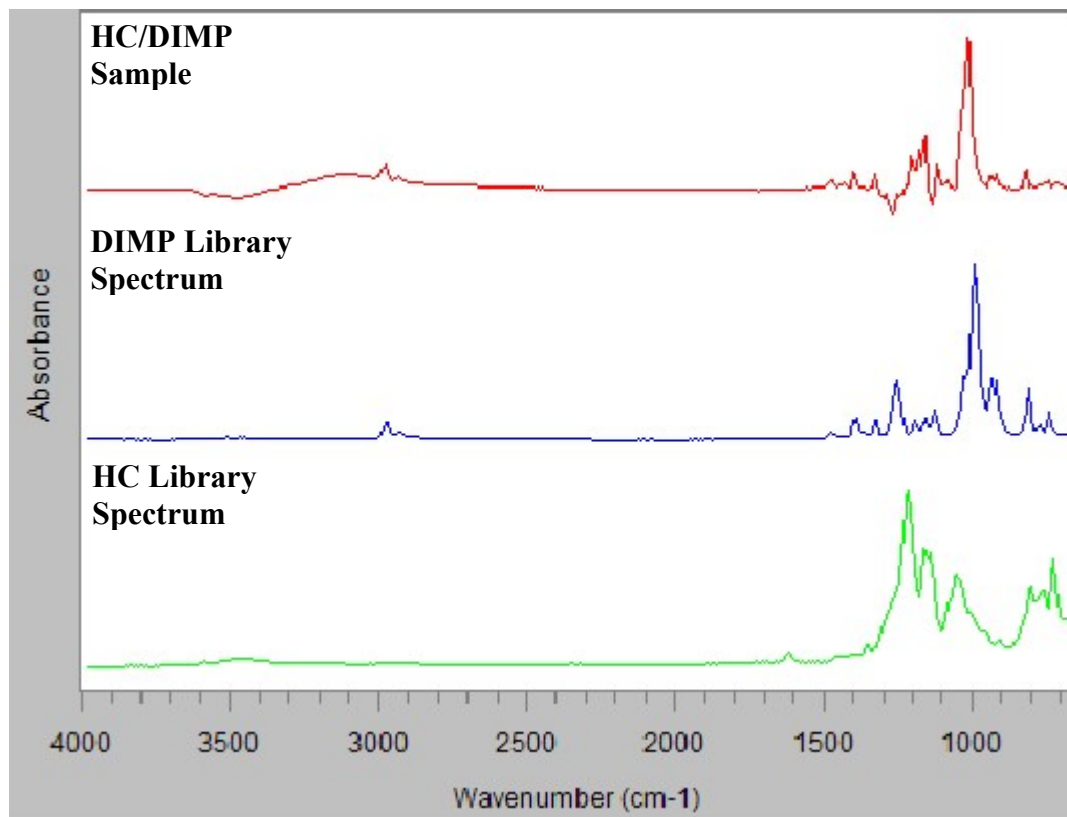
- The sample spectrum has a high correlation to the library spectrum of the analyte of interest and is significantly different from any other library spectrum.
- The sample spectrum is significantly different from any other library spectrum and the absorbance peaks of the sample spectrum can be attributed to the chemical bonds from the sample analyte or polymer.

#### 4.1.1.1 Identification by Library Matching

With the IR absorbance of the polymer already accounted for in the background, ideally, the sample spectrum following the uptake of analyte into the SPME film would correlate well with the library spectrum of the pure analyte. However, this was not the case since spectra from the analysis of the polymer/analyte sample were not well correlated to any existing library spectra. When compared to the library spectrum of the analyte, the HQIs of all samples were below 0.35. When compared to the entire library, the polymer/analyte samples had a top library match HQI of 0.7 or below to structurally similar but incorrect chemicals. Figure 4-1 shows a spectrum from a HC/DIMP sample, the library spectrum of DIMP, and the library spectrum of HC polymer. As can be seen in the figure, the sample spectrum did not correlate well with either of these library spectra. Results for all polymer/analyte combinations had results that did not correlate well with any library spectra (Appendix A).

#### 4.1.1.2 Identification by Spectral Analysis

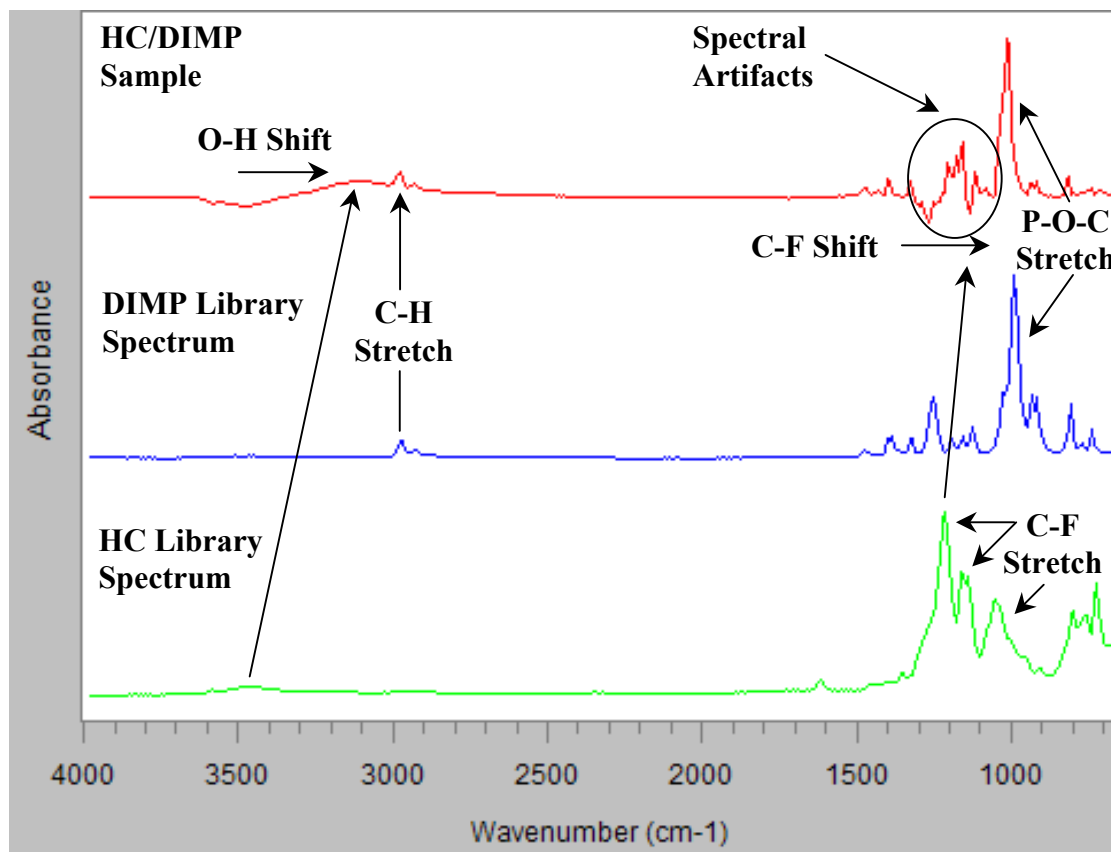
Since the sample spectrum did not correlate well to the library spectrum of the analyte, the next step to demonstrating that the instrument was detecting the analyte was to show that the absorbance peaks of the sample spectrum could be attributed to the chemical bonds from the sample analyte and/or polymer. Figure 4-2 shows a spectrum from a HC/DIMP sample. The main peak in the sample spectrum was a P-O-C stretch at 996 wavenumbers which is only a slight shift when compared to the DIMP library spectrum where the P-O-C peak occurs at 972 wavenumbers. Other peaks such as the asymmetric/symmetric methyl C-H stretches at 2986 and 2933  $\text{cm}^{-1}$  show very little shifting and are also evidence that the analyte is present in the sample spectrum.



**Figure 4-1: HC/DIMP Direct Sampling Spectrum (10 ppm, 2 min, 1 lpm) Compared to Library Spectra of the Sample Components**

The negative absorbance in Figure 4-2 at 3500 wavenumbers and the corresponding positive absorbance at 3100 wavenumbers are consistent with the shifting of the O-H stretch of the HC polymer. The shift to a lower frequency is due to increased hydrogen bonding of the HC polymer's hydroxyl groups with the analyte. This demonstrates the expected mechanism of interaction between the molecules of analyte and polymer is occurring. This chemisorptive process will result in greater sensitivities and longer desorption times when compared to absorptive liquid polymers.

The dominant C-F stretch peaks from the HC polymer are located between 1300-1025 wavenumbers as seen in Figure 4-2. This same region corresponds with an area of many spectral artifacts in the HC/DIMP sample spectrum. The artifacts include



**Figure 4-2: Interpretation of HC/DIMP Direct Sampling Spectrum (10 ppm, 2 min, 1 lpm) Compared to Library Spectra of the Sample Components**

unaccounted positive peaks, negative peaks, and derivative shaped peaks (asymmetrical peaks with an inflection point both above and below the baseline), which can be seen more clearly in Figure 4-3. Derivative shaped peaks are caused by wavenumber shifts in the spectrum of the reference material versus its spectrum when in a mixture (Smith 1996). In this case, the dominant C-F peaks in the HC polymer appear to have shifted to a lower frequency and caused all three of the previously mentioned artifacts.

This shift could be caused by a change in the refractive index as the polymer extracts the analyte, or more probably, the increased hydrogen bonding between the analyte and the O-H group in the polymer is also affecting the nearby C-F<sub>3</sub> moieties, thereby shifting their observed spectral feature to a slightly lower frequency. In either

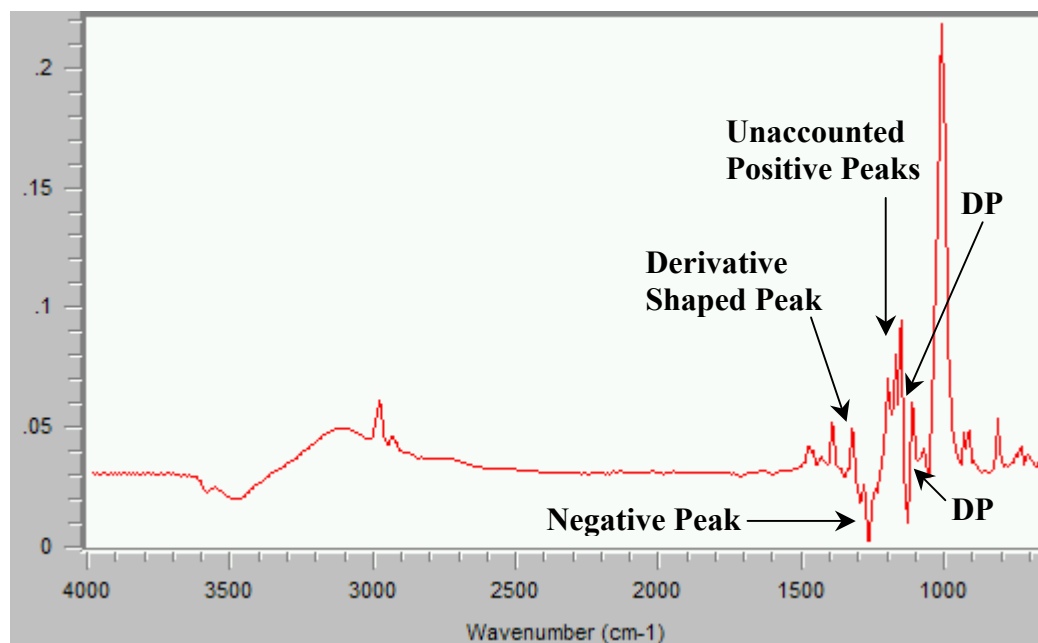


Figure 4-3: HC/DIMP Direct Sampling Spectrum (10 ppm, 2 min, 1 lpm)

DP = Derivative Shaped Peak

case, the shifting of the C-F peaks to a lower wavenumber would cause the sample spectrum to show less absorbance (negative peaks) at the original wavenumbers, higher absorbance (unaccounted positive peaks) at the lower wavenumbers and the shifting of the reference material would cause the derivative shaped peaks.

The peaks corresponding to the major analyte structures, the spectral confirmation of hydrogen bonding (O-H shift) which was the expected mechanism of interaction and a plausible explanation for the spectral artifacts in the 1300-1025 wavenumber range, strongly suggest the analyte is the primary contributor to the sample spectra.

Since the sample spectrum did not have a close correlation to any existing library spectrum, the instrument can be “trained” to identify future HC/DIMP samples by adding a representative spectrum of the sample to the library. Results for all polymer/analyte combinations had similar results and were also added to the library. Spectra from each combination can be seen in Appendix A.

### 4.1.1.3 Polymer Sensitivity

Since all three polymers were able to extract vapor phase analytes and provide polymer/analyte sample spectra that were different from all existing library spectra, replicate samples (Table 4-1) were recorded for each polymer/analyte combination and the relative sensitivities of the polymers were compared using the P-O-C peak height which is a main peak for both DIMP and DMMP.

Analyte	Polymer	Sample Size (n)
DIMP	HC	6
	HCM	5
	HCMAM	6
DMMP	HC	7
	HCM	5
	HCMAM	6

**Table 4-1: Polymer/Analyte Sample Sets for Sensitivity Comparison**

Graphical results can be seen in Figure 4-4 and Figure 4-5. The narrow bars represent the peak heights from individual samples and the wide bar represents the mean of each sample set. HC had the highest mean absorbance values for both DIMP and DMMP and was selected as the only polymer to continue in the rest of this research.

### 4.1.2 Direct Sampling Limit of Detection

This testing was to establish the LOD for DIMP and DMMP using HC SPME films and the new library entry for the polymer/analyte combination. Exposure concentrations were started at 100 ppm with an 8 minute sample time and were decreased by one order of magnitude after each positive identification. The decrease continued until the chemical could no longer be identified using the criteria listed in Section 3.4.3, Limit of Detection. The representative library entry for each polymer/analyte combination came from the

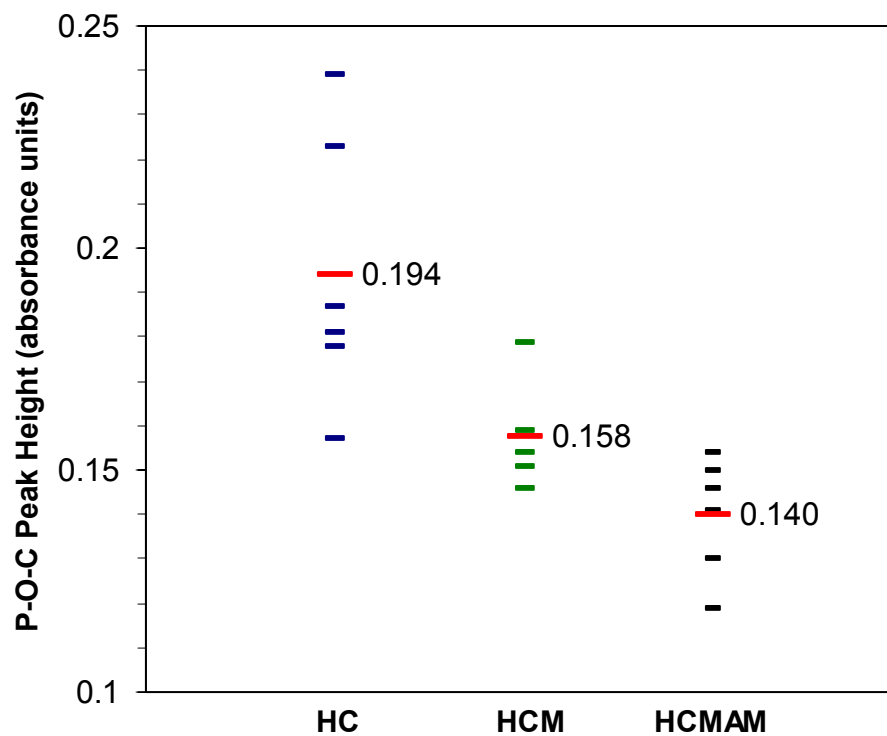


Figure 4-4: Relative Polymer Sensitivity to DIMP Extracted by Direct Sampling (10 ppm, 2min, 2L)

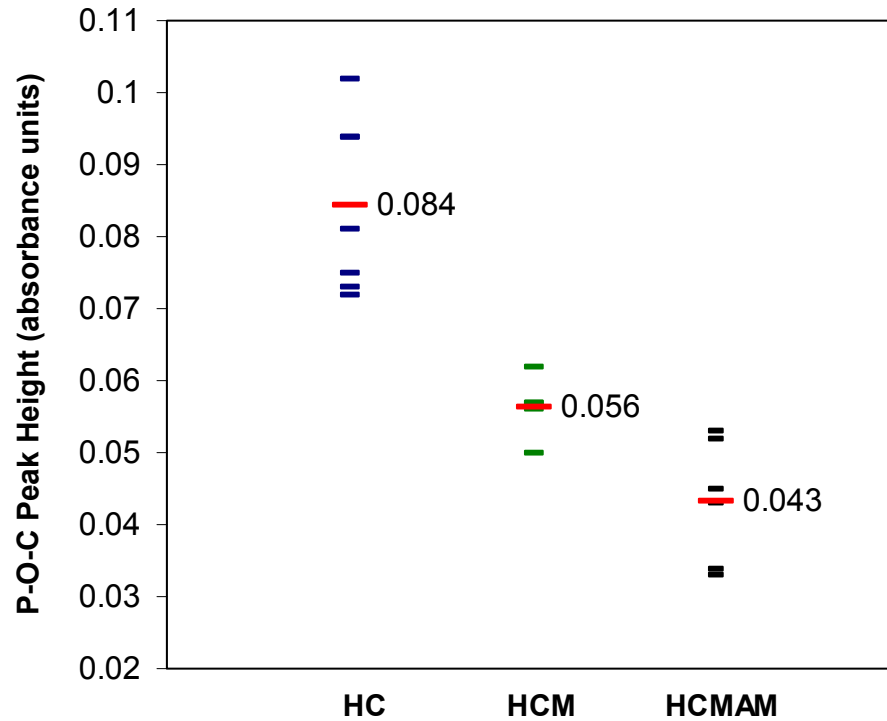


Figure 4-5: Relative Polymer Sensitivity to DMMP Extracted by Direct Sampling (10 ppm, 2min, 2L)

lowest concentration that could meet the spectral quality criteria explained in Section 3.6, Library Generation. Using a library spectrum from the lowest concentration optimizes detection near the LOD. Even though higher concentrations do not correlate as well to this spectrum, their stronger IR absorbance makes them easier to confirm by spectral interpretation. This maximizes the range of detection when only one library spectrum can be used for a polymer/analyte combination.

Table 4-2 shows the sample sets that were collected for HC/DIMP and HC/DMMP samples. The representative spectrum added to the library was from the 100 ppb sampling set for DIMP and the 1 ppm sampling set for DMMP since these were the lowest concentrations that meet all criteria listed in Section 3.6.

Analyte	Concentration (ppm)	Sample Size (n)
DIMP	100	5
	10	5
	1	7
	0.1*	5
	0.05	6
	0.01	5
DMMP	100	5
	10	5
	1*	4
	.25	7
	0.1	7

**Table 4-2: HC Polymer/Analyte Sample Sets for Limit of Detection**  
\*Concentration used to generate the polymer/analyte library spectrum

Based on the library spectra for DIMP at 100 ppb and DMMP at 1 ppm, the LOD for DIMP is 50 ppb and DMMP is 250 ppb. Below these concentrations the correct library match did not have the highest HQI. Figure 4-6 shows the 95% confidence intervals for the values of the correct HQI and the next best HQI for HC/DIMP samples and Figure 4-7 shows the 95% confidence intervals for HC/DMMP. A paired samples T

test determined there was a significant difference between the top two matches in all sample sets at or above the LOD ( $p \leq 0.001$ ). Despite small sample sizes, a normal distribution and equal variances were assumed. For each sample set, quantile-quantile (Q-Q) plots were generated to compare the observed values against the expected values of a normally distributed population. Visual inspection of the Q-Q- plots (Appendix B) showed that a normal distribution assumption was plausible. In addition, the differences in means and medians of the sample sets were small which suggests some symmetry of data points. Symmetry ensures the T test results are similar to non-parametric methods, such as the Kruskal-Wallis test that would be used if the above assumptions were not correct.

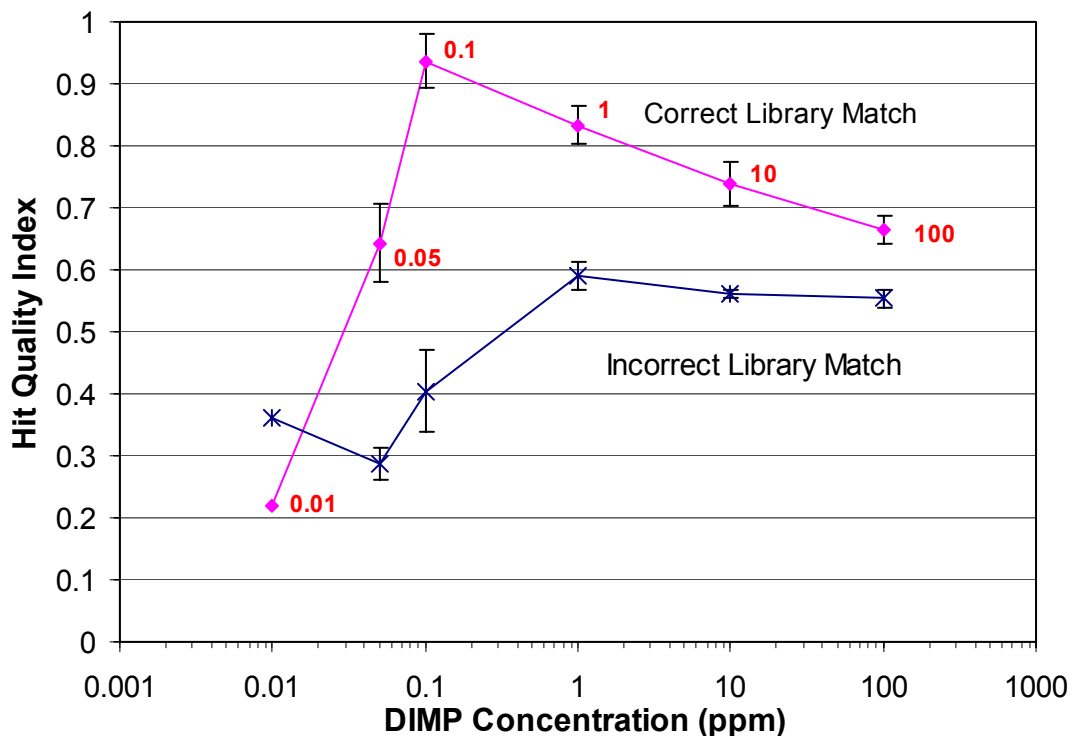


Figure 4-6: Comparison of the Correct Library Match and the First Incorrect Match with 95% Confidence Intervals (HC/DIMP Direct Sampling, 8 min, 1 lpm)

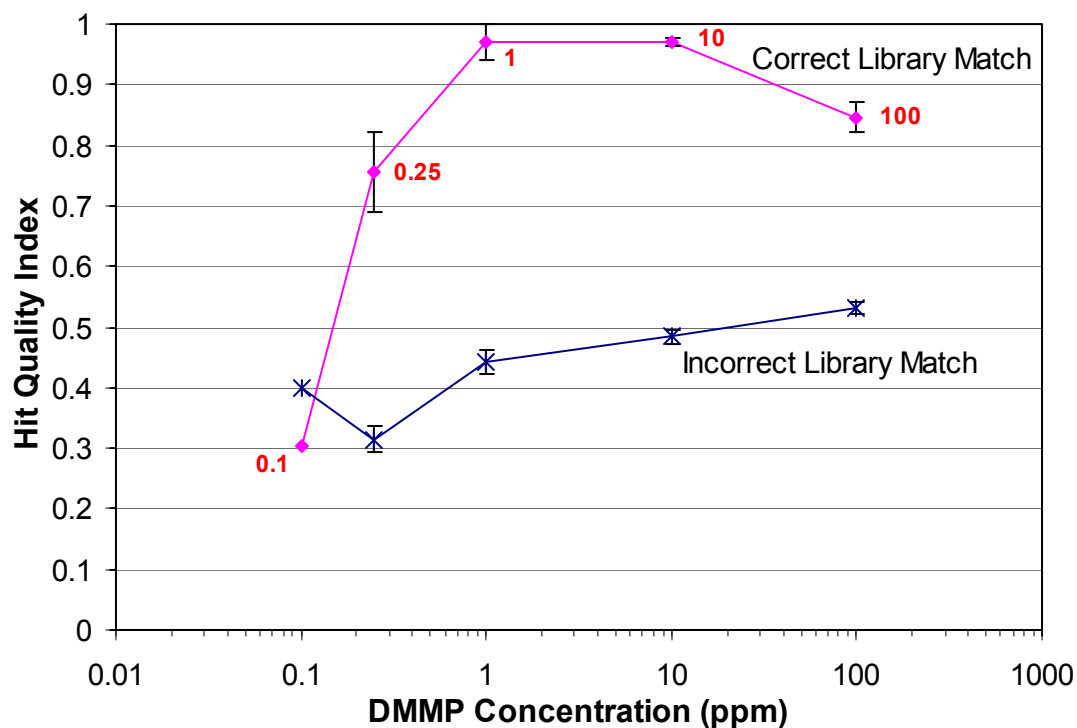


Figure 4-7: Comparison of the Correct Library Match and the First Incorrect Match with 95% Confidence Intervals (HC/DMMP Direct Sampling, 8 min, 1 lpm)

Figure 4-8 shows a HC/DIMP 50 ppb spectrum and Figure 4-9 shows a HC/DMMP 250 ppb spectrum. A spectrum from each concentration is available in Appendix C. The dominant peak in both samples continues to be the P-O-C stretch, located at 1006 wavenumber for DIMP and 1048 wavenumbers for DMMP. They are well over 3 times the surrounding noise. The effect of the polymer/analyte hydrogen bonding can still be seen in the O-H shift and the spectral artifacts are still present between 1300-1025 wavenumbers.

At lower concentrations, spectral properties of both analytes were still present for visual comparison; however, the instrument could no longer match the sample to the correct library spectrum with a HQI that was significantly greater than the first incorrect spectrum. In this study, the library matching software was the limiting factor in

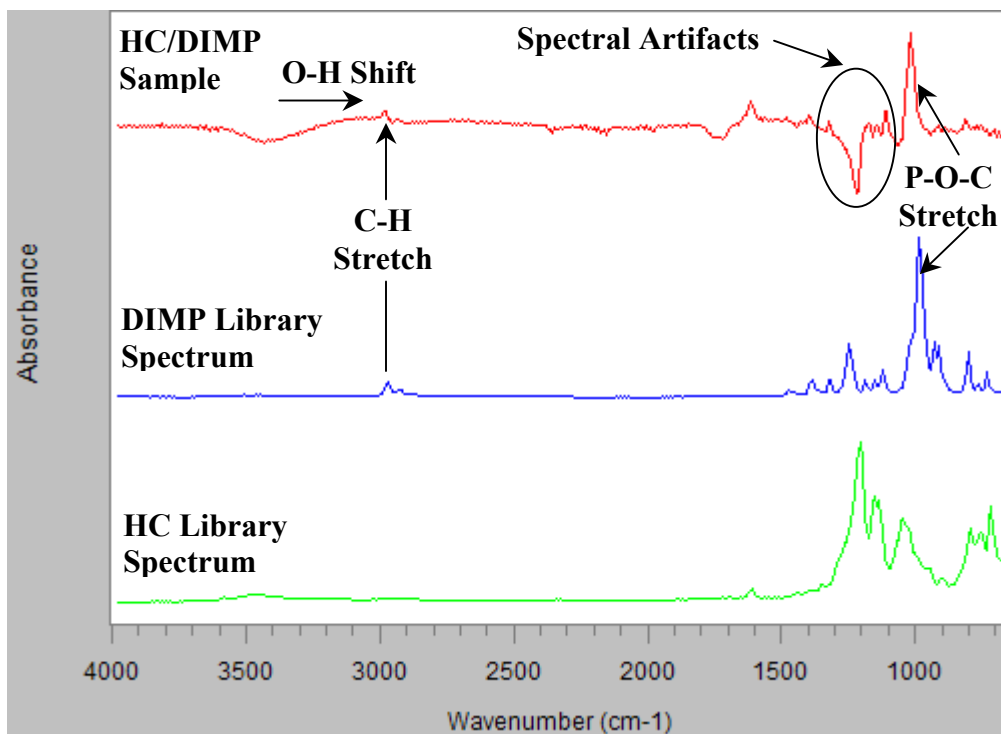


Figure 4-8: HC/DIMP Direct Sampling Spectrum (50 ppb, 8 min, 1 lpm)

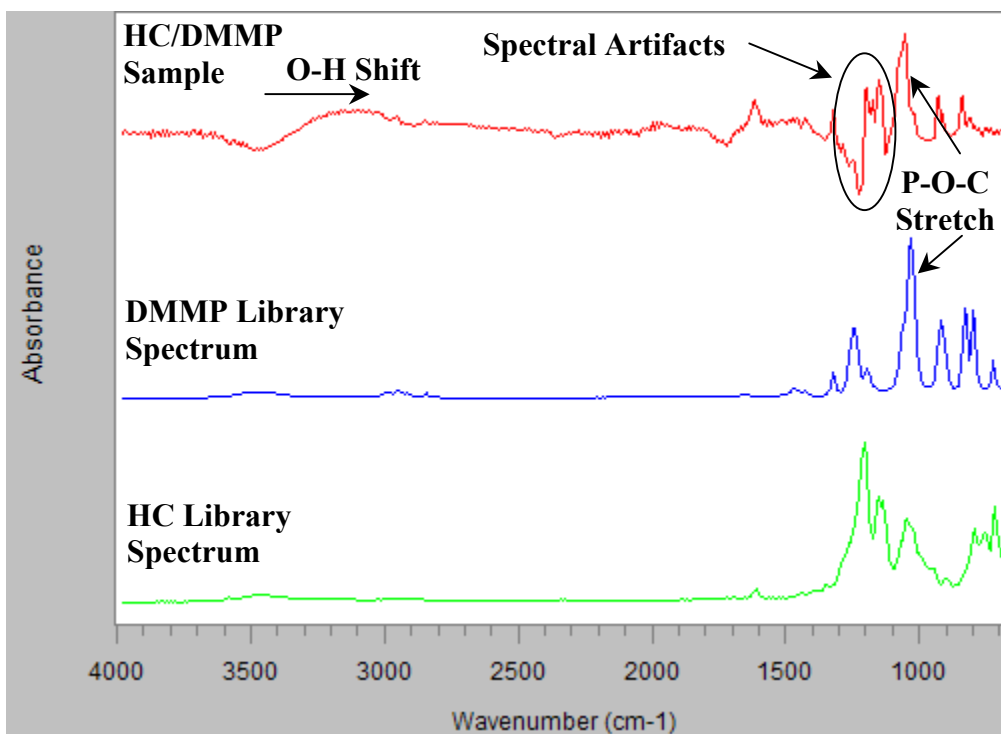


Figure 4-9: HC/DMMP Direct Sampling Spectrum (250 ppb, 8 min, 1 lpm)

establishing a LOD. At concentrations lower than the LOD, the instrument still produced spectral features that were more than 3 times the surrounding noise and could be used in spectral interpretation.

### 4.1.3 Extraction Time

The required extraction time must be short enough to allow for practical field sampling times. To explore the effects of changes to the extraction time, a HC SPME film ( $0.25 \pm 0.05$  AU) was exposed to a 1 ppm concentration of DIMP and DMMP for 2, 4, 8 and 12 minutes with a flowrate of 1 lpm. Table 4-3 shows the sample sets that were collected for HC/DIMP and HC/DMMP samples at 1 ppm concentrations.

Analyte	Sample Time	Sample Size (n)
DIMP	2	6
	4	7
	8	6
	12	3
DMMP	2	5
	4	5
	8	5
	12	3

**Table 4-3: HC Polymer/Analyte Sample Sets for Extraction Time**

As seen in Figure 4-10, the HC SPME film nears equilibrium with 1 ppm samples of DIMP and DMMP at 8 minutes. The percent increase in the mean absorbencies of the P-O-C stretch from the 8 and 12 minute extraction times were less than 1% for both analytes and the difference between 4 and 8 minutes was less than 11%. This small increase in absorbance, which is directly proportional to concentration, indicates that longer extraction times would not yield substantially higher concentrations of analyte in the SPME film. Although they will vary with the analyte of interest, field sample times of 4-8 minutes should suffice for HC SPME films to extract a high percentage of the

equilibrium amount of analyte. It should be noted however that SPME theory dictates that equilibration times increase with decreasing sample concentration (Pawliszyn, 1997). Therefore, increased sample times at lower concentrations may result in significantly larger extractions of analyte and a lower LOD.

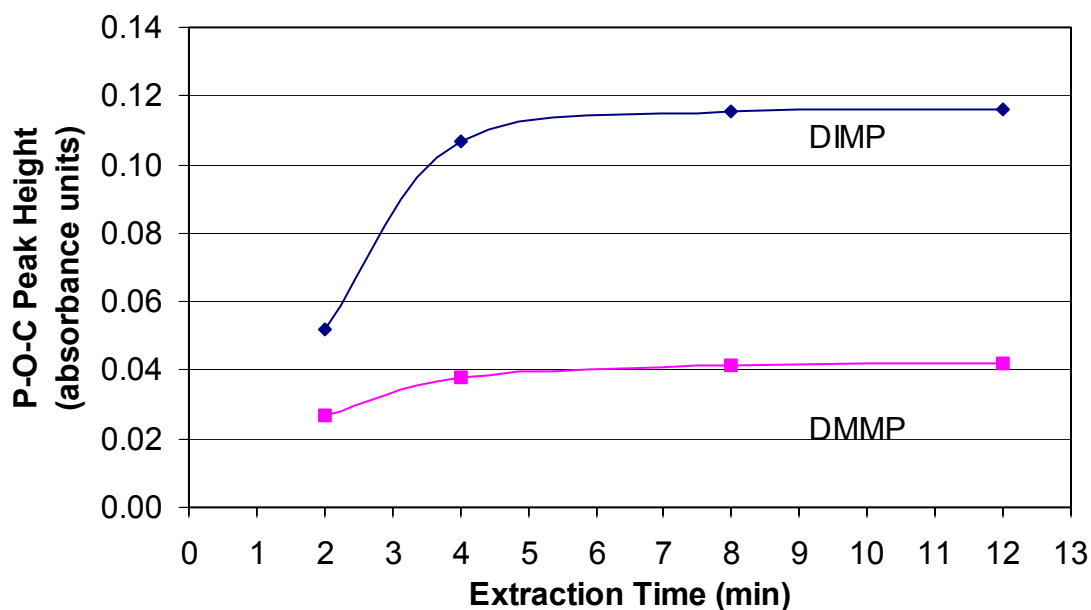


Figure 4-10: Extraction Time Profiles for HC/DIMP and HC/DMMP Direct Sampling (1 ppm)

#### 4.1.4 Sample Velocity

Increasing the sample's velocity over the SPME film should reduce the boundary layer between the film and the moving airflow. To explore the effects of air velocity on the extraction of analytes by HC SPME films, a film ( $0.25 \pm 0.05$  AU) was exposed to 2 L of analyte during exposure times of 2 and 4 minutes resulting in average velocities of 465 fpm and 232 fpm. A second set of samples was collected using 4 L of analyte for 2 and 4 minutes resulting in flowrates of 930 fpm and 465 fpm. Table 4-4 shows the sample sets that were collected for HC/DIMP and HC/DMMP samples at 1 ppm concentrations.

Analyte	Sample Time	Sample Flowrate (lpm)	Sample Size (n)
DIMP	2	465	6
	2	930	8
DMMP	2	465	5
	2	930	5
DIMP	4	232	5
	4	465	7
DMMP	4	232	5
	4	465	5

**Table 4-4: HC Polymer/Analyte Sample Sets for Sample Velocity**

Figure 4-11 shows the 95% confidence intervals of the mean absorbance at each sample time and velocity. Changes in velocity resulted in a significant difference ( $p \leq 0.001$ ) in the P-O-C stretch absorbencies at both sample times for DIMP and at the 4 minute sample set for DMMP. In the 2 minute sample set for DMMP, the mean absorbance increased with velocity although the difference was not statistically significant. One-way analysis of variance (ANOVA) was used to compare the difference in the means of each sample set. A normal distribution was assumed after visual inspection of Q-Q plots (Appendix B) and the requirement for similar sample size was met. A test for homogeneity of variances showed no significant differences in variance except for the 4 minute DIMP sample group. An independent samples T test, assuming non-equal variances, was run for that sample set and confirmed the significant difference found by ANOVA. The significant increase in absorbance in three out of the four sample sets indicates that higher sample velocities will yield higher concentrations of analyte in the HC SPME film.

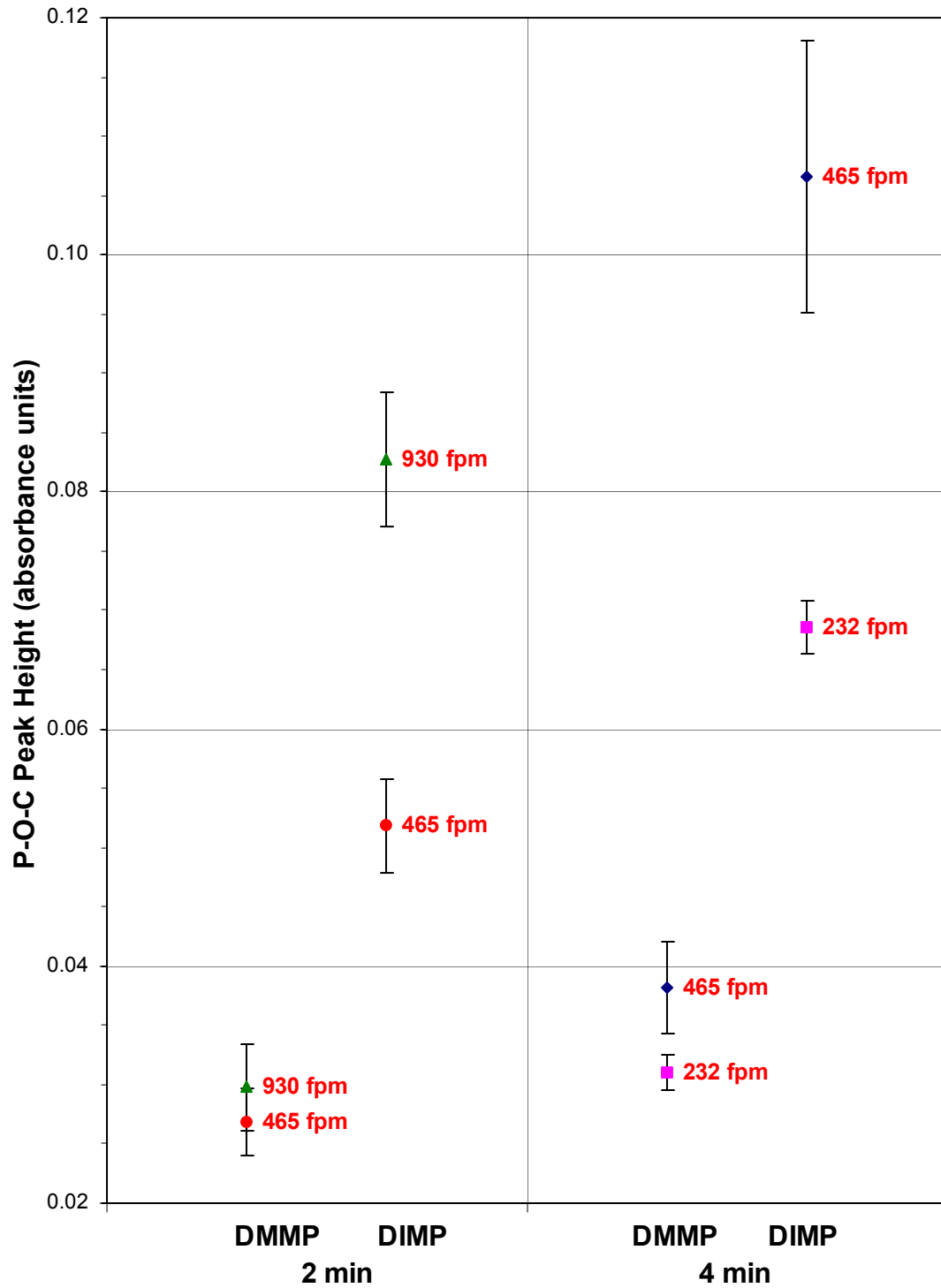


Figure 4-11: Comparison of IR Absorption to Changes in Sample Velocity with 95% Confidence Intervals (HC/DIMP and HC/DMMP Direct Sampling)

### 4.1.5 SPME Film Thickness

When SPME film sampling is combined with ATR analysis, increasing the thickness will increase the pathlength of interaction between the IR beam and the sample as long as the SPME film thickness is less than the IR penetration depth. As noted in Section 3.4.1, IRE SPME Film Coatings, any HC SPME film with an absorbance less than 0.68 AU at 1200 wavenumber (C-F stretch) will have a thickness less than the instrument's penetration depth of approximately 3  $\mu\text{m}$ . To study the effect of the SPME film thickness on the IR absorbance from a sample, the relative thickness of the film was varied while all other parameters remained constant. HC thicknesses of 0.1 ( $\pm 0.008$ ), 0.3 ( $\pm 0.025$ ), and 0.5 ( $\pm 0.042$ ) AU, as measured by IR absorption at the 1200 wavenumber C-F peak, were exposed to 4 L of analyte over 4 minutes at a concentration of 10 ppm. Table 4-5 shows the sample sets that were collected for HC/DIMP and HC/DMMP samples at 10 ppm concentrations.

Analyte	HC Absorption (AU at 1200 $\text{cm}^{-1}$ )	Sample Size (n)
DIMP	0.1	5
	0.3	6
	0.5	4
DMMP	0.1	5
	0.3	5
	0.5	5

**Table 4-5: HC Polymer/Analyte Sample Sets for Polymer Thickness**

**\*HC absorption is an indirect measure of HC thickness**

Changes in SPME film thickness resulted in a significant difference ( $p < 0.001$ ) in the absorbencies of the P-O-C stretch at each thickness for both DIMP and DMMP as determined by a one-way ANOVA with a Tukey HSD Post Hoc test. A normal distribution and equal variances were assumed after visual inspection of Q-Q plots (Appendix B) and the requirement for similar sample size was met. Due to the

exceptionally large F values (>200), small deviations from the ANOVA assumptions should not have a large impact on the test.

Figure 4-12 shows the 95% confidence intervals of the means, using one sample T tests. The significant increase in absorbance indicates that increased SPME film thickness increases instrument response while sample concentration remains constant. This trend should continue until the relative film thickness reaches 0.68 AU, after which it will be thicker than the penetration depth and yield no increase in IR absorption from the analyte.

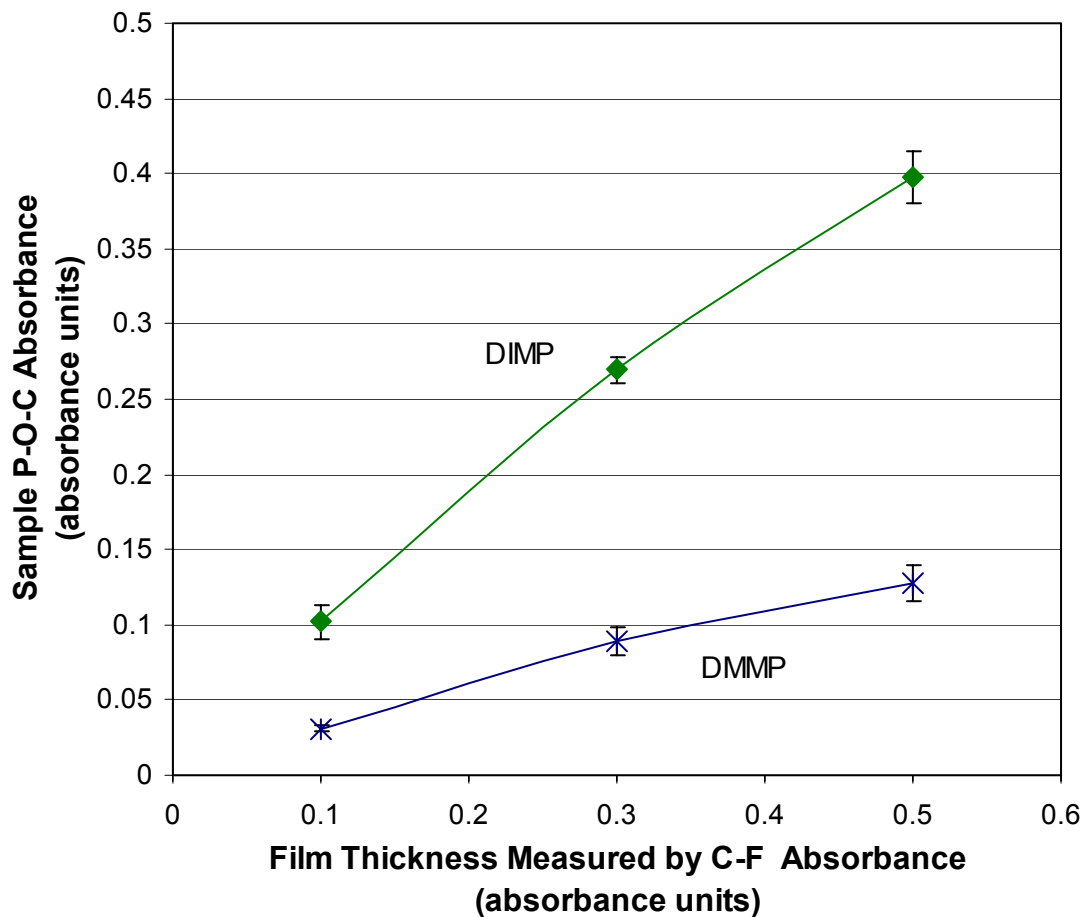


Figure 4-12: Comparison of IR Absorption to Changes in Film Thickness with 95% Confidence Intervals (HC/DIMP and HC/DMMP Direct Sampling, 10 ppm, 4 min, 1 lpm)

Two limiting factors regarding the SPME film thickness variable should be noted. First, as the film thickness increases, the time required to reach equilibration will

increase; therefore, longer sample times at lower concentrations may be required. Also, since a new baseline is recorded after application of the SPME film, the absorbance peaks from the polymer are adjusted to achieve a flat spectrum. However, despite a flat baseline, the polymer is still absorbing a large fraction of the radiation at many points in the spectrum. Increased SPME film thickness may increase spectral artifacts, such as the negative peaks seen in many of the sample spectra in previous sections, or in lower radiation absorbance attributed to the analyte of interest. Both of these side effects could hamper spectral analysis at lower concentrations. Therefore, the SPME film thickness should be increased until the penetration depth is reached or spectral quality is reduced.

#### **4.1.6 Quantitative Analysis**

When using SPME sampling and ATR analysis, factors from both Beer's Law and SPME theory must be addressed. Pathlength, IR absorptivity, analyte/polymer distribution coefficient, and equilibrium times are some of the factors that would have to be addressed to find an equation for quantification of SPME samples by ATR analysis. To explore the possibility of using an algorithm to quantify analyte concentrations, a calibration curve based on the peak heights of the P-O-C stretch in the analyte was created.

Figures 4-13 and 4-14 illustrate that, at the middle and high concentrations, a logarithmic relationship appears to exist for both DIMP and DMMP between the peak height and the analyte concentration. The problem with this logarithmic relationship is that both the Beer-Lambert Law and SPME theory dictate that the concentration should be directly proportional to absorbance. If Equations 2-2 and 2-4 are combined,

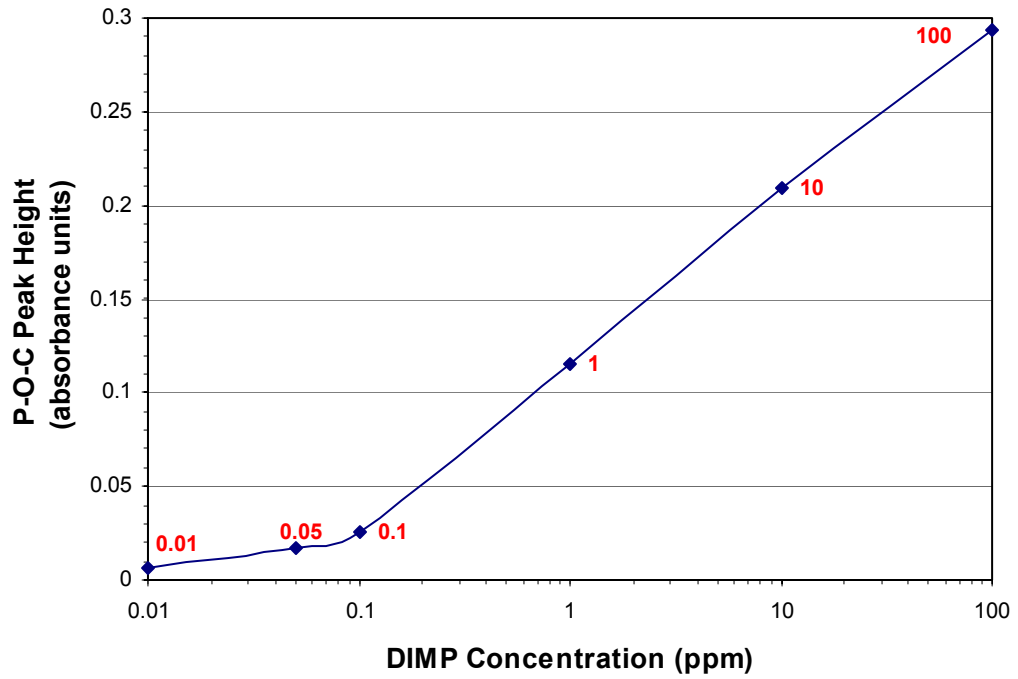


Figure 4-13 IR Absorbance vs. Concentration for HC/DIMP Direct Sampling (8 min, 1 lpm)

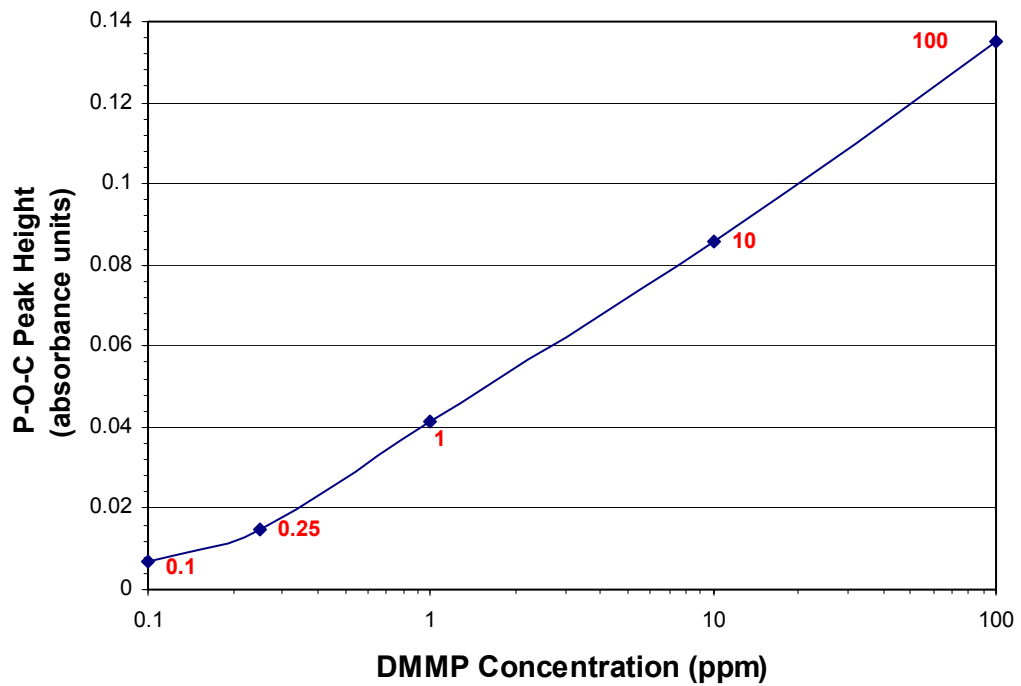


Figure 4-14: IR Absorbance vs. Concentration for HC/DMMP Direct Sampling (8 min, 1 lpm)

absorbance and concentration should be related by:

$$A = \varepsilon l K_{fs} C_o \quad \text{Equation 4-1}$$

where:

- A = absorbance (AU)
- $\varepsilon$  = absorptivity (L/mol $\cdot\mu\text{m}$ )
- l = pathlength ( $\mu\text{m}$ )
- $K_{fs}$  = film/sample distribution constant
- $C_o$  = concentration of analyte in the sample (mol/L)

There are two theories why the data in Figures 4-13 and 4-14 did not follow the directly proportional relationship seen in Equation 4-1. First, as the concentration of a sample increases, intense absorbance bands do not always follow the Beer-Lambert Law (Smith 1996). Using a less intense reference peak could result in a more linear relationship. Second, as the SPME film extracts analyte, the film thickness increases due to the additional mass. This means that the pathlength in Equation 4-1 will increase proportionally with the concentration. At high concentrations, the SPME film might have extracted enough analyte that the thickness of the film surpassed the penetration depth of the IR beam thus ending the proportional increase in pathlength and reducing the change in absorbance when compared to lower concentrations.

With this in mind, the 10 and 100 ppm data points were removed and the remaining data were plotted in Figures 4-15 and 4-16. Without the high concentrations, the data follow a directly proportional relationship as predicted by Equation 4-1. A linear calibration curve can be established and should be useful in quantifying analysis results. Sampling parameters such as sample time, velocity, and SPME film thickness would have to be controlled for a consistent calibration curve. For concentrations at 1 ppm and below, the samples were probably not at equilibrium so particular attention would need to be paid to sample time since the extraction time profile (as described in Section 4.1.3,

Extraction Time) could still be relatively steep and result in large changes in absorbance. In addition, as with all ATR instruments, this calibration curve is only applicable to the IRE crystal used to generate it and it should not be used on other instruments.

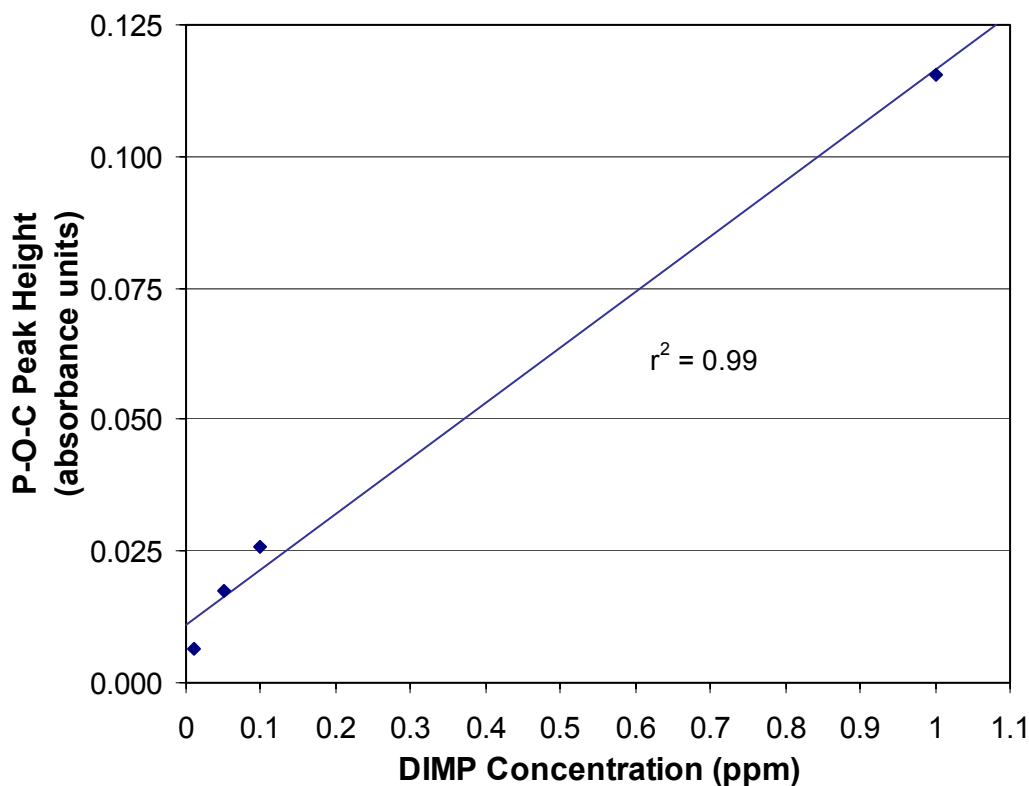


Figure 4-15: IR Absorbance vs. Concentration for HC/DIMP Direct Sampling (8 min, 1 lpm)

#### 4.1.7 Desorption Time

To measure the desorption of the analyte from the SPME film over time, a HC SPME film was placed on the IRE and exposed to varying concentrations. The samples were reanalyzed at 5 minute intervals for a period of 30 minutes. Triplicate samples were run at each concentration.

As expected, samples at the highest concentrations desorb more quickly and release a larger percentage of analyte than the lower concentrations (see Figures 4-17 and 4-18).

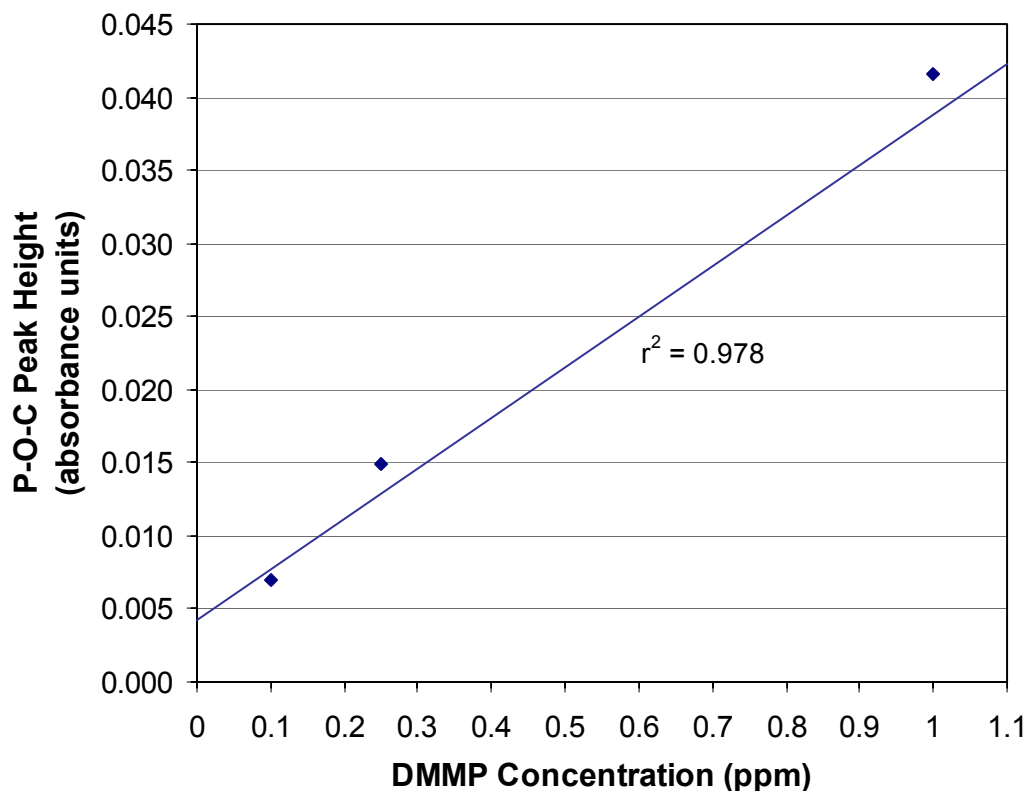


Figure 4-16: IR Absorbance vs. Concentration for HC/DMMP Direct Sampling (8 min, 1 lpm)

Results from samples at lower concentrations show only a small percentage of analyte is lost. For DIMP, the absorbance values after 10 minutes for 10 ppm, 1 ppm and 0.1 ppm samples were 75%, 86% and 100% of their original absorbance values. DMMP samples at 100 ppm, 10 ppm, and 1 ppm, retained 53%, 62%, and 82% of their absorbance. Low desorption rates over 10 to 15 minute periods indicate that remote SPME sampling and later ATR analysis is feasible and quantification of results at low concentrations could be representative of the original concentration.

## 4.2 Remote Sampling

To explore whether or not chemical vapors can be sampled in a remote location and brought to an ATR-FTIR instrument for analysis, a transportable sampling device was

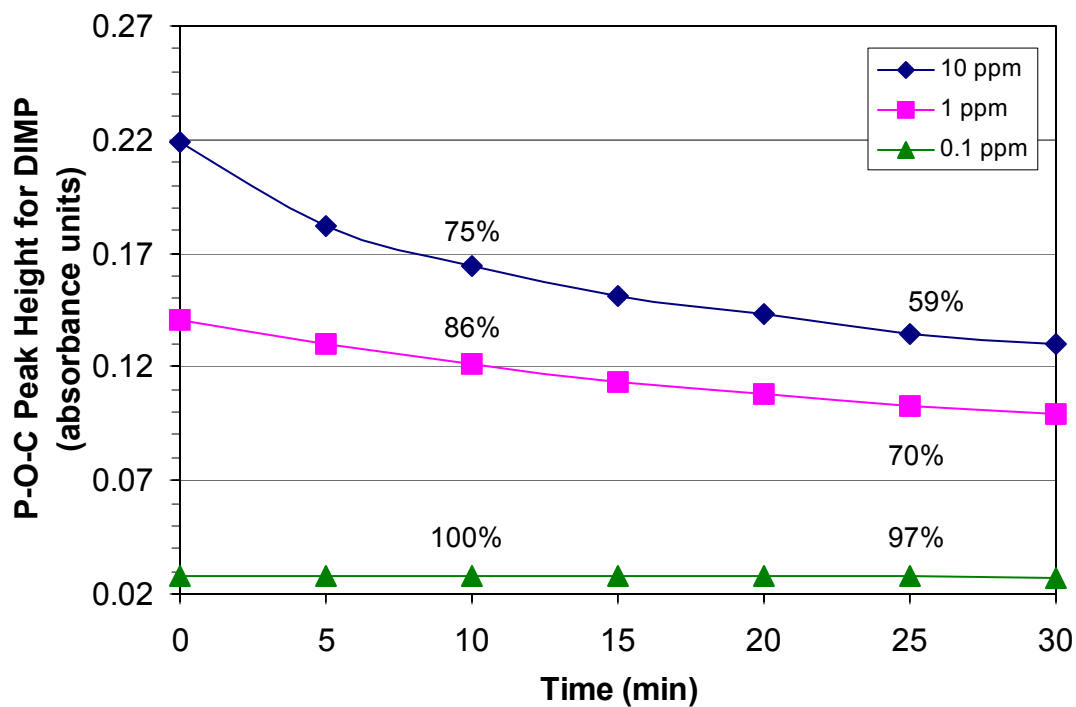


Figure 4-17: Desorption Time Profiles for HC/DIMP Direct Sampling with Percent of Original Peak Height Remaining (8 min, 1 lpm)

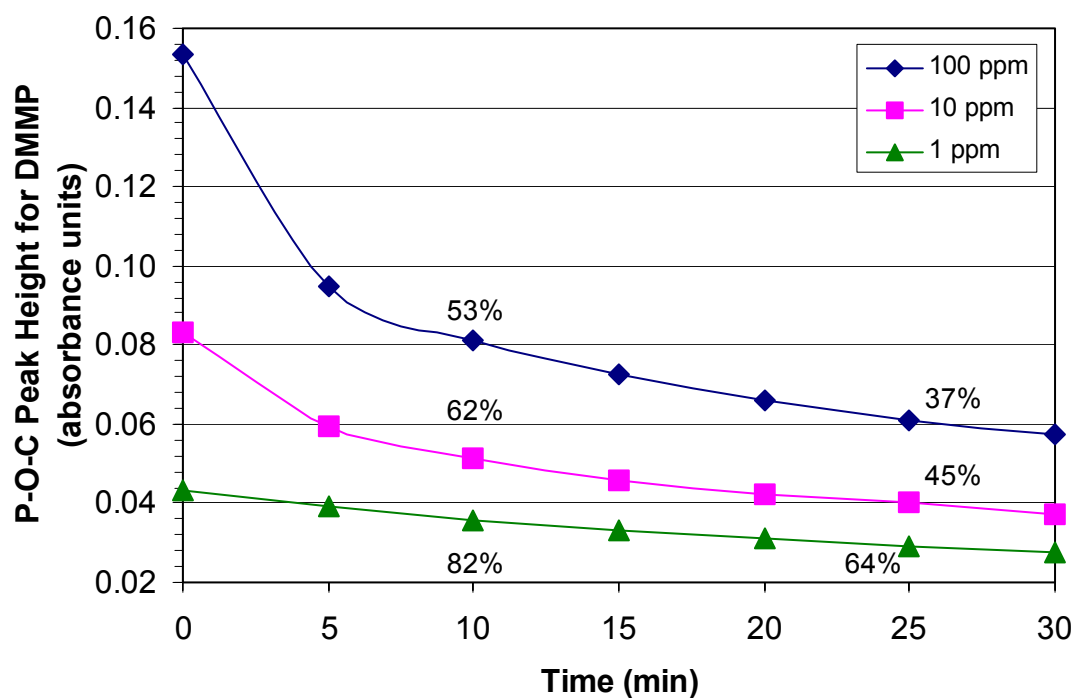


Figure 4-18: Desorption Time Profiles for HC/DMMP Direct Sampling with Percent of Original Peak Height Remaining (8 min, 1 lpm)

assembled. A HC SPME film on an acrylic strip backing was placed inside a UTH where DMMP samples were pumped over the film. Since the SPME film is on the acrylic sampling strip and not on the instrument's IRE, a new background to zero out the absorbance of the polymer could not be established. Placing the film on the IRE to record a new background would cause the polymer to adhere to both the IRE and the acrylic strip and alter the film's original thickness. Therefore, unlike in the direct sampling method, the sample spectra were a combination of both the analyte and the SPME film without the benefit of the polymer "background subtraction."

#### **4.2.1 Analyte Identification**

Figure 4-19 shows the spectrum from a 10 ppm, 15 minute, remote sample. A spectrum from each concentration is available in Appendix D. The dominant peak is the C-F stretch from the HC polymer at 1196 wavenumbers but the P-O-C stretch from the analyte combines with the C-F peak of the HC polymer at 1037 wavenumbers to produce an increased absorbance value. The effect of the polymer/analyte hydrogen bonding can still be seen in the slight increase in absorbance at 3100 wavenumbers. The combination of hydrogen bonding and the increased absorbance at the P-O-C wavenumber indicate that the analyte is a significant contributor to the sample spectra. The instrument can be "trained" to identify the future HC/DMMP remote samples by adding a representative spectrum of the sample to the library. However, the differences between the sample spectrum and the unexposed polymer were much smaller than the direct method where the SPME film was placed directly on the IRE and a new background was established. This will result in a higher LOD since the samples will have a high correlation to

unexposed SPME films making it harder to match the sample spectrum to the correct library spectrum.

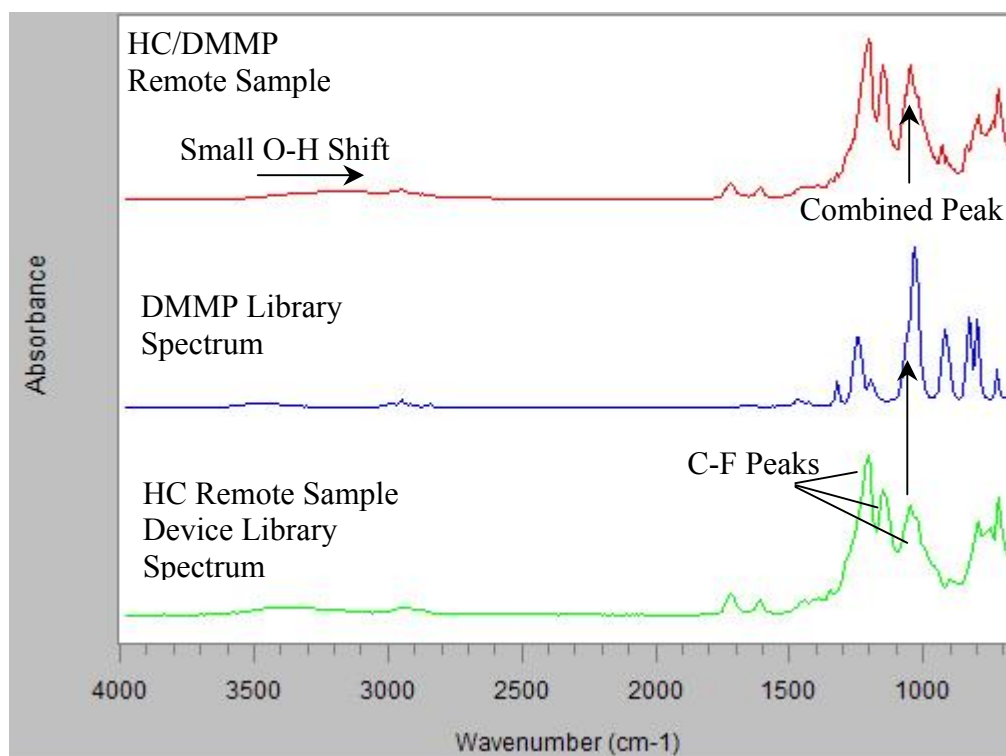


Figure 4-19: HC/DMMP Remote Sample Spectrum (10 ppm, 15 min, 0.2 lpm)

#### 4.2.2 Remote Sampling Limit of Detection

Table 4-6 shows the sample sets that were collected for remote HC/DMMP samples. The representative spectrum added to the library was from the 100 ppm, 15 minute sampling since this was the lowest concentration that met all criteria listed in Section 3.6, Library Generation.

DMMP	Concentration		
	10 ppm	100 ppm	1265 ppm
Sample Time (min)			
15	3	3*	3
5	4	3	3
1	5	5	3

Table 4-6: Remote HC/DMMP Sample Sets

\* Concentration and sample time used to generate the polymer/analyte library spectrum

Based on the 100 ppm sample library spectrum, a LOD of 10 ppm was observed for remote HC/DMMP 15 minute samples. Below that concentration, the difference between the correct library match and the first incorrect library match was no longer statistically different. Shorter sample times of 5 and 10 minutes could not differentiate a 10 ppm sample from the library spectrum of an unexposed SPME film coated acrylic strip. Figure 4-20 shows the 95% confidence intervals for the correlation values of the correct HQI and the next best HQI. A paired samples T test demonstrated a significant difference between the top two matches in all 15 minute sample sets ( $p \leq 0.012$ ). Despite small sample sizes, a normal distribution and equal variances were assumed after visual inspection of Q-Q plots (Appendix B) for each sample set and the ratios of the variances were small.

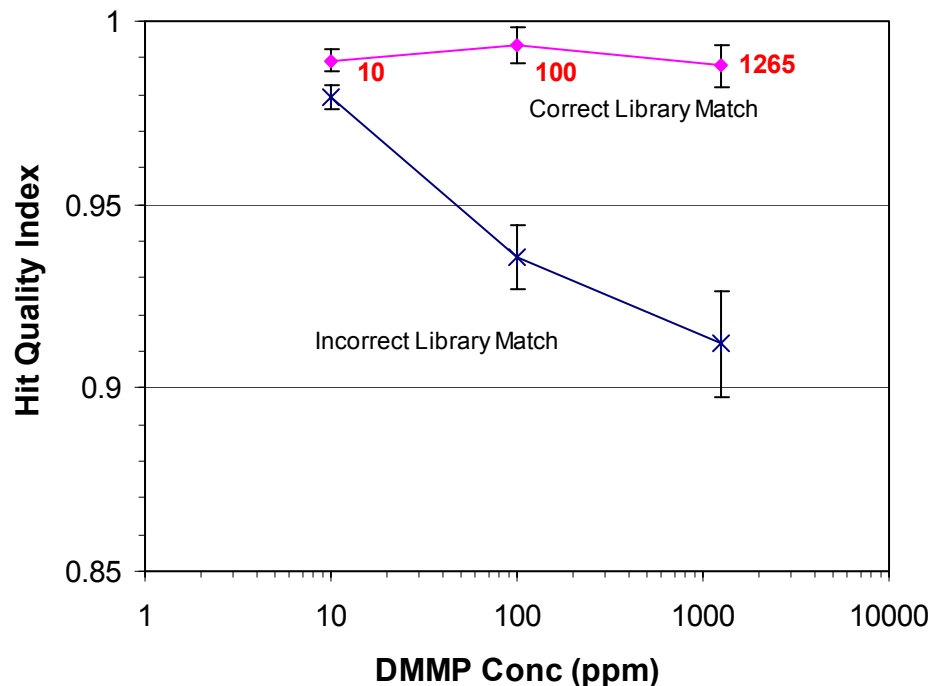


Figure 4-20: Comparison of the Correct Library Match and the First Incorrect Match with 95% Confidence Intervals (HC/DMMP Remote Sampling, 15 min, 0.2 lpm)

## 5 Discussion and Conclusions

This research was intended to broaden the capability of field portable ATR-FTIR spectrometers to identify chemicals in the vapor phase without elaborate sample preparations. Three polymeric SPME films (HC, HCM, and HCMAM) were used to collect samples of DIMP and DMMP. Spectral analysis of the SPME film samples from each of the three polymers confirmed that the analyte could be identified. SPME film sampling coupled with ATR analysis can enhance the capability of ATR-FTIR in identifying chemicals in the vapor phase.

LODs established in this study for the identification of DIMP and DMMP using the TravelIR™ with HC SPME film were 50 ppb and 250 ppb respectively. However, the LOD set in this study was based on a library spectrum that could identify the analytes at concentrations as high as 100 ppm. Since these extremely high concentrations are not typically relevant to field sampling for CWAs, a spectrum from a lower concentration could be added to the library to reduce the LOD.

Instrument response to the analyte increased as both the velocity of the sample over the SPME film and the thickness of the film increased. As the sample velocity was increased, the concentration of analyte in the SPME film also increased. Increasing the SPME film thickness increases the pathlength and allows more interaction between the analyte and the instrument. Optimizing the combination of these variables could further reduce the LODs.

Linear calibration curves based on P-O-C peak heights vs. concentration values were demonstrated for concentrations at and below 1 ppm. This suggests that quantitative analysis of SPME-ATR sampling is feasible. An equation based on the Beer-Lambert

Law and SPME theory was proposed to explain the observed directly proportional relationship.

Extraction time profiles for 1 ppm samples of DIMP and DMMP with HC SPME film suggest that the majority of analyte extraction will take place within the first 4 minutes of sampling, which is a reasonable time frame for field sampling. Desorption curves show that almost no analyte is lost in the first 10 minutes for the lowest concentrations and the IR absorption peaks for higher concentrations are still very intense. The slow desorption times make remote sampling feasible.

The LOD for a remote sampling technique using a HC SPME film on an acrylic strip was 10 ppm for DMMP. This LOD was much higher than the LOD for the direct sampling method but it could be lowered with changes to the sampling variables or the sampling device.

## **5.1 Applications**

One application of SPME-ATR sampling and analysis may be as a continuous area monitoring device. Current technologies used by the military rely on analytical techniques such as SAW and ion mobility spectrometry (IMS), which are prone to false positive results. In addition, the LODs of most commercially fielded systems are relatively high. The fundamental principles behind IR spectrometry mean that instrument response is based on the specific chemical structure of analytes and not just the presence or absence of a chemical. The spectral “fingerprint” from the instrument can be used to screen out false positives through spectral interpretation. In addition, the selectivity of the polymer used for sample collection reduces many of the sources of false positives associated with other technologies. As evidenced by this research, SPME-ATR is capable

of LODs in the ppb range and those limits may be lowered if the sampling variables covered in this study are changed. Current technology has already produced rugged and portable ATR-FTIR instruments and continuous area monitors could potentially be produced by modifying current instrumentation.

A second application would be for air sampling by first responders or industrial hygienists. If the remote sampling method can be improved to provide lower detection limits with pre-manufactured sampling devices, large numbers of samples could be collected and rapidly analyzed. The system has a very small footprint with low power consumption and no need for special gases or large amounts of supplies. The development of methods for quick and reproducible SPME film films could also make SPME-ATR sampling and analysis a valuable tool in the field. A SPME film could be placed on the IRE and the instrument can be taken to the sampling location to supplement other field analysis methods.

## **5.2 Study Limitations**

Inaccuracies in the analyte concentrations used in this study could arise from using two different methods to make the concentrations: liquid injection and saturated air injection. However, highly precise concentrations were not considered critical to this type of exploratory research. The analyte concentrations were not independently verified and analyte losses to the syringe, bag, or sample train were possible. Standard temperature and pressures were assumed throughout the study and some fluctuations in these variables may have had a minor influence on actual concentrations. Measurement error may have occurred during the injection of small amounts of liquid and air to create sample concentrations in Tedlar bags.

For most of the sampling, hand pressure was used to force the sample over the SPME film. Because of this, variations in velocity likely occurred during the exposure period and only an average velocity could be calculated. Air pumps that could provide a more consistent velocity were tested but there was a substantial loss of analyte to the pump before it reached the film. It was decided that hand pressure was better than the losses to the pump and care was taken to apply even pressure through the sampling period.

Equipment was not available to ensure even and accurate SPME film thickness on the IRE or acrylic strips. Absorbance values were used to ensure relative thickness remained constant but the tolerances for most samples were large (20%). Uneven film and thickness variations may affect observed results.

### **5.3 Additional Research**

Follow-on research in this area should include:

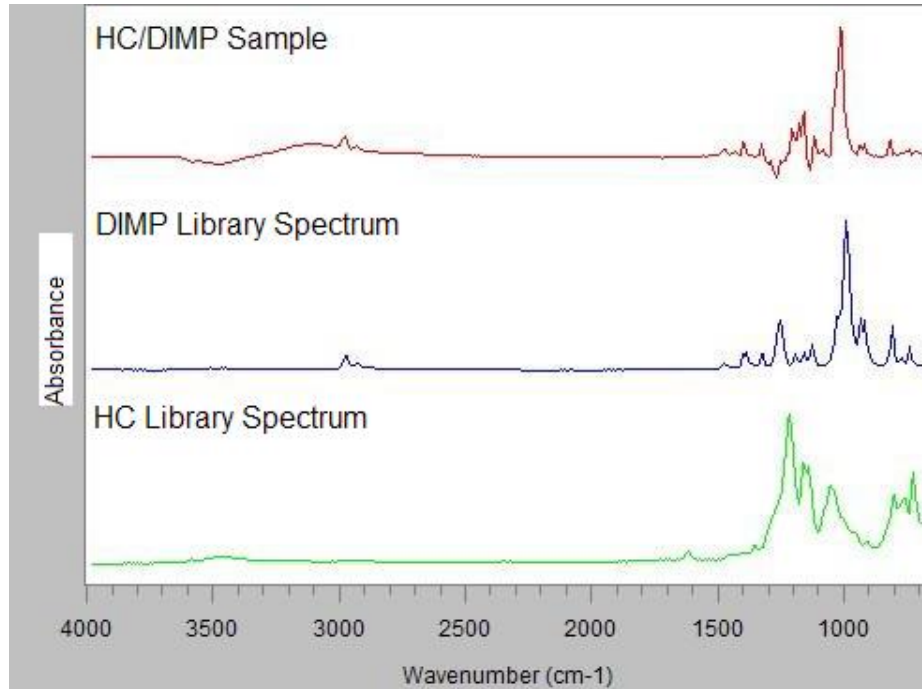
1. Optimization of sample variables: Variables such as sample velocity, SPME film thickness, and sample time were evaluated independently in this study. Additional research should find the optimal combination of these variables to establish a lower LOD for both direct and remote sampling.
2. Quantitative testing: A linear calibration curve was observed during this testing suggesting that sample quantification is possible; however, analysis of concentrations between the points used to generate the curve were not tested. Further research to confirm that quantification is possible should be explored. Determination of constants such as the polymer/analyte absorptivity coefficient,

analyte/polymer distribution coefficient, and equilibrium times would also be beneficial.

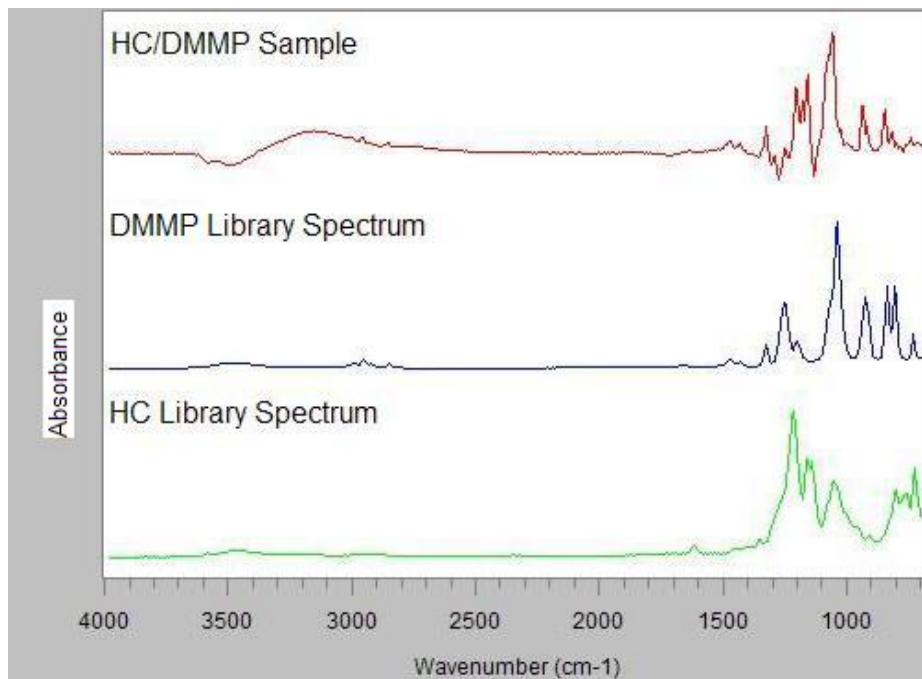
3. Interferences: Most sample spectra in this study have spectral artifacts due to spectral shifting caused by the hydrogen bonding of analyte to the polymer. These artifacts are not seen in most IR spectrometry applications and significantly lower the HQIs from library spectra without these artifacts. As more analytes are sampled using the SPME-ATR sampling and analysis technique, more spectra with similar artifacts will be added to spectral libraries. The increase in similar spectra could increase the HQIs of incorrect spectra and raise the LODs established in this study. However, the lack of spectral matching interference between the two structurally similar analytes used in this study indicate that this will not be a significant problem.
4. Establishment of LODs for Nerve Agents: This study used common simulants for nerve agents. Even though the two simulants were similar in structure, the LOD for DMMP was 5 times higher than DIMP. The LODs for these simulants may not accurately reflect the LODs for nerve agents.
5. Additional polymer and analyte testing: The polymers used in this study selectively concentrated hydrogen bond basic analytes. The testing of polymers that target different classes or a broader range of toxic industrial chemicals would greatly increase the versatility of this sampling and analysis method.

## Appendix A

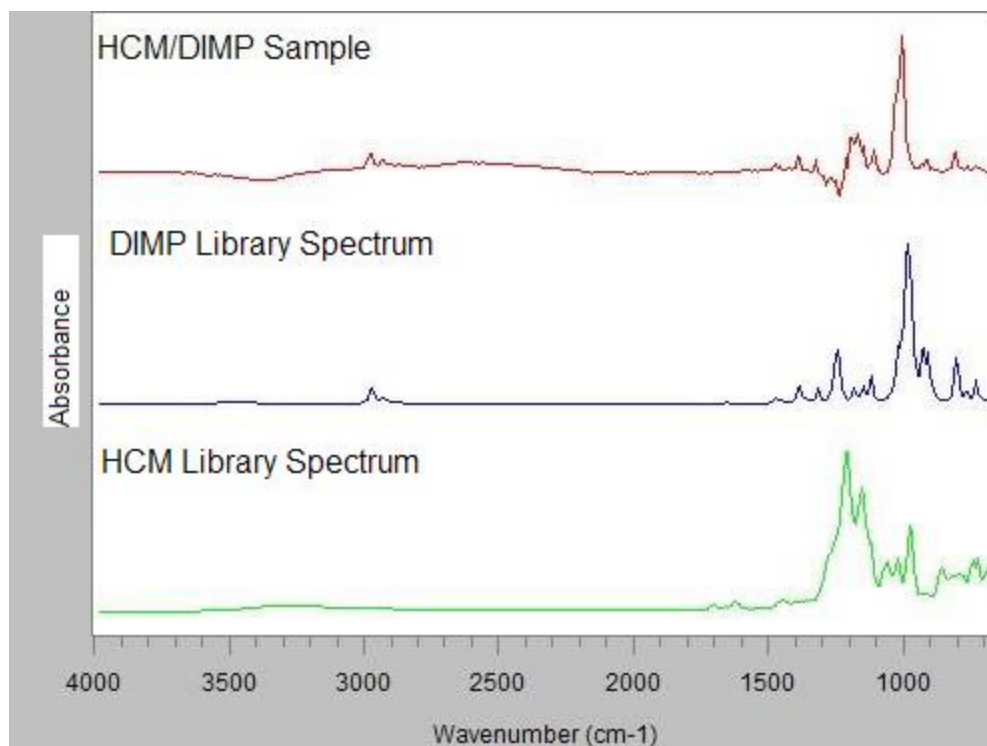
### Direct Sampling Comparison Spectra



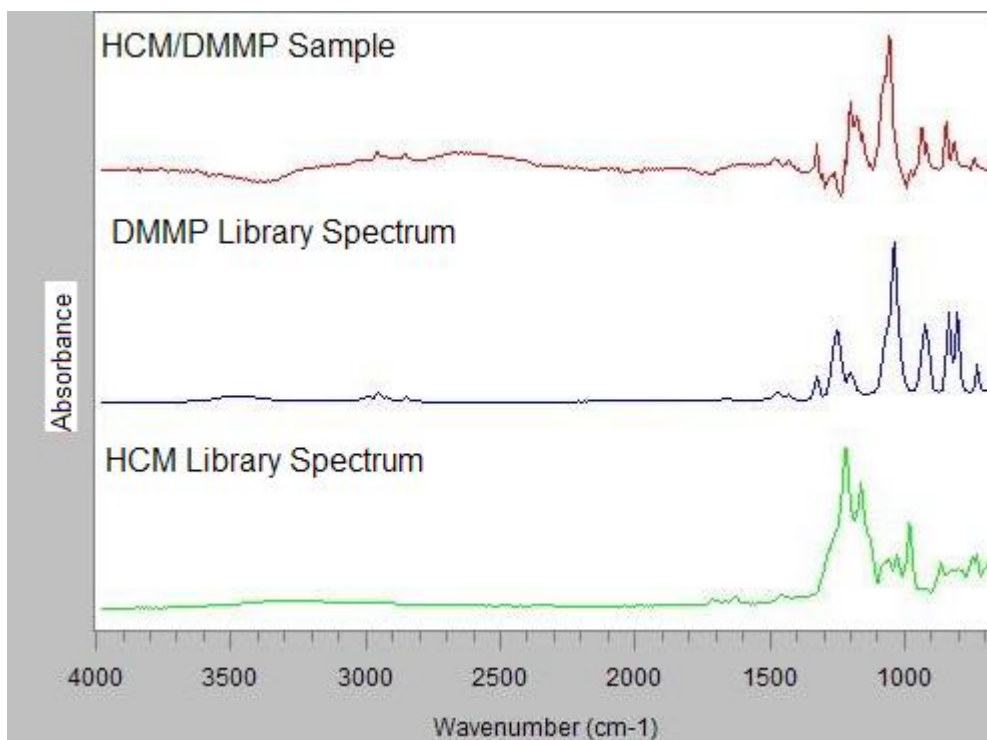
DIMP Extracted by HC Direct Sampling (10 ppm, 2L, 2 min)



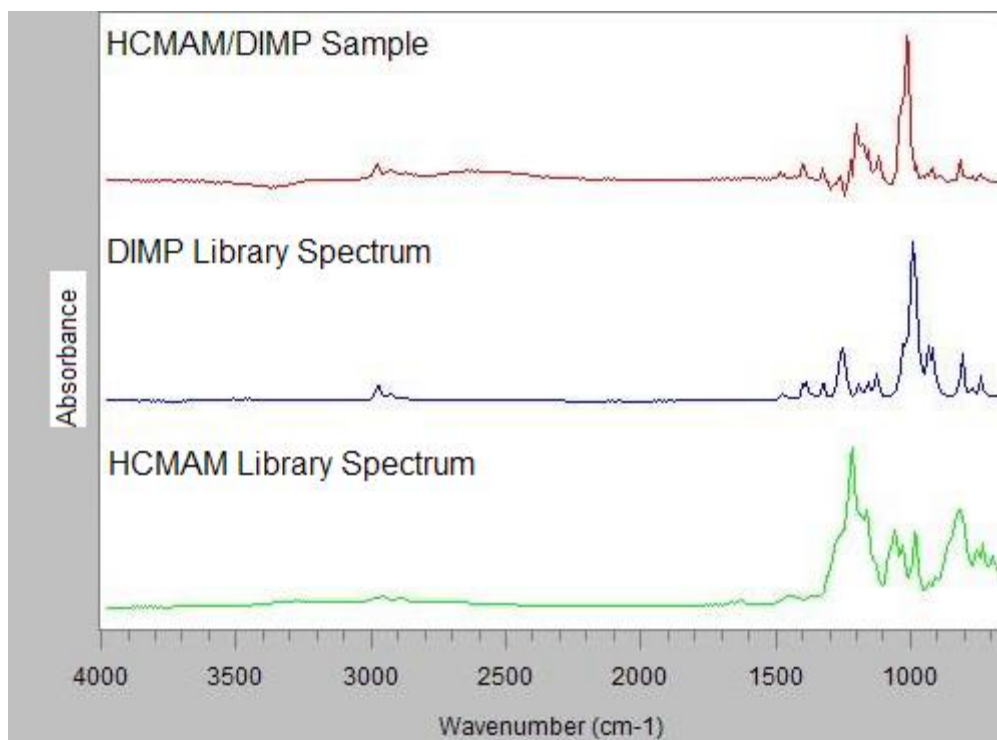
DMMP Extracted by HC Direct Sampling (10 ppm, 2L, 2 min)



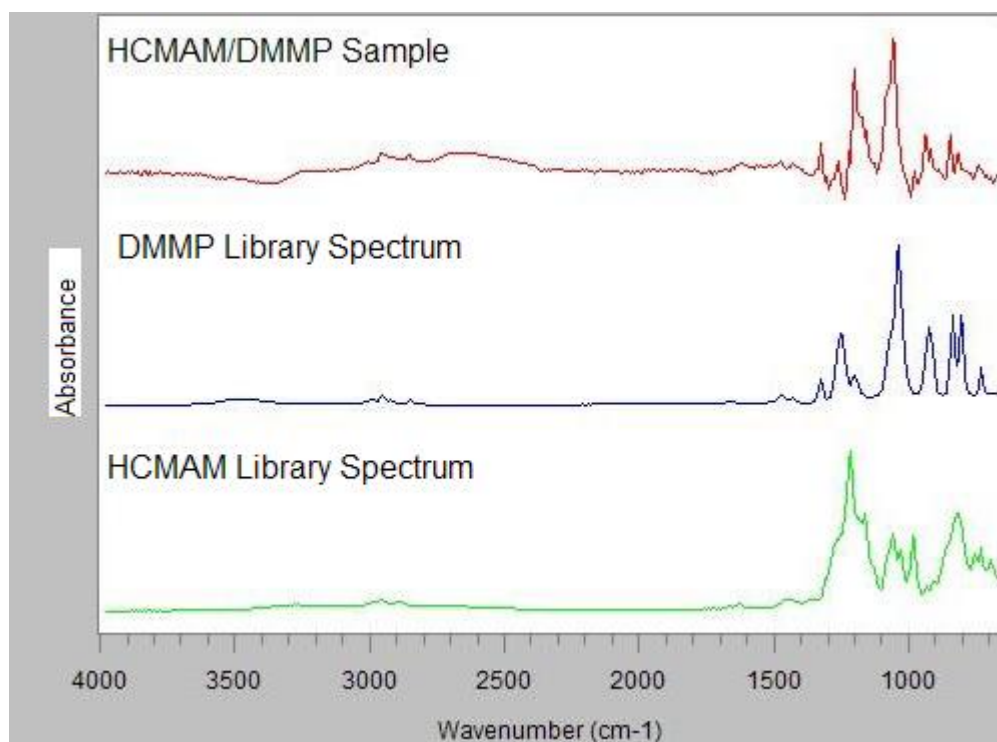
DIMP Extracted by HCM Direct Sampling (10 ppm, 2L, 2 min)



DMMP Extracted by HCM Direct Sampling (10 ppm, 2L, 2 min)



DIMP Extracted by HCMAM Direct Sampling (10 ppm, 2L, 2 min)



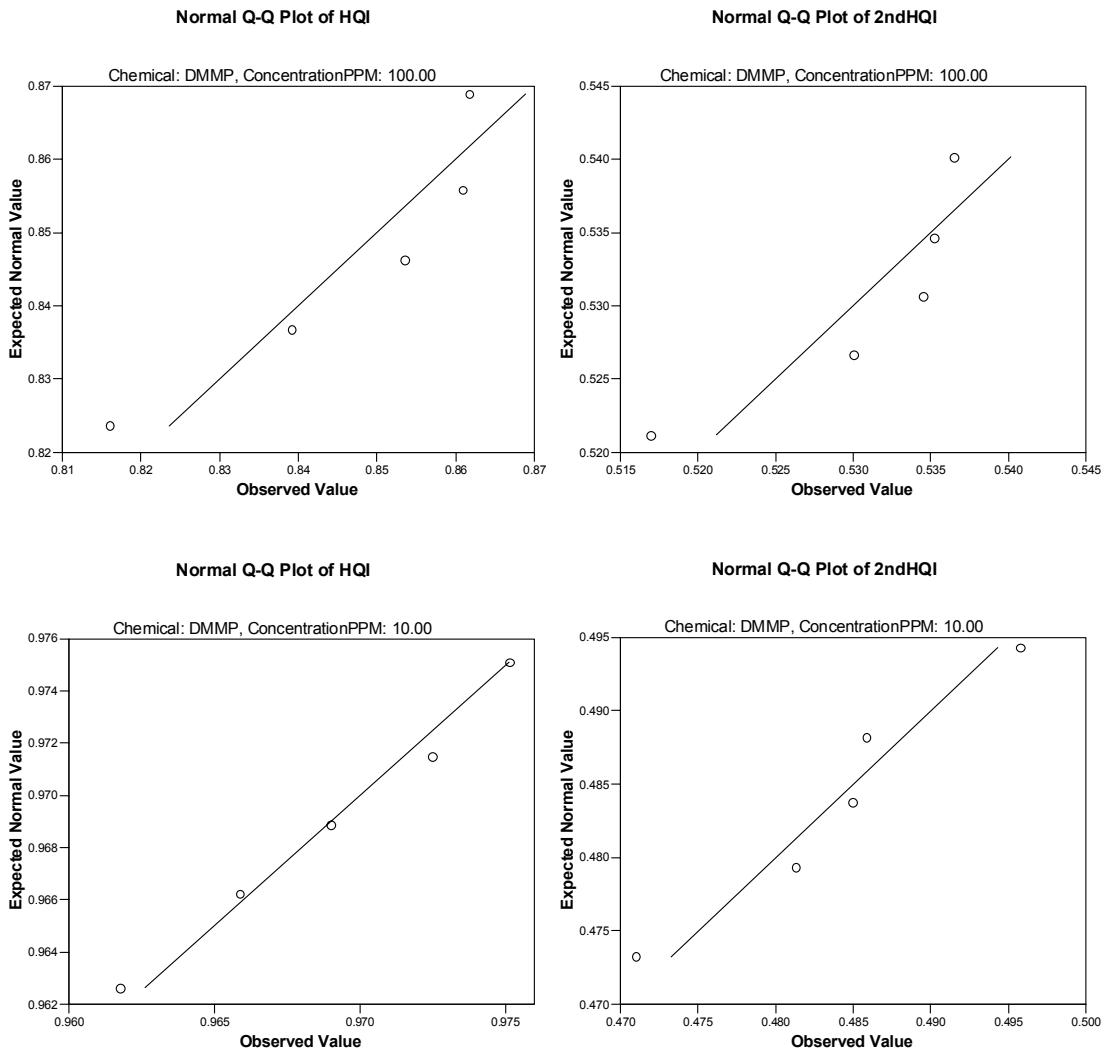
DMMP Extracted by HCMAM Direct Sampling (10 ppm, 2L, 2 min)

# Appendix B

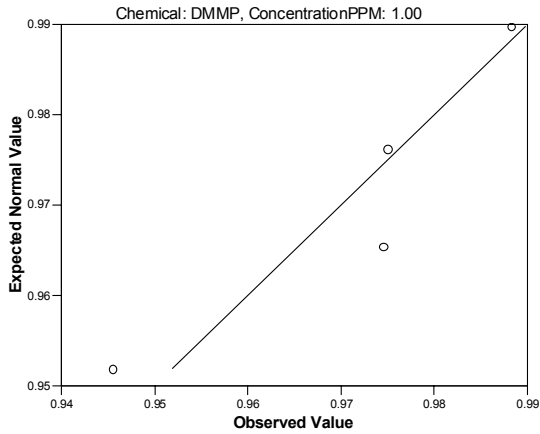
## Quantile-Quantile Plots

- Section 4.1.2 Direct Sampling Limit of Detection

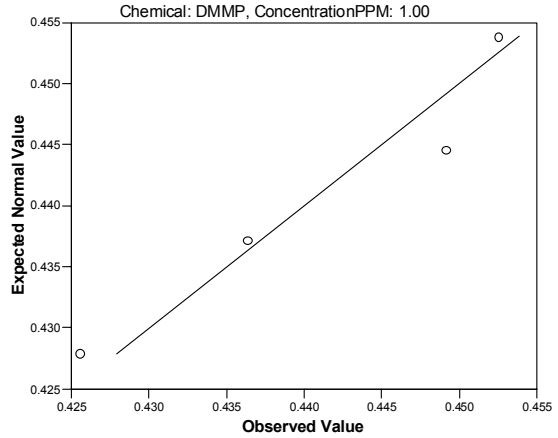
HQI is quality index of the sample spectrum compared to the correct library spectrum and 2<sup>nd</sup> HQI is the quality index of the sample spectrum compared to the first incorrect library spectrum.



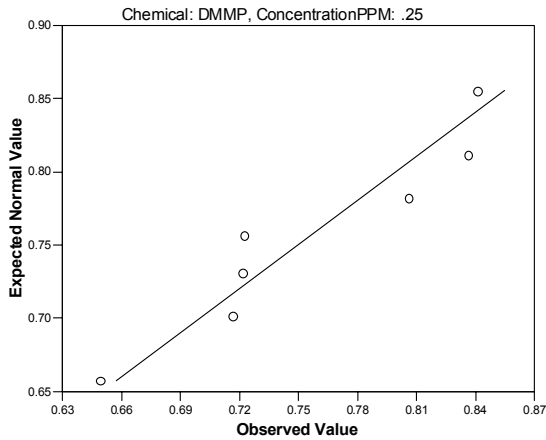
Normal Q-Q Plot of HQI



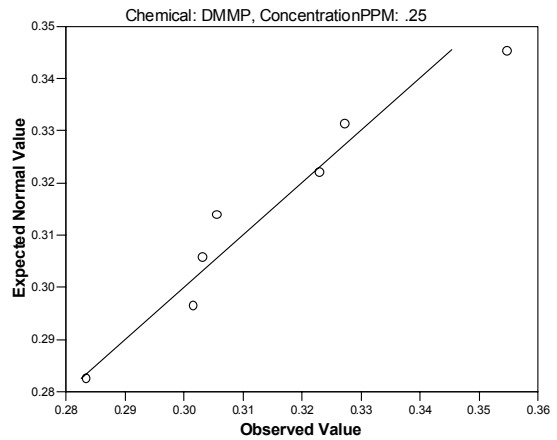
Normal Q-Q Plot of 2ndHQI



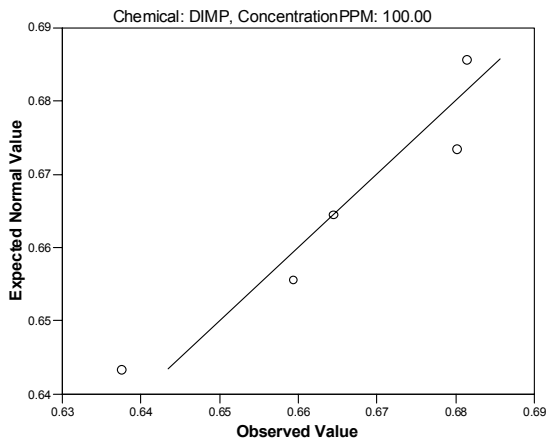
Normal Q-Q Plot of HQI



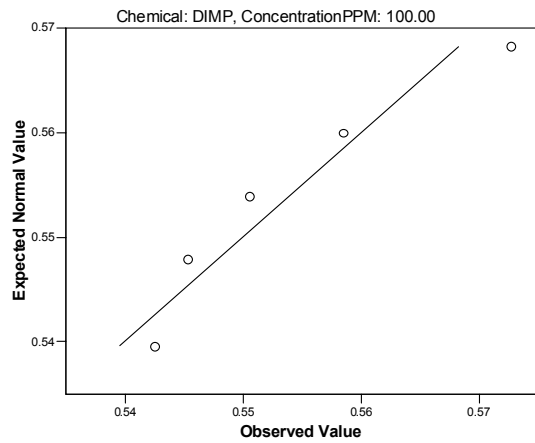
Normal Q-Q Plot of 2ndHQI



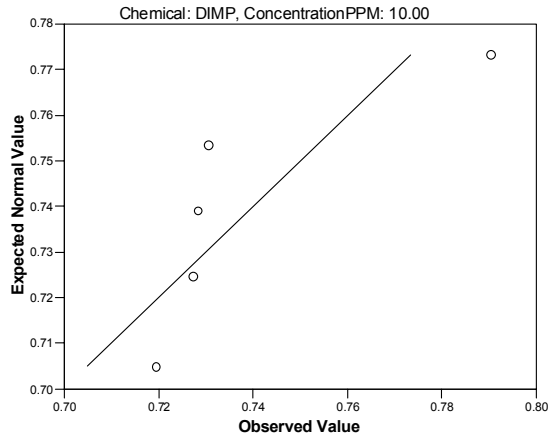
Normal Q-Q Plot of HQI



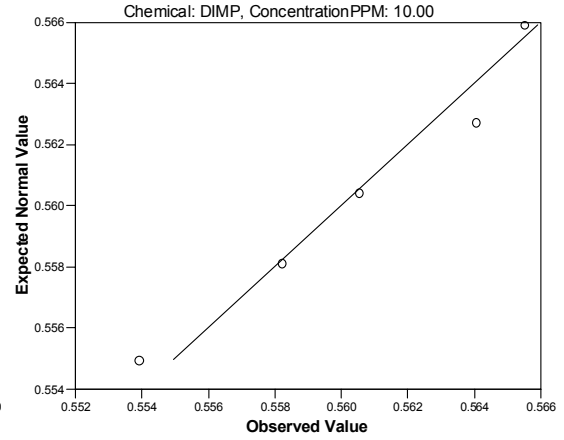
Normal Q-Q Plot of 2ndHQI



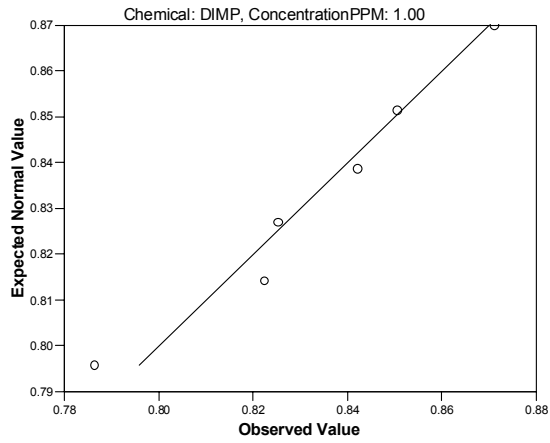
Normal Q-Q Plot of HQI



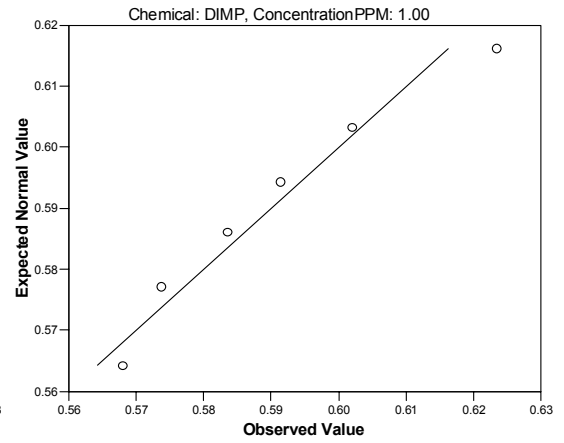
Normal Q-Q Plot of 2ndHQI



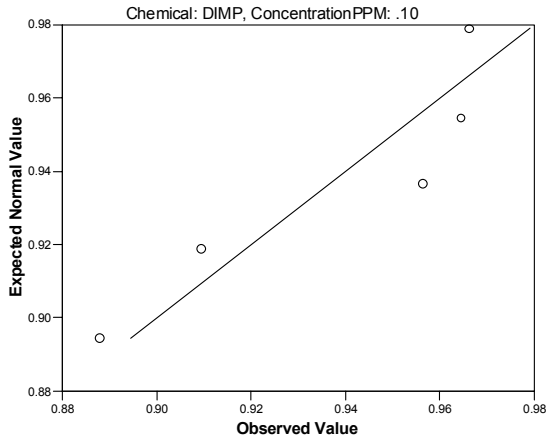
Normal Q-Q Plot of HQI



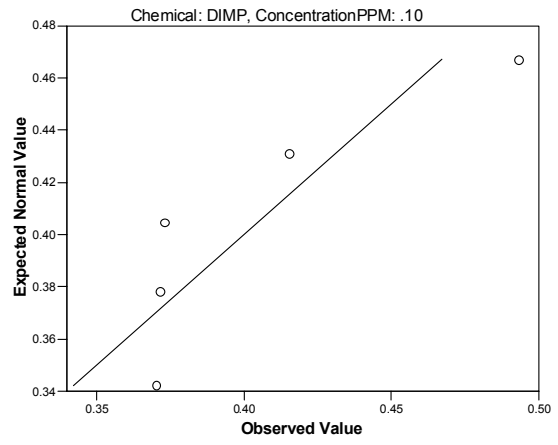
Normal Q-Q Plot of 2ndHQI



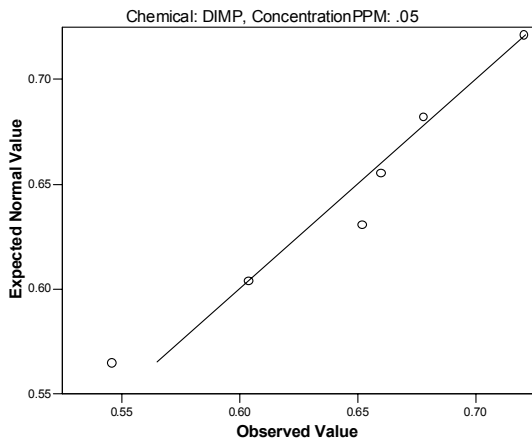
Normal Q-Q Plot of HQI



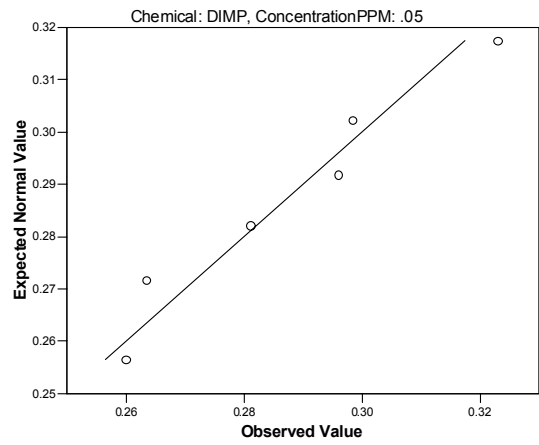
Normal Q-Q Plot of 2ndHQI



Normal Q-Q Plot of HQI

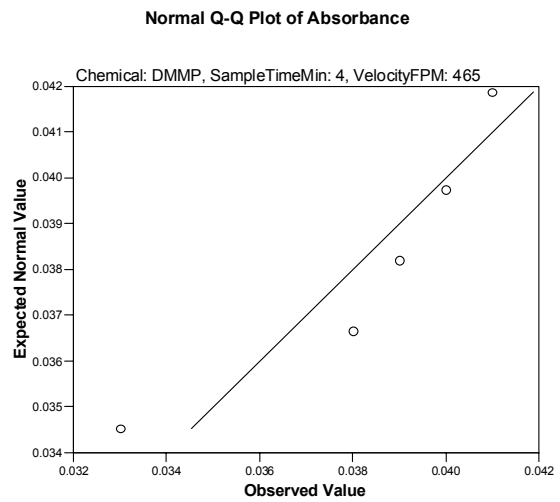
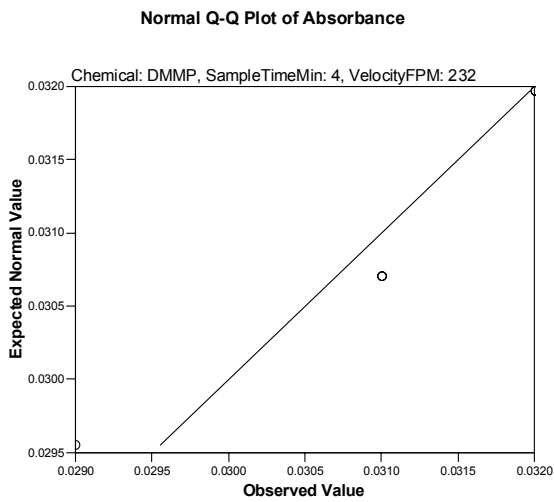
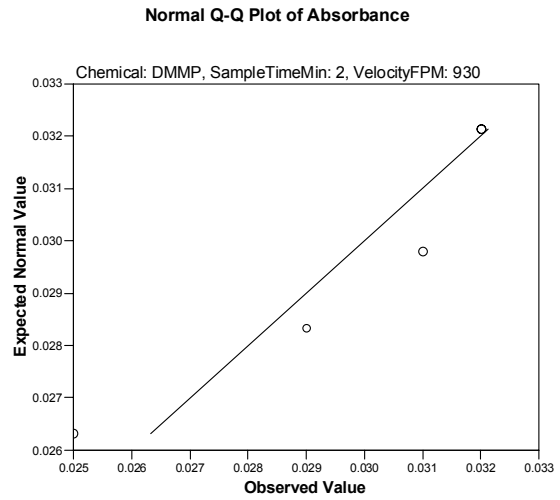
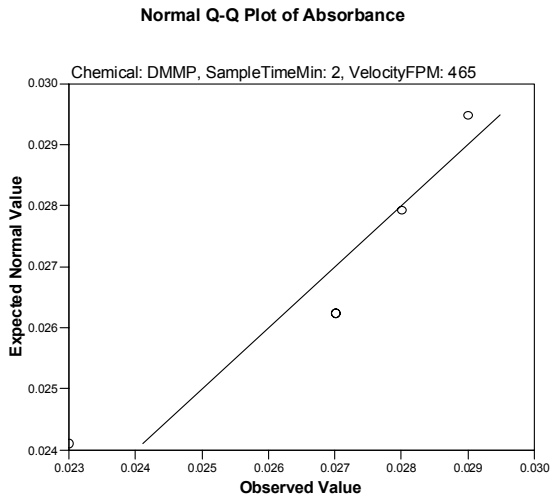


Normal Q-Q Plot of 2ndHQI

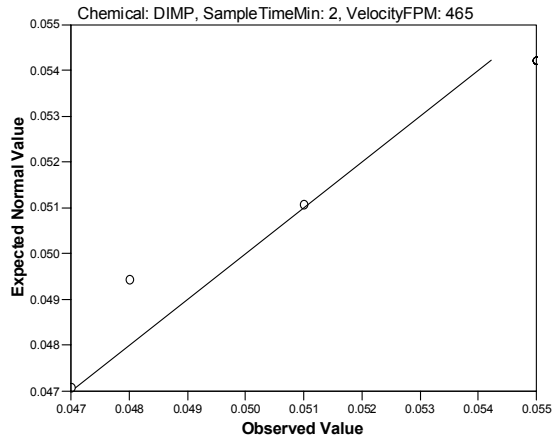


- Section 4.1.4 Sample Velocity

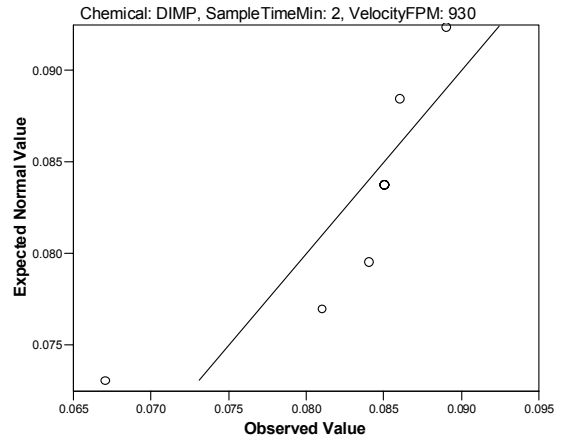
The observed absorbance values in the plots are from a sample's P-O-C peak height.



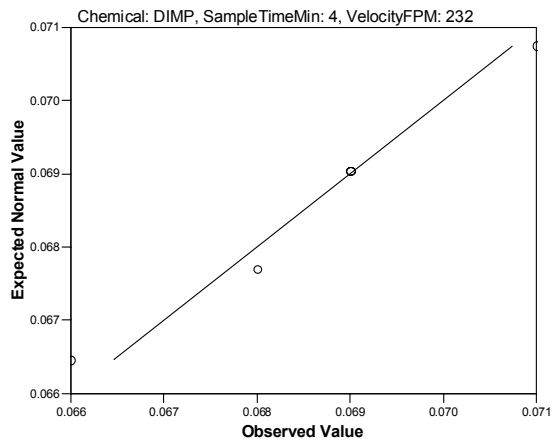
Normal Q-Q Plot of Absorbance



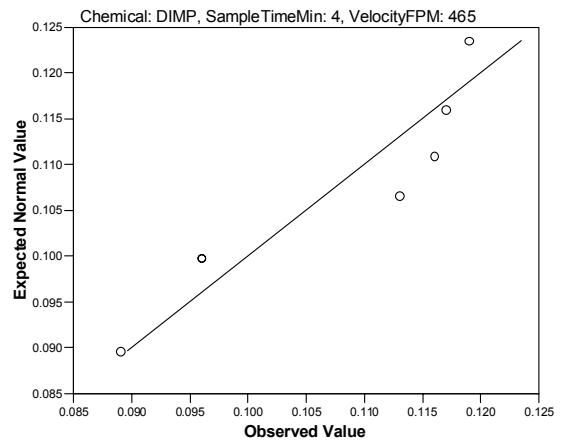
Normal Q-Q Plot of Absorbance



Normal Q-Q Plot of Absorbance

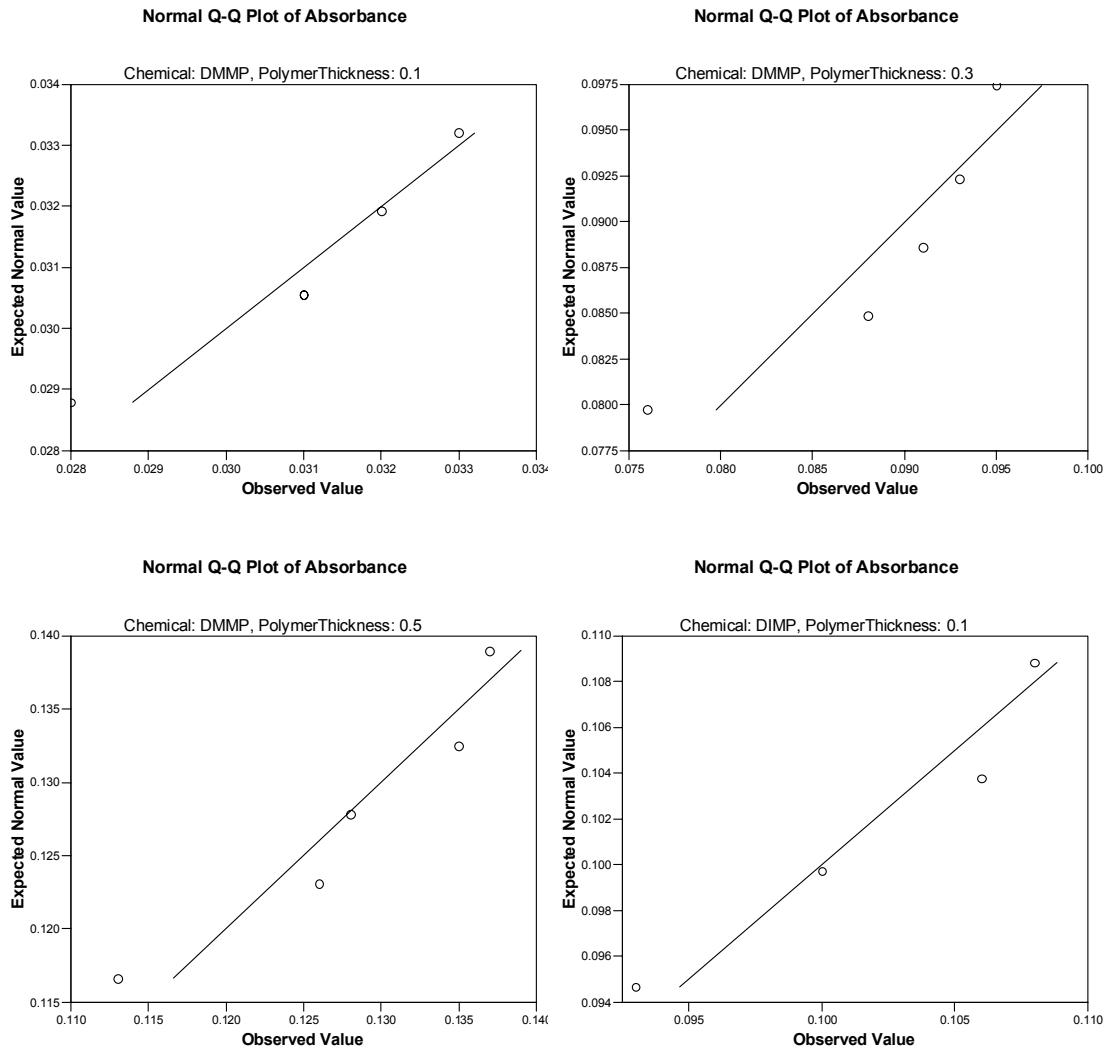


Normal Q-Q Plot of Absorbance

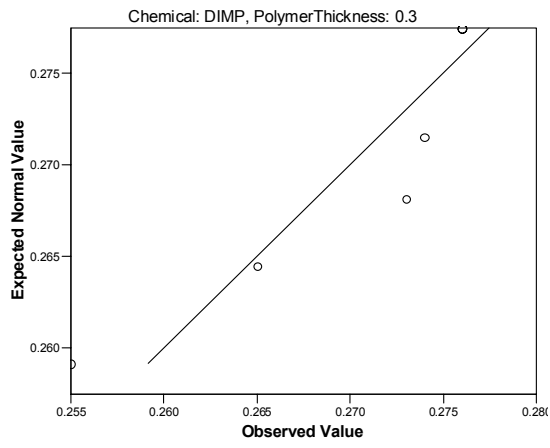


- Section 4.1.5 SPME Film Thickness

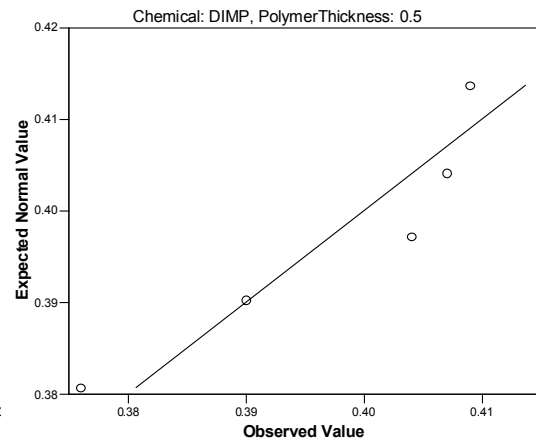
The observed absorbance values in the plots are from a sample's P-O-C peak height. Polymer thickness is the absorbance value of the C-F peak height from the SPME film. This was used to indirectly gauge the film's thickness.



Normal Q-Q Plot of Absorbance



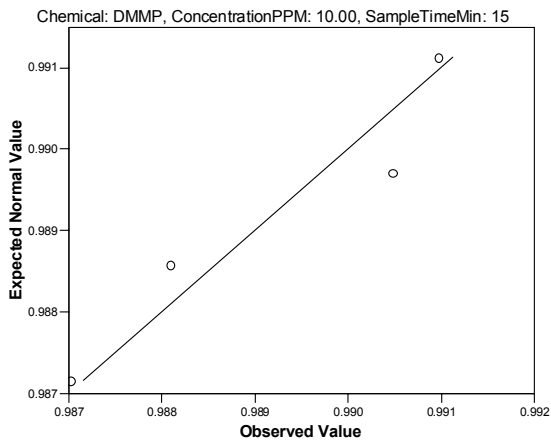
Normal Q-Q Plot of Absorbance



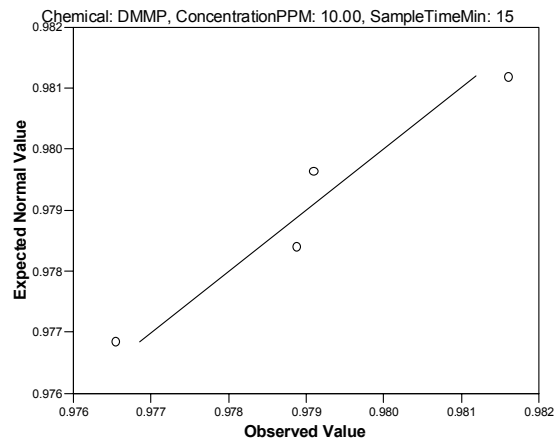
- **Remote Sampling**

HQI is quality index of the sample spectrum compared to the correct library spectrum and 2<sup>nd</sup> HQI is the quality index of the sample spectrum compared to the first incorrect library spectrum.

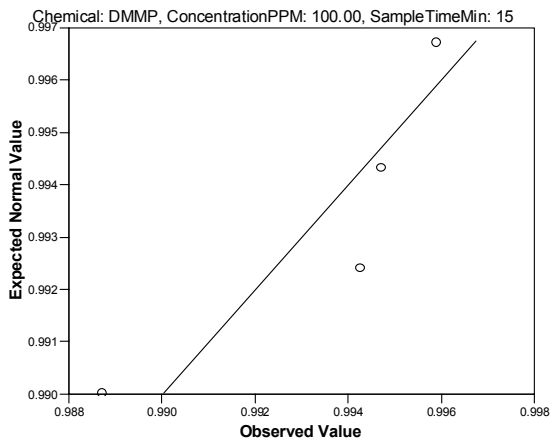
**Normal Q-Q Plot of HQI**



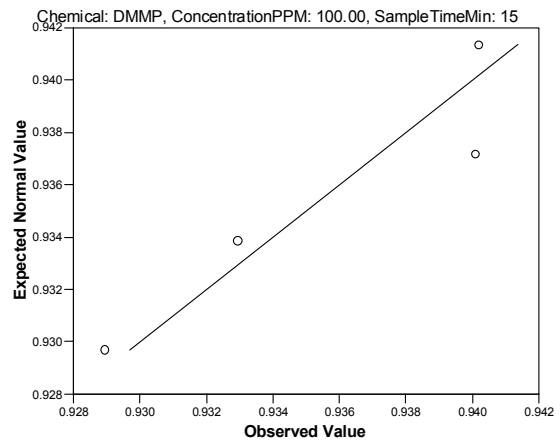
**Normal Q-Q Plot of 2ndHQI**



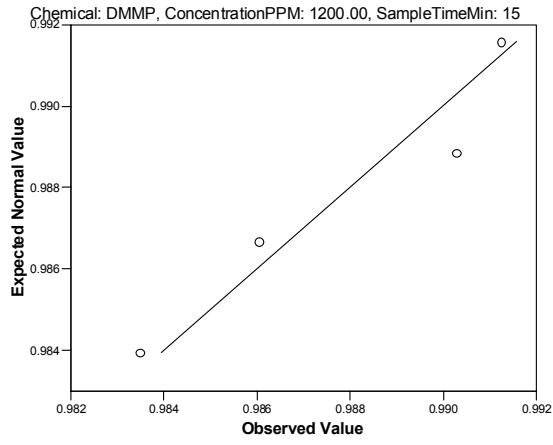
**Normal Q-Q Plot of HQI**



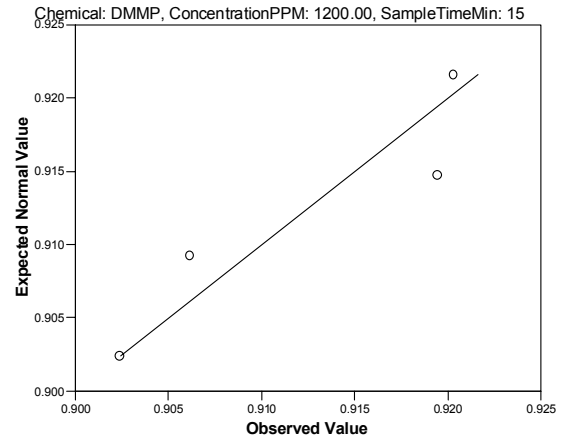
**Normal Q-Q Plot of 2ndHQI**



Normal Q-Q Plot of HQI



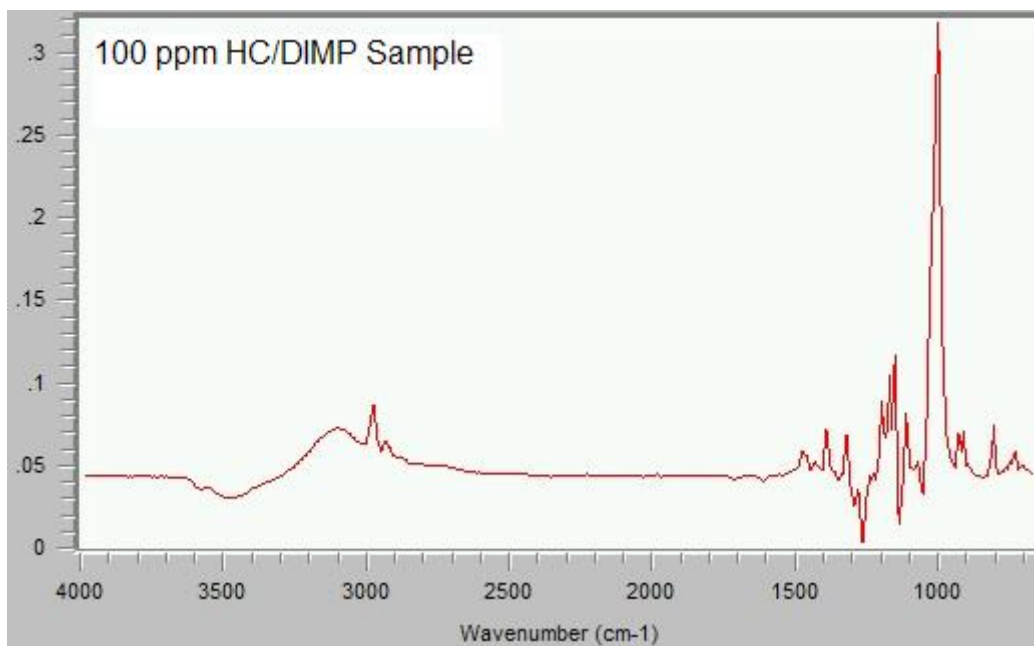
Normal Q-Q Plot of 2ndHQI



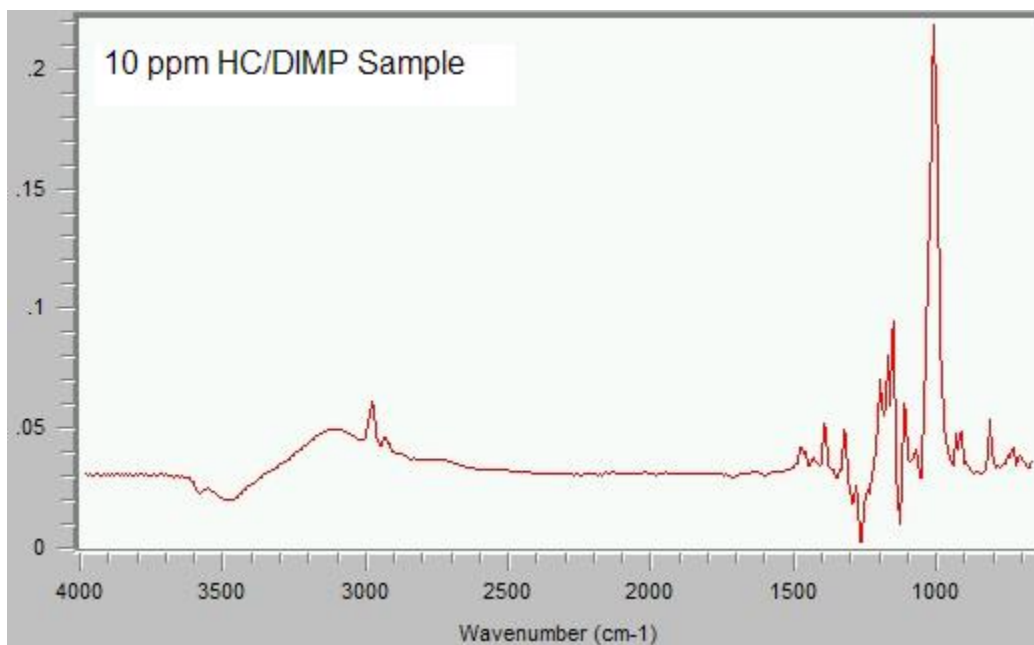
## Appendix C

### Direct Sampling Spectra

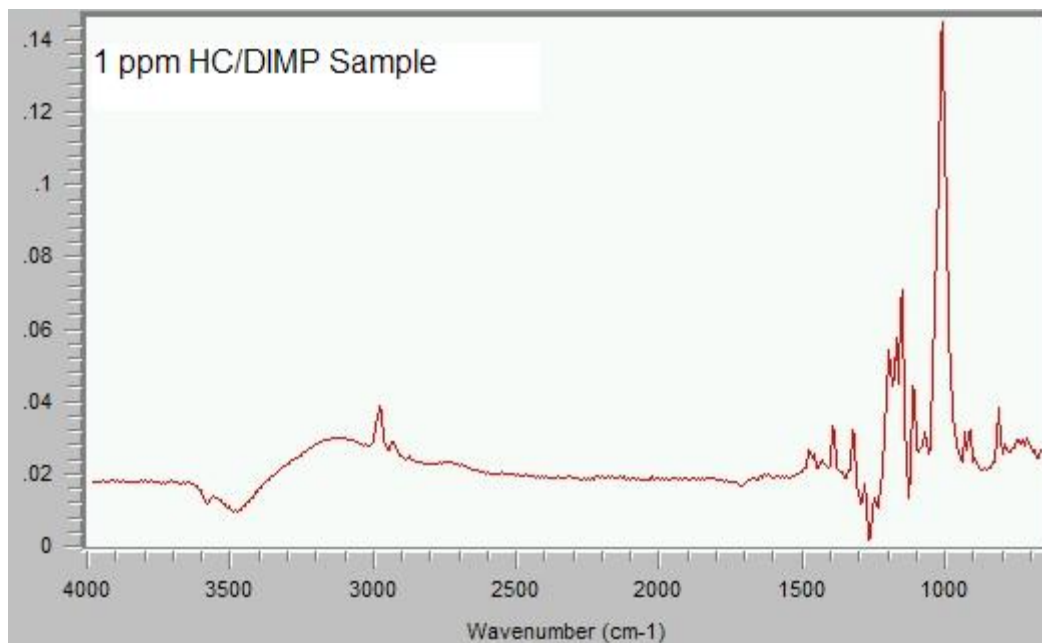
- **DIMP Samples**



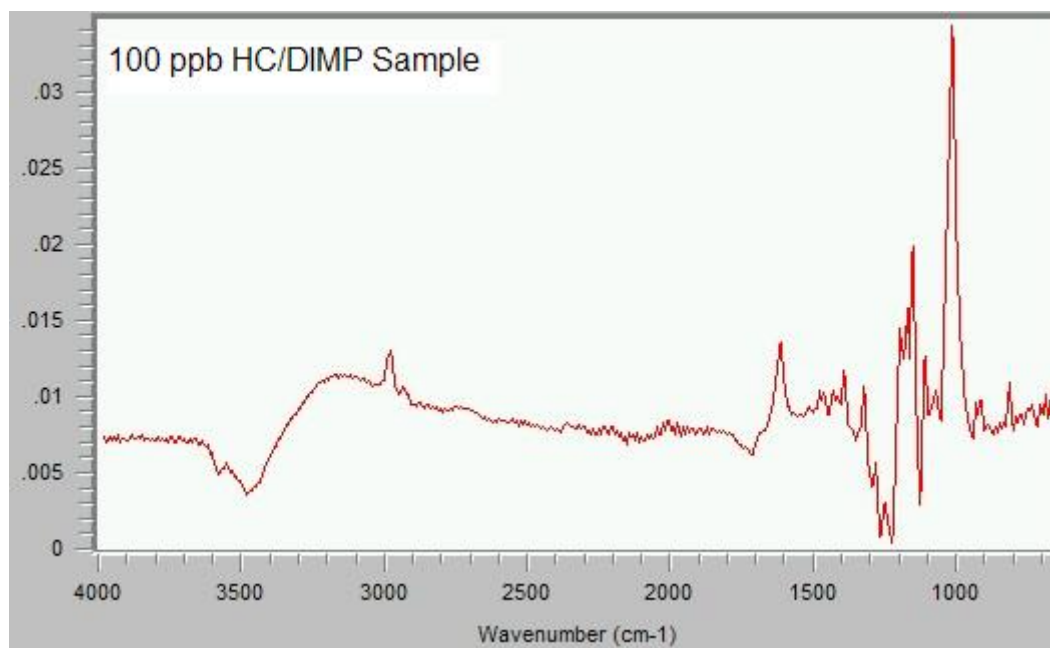
DIMP Extracted by HC Direct Sampling (100 ppm, 8L, 8 min)



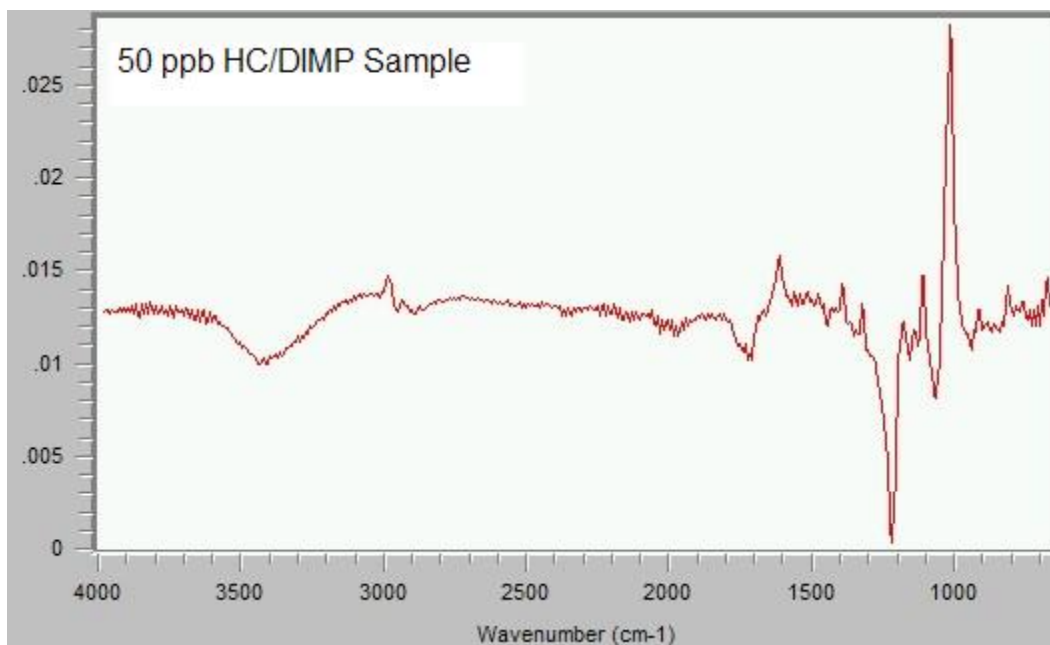
DIMP Extracted by HC Direct Sampling (10 ppm, 8L, 8 min)



DIMP Extracted by HC Direct Sampling (1 ppm, 8L, 8 min)

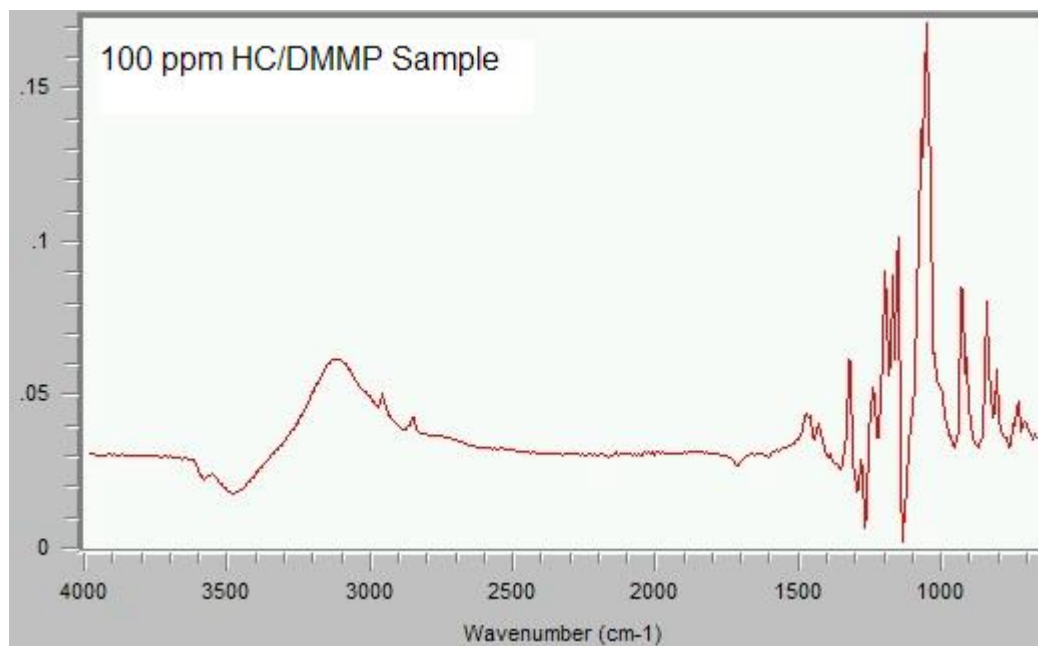


DIMP Extracted by HC Direct Sampling (100 ppb, 8L, 8 min)

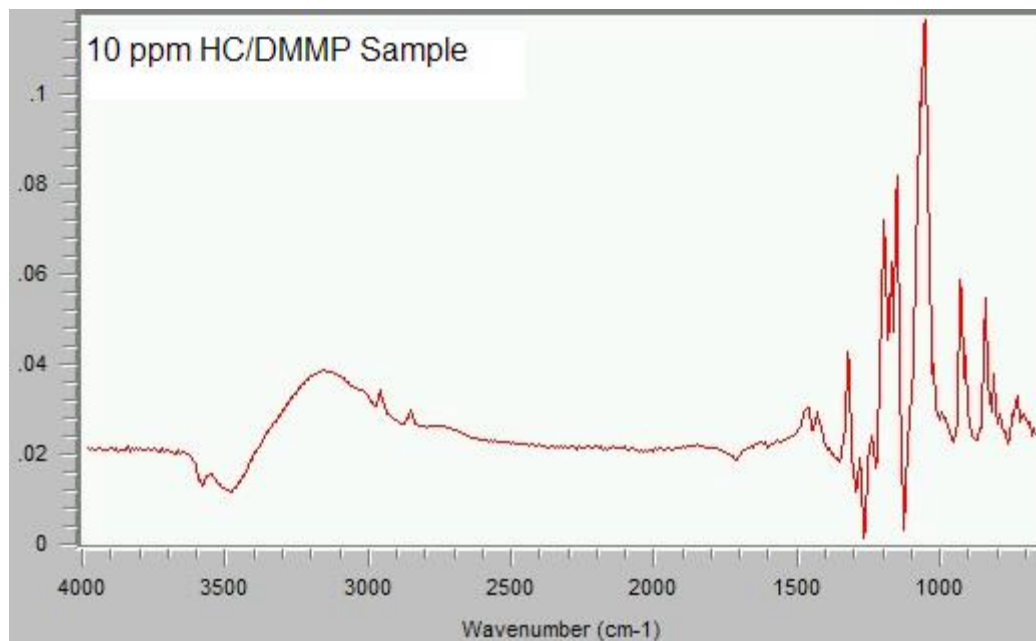


DIMP Extracted by HC Direct Sampling (50 ppb, 8L, 8 min)

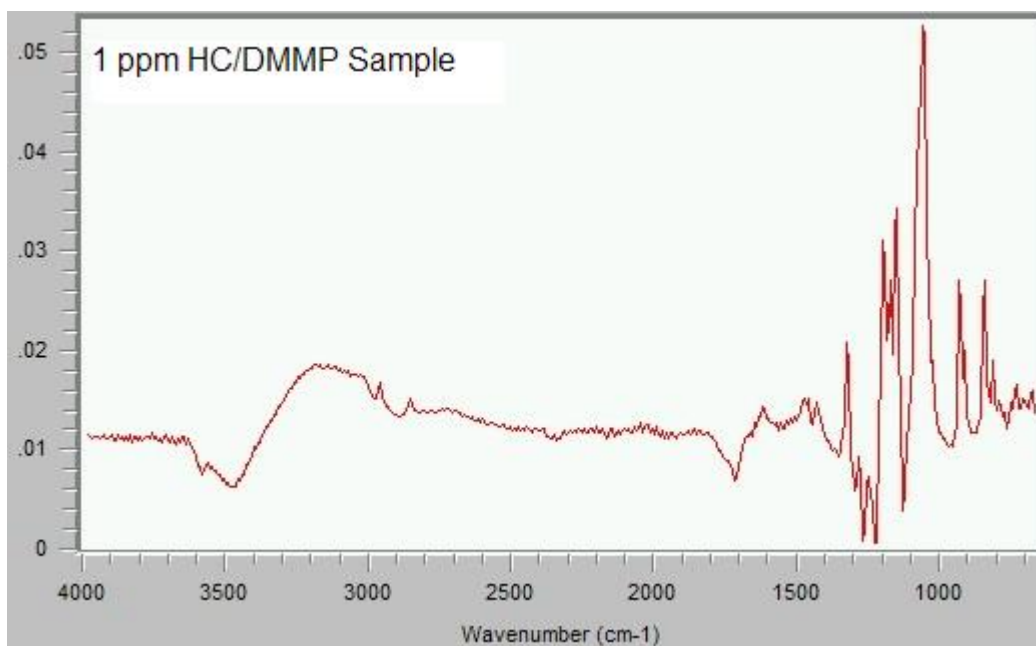
- **DMMP Samples**



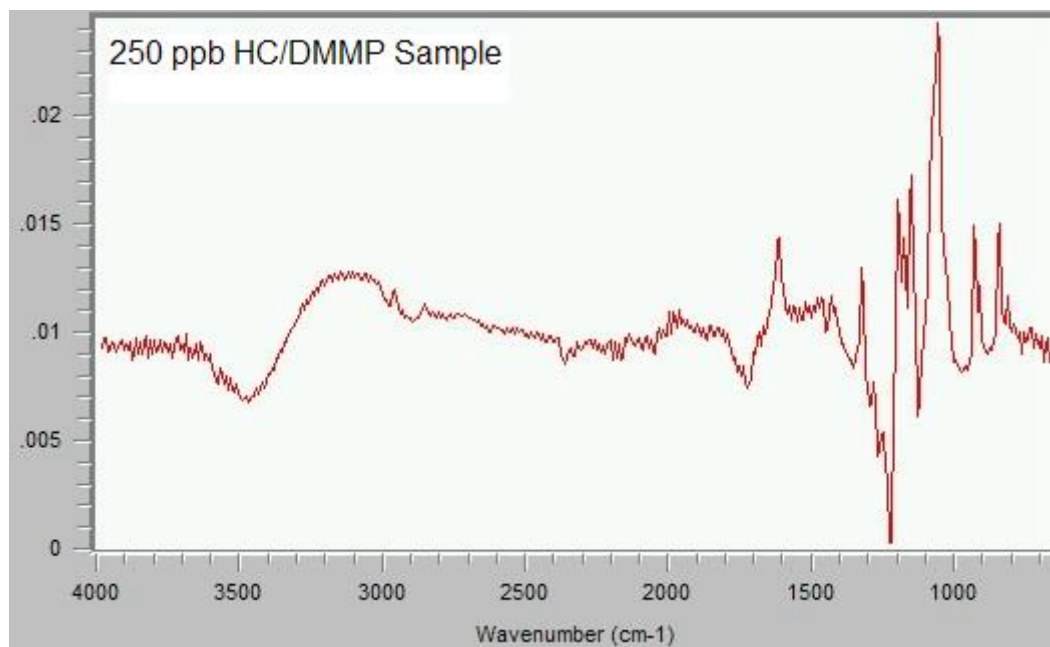
DMMP Extracted by HC Direct Sampling (100 ppm, 8L, 8 min)



DMMP Extracted by HC Direct Sampling (10 ppm, 8L, 8 min)



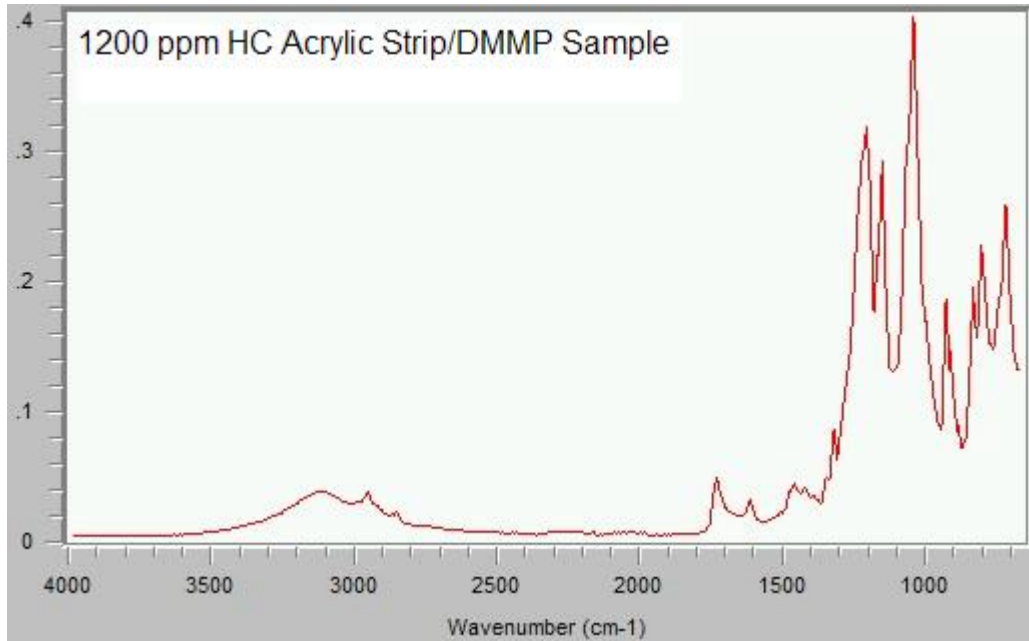
DMMP Extracted by HC Direct Sampling (1 ppm, 8L, 8 min)



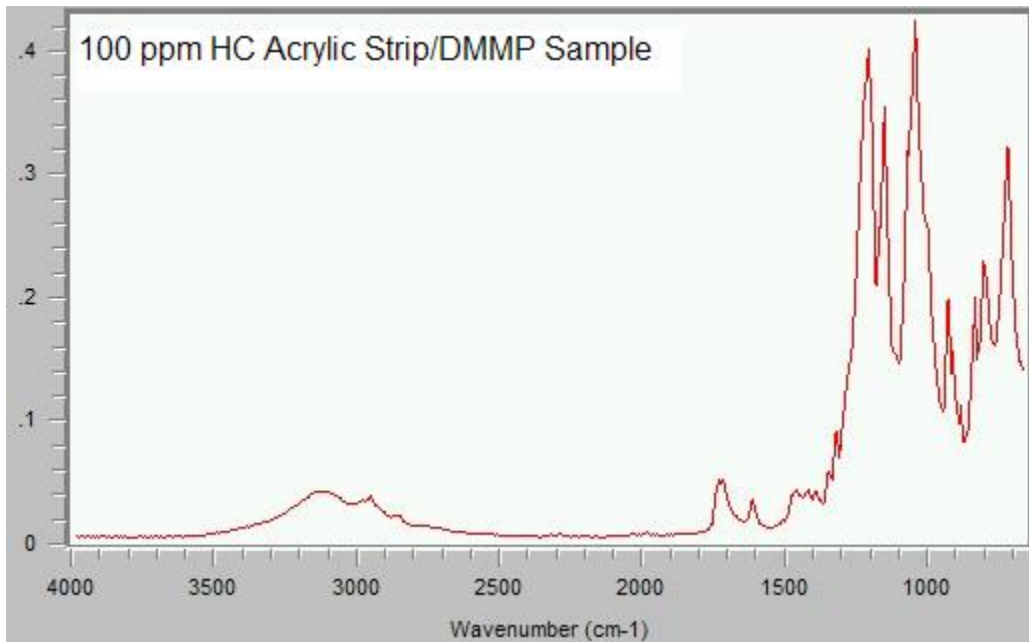
DMMP Extracted by HC Direct Sampling (250 ppb, 8L, 8 min)

## Appendix D

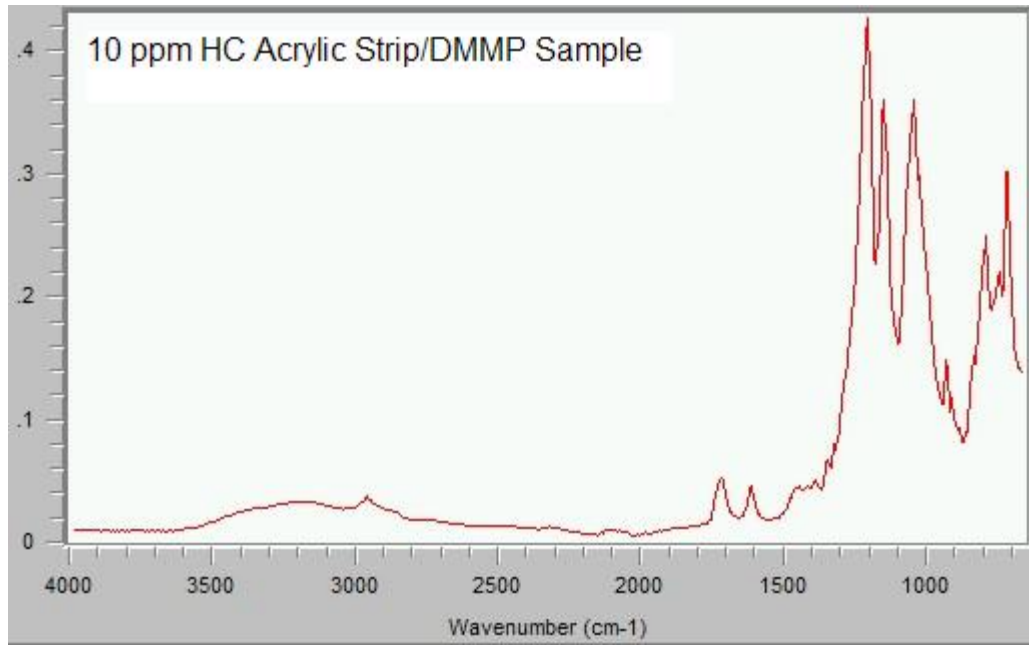
### Remote Sampling Spectra



DMMP Extracted by HC Remote Sampling (1200 ppm, 0.195 lpm, 15 min)



DMMP Extracted by HC Remote Sampling (100 ppm, 0.195 lpm, 15 min)



DMMP Extracted by HC Remote Sampling (10 ppm, 0.195 lpm, 15 min)

## Appendix E

### Statistical Tests and Information

This appendix gives supplementary statistical information on the data generated during this study and summarized in Chapter 4, Experimental Results. Sampling conditions and variables were described in the corresponding sections of Chapter 4.

- **Section 4.1.2 Direct Sampling Limit of Detection**

HQI is quality index of the sample spectrum compared to the correct library spectrum and 2<sup>nd</sup> HQI is the quality index of the sample spectrum compared to the first incorrect library spectrum.

**Paired Samples Statistics**

Chemical	ConcentrationPPM			Mean	N	Std. Deviation	Std. Error Mean
DMMP	.25	Pair	HQI	.7561871	7	.07245009	.02738356
		1	2ndHQI	.3140071	7	.02305930	.00871559
	1.00	Pair	HQI	.9708025	4	.01804967	.00902484
		1	2ndHQI	.4408775	4	.01237641	.00618820
	10.00	Pair	HQI	.9688580	5	.00529785	.00236927
		1	2ndHQI	.4837640	5	.00892601	.00399183
	100.00	Pair	HQI	.8462640	5	.01918718	.00858077
		1	2ndHQI	.5306480	5	.00804567	.00359813
DIMP	1.00	Pair	HQI	.8329033	6	.02893496	.01181265
		1	2ndHQI	.5902700	6	.02027224	.00827611
	10.00	Pair	HQI	.7391180	5	.02893921	.01294201
		1	2ndHQI	.5604320	5	.00464647	.00207797
	100.00	Pair	HQI	.6645280	5	.01792606	.00801678
		1	2ndHQI	.5539120	5	.01213763	.00542811
	.05	Pair	HQI	.6431600	6	.06097185	.02489166
		1	2ndHQI	.2869567	6	.02376746	.00970302
	.10	Pair	HQI	.9367720	5	.03585103	.01603307
		1	2ndHQI	.4046280	5	.05292854	.02367036

## Paired Samples Test

Chemical	ConcentrationPPM	Pair	HQI - 2nd HQI	Paired Differences					t	df	Sig. (2-tailed)
				Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
							Lower	Upper			
DMMP	.25	Pair 1	HQI - 2nd HQI	.4421800	.06187486	.0233865	.38495529	.49940471	18.907	6	.000
	1.00	Pair 1	HQI - 2nd HQI	.5299250	.02510371	.0125519	.48997940	.56987060	42.219	3	.000
	10.00	Pair 1	HQI - 2nd HQI	.4850940	.01212597	.0054229	.47003762	.50015038	89.453	4	.000
	100.00	Pair 1	HQI - 2nd HQI	.3156160	.01912609	.0085534	.29186782	.33936418	36.899	4	.000
DIMP	1.00	Pair 1	HQI - 2nd HQI	.2468657	.04519487	.0170821	.20506743	.28866400	14.452	6	.000
	10.00	Pair 1	HQI - 2nd HQI	.1786860	.03088761	.0138134	.14033397	.21703803	12.936	4	.000
	100.00	Pair 1	HQI - 2nd HQI	.1106160	.02926017	.0130855	.07428470	.14694730	8.453	4	.001
	.05	Pair 1	HQI - 2nd HQI	.3562033	.07227553	.0295064	.28035482	.43205185	12.072	5	.000
	.10	Pair 1	HQI - 2nd HQI	.5321440	.08055450	.0360251	.43212237	.63216563	14.771	4	.000

- Section 4.1.4 Sample Velocity

The following statistical tests compare the observed absorbance values from a sample's P-O-C peak height.

### Test of Homogeneity of Variances

Absorbance

Chemical	SampleTimeMin	Levene Statistic	df1	df2	Sig.
DMMP	2	.547	1	8	.481
	4	2.025	1	8	.193
DIMP	2	.347	1	12	.567
	4	37.573	1	10	.000

### ANOVA

Absorbance

Chemical	SampleTimeMin		Sum of Squares	df	Mean Square	F	Sig.
DMMP	2	Between Groups	.000	1	.000	3.237	.110
		Within Groups	.000	8	.000		
		Total	.000	9			
	4	Between Groups	.000	1	.000	23.143	.001
		Within Groups	.000	8	.000		
		Total	.000	9			
DIMP	2	Between Groups	.003	1	.003	101.8	.000
		Within Groups	.000	12	.000		
		Total	.004	13			
	4	Between Groups	.004	1	.004	44.789	.000
		Within Groups	.001	10	.000		
		Total	.005	11			

## Independent Samples Test

				Levene's Test for Equality of Variances		t-test for Equality of Means						
				F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
Chemical	Sample TimeMin	Absorbance	Equal variances assumed Equal variances not assumed								Lower	Upper
DMMP	4	Absorbance	Equal variances assumed	2.025	.193	-4.811	8	.001	-.007200	.001497	-.01065	-.00375
			Equal variances not assumed			-4.811	5.208	.004	-.007200	.001497	-.01100	-.00340
DIMP	4	Absorbance	Equal variances assumed	37.6	.000	-6.692	10	.000	-.037971	.005674	-.05061	-.02533
			Equal variances not assumed			-7.970	6.356	.000	-.037971	.004765	-.04947	-.02647

a. No statistics are computed for one or more split files

- **Section 4.1.5 SPME Film Thickness**

The following statistical tests compare the observed absorbance values from a sample's P-O-C peak height. Polymer thickness is the absorbance value of the C-F peak height from the SPME film. This was used to indirectly gauge the film's thickness.

### Test of Homogeneity of Variances

Absorbance

Chemical	Levene Statistic	df1	df2	Sig.
DMMP	2.082	2	12	.167
DIMP	2.340	2	12	.139

### ANOVA

Absorbance

Chemical		Sum of Squares	df	Mean Square	F	Sig.
DMMP	Between Groups	.024	2	.012	237.870	.000
	Within Groups	.001	12	.000		
	Total	.024	14			
DIMP	Between Groups	.194	2	.097	919.320	.000
	Within Groups	.001	12	.000		
	Total	.195	14			

### Multiple Comparisons

Dependent Variable: Absorbance

Tukey HSD

Chemical	(I) Polymer Thickness	(J) Polymer Thickness	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
DMMP	0.1	0.3	-.057600*	.004465	.000	-.06951	-.04569
		0.5	-.096800*	.004465	.000	-.10871	-.08489
	0.3	0.1	.057600*	.004465	.000	.04569	.06951
		0.5	-.039200*	.004465	.000	-.05111	-.02729
	0.5	0.1	.096800*	.004465	.000	.08489	.10871
		0.3	.039200*	.004465	.000	.02729	.05111
DIMP	0.1	0.3	-.168083*	.006631	.000	-.18577	-.15039
		0.5	-.295450*	.006891	.000	-.31383	-.27707
	0.3	0.1	.168083*	.006631	.000	.15039	.18577
		0.5	-.127367*	.006221	.000	-.14396	-.11077
	0.5	0.1	.295450*	.006891	.000	.27707	.31383
		0.3	.127367*	.006221	.000	.11077	.14396

\*. The mean difference is significant at the .05 level.

### Independent Samples Test

			Levene's Test for Equality of Variances		t-test for Equality of Means						
			F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
Chemical									Lower	Upper	
DMMP	Absorbance	Equal variances assumed	3.595	.095	-16.66	8	.000	-.057600	.003458	-.06557	-.04963
		Equal variances not assumed			-16.66	4.495	.000	-.057600	.003458	-.06680	-.04840
DIMP	Absorbance	Equal variances assumed	.283	.609	-33.49	8	.000	-.168083	.005019	-.17966	-.15651
		Equal variances not assumed			-35.08	7.527	.000	-.168083	.004791	-.17925	-.15691

- Section 4.2.2 Remote Sampling Limit of Detection

HQI is quality index of the sample spectrum compared to the correct library spectrum and 2<sup>nd</sup> HQI is the quality index of the sample spectrum compared to the first incorrect library spectrum.

Paired Samples Test

Sample TimeMin	Concentration PPM			Paired Differences					t	df	Sig. (2-tailed)
				Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
							Lower	Upper			
1	10.00	Pair 1	HQI - 2ndHQI	-.030450	.00476148	.00194387	-.035447	-.025453	-15.665	5	.000
		Pair 2	SpecIDHQI1 - SpecIDHQI2	-.022326	.02541367	.01037509	-.048996	.0043437	-2.152	5	.084
		Pair 3	DerivHQI1 - DerivHQI2	-.309399	.04599027	.01877545	-.357663	-.261135	-16.479	5	.000
	100.00	Pair 1	HQI - 2ndHQI	-.001683	.01829217	.00746775	-.020880	.0175131	-.225	5	.831
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.00185283	.02342014	.00956123	-.022725	.0264308	.194	5	.854
		Pair 3	DerivHQI1 - DerivHQI2	.01418767	.24341625	.09937427	-.241262	.2696374	.143	5	.892
	1200.00	Pair 1	HQI - 2ndHQI	.02155750	.00272907	.00136454	.0172149	.0259001	15.798	3	.001
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.02938075	.00312381	.00156190	.0244101	.0343514	18.811	3	.000
		Pair 3	DerivHQI1 - DerivHQI2	.20469875	.03078944	.01539472	.1557059	.2536916	13.297	3	.001
5	10.00	Pair 1	HQI - 2ndHQI	.00473800	.01494185	.00668220	-.013815	.0232908	.709	4	.517
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.01163660	.01726269	.00772011	-.009798	.0330711	1.507	4	.206
		Pair 3	DerivHQI1 - DerivHQI2	.06656120	.14105729	.06308274	-.108585	.2417070	1.055	4	.351
	100.00	Pair 1	HQI - 2ndHQI	.05457000	.00800671	.00400336	.0418295	.0673105	13.631	3	.001
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.06717975	.00889106	.00444553	.0530321	.0813274	15.112	3	.001
		Pair 3	DerivHQI1 - DerivHQI2	.50101200	.02363445	.01181723	.4634043	.5386197	42.397	3	.000
	1200.00	Pair 1	HQI - 2ndHQI	.06993000	.00341897	.00170948	.0644897	.0753703	40.907	3	.000
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.08239825	.00331400	.00165700	.0771249	.0876716	49.727	3	.000
		Pair 3	DerivHQI1 - DerivHQI2	.51498825	.00448697	.00224348	.5078485	.5221280	229.549	3	.000
15	10.00	Pair 1	HQI - 2ndHQI	.01011500	.00373529	.00186764	.0041713	.0160587	5.416	3	.012
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.01424650	.00462831	.00231415	.0068818	.0216112	6.156	3	.009
		Pair 3	DerivHQI1 - DerivHQI2	.10724200	.04945161	.02472581	.0285534	.1859306	4.337	3	.023
	100.00	Pair 1	HQI - 2ndHQI	.05785250	.00532972	.00266486	.0493717	.0663333	21.709	3	.000
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.07063725	.00507577	.00253788	.0625606	.0787139	27.833	3	.000
		Pair 3	DerivHQI1 - DerivHQI2	.52871850	.01889237	.00944619	.4986565	.5587805	55.972	3	.000
	1200.00	Pair 1	HQI - 2ndHQI	.07573750	.00561695	.00280848	.0667997	.0846753	26.967	3	.000
		Pair 2	SpecIDHQI1 - SpecIDHQI2	.09117100	.00481483	.00277984	.0792103	.1031317	32.797	2	.001
		Pair 3	DerivHQI1 - DerivHQI2	.54023033	.00631460	.00364574	.5245440	.5559167	148.181	2	.000

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## **Curriculum Vitae**

Capt Chet Bryant graduated from the United States Air Force Academy in 1998 with a Bachelor of Science in Environmental Engineering. He served as the Environmental Protection Element Chief at Shaw AFB from 1998-2000 where he was in charge of developing and implementing drinking water and water pollution programs. While stationed at Hill AFB from 2000-2003 he was the Industrial Hygiene Team Chief in charge of the health risk assessment and surveillance of the 5000 person directorate responsible for the heavy maintenance and overhaul of the Air Force fleet of F-16, A-10 and C-130 aircraft. In 2003, he entered the Graduate School of Biomedical Sciences and Public Health, Uniformed Services University. Upon graduation in Jun 2005, he will be assigned to the Air Force Research Laboratory at Wright Patterson Air Force Base.