



UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES  
 F. EDWARD HÉBERT SCHOOL OF MEDICINE  
 4301 JONES BRIDGE ROAD  
 BETHESDA, MARYLAND 20814-4799



PREVENTIVE MEDICINE  
 AND  
 BIOMETRICS

5 June, 2006

APPROVAL SHEET

Title of Thesis: Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid Phase Microextraction for the Collection of Nerve Agent Simulant

Name of Candidate: Capt Stephen L. Boglarski  
 Master of Science in Public Health  
 Department of Preventive Medicine and Biometrics

Thesis and Abstract Approval:

*Gary L. Hook*  
 Chairman, OICDR Gary L. Hook, PhD

15 June 06  
 Date

*Peter T. LaPuma*  
 Lt Col Peter T. LaPuma, PhD

15 JUN 06  
 Date

*Gary A. Morris*  
 LCDR Gary A. Morris, PhD

15 June 06  
 Date

# Report Documentation Page

Form Approved  
OMB No. 0704-0188

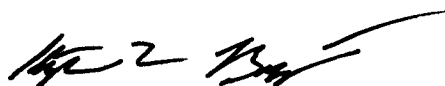
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

|  |                                    |                                     |                            |   |                                 |
|--|------------------------------------|-------------------------------------|----------------------------|---|---------------------------------|
| 1. REPORT DATE<br><b>2006</b>  |                                    | 2. REPORT TYPE                      |                            | 3. DATES COVERED<br><b>00-00-2006 to 00-00-2006</b> |                                 |
| 4. TITLE AND SUBTITLE<br><b>Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microextraction for the Collection of Nerve Agent Simulant</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)<br><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<br><b>Approved for public release; distribution unlimited</b>  |                                    |                                     |                            |   |                                 |
| 13. SUPPLEMENTARY NOTES<br><b>The original document contains color images.</b>   |                                    |                                     |                            |   |                                 |
| 14. ABSTRACT   |                                    |                                     |                            |   |                                 |
| 15. SUBJECT TERMS  |                                    |                                     |                            |   |                                 |
| 16. SECURITY CLASSIFICATION OF:  |                                    |                                     | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES<br><b>94</b>                    | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT<br><b>unclassified</b>   | b. ABSTRACT<br><b>unclassified</b> | c. THIS PAGE<br><b>unclassified</b> |                            |   |                                 |

The author hereby certifies that the use of any copyrighted material in the thesis manuscript entitled:

Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microextraction for the Collection of Nerve Agent Simulant

is appropriately acknowledged and, beyond brief excerpts, is with the permission of the copyright owner.



Stephen L. Boglarski, Capt, USAF, BSC  
Department of Preventive Medicine and Biometrics  
Uniformed Services University of the Health Sciences

## ABSTRACT

Title: Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microextraction for the Collection of Nerve Agent Simulant

Stephen L. Boglarski, Master of Science in Public Health, 2006

Directed By: Gary L. Hook, CDR, USN  
Assistant Professor, Department of Preventive Medicine and Biometrics

Solid phase microextraction (SPME) is used to conduct analyses for trace levels of nerve agent. Measurements can be improved by using a SPME polymer coating that is selective for nerve agents in place of current commercial polymers. This research focuses on three hydrogen bond acidic polymers developed by the Naval Research Laboratory that have an increased affinity for nerve agents. These polymers were coated onto fused silica fibers using three methods: dip coating, applicator coating, and ink jet coating. Vapor and aqueous phase sampling of nerve agent simulant was conducted to evaluate the performance of these polymers. The hydrogen bond acidic polymers showed significantly higher uptakes than commercial polymers and were able to detect vapor phase nerve agent simulant at  $0.005 \text{ mg/m}^3$  for a 1 minute sample and aqueous phase simulant at 1 ppm for a 10 minute sample. The use of these polymers with SPME extraction has the potential to provide rapid field sampling for the detection of trace levels of nerve agent.

APPLICATION OF HYDROGEN BOND ACIDIC POLYCARBOSILANE  
POLYMERS AND SOLID-PHASE MICROEXTRACTION FOR THE COLLECTION  
OF NERVE AGENT SIMULANT

By

Stephen L. Boglarski

Thesis submitted to the Faculty of the Preventive Medicine and Biometrics Graduate  
Program 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

2006

## **Dedication**

- To my wife, Amanda, for your never-ending love and support throughout our life together.
- To my parents, for the guidance you provided throughout my life and for teaching me the many reasons to strive for a good education.

## **Acknowledgements**

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

- My thesis advisory committee: CDR Gary Hook, LtCol Peter LaPuma, and LCDR Gary Morris.
- Dr. R. Andrew McGill, Dr. Duane Simonson, and Dr. Jennifer Stepnowski from the Naval Research laboratory who facilitated the ink jet coating and provided several of the polymers used in this study.
- Dr. Eric Houser from the Department of Homeland Security who facilitated the dip coating and provided several of the polymers used in this study.
- Dr. Venkat Mani from American Analytical, who facilitated the applicator coating and provided assistance with polymer crosslinking.

# Table of Contents

|  |     |
|--|-----|
| Dedication.....  | v   |
| Acknowledgements .....                                     | vi  |
| Table of Contents .....                                    | vii |
| List of Figures .....                                      | ix  |
| List of Tables .....                                       | x   |
| 1. Introduction.....                                       | 1   |
| 1.1. Background.....                                       | 1   |
| 1.1.1. Gas Chromatography/Mass Spectrometry .....          | 2   |
| 1.1.2. Solid Phase Microextraction.....                    | 3   |
| 1.1.3. Polymer Coatings.....                               | 3   |
| 1.2. Research Question and Specific Aims .....             | 4   |
| 2. Literature Review .....                                 | 6   |
| 2.1. G-Series Nerve Agents.....                            | 6   |
| 2.2. Solid Phase Microextraction.....                      | 10  |
| 2.3. Solid Phase Microextraction Sampling.....             | 12  |
| 2.4. Polymer Coatings.....                                 | 13  |
| 3. Methodology .....                                       | 20  |
| 3.1. Application of Polymer Coatings .....                 | 20  |
| 3.1.1. Dip Coating.....                                    | 20  |
| 3.1.2. Applicator Coating .....                            | 23  |
| 3.1.3. Ink Jet Coating .....                               | 25  |
| 3.2. Fiber Imaging .....                                   | 29  |
| 3.3. Nerve Agent Simulant.....                             | 30  |
| 3.4. Vapor Phase Extraction.....                           | 31  |
| 3.4.1. Sample Preparation .....                            | 32  |
| 3.4.2. Solid Phase Microextraction Sampling Protocol ..... | 33  |
| 3.5. Aqueous Phase Extraction.....                         | 34  |
| 3.5.1. Sample Preparation .....                            | 34  |
| 3.5.2. Solid Phase Microextraction Sampling Protocol ..... | 35  |
| 3.6. Gas Chromatography/Mass Spectrometry Analysis .....   | 36  |
| 3.7. Polymer Comparison and Data Analysis .....            | 36  |
| 4. Experimental Results and Discussion.....                | 38  |
| 4.1. Application of Polymer Coatings .....                 | 38  |
| 4.1.1. Dip Coating.....                                    | 38  |
| 4.1.2. Applicator Coating .....                            | 39  |
| 4.1.3. Ink Jet Coating .....                               | 41  |
| 4.2. Vapor Phase Extraction.....                           | 43  |
| 4.2.1. Vapor Phase Sampling Results .....                  | 43  |
| 4.2.2. Data Analysis .....                                 | 51  |
| 4.3. Aqueous Phase Extraction.....                         | 52  |
| 4.3.1. Aqueous Phase Sampling Results .....                | 52  |
| 4.3.2. Data Analysis .....                                 | 56  |



|  |    |
|--|----|
| 5. Conclusions and Recommendations .....     | 58 |
| 5.1. Data Analysis Conclusions.....          | 58 |
| 5.2. Study Limitations.....                  | 60 |
| 5.3. Additional Research.....                | 61 |
| Appendix A. Ink Jet Coating Parameters ..... | 65 |
| Appendix B. DMMP Uptake Data Tables.....     | 67 |
| Appendix C. Statistical Comparisons.....     | 70 |
| Bibliography .....                           | 82 |
| Curriculum Vitae.....                        | 84 |

## List of Figures

|  |    |
|--|----|
| Figure 2-1. Chemical Structure of Tabun (GA).....  | 7  |
| Figure 2-2. Chemical Structure of Sarin (GB).....  | 7  |
| Figure 2-3. Chemical Structure of GF.....  | 8  |
| Figure 2-4. Chemical Structure of Soman (GD).....  | 8  |
| Figure 2-5. (a) SPME Fiber Holder and (b) Fiber Assembly (Bryant, 2005).....   | 10 |
| Figure 2-6. Chemical Structure of Linear PDMS Polymer.....   | 14 |
| Figure 2-7. Basic Chemical Structure of HC.....  | 15 |
| Figure 2-8. Hydrogen Bonding Between HC and DMMP (Bryant, 2005).....   | 16 |
| Figure 2-9. Basic Chemical Structure of FPOL.....  | 17 |
| Figure 3-1. Crosslinking of PDMS and HC Polymer Chains.....  | 21 |
| Figure 3-2. Polymer Application Using Silicon Applicator.....  | 24 |
| Figure 3-3. Ink Jet Coating Set-Up.....  | 26 |
| Figure 3-4. SPME Fiber Measurements.....   | 30 |
| Figure 3-5. Basic Chemical Structure of DMMP.....  | 31 |
| Figure 4-1. Commercial PDMS (30 $\mu$ m) Fiber (10X Magnification).....  | 39 |
| Figure 4-2. HC/PDMS (Dipped#1) Fiber (10X Magnification).....  | 39 |
| Figure 4-3. HC/PDMS (Dipped#2) Fiber (10X Magnification).....  | 39 |
| Figure 4-4. HC/PDMS (Applicator) Fiber (10X Magnification).....  | 40 |
| Figure 4-5. FPOL/PDMS (Applicator) Fiber (10X Magnification).....  | 40 |
| Figure 4-6. HC (Ink Jet) Fiber Before Sampling (10X Magnification).....  | 42 |
| Figure 4-7. HC (Ink Jet) Fiber After Sampling (10X Magnification).....   | 42 |
| Figure 4-8. NM <sub>2</sub> A (Ink Jet) Fiber (10X Magnification).....   | 42 |
| Figure 4-9. Total Ion Chromatograms for DMMP Uptake at 0.5, 0.05, and 0.005 mg/m <sup>3</sup><br>Using Fiber HC/PDMS (Dipped#2)..... | 44 |
| Figure 4-10. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at<br>0.5 and 0.05 mg/m <sup>3</sup> .....                | 45 |
| Figure 4-11. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at<br>0.005 mg/m <sup>3</sup> .....                       | 45 |
| Figure 4-12. Total Polymer Volumes of Test Fibers.....   | 46 |
| Figure 4-14. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of<br>DMMP at 0.005 mg/m <sup>3</sup> .....              | 47 |
| Figure 4-13. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of<br>DMMP at 0.5 and 0.05 mg/m <sup>3</sup> .....       | 48 |
| Figure 4-14. Relative Standard Deviations for Vapor Phase Extraction of DMMP.....  | 51 |
| Figure 4-15. Total Ion Chromatograms for DMMP Uptake at 100 and 1 ppm Using Fiber<br>HC/PDMS (Dipped#2).....                         | 52 |
| Figure 4-16. GC/MS Peak Area Comparison for Aqueous Phase Extraction of DMMP at<br>100 and 1 ppm.....                                | 53 |
| Figure 4-17. GC/MS Peak Area/Polymer Volume Comparison for Aqueous Phase<br>Extraction of DMMP at 100 and 1 ppm.....                 | 54 |
| Figure 4-18. Relative Standard Deviations for Aqueous Phase Extraction of DMMP..   | 56 |
| Figure 5-1. Reaction of PEHS with HC Polymer.....  | 62 |

## List of Tables

|  |    |
|--|----|
| Table 2-1. Airborne Exposure Limits for G-Series Nerve Agents for the U.S. Army<br>(Department of the Army, 2004).....       | 9  |
| Table 3-1. Test Fiber Information.....   | 32 |
| Table 3-2. Expected Advantage in DMMP Uptake of Hydrogen Bond Acidic Polymers<br>Over a PDMS Polymer of Equal Thickness..... | 37 |
| Table 4-1. Expected and Actual Advantage in DMMP Uptake for Vapor Phase<br>Extraction .....                                  | 50 |
| Table 4-5. Expected and Actual Advantage in DMMP Uptake for Aqueous Phase<br>Extraction.....                                 | 55 |
| Table 5-1. Summary of Hydrogen Bond Acidic Polymer Coatings.....   | 58 |

## **Introduction**

### **1.1. Background**

The field detection and identification of chemical warfare agents (CWAs) has become an increasingly critical challenge faced by today's military and civilian responders. The proliferation of WMD-related technologies and materials and the willingness of terrorist groups to obtain and employ these weapons have increased the threat of mass casualty attacks. The advent of the internet and digital mobile communications have enabled terrorist groups and rogue states to more readily acquire the technical expertise needed to develop these weapons. Terrorist groups such as Al Qaeda have openly declared their intentions to acquire and employ these weapons against civilian and military targets. In addition, factors such as the fall of the former Soviet Union have increased the probabilities that groups may attempt to steal or smuggle these weapons from nations that no longer possess tight control over their current stockpiles. (U.S. Department of State, 2006).

The use of CWAs against military and civilian populations has become an increasing realistic concern. Nerve agents, in particular, are among the most lethal CWAs. The 1995 release of the nerve agent sarin in the Tokyo subway system by the Aum Shinrikyo cult and the use of CWAs by the Iraqi Army against Kurdish refugees are both recent examples of the threat posed by these weapons (McCafferty and Lennarson, 2002). In addition to military and terrorist actions, nerve agent leakage from aging weapon storage bunkers, the decommissioning of CWA production facilities, and the demilitarization of munitions continue to pose a significant concern to human health.

Responders to any type of nerve agent incident or threat need to quickly and accurately identify the agent and to quantify the potential exposure to military and civilian personnel. Due to the lethality of these agents, field sampling techniques and equipment need to provide accurate information at trace concentrations. Although there are many different types of field sampling and detection instruments available for nerve agents, few have the accuracy and sensitivity needed to detect and quantify levels below concentrations that are immediately dangerous to life and health (IDLH). One proven technology that continues to show promise for detecting trace concentrations of nerve agents is solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (GC/MS).

#### **1.1.1. Gas Chromatography / Mass Spectrometry (GC/MS)**

GC/MS analysis is a proven technology for the analysis of volatile and semi-volatile chemicals. The GC separates the chemical components in a sample mixture. The MS is then used to identify the chemical agent by comparing the mass of the fragments in the resulting spectrum to a reference library and/or through mass spectral interpretation. The use of GC/MS for the detection and identification of CWAs has been proven to be an effective technology that is capable of identifying multiple chemicals, including nerve agents. GC/MS analysis provides both qualitative and quantitative compound-specific data, with detection sensitivities in the high parts-per-trillion (ppt) to low parts-per-billion (ppb) range (Smith et al, 2004).

### **1.1.2. Solid Phase Microextraction (SPME)**

SPME was first developed in 1990 to address the need for simple, rapid sample preparation in a field environment. It relies on a solvent-free partitioning process that combines sampling, extraction, and concentration into a single step (Pawliszyn, 1999). SPME has been used to extract compounds directly from air and water and indirectly from soils (Harvey, 2002). SPME uses a polymeric extracting phase attached to a small fused silica fiber. The polymer extracts and concentrates chemicals from a sample matrix. The SPME fiber is then inserted directly into a GC/MS or other analytical instrument and is thermally desorbed. When coupled with GC/MS analysis, SPME provides a rapid field sampling method for the detection and identification of many chemical agents at trace concentrations (Hook, 2003a).

### **1.1.3. Polymer Coatings**

Commercially available SPME polymer coatings are currently limited to polydimethylsiloxane (PDMS), polyacrylate (PA), or carbowax (CW) which are liquid phase polymers. These can also be combined with a solid phase polymer such as divinylbenzene (DVB) or carboxen. Each polymer differs in its adsorptive characteristics, affinity for polar and nonpolar compounds, and sensitivity and selectivity for certain analytes. Commercially available polymer coatings can concentrate and detect many CWAs (Hook, 2004), but more specialized polymers designed specifically to selectively concentrate CWAs are desirable in order to achieve lower detection limits.

The Naval Research Laboratory (NRL) has developed and tested high molecular weight sorbant polymer materials known as hydrogen bond acidic polycarbosilanes.

These polymers were used as chemical sensor coatings in CWA detection devices and were able to detect nerve agents at significantly lower airborne concentrations when compared to commercially manufactured polymers (Houser, 2004). If these hydrogen bond acidic polymers were used to make SPME fibers, they may provide lower detection limits for nerve agents when used with GC/MS analysis. These hydrogen bond acidic polymer SPME fibers could provide a rapid field collection system for first responders capable of detecting trace concentrations of these agents.

## **1.2. Research Question and Specific Aims**

### Research Question #1:

Can hydrogen bond acidic polymers be coated onto fused silica fibers and be used for SPME extraction of nerve agent simulant?

### Specific Aims:

1. Test and compare three different methods for coating hydrogen bond acidic polymers onto fused silica fibers. These methods will include dip coating, applicator coating, and ink jet coating.
2. Test and compare three different hydrogen bond acidic polymers for their ability to be coated onto SPME fibers. These polymers will include the HC, FPOL, and NM<sub>2</sub>A polymers.

Research Question #2:

Will SPME fibers coated with hydrogen bond acidic polymers have a greater collection efficiency for G-series nerve agent simulant when compared to commercially available polymers?

Specific Aims:

1. Perform vapor phase and aqueous phase sampling at multiple concentrations using SPME fibers coated with the three hydrogen bond acidic polymers and three commercially manufactured fibers.
2. Using GC/MS analysis, compare the total analyte uptake of hydrogen bond acidic polymers to that of the commercially available polymers.
3. Determine if the hydrogen bond acidic polymers can meet analyte uptake expectations established by the NRL for each type of polymer. These analyte uptake expectations compare the expected uptake of nerve agent simulant for NRL polymers in comparison with commercial PDMS.



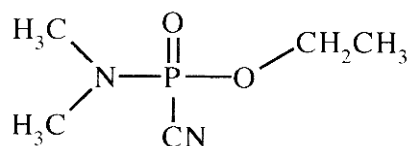
## **2. Literature Review**

This research brings together hydrogen bond acidic polymers and SPME to enhance field sampling and analysis techniques for nerve agents. This research will focus on G-series nerve agent simulant. Considerable research and testing has been conducted proving the effectiveness of SPME analysis of G-series nerve agents. Research has also been conducted on the effectiveness of hydrogen bond acidic polymers that demonstrates this polymer's affinity for G-series nerve agents. This chapter will provide insight on G-series nerve agents, the development of SPME and hydrogen bond acidic polymers, along with the testing conducted that provides the foundation for this thesis.

### **2.1. G-Series Nerve Agents**

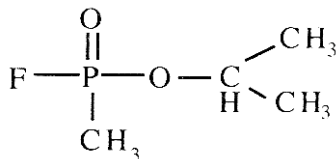
G-series nerve agents are organophosphorous compounds developed by German chemists in the 1930's and 1940's and include tabun (O-ethyl dimethylamidophosphoryl cyanide (GA)), sarin (isopropyl methylphosphonofluoridate (GB)), soman (pinacolyl methylphosphonofluoridate (GD)), and GF (cyclohexyl methylphosphonofluoridate). These agents are relatively stable compounds that can be easily dispersed. The raw materials needed for their manufacture are inexpensive and to some degree readily available. Nerve agents affect the transmission of nerve impulses by inhibiting the function of the enzyme acetylcholinesterase, which is vital to the normal biological activity of the nervous system. When inhaled or absorbed through the skin, nerve agents are highly toxic and produce rapid neurotoxic effects. Death from exposure to nerve agents can result within several minutes to several hours, depending on the dose and route of exposure (Sun and Ong, 2005).

Tabun (Figure 2-1), is the easiest nerve agent to manufacture, and thus, is the most likely agent to be initially synthesized by developing nations and terrorist groups who are just starting to produce nerve agents (Sun and Ong, 2005). Tabun is an organophosphate, characterized by an oxygen phosphorous double bond, and contains a cyanide (-CN) functional group. Tabun has a moderate volatility of 328 mg/m<sup>3</sup> at 20° C and poses both an inhalation and skin contact hazard (Sun and Ong, 2005).



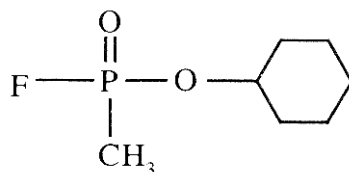
**Figure 2-1. Chemical Structure of Tabun (GA)**

Nations with a more mature chemical weapons program are more likely to produce sarin, soman, and GF. Sarin (Figure 2-2), differs from tabun in that it contains a fluorine atom (-F) in place of the -CN group. Sarin has a high volatility of 16,091 mg/m<sup>3</sup> at 20° C and poses a significant inhalation hazard (Sun and Ong, 2005).



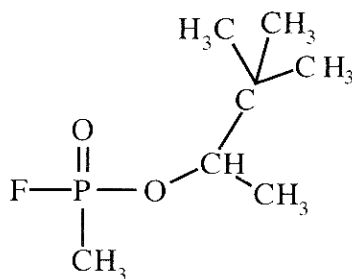
**Figure 2-2. Chemical Structure of Sarin (GB)**

GF (Figure 2-3), contains both the (-F) functional group and a cyclohexane ring. It exhibits a moderate volatility of 438 mg/m<sup>3</sup> at 20° C and poses both an inhalation and skin contact hazard (Sun and Ong, 2005).



**Figure 2-3. Chemical Structure of GF**

Soman (Figure 2-4), also contains a fluorine (-F) functional group. It exhibits a moderate volatility of 3900 mg/m<sup>3</sup> at 20° C and poses both an inhalation and skin contact hazard. Soman is the most toxic of the G-series agents because it penetrates the central nervous system very quickly and irreversibly binds to acetylcholinesterase receptors in the body making medical treatment very difficult (Sun and Ong, 2005).



**Figure 2-4. Chemical Structure of Soman (GD)**

Specific airborne exposure limits for G-series nerve agents are provided in Table 2-1.

| <b>Airborne Exposure Limit</b>                  | <b>Exposure Scenario</b>      | <b>Tabun (mg/m<sup>3</sup>)</b> | <b>Sarin (mg/m<sup>3</sup>)</b> | <b>Soman &amp; GF (mg/m<sup>3</sup>)</b> |
|---|-------------------------------|---------------------------------|---------------------------------|--|
| IDLH (Immediately Dangerous to Life and Health) | One time exposure             | 0.1                             | 0.1                             | 0.05                                     |
| STEL (Short-Term Exposure Limit)                | Occasional 15 minute exposure | 0.0001                          | 0.0001                          | 0.00005                                  |
| TWA (Time-Weighted Average)                     | Daily, 8h r, 30 year exposure | 0.00003                         | 0.00003                         | 0.00003                                  |

**Table 2-1. Airborne Exposure Limits for G-Series Nerve Agents for the U.S. Army**  
(Department of the Army, 2004)

Due to the high toxicity and rapid mechanism of action of these nerve agents, expedient field detection is needed at trace concentrations in order to protect military and civilian populations. Traditional rapid field sampling technologies for nerve agents generally do not have the sensitivities required to detect agents at very low toxicologically relevant concentrations. These technologies also tend to have a larger footprint, less portability, and require additional logistical support. The goal of field technology development for nerve agent detection is to produce sampling and analytical instrumentation that is small, lightweight, easy to use, and provides qualitative and quantitative information for multiple chemicals while maintaining a high selectivity and sensitivity for nerve agents. The application of SPME and GC/MS offers many of these benefits for the detection of nerve agents (Hook, 2003a).

## 2.2. Solid Phase Microextraction

A SPME fiber usually consists of a 1 cm length of fused silica, approximately 80-125  $\mu\text{m}$  in diameter, attached to a needle assembly. The fiber is coated with a small quantity of polymer. The polymer coating thicknesses ranges between 5-100  $\mu\text{m}$  and serves as the extracting phase. Total polymer volume is usually less than 1  $\mu\text{l}$ . Thicker polymer coatings generally lead to increased sensitivity, but require a longer sampling time (Pawliszyn, 1997). The coated fiber is housed inside a syringe-type needle that protects and isolates the fiber from exposure and can safely puncture the septum of a sample container (Figure 2-5).

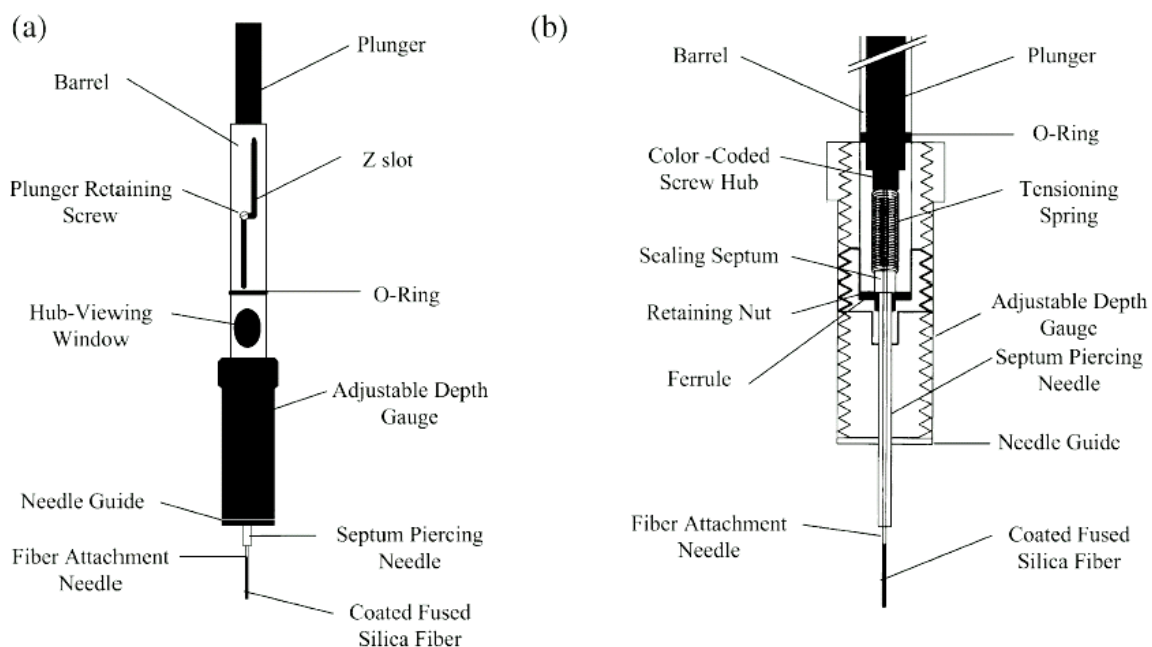


Figure 2-5. (a) SPME Fiber Holder and (b) Fiber Assembly (Bryant, 2005)

During SPME sampling, the coated fiber is extended out of the end of the needle and is exposed to a gas or a liquid for a specific period of time. During this time, volatile

and semi-volatile chemicals partition to the polymer through adsorption or absorption, depending on the type of polymer used (Pawliszyn, 1997). Since the quantity of polymer is generally very small compared to the volume of sample media, the polymer will come to equilibrium with its surroundings in a relatively short period of time. As the fiber reaches equilibrium, additional collection of analyte by the exposed fiber will not occur. When sampling is completed, the fiber is retracted back into the protective needle and sealed with a septum if it is not immediately analyzed. When used with GC/MS analysis, the retracted fiber is inserted into a heated GC injection port. The fiber is then extended out of the needle and the analytes are thermally desorbed from the fiber into the GC/MS for analysis (Pawliszyn, 1999).

The quantity of analyte extracted by a polymer at equilibrium can be determined by the partition coefficient between the analyte and the polymer coating material. Equation 2-1 describes the mass of analyte extracted by the polymer after equilibrium has been reached.

$$n = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \quad \text{Equation 2.1}$$

- 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 ( $\mu\text{g}/\text{m}^3$ )

Equation 2-1 indicates that there is a direct proportional relationship between sample concentration and the amount of analyte extracted. When the sample volume is very large relative to the fiber coating volume ( $K_{fs} V_f \ll V_s$ ), equation 2-1 can be simplified to:

$$n = K_{fs} V_f C_o$$

Equation 2.2

Equation 2.2 demonstrates that the quantity of analyte extracted can be determined independent of sample volume. It is not necessary to measure the volume of air that is sampled, which is commonly required for most traditional air sampling procedures. This makes SPME an ideal technique for field sampling (Pawliszyn, 1999).

SPME is usually considered a passive sampling technique since the fiber is simply placed into a sample matrix and chemicals partition to the polymeric phase. To collect volatile and semi-volatile compounds from soil or liquid, fibers can be exposed in air, directly immersed into a liquid, or can be placed in a container's headspace. For air sampling, the natural convection of air is generally sufficient to facilitate the partitioning of analytes to the polymer. For liquid sampling, however, a zone of depletion can form around the fibers as chemical compounds are partitioned out of the liquid. However, this can be corrected by continuously stirring the sample while the fiber is immersed in the liquid (Pawliszyn, 1999).

### 2.3. Solid Phase Microextraction Sampling

Rapid sampling and quantitative analysis of nerve agents using SPME and GC/MS have been demonstrated in numerous studies. Hook *et al.* (2003a) described the benefits of using SPME sampling coupled with GC/MS analysis for the detection of VX nerve agent contamination. This research found that PDMS coated fibers were capable of detecting 1.0  $\mu\text{g}$  of VX per gram of soil. Schneider *et al.* (2001) established the effectiveness of SPME for rapid field detection of sarin in both air and water. This study

found a limit of detection (LOD) of 0.1 µg/L of sarin in headspace sampling and a LOD of 12 µg/L using direct immersion of the fiber into an aqueous solution. Headspace sampling of VX by Hook *et al.* (2003b) was performed to compare the performance of five commercially available polymer coatings. Results showed that the PDMS, PA, CW/DVB, and PDMS/DVB polymers provided similar uptake kinetics. Lasko and Ng (1997) demonstrated the effectiveness of SPME and GC/MS in detecting 60 ppb of sarin, soman, tabun, and VX in samples of tap water, river water, sea water and sewage. The detection of airborne sarin using both static and dynamic SPME was studied by Hook *et al.* (2004). A dynamic system where contaminated air was pumped across a SPME fiber inside a sampling chamber demonstrated that more sarin was captured in comparison to a static sampling system. The success of these studies shows that SPME sampling, when coupled with GC/MS analysis, is an effective method for the detection and quantification of nerve agents in many different sample media.

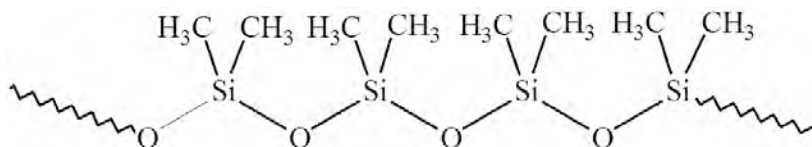
#### **2.4. Polymer Coatings**

Commercially available polymer coatings for SPME fibers differ in their mechanism of extraction (absorption or adsorption), and in their affinity for polar or nonpolar analytes. Coatings are classified into two separate types: 1) homogenous pure polymer coatings and 2) porous particles embedded in a polymeric phase. There are two commercially available homogenous pure polymer coatings that have absorptive characteristics. Polydimethylsiloxane (PDMS) has a high affinity for nonpolar analytes and is the most widely used general purpose polymer. Polyacrylate (PA) possesses an affinity for polar analytes. The remaining polymer coatings use a mixed phase system



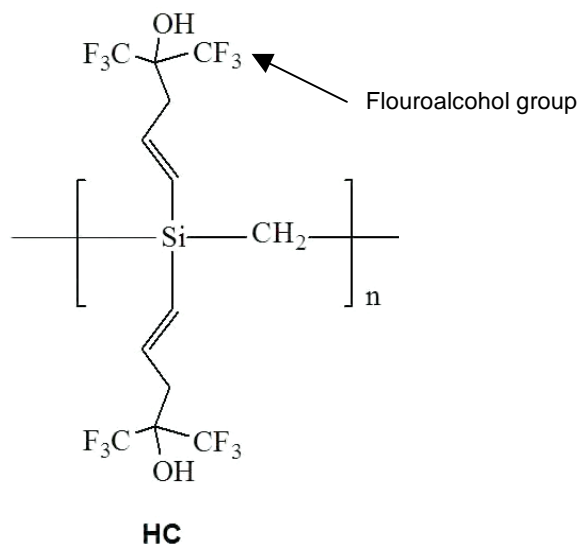
containing porous particles, either divinyl benzene (DVB) or carboxen, embedded in a partially cross-linked polymeric phase, either PDMS or carbowax (CW). These mixed phase polymers have adsorptive characteristics and have a higher selectivity and sensitivity for certain analytes (Pawliszyn, 1999).

Recent research and development has yielded new polymers that have hydrogen bond acidic functional groups. These functional groups are characterized by an electron deficient hydrogen atom that allows the polymer to extract analytes by chemisorption rather than adsorption. It can also increase selectivity towards specific analytes as well as improve sensitivity. These qualities offer a distinct advantage over commercially available polymers. PDMS, for example, is a highly viscous linear chained polysiloxane and does not have hydrogen bond acidic functional groups (Figure 2-6). It absorbs most nonpolar substances and, therefore, cannot target specific analytes (Pawliszyn, 1999).



**Figure 2-6. Chemical Structure of Linear PDMS Polymer**

The NRL has recently developed and tested hydrogen bond acidic polymers characterized by fluoroalcohol-substituted polycarbosilane chains. The basic structure of the hydrogen bond acidic polymer designated as HC is shown in Figure 2-7.

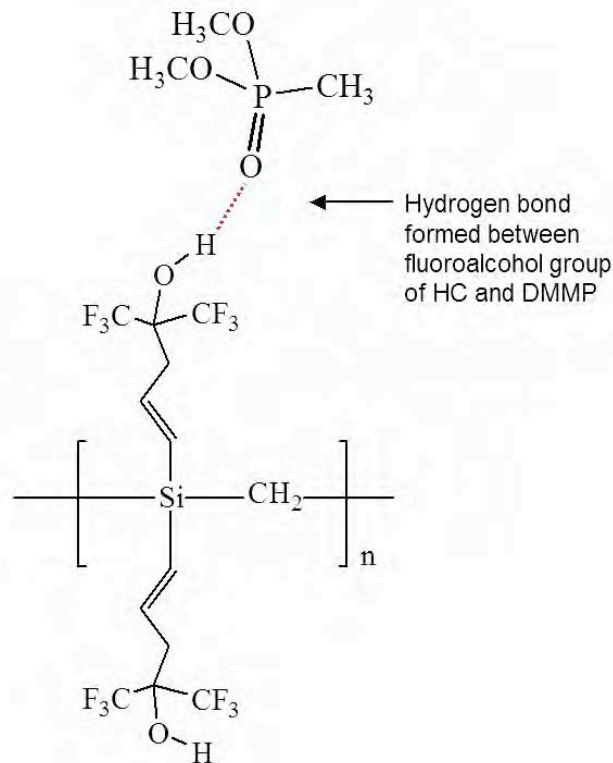


**Figure 2-7. Basic Chemical Structure of HC**

The carbosilane backbone offers thermal stability while the fluoroalcohol functional end groups have an electron withdrawing effect on the oxygen atom in the O-H group, thus making them hydrogen bond acidic. The absence of hydrogen bond basic sites in the polymer backbone, such as the oxygen atoms contained in linear PDMS, reduces hydrogen bonding internal to the molecule. This increases the number of fluoroalcohol groups available for hydrogen bonding with hydrogen bond basic analytes such as organophosphates and nerve agents and leads to higher uptake of these agents (Bryant, 2005). Hydrogen bond acidic polymers can be either linear or hyperbranched. While the two types perform similarly in regards to their uptake of nerve agent, the linear polymers are generally more viscous and have a higher molecular weight than the hyperbranched polymers (NRL, 2006).

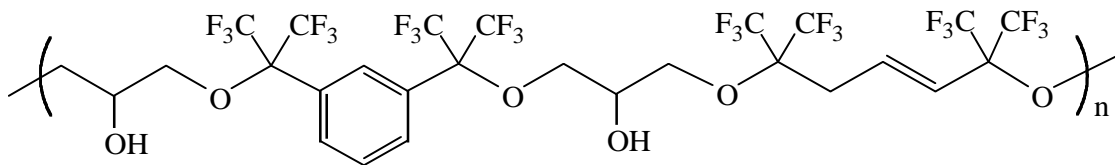
The vapor sorptive properties of hydrogen bond acidic polymers were evaluated by Houser *et al.* (2004) in surface acoustic wave (SAW) sensors. Results showed that these polymers had a high sensitivity to hydrogen bond basic vapors such as the nerve

agent simulant dimethyl methylphosphonate (DMMP). DMMP is hydrogen bond basic at the terminal oxygen atom of the P=O bond. The bonding mechanism between the HC polymer and DMMP is shown in Figure 2-8. Previous experimentation by the NRL shows that HC will absorb an average of 20 times more nerve agent as compared to commercial PDMS (NRL, 2006).



**Figure 2-8. Hydrogen Bonding Between HC and DMMP (Bryant, 2005)**

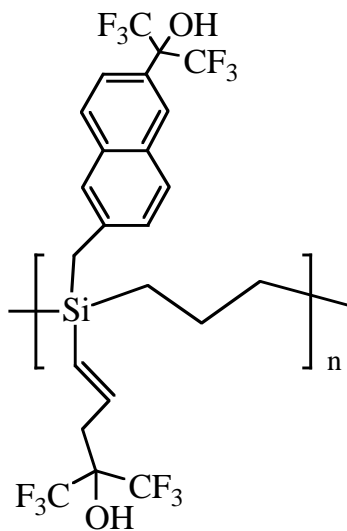
Another polymer currently being tested by the NRL is FPOL (Figure 2-9). This polymer is also characterized by multiple fluorocarbon and O-H functional groups.



**Figure 2-9. Basic Chemical Structure of FPOL**

Unlike the HC polymer, FPOL is a fluoro-ether where the O-H groups are not located next to the FI groups but are connected to the polymer backbone. FPOL also has oxygen groups within the polymer backbone. Due to this configuration, FPOL should still have an affinity for hydrogen bond basic analytes, but will not be nearly as selective as HC. Previous experimentation shows that FPOL will absorb an average of 2-3 times more nerve agent as compared to commercial PDMS. FPOL also has a lower molecular weight and lower viscosity than HC (NRL, 2006).

The NM<sub>2</sub>A polymer is another hyperbranched hydrogen bond acidic polycarbosilane that is being tested by the NRL (Figure 2-10). NM<sub>2</sub>A is a linear polymer



**Figure 2-9. Basic Chemical Structure of NM<sub>2</sub>A**

with a carbosilane backbone and fluoroalcohol groups attached to naphthylmethyl groups. As with the HC polymer, the fluoroalcohol groups create strong hydrogen bond acidity. The increased electron density due to the aromatic naphthyl rings may increase the interaction between the polymer and target analytes. NM<sub>2</sub>A has a higher molecular weight and viscosity than HC due to the naphthyl rings but has fewer fluoroalcohol end groups. Previous experimentation by the NRL has shown that it can absorb, on average, ten times the amount of nerve agent simulant when compared to commercial PDMS (NRL, 2006).

Further comparison studies by other researchers have shown that hydrogen bond acidic polymers exhibit a significantly higher selectivity to nerve agent simulants relative to general purpose polysiloxane polymers. Houser *et al.* (2004) demonstrated that fluoroalcohol substituted polycarbosilanes have higher sensitivity toward nerve agent simulant due to the absence of hydrogen bond basic sites (oxygen atoms) within the polymer backbone. Grate *et al.* (1993) also demonstrated that hydrogen bond acidic polymers provide a high selectivity and sensitivity for nerve agent simulants and actual nerve agents. Pacific Northwest National Laboratories (PNNL) designed several polymers that consisted of hydrogen bond acidic hexafluorobisphenol groups between polydimethylsiloxane spacers. The PNNL polymers were tested by Grate *et al.* (1999) in SAW vapor sensors and the results showed they provided better detection of trace concentrations of organophosphates when compared to commercially available polymers. Harvey *et al.* (2002) coated SPME fibers with a phenol-based hydrogen bond acidic polycarbosilane polymer and evaluated its selectivity towards sarin as compared to

standard PDMS polymers. This study showed the hydrogen bond acidic polymer exhibited a 20-fold higher uptake of sarin than PDMS, coupled with a lower selectivity towards total hydrocarbons. Overall, these studies have shown the use of hydrogen bond acidic polymers can provide superior uptake for selected analytes such as nerve agents. Successfully coating SPME fibers with the hydrogen bond acidic polymers developed by the NRL will allow samples to be rapidly collected and analyzed on a GC/MS with a SPME injection port.

### **3. Methodolgy**

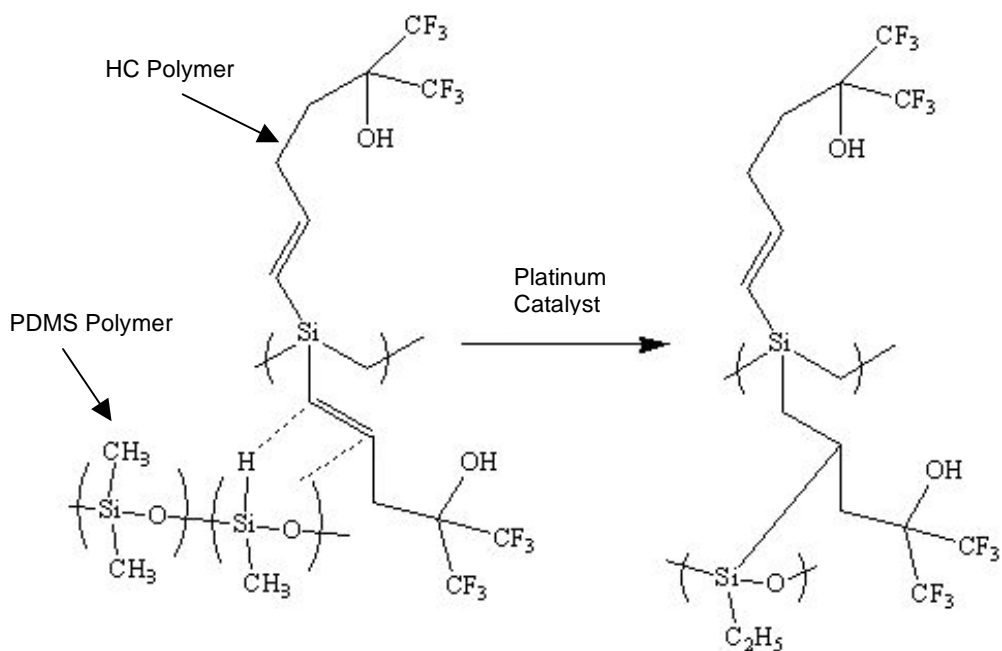
This chapter describes the methods used to answer the research questions discussed in Chapter 1. The first objective of this research was to determine if the hydrogen bond acidic polymers can be effectively coated onto SPME fibers and to test three different coating methods. Dip coating, applicator coating, and ink jet coating methods are examined. The second objective was to test the coated fibers against known concentrations of nerve agent simulant and compare the performance of the hydrogen bond acidic polymers to commercially available polymers and to analyte uptake expectations established by the NRL for each type of polymer. Two methods of simulant sampling were tested: static vapor phase sampling and direct immersion aqueous phase sampling.

#### **3.1. Application of Polymer Coatings**

##### **3.1.1. Dip Coating**

Dip coating was the first method tested for applying hydrogen bond acidic polymers to SPME fibers. The dipping solutions were prepared by dissolving a selected quantity of HC polymer and an adhesive PDMS polymer in a methylene chloride (Aldrich Chemical Co., Cas#75-09-2) solvent along with a platinum catalyst. The low viscosity of the HC polymer made it unsuitable for coating the fiber using only the neat polymer as it did not adhere to fiber. Therefore, the adhesive PDMS polymer was added to the HC polymer to both increase the viscosity of the mixed solution and promote crosslinking within the polymer matrix. The adhesive PDMS polymer is a linear PDMS,

with 5-7% of its functional groups being Si-H groups (Figure 3-1). These silicon-bonded hydrogen atoms readily crosslink the chains of the PDMS polymer with other PDMS chains and with the chains of the HC polymer in the presence of a platinum catalyst.



**Figure 3-1. Crosslinking of PDMS and HC Polymer Chains**

The catalyst is a platinum (0)-2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane complex solution (Aldrich Chemical Co., Cas#68585-32-0). In order to achieve the appropriate amount of crosslinking needed to stabilize both polymers in a solid matrix, the HC polymer was combined with the adhesive PDMS polymer in a 50/50 mixture by weight.

The first step in creating the dipping solution involved adding 250 mg of the HC polymer to a glass vial. A microbalance (Sartorius, model BP-615) was used to weigh the appropriate amount. An equal mass of the adhesive PDMS polymer was then added



to the vial. The next step involved adding a selected quantity of methylene chloride. Three separate dipping solutions were created by adding 1.0, 2.0, or 3.0 ml of methylene chloride. This was done to determine which concentration would result in the best coating. Once the polymers were fully dissolved in the solvent (approximately 30 minutes), 5.0  $\mu$ l of platinum catalyst was added to the vial to initiate crosslinking. The mixed polymer solution was stirred until a uniform viscosity was achieved. The vial was then secured to a laboratory stand in preparation for dip coating.

Standard Supelco fiber assemblies with uncoated fused silica fibers, 1 cm in length and 110  $\mu$ m in diameter, were used for the dip coating. The fiber assembly was placed in a standard Supelco SPME fiber holder, and the fiber was extended out of the assembly. The fiber was then repeatedly dipped, 3-6 times, into the polymer solution until a visible coating was achieved. The fiber was then removed from the solution and was held horizontally and rotated to prevent the polymer from collecting at one end of the fiber and ensure a more even distribution of the coating along the fiber. The fiber was rotated for 30 seconds while the solvent evaporated. This dipping and evaporation process was then repeated 2-3 additional times until a semi-uniform coating was present along the entire length of the fiber.

A problem with this method involved the tendency of the polymer to clump together in beads on the surface of the fiber instead of attaching as a smooth coating as seen in commercial polymer coatings. The beads of polymer were manually smoothed by using a second uncoated fiber like a paint brush to break up the beads and spread the polymer along the surface of the fiber. This helped to improve the uniformity of the polymer coating.

The fiber was then partially cured by placing it in a vacuum oven (Cole Parmer, StableTemp) at 100° C under a vacuum of 20 in. Hg for 30 minutes. This was done to evaporate any remaining solvent and to promote polymer crosslinking. A vacuum pump (GE, model 5KH36KNA510X) was used to create the vacuum. After removal from the oven, the fiber was re-dipped in the solution using the same dipping procedures to add an additional layer of polymer to the fiber. Some additional beading of the polymer was observed and the beads were again manually smoothed. The target polymer thickness was 30 µm. This thickness was chosen to make it comparable with a commercial 30 µm PDMS fiber. After the final dip coated layer, the fiber was hardened by placing it in the vacuum oven for 16 hours at a temperature of 120° C and 20 in. Hg pressure.

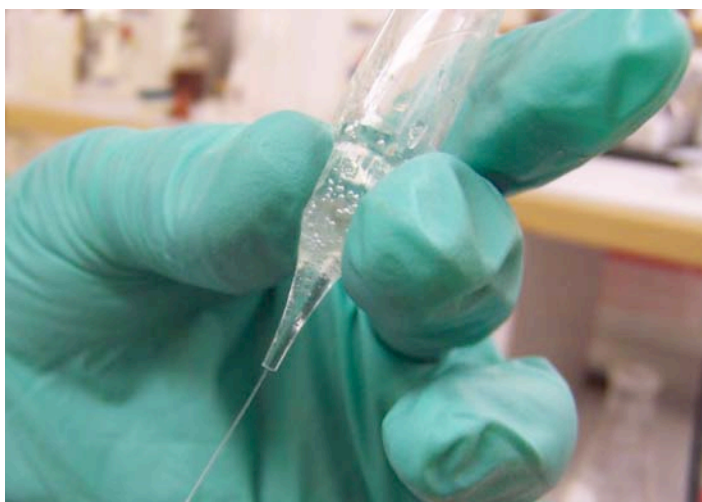
The dipping solution that contained the 3.0 ml of methylene chloride was found to be too dilute and did not result in any of the polymer mixture adhering to the fiber. The dipping solutions with 1.0 ml and 2.0 ml of methylene chloride resulted in semi-uniform polymer coatings. The fibers created from these dipping solutions were used for vapor and aqueous phase sampling and are designated as fibers “HC/PDMS (Dipped#1)” and “HC/PDMS (Dipped#2)” respectively.

### **3.1.2. Applicator Coating**

Applicator coating was performed with assistance from Dr. Venkat Mani, American Analytical, State College, PA. Both the HC and FPOL polymers were selected for applicator coating. For coating with the HC polymer, a 50/50 mixture of the HC and the adhesive PDMS polymer was used. First, 6.0 ml of methylene chloride was added to a glass vial. Then 750 mg of the HC polymer and 750 mg of the adhesive PDMS

polymer were added to the vial and allowed to dissolve into solution. After approximately 30 minutes, 15.0  $\mu\text{l}$  of the platinum catalyst (same as with dip coating) was added to the vial to initiate the crosslinking process. The mixed polymer solution was then stirred until a uniform viscosity was achieved.

A 12 inch long uncoated fiber made of fused silica polyacrolate (FSA) (Polymicro Technologies, FSA080120) was used for the applicator coating. The FSA fiber had a fused silica diameter of 83  $\mu\text{m}$  with a 21  $\mu\text{m}$  thickness of polyacrolate for a total fiber diameter of 125  $\mu\text{m}$ . The polyacrolate coating strengthened the silica fiber and provided a favorable surface for attaching the polymer. The FSA fiber was first pretreated by dipping it in a methylene chloride solution for 20 seconds. Approximately 4.0 ml of the mixed polymer solution was poured into a funnel-shaped silicon applicator. The end of the fiber was inserted into the top of the applicator and drawn out the bottom through the small end of the funnel (Figure 3-2).



**Figure 3-2. Polymer Application Using Silicon Applicator**

The entire fiber was pulled through the applicator, applying a uniform coating of the polymer mixture along the FSA fiber approximately 10  $\mu\text{m}$  in thickness. The fiber was then held in front of a desktop flameless heater for 2 minutes to enhance evaporation of the methylene chloride solvent and crosslinking of the polymer matrix. The fiber was passed through the applicator and heated in the same manner a total of 4 times in order to add additional layers of polymer to the FSA fiber and bring the total polymer thickness to approximately 40  $\mu\text{m}$ .

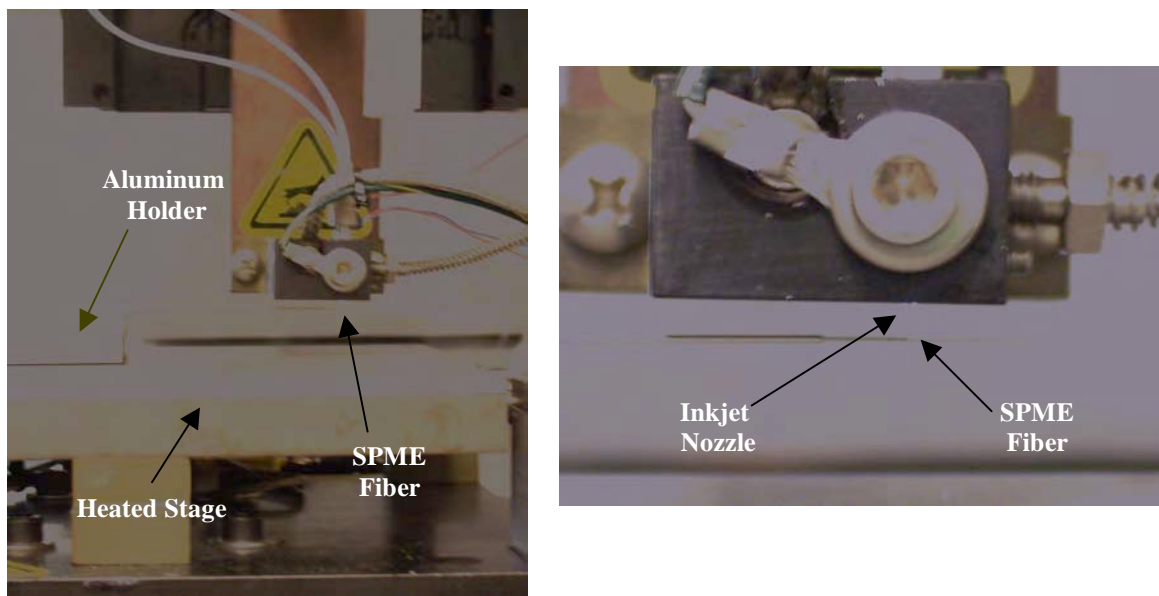
The coated fiber was then placed in an oven (Blue M, Stabil-Therm) inside a glass cylinder containing a nitrogen atmosphere. It was cured at 200° C for 16 hours in order to evaporate the remaining methylene chloride and promote additional crosslinking of the polymer mixture. A nitrogen atmosphere was used to prevent degradation of the PDMS polymer that could occur in the presence of oxygen. The fiber was then removed from the oven and allowed to cool to room temperature. The fiber was then cut into 2 cm lengths. Each length of fiber was inserted 1 cm into the needle of a standard Supelco SPME fiber assembly and glued into place. This allowed 1 cm of the fiber to be exposed for sampling. The entire process was then repeated using the FPOL polymer combined in a 50/50 mixture of FPOL and adhesive PDMS. The fibers created from these mixtures and used in further vapor and aqueous phase testing are designated as fibers “HC/PDMS (Applicator)” and “FPOL/PDMS (Applicator)”.

### **3.1.3. Ink Jet Coating**

The third method evaluated in this study is the ink jet coating method. This method was performed in conjunction with the NRL using a Jet Lab II (Microfab

Technologies, Inc.) ink jet printing platform. The goal of the ink jet coating method was to produce a fiber with a more uniform polymer coating that could be easily replicated. The two coatings chosen for the ink jet coating method were the HC and NM<sub>2</sub>A polymers. The NM<sub>2</sub>A polymer was chosen in place of the FPOL polymer since the NM<sub>2</sub>A has a higher molecular weight and higher viscosity which would make it easier to coat onto a SPME fiber.

Standard Supelco fiber assemblies with uncoated fused silica fibers, 1 cm in length and 110  $\mu$ m in diameter, were used for the ink jet coating method. The uncoated fused silica fiber was inserted into a standard SPME fiber holder which was then secured to an aluminum holder. The fiber was positioned on the stage of the ink jet printing platform so that the fiber was situated approximately 3mm directly below the ink jet nozzle and 2 cm above the heated stage as shown in Figure 3-3. For all ink jet coatings,



**Figure 3-3. Ink Jet Coating Set-Up**

the stage was heated to 110 °C to aid in solvent evaporation as the droplets were dispersed and adhered to the fiber.

The HC polymer was first dissolved in a butanol solvent in order to decrease its viscosity prior to jetting. This was done to ensure that the polymer solution would not clog the ink jet nozzle. A solution of 1.0% HC polymer (by weight) in 1-butanol (CAS#71-36-3, Aldrich Chemical Co.) was used. The 1.0% HC polymer solution was then loaded into the well of the ink jet nozzle.

Eight layers of the HC coating were applied to the uncoated fused silica fiber. The specific ink jet settings used for the formation of the droplets and the coating pattern are given in Appendix A. The first layer of polymer was applied to the fiber by jetting 100 bursts along the entire 1 cm length of the fiber in two parallel rows for a total of 200 bursts. The fiber remained stationary. Each burst contained 200 droplets of the polymer solution. Each droplet was approximately 100 μm in diameter. While coating the first layer, formations of combined droplets appeared as small beads of polymer on the fiber. These small beads moved along the fiber due to capillary action and surface tension. The beads became larger as they moved along the surface of the fiber and collected additional droplets of polymer.

The second layer of polymer coating was then applied to the HC fiber approximately two minutes after the first layer. For the second layer, the coating pattern was expanded to three parallel rows to maximize the amount of solution deposited on the fiber. At 100 bursts per row, this increased the total number of bursts to 300. The third and fourth layers were also coated onto the fiber using the three parallel rows and 300 total bursts.

The fiber was then rotated 180 degrees to apply an additional four layers to the opposite side of the fiber. For the fifth layer (the first just after the fiber rotation), the spacing between each burst was doubled to reduce large bead formation. Therefore, the number of bursts in each row was reduced from 100 to 50 bursts for a total of 150 bursts. Increasing the burst spacing did not appear to reduce the capillary effect. For the sixth, seventh and eighth layers, the same three rows at 150 total bursts were maintained but the number of droplets per burst was reduced. The droplets were reduced from 100 to 50 to 25 drops per burst, respectively. The lower burst rates were found to reduce large bead formation and their movement along the fiber. The HC fiber created from the ink jet coating method and used in further vapor and aqueous phase sampling is designated as fiber “HC (Ink Jet)”.

A second fused silica fiber was coated using the  $\text{NM}_2\text{A}$  polymer. A jetting solution of 0.4%  $\text{NM}_2\text{A}$  polymer (by weight) in a 20/80 mixture (by weight) of toluene (CAS#108-88-3, Aldrich) and 1-butanol was used. The 0.4% concentration of  $\text{NM}_2\text{A}$  polymer and the mixture of the two solvents had to be used to achieve complete dissolution of the  $\text{NM}_2\text{A}$  in the solvent.

A total of 16 layers (8 per side) of  $\text{NM}_2\text{A}$  polymer were applied to the fiber using a burst rate of 50 droplets per burst. Three parallel rows were again applied for each layer but the distance between each burst was increased which resulted in 44 bursts per row (instead of 50) for a total of 132 bursts per layer (instead of 150). The fiber created from ink jet coating the  $\text{NM}_2\text{A}$  solution and used in further vapor and aqueous phase sampling was designated as fiber “ $\text{NM}_2\text{A}$  (Ink Jet)”. Microscopic images and further

analysis of all ink jet coated fibers are given in section 4.1.3. The ink jet settings used for droplet formation and the coating pattern are given in Appendix A.

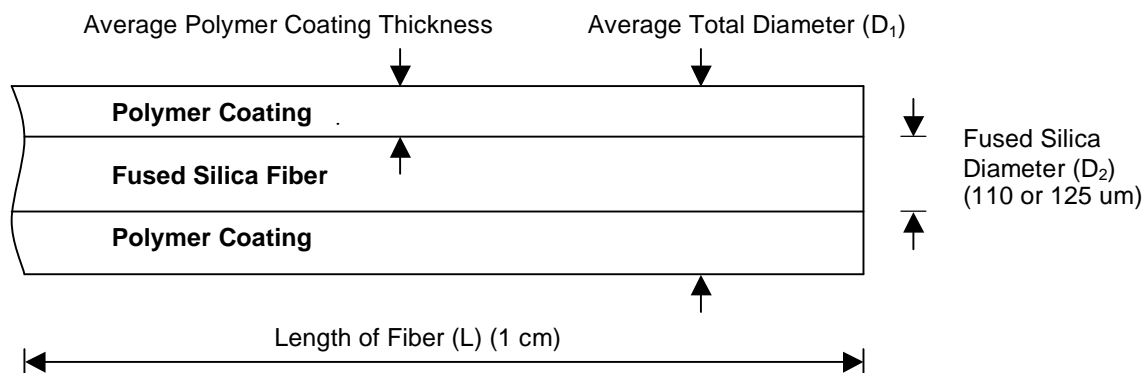
### **3.2. Fiber Imaging**

Measurement of the polymer thickness of each fiber was made by imaging each fiber under a Leica Model DM LB microscope using the 20X magnification lens. The fiber to be measured was inserted into a SPME fiber holder, which was then secured to a laboratory stand. The position of the fiber on the stand was adjusted so that the SPME fiber holder laid flat on the microscope stage. It was supported by four stacked glass slides to ensure that the distance from the lens was always the same and repeatable measurements could be achieved. The microscope was focused so the edges of the fiber were clear. This ensured that the depth of the focus was half way into the fiber. A video image of the fiber under the 20X magnification lens was then captured using the microscope's camera (QImaging, Micropublisher) and imaging software (QImaging, QCapture 1394) and displayed on a computer screen.

Using the Image-Pro Discovery software, a measurement of the total fiber diameter of an uncoated Supelco fused silica fiber was made using the software's built-in measurement tools. This procedure optically calibrated the measurement tool. Images of the test fibers were obtained using the same procedures and total fiber diameter measurements were obtained. Ten measurements were taken every 1mm along the length of the polymer coating in order to obtain an average fiber diameter. Average polymer coating thickness was obtained by subtracting the diameter of the uncoated fused silica fiber (either 110 or 125  $\mu\text{m}$ ) from the average total fiber diameter and dividing by two.



The total volume of polymer coating was then determined by calculating the total combined volume of both the polymer coating and fused silica fiber and subtracting the volume of the fused silica fiber (Figure 3-4).



$$\text{Average Polymer Coating Thickness} = (D_1 - D_2) / 2$$

$$\text{Total Polymer Coating Volume} = \pi (D_1 / 2)^2 L - \pi (D_2 / 2)^2 L$$

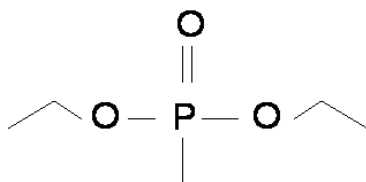
**Figure 3-4. SPME Fiber Measurements**

Microscopic fiber imaging was also used to visually analyze the overall quality of and uniformity of the polymer coatings. Digital photographs of the test fibers were taken both before and after sampling was performed to determine if the polymer coatings had been damaged or degraded through repeated vapor and aqueous phase sampling.

### 3.3. Nerve Agent Simulant

Nerve agent simulants are chemicals that are produced in order to mimic the behavior of actual nerve agents. Simulants have similar structure and functional groups

as nerve agents. Simulants also have similar physical properties such as vapor pressure and ionization affinity. The major advantage of using nerve agent simulants is that they are much less toxic and easier to work with. Dimethyl methylphosphonate or DMMP (97%, Aldrich Chemical Co., CAS# 756-79-6) was the simulant selected due to its structural similarities to military nerve agents and the many organophosphate based chemicals and pesticides used in industry (Figure 3-9). DMMP was used for both vapor phase and aqueous phase sampling.



**Figure 3-5. Basic Chemical Structure of DMMP**

### **3.4. Vapor Phase Extraction**

The six different SPME fibers coated with the hydrogen bond acidic polymers discussed in the previous sections were tested using static vapor phase extraction from tedlar bags. Three commercially manufactured fibers were used for comparison for a total of nine test fibers. The three commercial fibers included two PDMS fibers with coating thicknesses of 30  $\mu\text{m}$  and 7  $\mu\text{m}$  and a DVB/PDMS fiber with a 65  $\mu\text{m}$  thickness. The PDMS fibers were tested to give a basis of comparison between the hydrogen bond acidic polymers and general purpose commercial polymers of similar thickness. The DVB/PDMS (65 $\mu\text{m}$ ) fiber was used due to the fact that previous research (Lasko, 1997) has shown that this coating gave much higher GC/MS peak areas when compared to other

commercial polymers for the aqueous phase extraction of sarin. Table 3-1 shows all of the polymers that were tested using vapor phase extraction.

| Fiber                     | Coating Method         |
|---------------------------|------------------------|
| Dip Coated                | HC/PDMS (Dipped #1)    |
|                           | HC/PDMS (Dipped #2)    |
| Applicator Coated         | HC/PDMS (Applicator)   |
|                           | FPOL/PDMS (Applicator) |
| Ink Jet Coated            | HC (Ink Jet)           |
|                           | NM2A (Ink Jet)         |
| Commercially Manufactured | PDMS (30um)            |
|                           | PDMS (7um)             |
|                           | DVB/PDMS (65um)        |

**Table 3-1. Test Fiber Information**

### 3.4.1. Sample Preparation

To compare the uptake of vapor phase simulants for each of the test fibers, known concentrations of DMMP were created in a 5.0 L tedlar bag (SKC). DMMP concentrations of 0.5, 0.05, and 0.005 mg/m<sup>3</sup> were selected to challenge each of the polymers against concentrations that would compare to the IDLH values of G-series nerve agents (0.05-0.1 mg/m<sup>3</sup>).

The 5.0 L tedlar bag was filled with 4.0 L of ambient air using a 2.0 L macro-volume syringe (SGE Inc.). In order to achieve the 0.5 mg/m<sup>3</sup> concentration in the bag, a stock solution of 2.0 mg/ml DMMP in methylene chloride was mixed in a 15 ml silanized glass vial. One microliter of the stock solution was drawn from the vial using a 10.0 ul

syringe (Hamilton, #701), and injected into the tedlar bag through its PTFE-lined silicone septa. A solvent chase method was used to draw the stock solution, where 1.0  $\mu\text{l}$  of methylene chloride was drawn into the syringe, followed by 1.0  $\mu\text{l}$  of air, followed by the 1.0  $\mu\text{l}$  of stock DMMP solution, followed by an additional 1.0  $\mu\text{l}$  of air. This method was used in order to ensure that 1.0  $\mu\text{l}$  of the stock solution was accurately injected into the bag. After injection of the DMMP stock solution, the bag was allowed to equilibrate for 30 minutes. The bag was then purged using a high flow pump (Gilian, model 800485). This process was repeated two additional times to minimize loss of analyte to the walls of the tedlar bag. After the third evacuation, the bag was filled to the desired concentration for sample collection. To achieve the 0.05 and 0.005  $\text{mg}/\text{m}^3$  concentrations in tedlar bags, stock solutions of 0.2 and 0.02  $\text{mg}/\text{ml}$  DMMP in methylene chloride were used.

### **3.4.2. SPME Sampling Protocol**

The hydrogen bond acidic test fibers were conditioned at 120° C for 30 minutes prior to use. This temperature was recommended by the NRL to minimize the chance for degradation of these polymers. All commercial test fibers were conditioned at 250° C for 30 minutes according to the manufacturer's recommendations. Sampling was conducted at ambient room temperature. The fiber to be tested was first inserted into a SPME fiber holder. Then the septum of the tedlar bag was pierced with the SPME fiber needle and the fiber was extended inside the bag. A standard extraction time of 10 minutes was used. Longer sampling times are generally undesirable in field sampling conditions. After 10 minutes, the fiber was retracted back into the needle and the SPME sampler was removed from the bag. The fiber was then promptly inserted into a heated

GC injection port. The fiber was extended into the mid-range region of the injection port liner and GC/MS analysis was conducted.

Triplicate samples of the test fibers listed in Table 3-1 were obtained at the 0.5 and 0.05 mg/m<sup>3</sup> test concentrations. Hydrogen bond acidic polymers that showed a significantly higher analyte uptake per μm<sup>3</sup> of polymer volume versus commercial polymers at the 0.05 mg/m<sup>3</sup> concentration were then challenged at 0.005 mg/m<sup>3</sup> along with the two commercial PDMS fibers for comparison. Triplicate samples of these fibers were obtained using both 10 and 1 minute sampling times. The 1 minute extractions were performed in order to determine if this shorter extraction time would still be sufficient to detect the analyte of interest at the lowest test concentration.

### **3.5. Aqueous Phase Extraction**

Direct immersion sampling was used to test the uptake of DMMP in an aqueous phase. The same six hydrogen bond acidic fibers and three commercial fibers that were tested during the vapor phase sampling were also used for aqueous phase sampling (Table 3-1).

#### **3.5.1. Sample Preparation**

For aqueous phase sampling, test concentrations of 100 ppm and 1 ppm DMMP in water were created. To prepare the 100 ppm concentration, a stock solution of 10% DMMP in methylene chloride was mixed by adding 0.5 ml of DMMP to 4.5 ml of methylene chloride in a silanized glass vial. From this stock solution, 1.2 μl was extracted and injected into a separate vial containing 12.0 ml of deionized water. This

resulted in a final concentration of 100 ppm DMMP. A solvent chase method was again used to ensure accuracy and reproducibility of the injections. To prepare the 1.0 ppm concentration, a stock solution of 0.1% DMMP in methylene chloride was mixed by adding 0.1 ml of DMMP to 9.9 ml of methylene chloride in a silanized glass vial. From this stock solution, 1.2  $\mu$ l was extracted using a 10.0  $\mu$ l syringe and injected into a separate vial containing 12.0 ml of deionized water to create the final concentration of 1 ppm DMMP. Each test vial was placed on a magnetic stirrer (Barnant Co., model 700-5011) and mixed for 30 minutes prior to sampling.

### **3.5.2. SPME Sampling Protocol**

The hydrogen bond acidic test fibers were conditioned at 120° C for 30 minutes prior to use. This temperature was recommended by the NRL to minimize the chance for degradation of these polymers. All commercial test fibers were conditioned at 250° C for 30 minutes according to the manufacturer's recommendations. Sampling was conducted at ambient room temperature. The fiber to be tested was first inserted into a SPME fiber holder. Then the septum of the test vial was pierced with the SPME fiber needle and the fiber was extended into the vial so that the entire length of the exposed fiber was immersed in the liquid. The liquid in the vial was continuously stirred during sampling using a magnetic stirrer. An extraction time of 10 minutes was used. After 10 minutes the fiber was retracted back into the needle and removed from the vial. The SPME fiber was then promptly inserted into a heated GC injection port. The fiber was extended into the mid-range region of the injection port liner and GC/MS analysis was

conducted. Triplicate samples of the nine of the test fibers were obtained at both the 100 ppm and 1 ppm test concentrations.

### **3.6. GC/MS Analysis**

GC/MS analysis of the SPME samples were performed using an Agilent GC with a noncoated inert electron impact ionization source and monolithic hyperbolic quadrupole mass selective detector. The GC used a 30m x 0.25 mm I.D. DB5-MS column having a film thickness of 0.25  $\mu\text{m}$ . Helium at a linear velocity of 1.4 ml/min and constant flow was used as the carrier gas. The oven was programmed to hold at 40° C for 2 minutes and then increase to 250° C at 20° C per minute. Desorption of the SPME fiber samples was accomplished in the splitless injection mode. A 0.75 mm deactivated glass injection port liner (Supelco) was used and the injector temperature was maintained at 150° C throughout the analysis. The MS transfer line was held at 270° C. Mass spectra were collected over the range of 30-250 mass-to-charge (m/z). Sample mass spectral information was stored and analyzed using the Agilent Chemstation software package. Blank samples were run, at a minimum, once per day prior to the start of SPME samples.

### **3.7. Polymer Comparison and Data Analysis**

The relative standard deviation (RSD) between the triplicate samples for each test fiber at each sampling concentration was calculated to analyze the reproducibility of the measurements. The total uptake (total GC/MS peak area) of DMMP as well as total uptake per  $\mu\text{m}^3$  of polymer volume for each fiber was compared using a one-way analysis of variance (ANOVA) followed by a Tukey HSD Post Hoc comparison test.

Comparisons were made between the test fibers to determine which polymer and coating method gave the best performance at each sampling concentration. Results for the hydrogen bond acidic polymers were also compared with results from prior testing by the NRL that provide expected DMMP uptake for each polymer type. These uptake expectations are given in Table 3-2 and detail the average advantage in DMMP uptake that the polymer is expected to provide when compared to a PDMS fiber of equal

| Polymer                   | Expected Advantage in DMMP Uptake |
|---------------------------|-----------------------------------|
| HC                        | 20 fold                           |
| HC/PDMS (50/50 mixture)   | 10 fold                           |
| FPOL/PDMS (50/50 mixture) | 1.5 fold                          |
| N <sub>2</sub> MA         | 10 fold                           |

**Table 3-2. Expected Advantage in DMMP Uptake of Hydrogen Bond Acidic Polymers Over a PDMS Polymer of Equal Thickness**

polymer thickness. In addition, previous research of the hydrogen bond acidic polymers has found that the expected advantage in DMMP uptake should be higher at lower concentrations (NRL, 2006).



## **4. Experimental Results and Discussion**

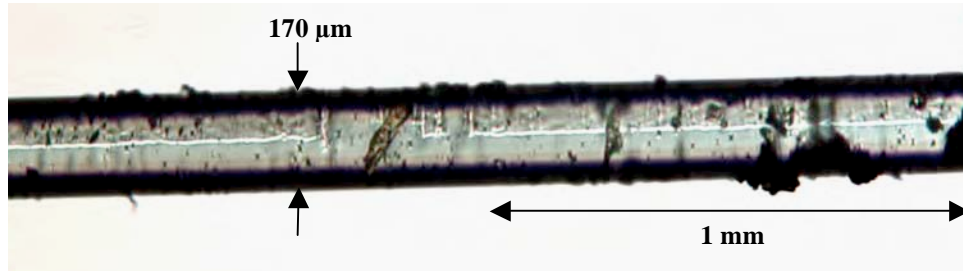
### **4.1. Application of Polymer Coatings**

The results from the three coating methods (dip coating, applicator coating, and ink jet coating) will be discussed in the following sections.

#### **4.1.1. Dip Coating**

Dip coating was performed using the HC polymer as described in chapter 3.1.1. The addition of the adhesive PDMS polymer and the platinum catalyst provided crosslinking and a bonded polymer coating. A microscopic image of a commercially manufactured PDMS (30 $\mu$ m) fiber under the 10X magnification lens is shown in Figure 4-1. Images of the HC/PDMS (Dipped#1) and HC/PDMS (Dipped#2) fibers are shown in Figures 4-2 and 4-3 respectively.

The polymer coatings of the HC/PDMS (Dipped#1 and #2) fibers were not as uniform as commercial fibers, exhibiting a slight variability in thickness along the length of the fiber. The coating of the HC/PDMS (Dipped#2) fiber was created with the more dilute dipping solution (250 mg polymer per 1.0 ml methylene chloride) which led to a slightly thinner but more uniform coating than the HC/PDMS (Dipped#1) fiber that used the thicker dipping solution (250 mg polymer per 2.0 ml methylene chloride). Both coatings fully hardened into a solid matrix and were firmly bonded to the fused silica fibers.



**Figure 4-1. Commercial PDMS (30μm) Fiber (10X Magnification)**



**Figure 4-2. HC/PDMS (Dipped#1) Fiber (10X Magnification)**



**Figure 4-3. HC/PDMS (Dipped#2) Fiber (10X Magnification)**

#### **4.1.2. Applicator Coating**

Applicator coating was performed using the HC and FPOL polymers, combined with the adhesive PDMS polymer as described in chapter 3.1.2. The fibers created through the applicator coating method are shown in Figures 4-4 and 4-5.



**Figure 4-4. HC/PDMS (Applicator) Fiber (10X Magnification)**



**Figure 4-5. FPOL/PDMS (Applicator) Fiber (10X Magnification)**

Both fibers were able to be fully hardened into a solid matrix and bonded to the surface of the fused silica fiber. However, there were variations in the quality of each polymer coating. The HC/PDMS (Applicator) fiber exhibited a very smooth and uniform coating. The FPOL/PDMS (Applicator) fiber coating was less uniform, having slight variations in thickness along the length of the coating. In addition, some sections of the FPOL/PDMS (Applicator) fiber had no coating. This could have been due to the FPOL polymer having a lower molecular weight and lower viscosity than the HC polymer, thus requiring a greater amount of crosslinking in order to evenly bond to the fiber.

### 4.1.3. Ink Jet Coating

Ink jet coating was performed using the HC and NM<sub>2</sub>A polymers as described in chapter 3.1.3. The amount of polymer that adhered to the fiber and the overall quality of polymer coating was dependant on both the type of polymer used and the ink jet parameters.

The HC (Ink Jet) fiber is shown in Figures 4-6 and 4-7. From Figure 4-6, it can be seen that the polymer tended to clump together and form a jagged non-uniform coating. An additional problem with the HC (Ink Jet) fiber was the polymer could not be fully crosslinked and bonded to the fused silica fiber since they were not mixed with the adhesive PDMS polymer. Images of the HC (Ink Jet) fiber taken before sampling (Figure 4-6) and after sampling (Figure 4-7) show the polymer was redistributed along the surface of the fiber. Migration of the polymer along the fiber may have occurred during desorption in the heated GC inlet. It is also possible the redistribution could be due to the polymer sticking to the inner walls of the needle assembly when retracted.

The NM<sub>2</sub>A (Ink Jet) fiber was coated using a setting of 50 droplets per burst and 132 total bursts per layer. Figure 4-8 illustrates how the reduced number of drops per burst and increased spacing between bursts limited the degree of beading and clumping of the polymer. However, these settings resulted in only a very thin layer of polymer adhering to the surface of the fiber and some areas of the fiber remaining uncoated. This may also have been due to the type of polymer and the lower 0.4% concentration of NM<sub>2</sub>A polymer in the ink jetting solution compared to the 1.0% concentration used with the HC polymer.

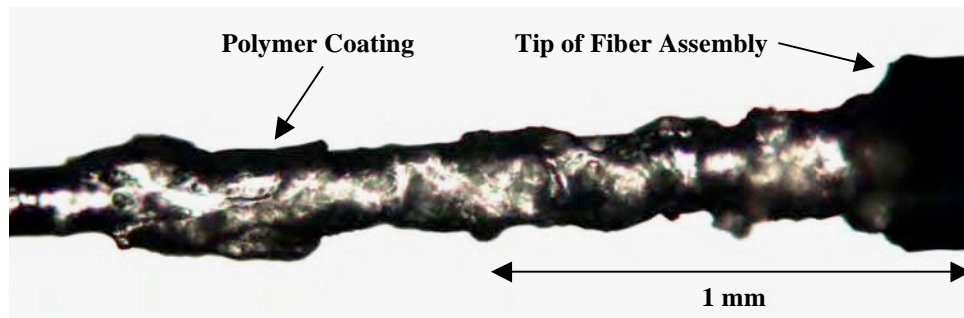


Figure 4-6. HC (Ink Jet) Fiber Before Sampling (10X Magnification)

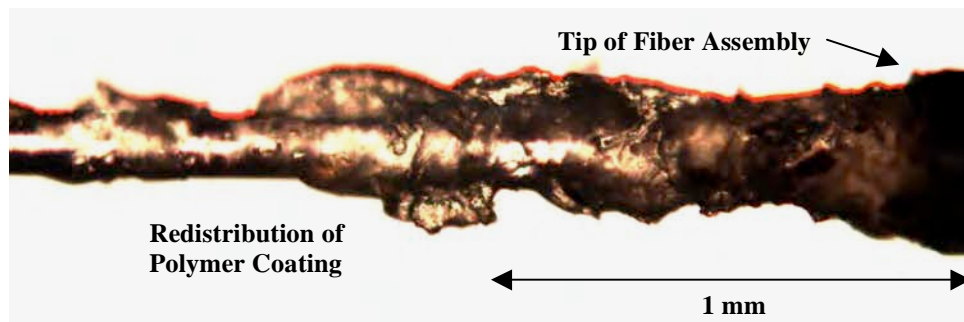


Figure 4-7. HC (Ink Jet) Fiber After Sampling (10X Magnification)

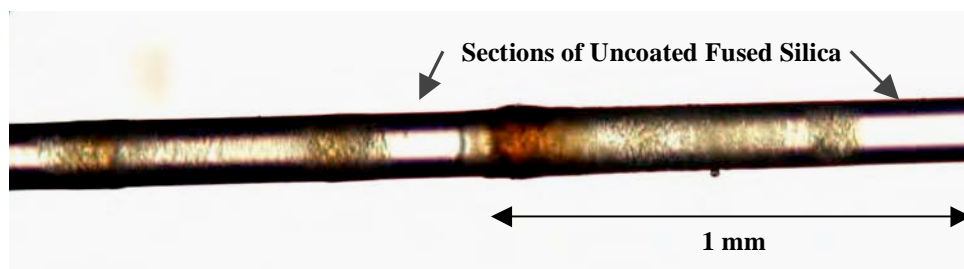


Figure 4-8. NM<sub>2</sub>A (Ink Jet) Fiber (10X Magnification)

The NM<sub>2</sub>A (Ink Jet) fiber coating did not exhibit any visible redistribution or degradation of its polymer coating after sampling as seen with the HC (Ink Jet) fiber. This could be due to the fiber having only a very thin polymer coating. It is also possible

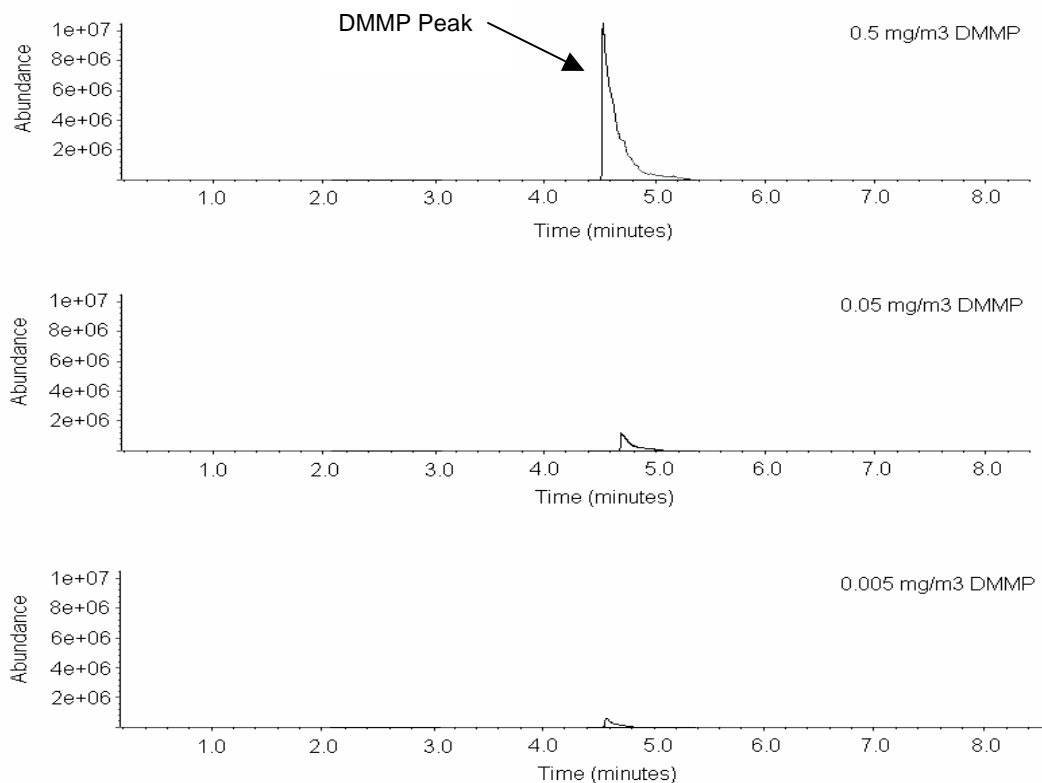
that the increased molecular weight and presence of the naphthyl groups within the polymer structure provided sufficient internal crosslinking of the polymer to increase its stability on the fiber.

Achieving a uniform polymer coating using the ink jet coating method may be possible with further testing and modification of the ink jet parameters. Adjusting the number of droplets per burst, the number of bursts per application layer, the number of layers, and continuous fiber rotation, should improve the quality of the coating. Other parameters that can be modified to possibly improve the coating process include the height of the spray nozzle above the fiber and the viscosity of the polymer solution. The use of higher molecular weight hydrogen bond acidic polymers, currently under development at the NRL, that exhibit more internal crosslinking may result in a more stable coating.

## **4.2. Vapor Phase Extraction**

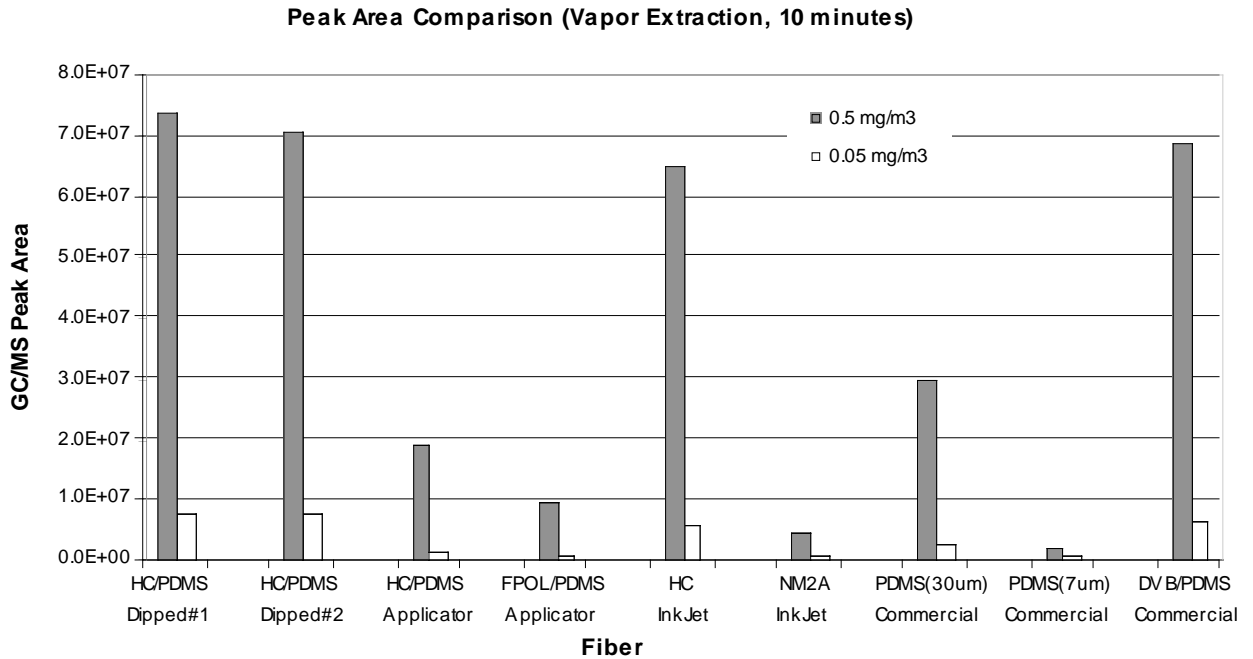
### **4.2.1. Vapor Phase Sampling Results**

Vapor phase extraction of DMMP using static air sampling in tedlar bags was conducted as described in section 3.4. Chromatograms resulting from the 10 minute extractions of vapor phase DMMP at 0.5, 0.05, and 0.005 mg/m<sup>3</sup> using the HC/PDMS (Dipped#2) fiber are given in Figure 4-9. The chromatograms are characterized by the DMMP peak at approximately 4.6 minutes. As expected, the chromatograms show how the total DMMP peak area was reduced as the vapor phase concentration was lowered. The chromatograms for the other test fibers exhibited similar characteristics.

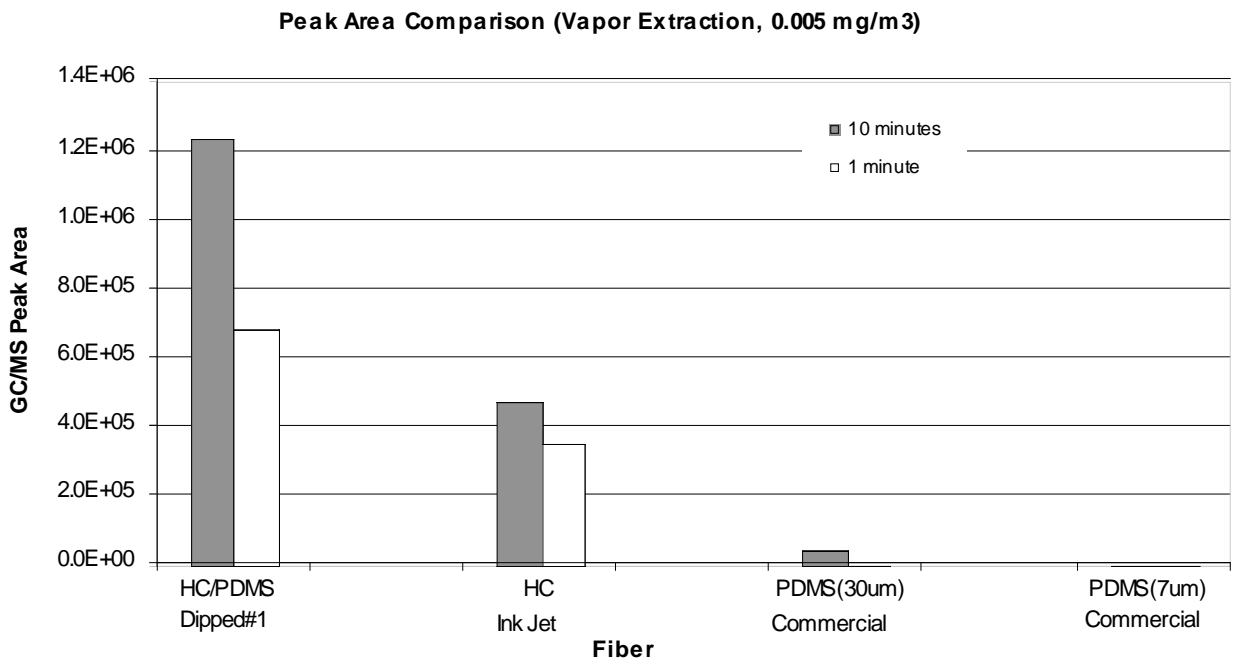


**Figure 4-9. Total Ion Chromatograms for Vapor Phase DMMP Uptake at 0.5, 0.05, and 0.005 mg/m<sup>3</sup> Using Fiber HC/PDMS (Dipped#2)**

Vapor phase DMMP uptake results comparing the total GC/MS peak area for each of the test fibers are shown graphically in Figures 4-10 and 4-11. In Figure 4-10 it can be seen that the HC/PDMS (Dipped#1 and #2) fibers, the HC (Ink Jet) fiber, and the commercial DVB/PDMS (65 $\mu$ m) fiber exhibited the highest total analyte uptake at both the 0.5 and 0.05 mg/m<sup>3</sup> sample concentrations. Results from these four fibers showed no statistical difference. The remaining fibers exhibited significantly lower ( $p < 0.001$ ) total uptakes of DMMP.



**Figure 4-10. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at 0.5 and 0.05 mg/m<sup>3</sup>**

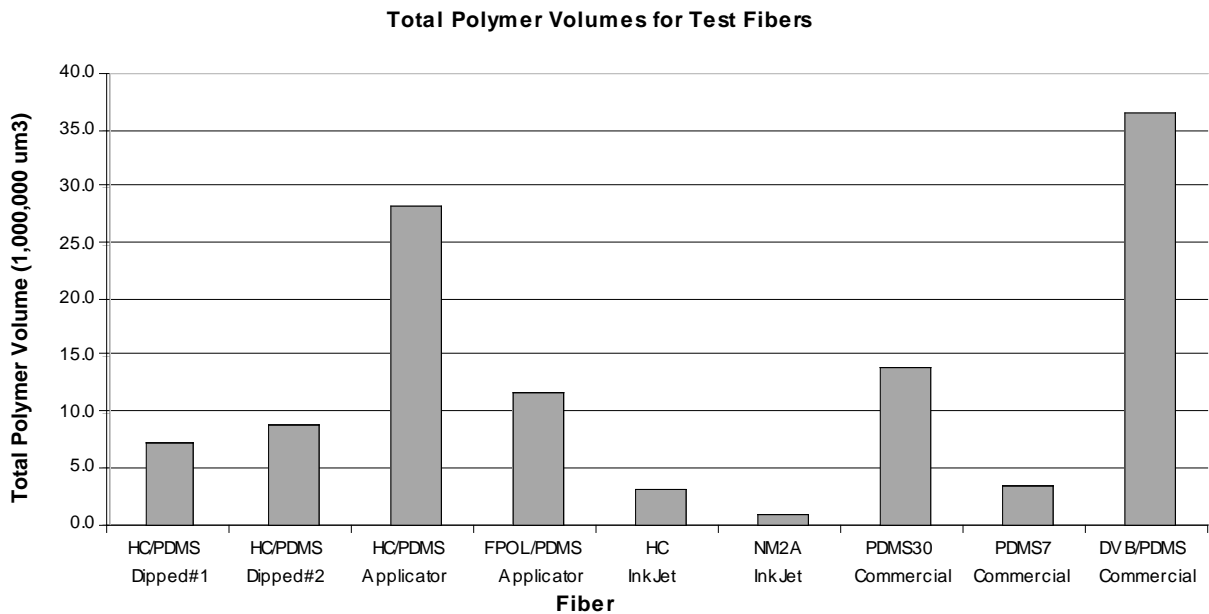


**Figure 4-11. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at 0.005 mg/m<sup>3</sup>**



Figure 4-11 shows that the advantage in DMMP uptake of the HC/PDMS (Dipped#1) and HC (Ink Jet) fibers over the commercial PDMS fibers was even more pronounced at a concentration of 0.005 mg/m<sup>3</sup> for both 1 and 10 minute samples. (Note: the HC/PDMS (Dipped#2) fiber was physically damaged prior to sampling at 0.005 mg/m<sup>3</sup> and therefore could not be included in this part of the study.) For the 1 minute extraction at 0.005 mg/m<sup>3</sup>, the PDMS (7µm) fiber did not detect the DMMP simulant, and the total GC/MS peak area for the PDMS (30µm) fiber was only about four times the background level. Neither of these fibers detected the DMMP at the 1 minute extraction. The HC/PDMS (Dipped#1) and HC (Ink Jet) fibers still exhibited large total GC/MS peak areas at both sampling times.

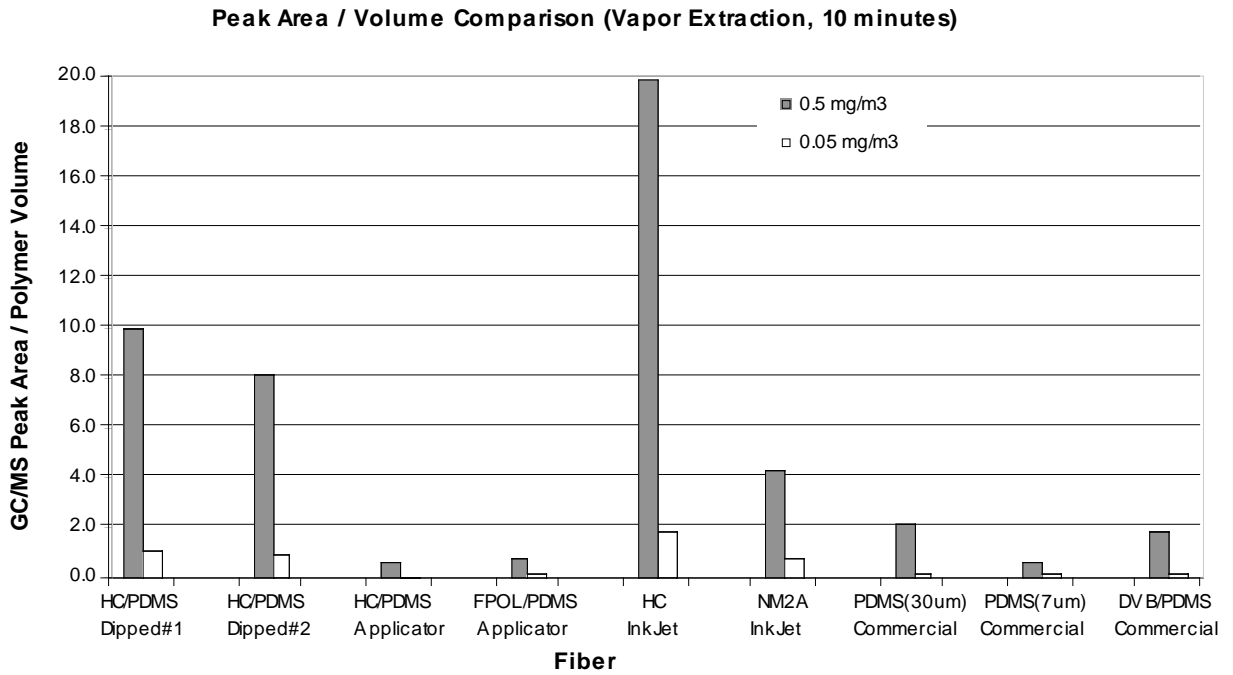
The total polymer volume of each of the test fibers is given in Figure 4-12. Due to the different polymer volumes on each of the test fibers, DMMP uptake was



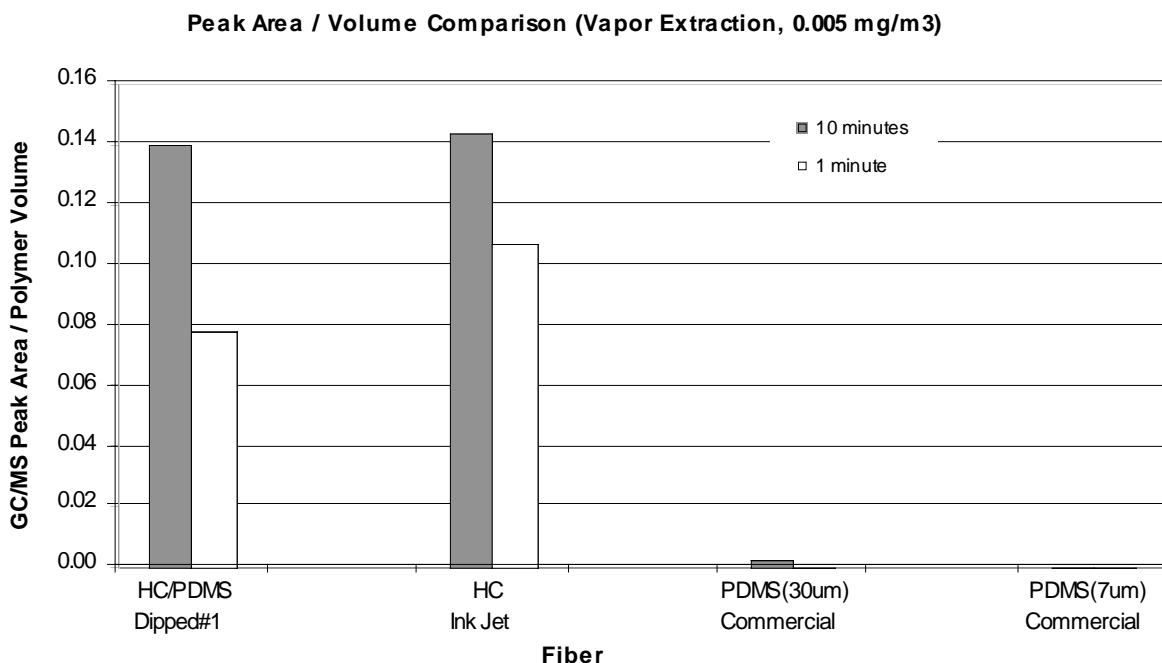
**Figure 4-12. Total Polymer Volumes of Test Fibers**

normalized by dividing the total GS/MS peak area by the polymer volume for each of the test fibers.

The total DMMP uptake per per  $\mu\text{m}^3$  of polymer volume for each of the test fibers are shown graphically in Figures 4-13 and 4-14. Figure 4-13 shows the results from the 0.5 and 0.05  $\text{mg}/\text{m}^3$  sample concentrations. From this comparison, it can be seen that the HC (Ink Jet) fiber exhibited the greatest DMMP uptake per  $\mu\text{m}^3$  of polymer volume, followed by the HC/PDMS (Dipped#1 and #2) fibers and then the NM<sub>2</sub>A (Ink Jet) fiber. Both of the applicator coated fibers and the commercial fibers exhibited lower total uptakes relative to their polymer volumes.



**Figure 4-13. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of DMMP at 0.5 and 0.05  $\text{mg}/\text{m}^3$**



**Figure 4-14. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of DMMP at 0.005 mg/m<sup>3</sup>**

Figure 4-14 illustrates the increased total DMMP uptake per  $\mu\text{m}^3$  of polymer volume of the HC/PDMS (Dipped#1) and HC (Ink Jet) fibers over both commercial PDMS fibers at a concentration of  $0.005 \text{ mg/m}^3$  for both 1 and 10 minute samples. Again, this graph highlights increased performance of these two hydrogen bond acidic polymers over commercial PDMS at trace concentrations.

The data in Figures 4-13 and 4-14 also shows a significant difference in DMMP uptake per  $\mu\text{m}^3$  of polymer volume between the HC/PDMS (Applicator) fiber compared to the HC/PDMS (Dipped#1 and #2) fibers. Although both types of fibers were coated with the same 50/50 mixture of HC and PDMS, the dip coated fibers performed much better than the applicator coated fiber. This indicates that the HC/PDMS mixture was effectively applied with dip coating but not with applicator coating. In addition, both the

dip coated and applicator coated HC/PDMS fibers exhibited polymer coatings that were clear prior to being cured. While the dip coated HC/PDMS polymer remained clear after being cured, both applicator coated fibers exhibited a visible change in the color and opacity of their polymer coatings. The applicator coated HC/PDMS polymer turned a golden color and the FPOL/PDMS polymer turned a light brown. This may be indicative of a change in the polymer chemistry brought about by the curing process. Curing the applicator coated polymers at a higher temperature of 200° C, may have caused thermal degradation of the HC and FPOL polymers which would lead to decreased amounts of DMMP being taken up. The NRL recommends a curing temperature of less than 150° C for these polymers. For future applicator coated fibers, lowering the curing temperature below 150° C may result in better performance.

An additional set of triplicate samples were taken using the HC/PDMS (Dipped#1 and #2) fibers and the two commercial PDMS fibers. This additional set was taken 8 days after the initial samples in order to determine if the HC/PDMS polymer mixture remained stable. It is possible that the PDMS would continue to polymerize with the HC, which would bind more reaction sites and inhibit analyte uptake. A significant difference was not observed between the two sample sets which suggests that the HC/PDMS mixture remained stable.

Results from the expected and actual average advantage in DMMP uptake of the hydrogen bond acidic polymers versus the PDMS (30µm) fiber are given in Table 4-1. Actual performance in DMMP uptake was calculated by comparing the total uptake per polymer volume ratios. At the 0.5 and 0.05 mg/m<sup>3</sup> concentrations, none of the hydrogen bond acidic polymers matched the expected performance advantage over the commercial

| Expected and Actual Advantage in DMMP Uptake of Hydrogen Bond Acidic Polymers over PDMS for Vapor Phase Sampling<br>(Comparison of Total Fiber Uptake Per Polymer Volume) |                    |   |                        |                         |
|---|--------------------|---|------------------------|-------------------------|
| Fiber   | Expected Advantage | Actual Advantage for Sampling Concentration |                        |                         |
|   |                    | 0.5 mg/m <sup>3</sup>                       | 0.05 mg/m <sup>3</sup> | 0.005 mg/m <sup>3</sup> |
| HC/PDMS<br>Dipped#1 and #2  | 10 fold            | 4.2   | 5.1                    | 46.7                    |
| HC/PDMS<br>Applicator   | 10 fold            | None  | None                   | (Not Sampled)           |
| FPOL/PDMS<br>Applicator   | 1.5 fold           | None  | None                   | (Not Sampled)           |
| HC<br>Ink jet   | 20 fold            | 9.4   | 9.2                    | 48.0                    |
| NM <sub>2</sub> A<br>Ink jet  | 10 fold            | 2.0   | 4.4                    | (Not Sampled)           |

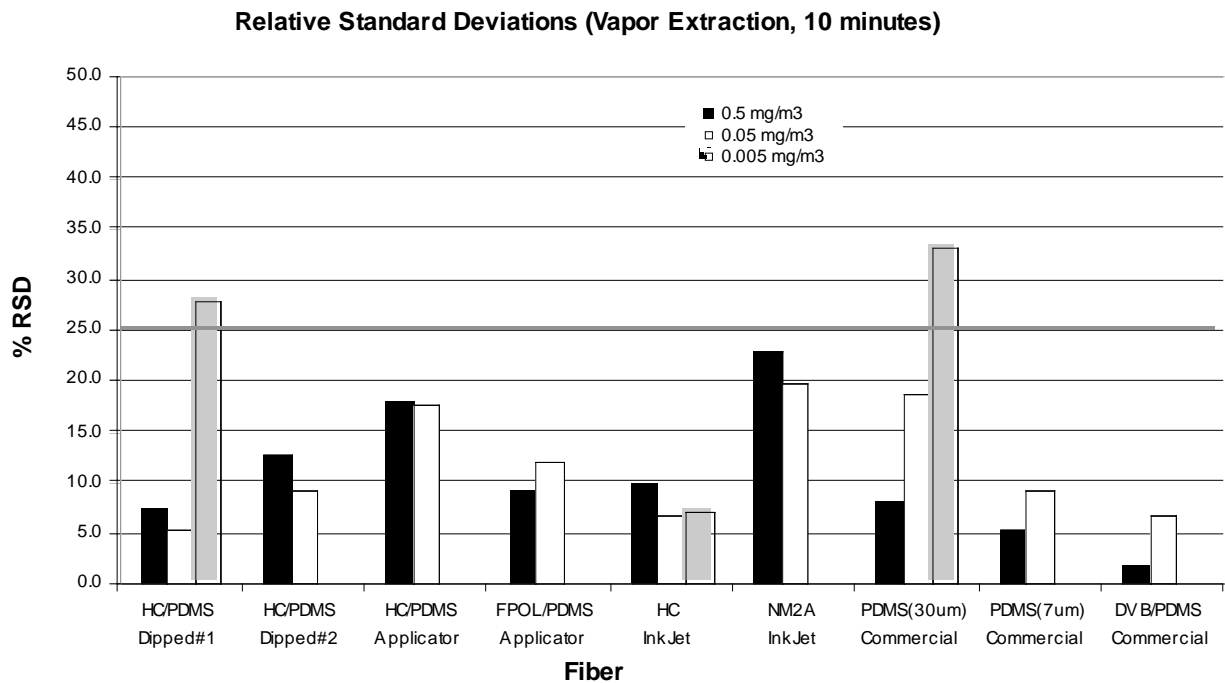
**Table 4-1. Expected and Actual Advantage in DMMP Uptake for Vapor Phase Extraction**

PDMS (30 $\mu$ m) fiber. At the 0.005 mg/m<sup>3</sup> concentration, the amount of DMMP taken up by the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers was almost 50 times higher than the commercial PDMS (30 $\mu$ m) fiber. These results support previous research by the NRL that found that the advantage in analyte uptake of the hydrogen bond acidic polymers over commercial polymers tends to increase at lower concentrations.

The NM<sub>2</sub>A (Ink Jet) fiber exhibited significantly higher levels of DMMP uptake over PDMS but did not meet expectations. Due to the very small quantity of polymer present on the NM<sub>2</sub>A (Ink Jet) fiber, results may be more prone to measurement error. If a thicker layer of the NM<sub>2</sub>A polymer could have been applied, the NM<sub>2</sub>A (Ink Jet) fiber may have shown improved DMMP uptake results.

#### 4.2.2. Data Analysis

In order to demonstrate repeatability in the sampling results, RSDs for all vapor phase sampling sets were calculated and are given in Figure 4-14. RSDs below 25% would generally be considered good repeatability for field sampling. All RSDs at both the 0.5 and 0.05 mg/m<sup>3</sup> concentrations were below 25%. Of the four fibers tested at the 0.005 mg/m<sup>3</sup> concentration, two of the fibers had RSDs above 25%, one remained below 25%, and the fourth fiber did not detect the DMMP simulant. This suggests that repeatable results were achieved for all of the fibers at the 0.5 and 0.05 mg/m<sup>3</sup> concentrations but, as the concentration was reduced to 0.005 mg/m<sup>3</sup>, some of the fibers may have been approaching their lower detection limits, resulting in higher RSDs.



**Figure 4-14. Relative Standard Deviations for Vapor Phase Extraction of DMMP**

Data tables for all vapor phase extraction results are given in Appendix B.

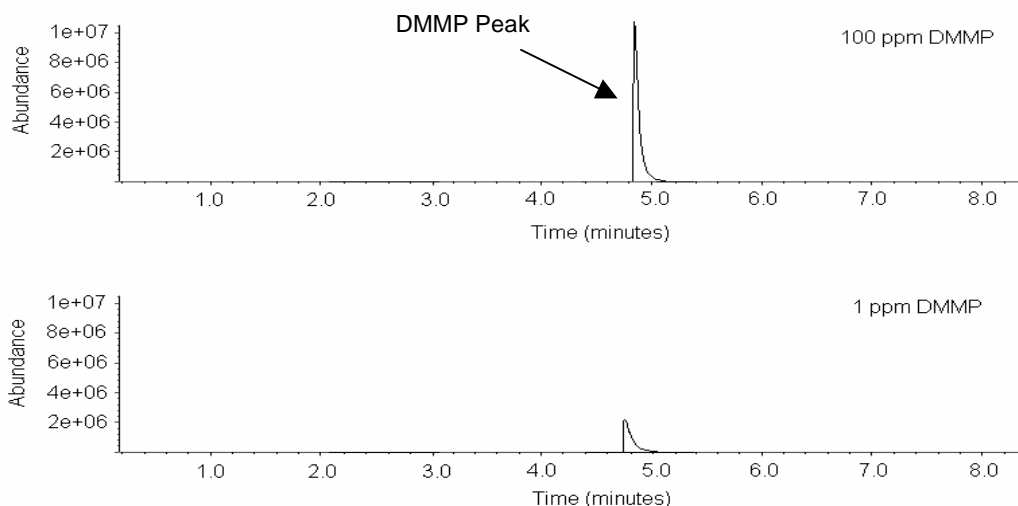
Statistical analysis of the data sets was performed using one-way ANOVA followed by

Tukey HSD Post Hoc comparison. Statistical results are provided in Appendix C.

### 4.3. Aqueous Phase Extraction

#### 4.3.1. Aqueous Phase Sampling Results

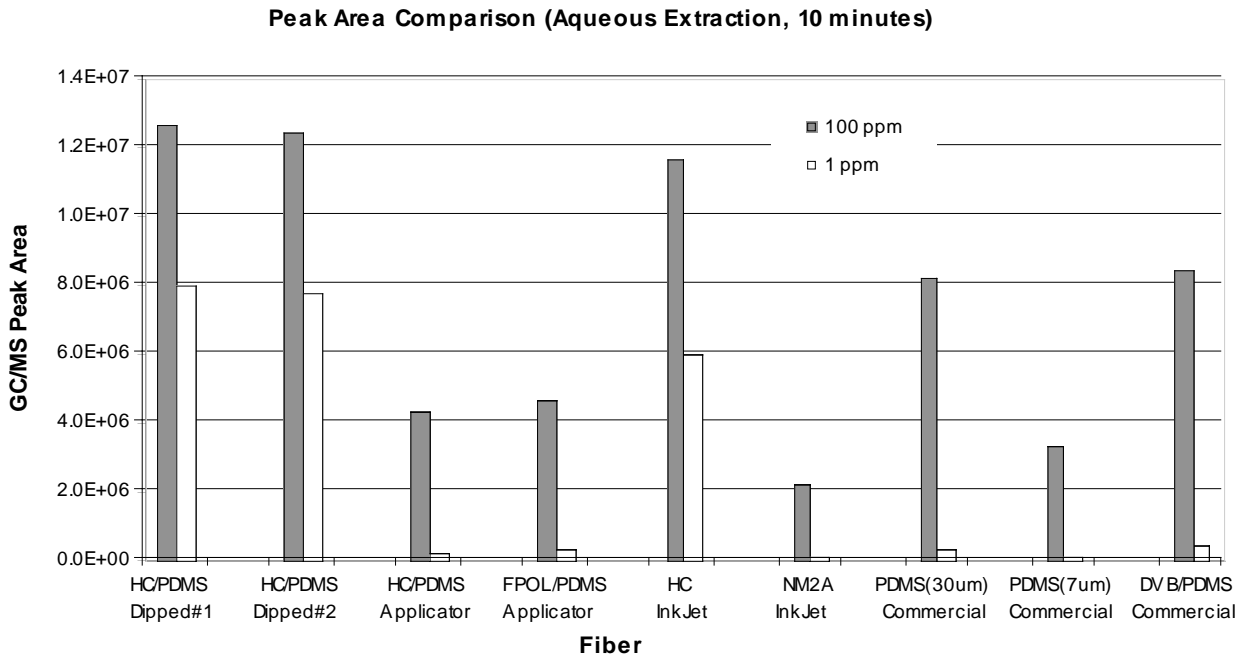
Aqueous phase extraction of DMMP using direct immersion water sampling in a glass vial was conducted as described in section 3.5. Total ion chromatograms resulting from the 10 minute extraction of aqueous phase DMMP at 100 and 1 ppm using the HC/PDMS (Dipped #2) fiber are given in Figure 4-15. The chromatograms are



**Figure 4-15. Total Ion Chromatogram for Aqueous Phase DMMP Uptake at 100 and 1 ppm Using Fiber HC/PDMS (Dipped#2)**

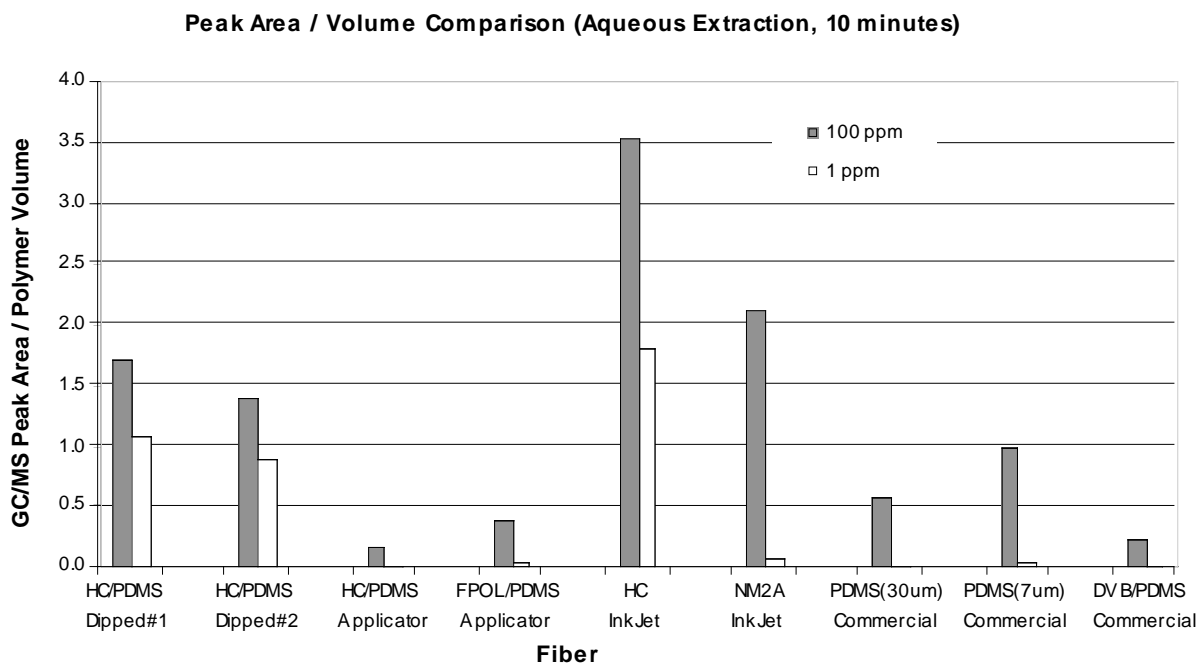
characterized by the DMMP peak at approximately 4.8 minutes. As expected, the chromatograms show how the total DMMP peak area was reduced as the aqueous phase concentration was lowered. The chromatograms for the other test fibers exhibited similar characteristics.

DMMP uptake results for aqueous phase sampling are shown graphically in Figures 4-16 and 4-17. These graphs compare the average GC/MS peak area and the peak area per  $\mu\text{m}^3$  of polymer volume for each of the test fibers. In Figure 4-16 it can be seen that the HC/PDMS (Dipped#1 and #2) fibers and the HC (Ink Jet) fiber had significantly greater ( $p < 0.001$ ) total uptakes of DMMP than the remaining fibers for both the 100 and 1 ppm concentrations. The graph also clearly shows the large increase in the difference in uptake between the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers and the remaining fibers when the test concentration was lowered to 1 ppm. Decreasing



**Figure 4-16. GC/MS Peak Area Comparison for Aqueous Phase Extraction of DMMP at 100 and 1 ppm**





**Table 4-17. GC/MS Peak Area/Polymer Volume Comparison for Aqueous Phase Extraction of DMMP at 100 and 1 ppm**

the concentration from 100 ppm to 1 ppm reduced uptake in the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers by less than 50%. The remaining fibers exhibited a 93-96% decrease in DMMP uptake.

Figure 4-17 gives the DMMP uptake results per  $\mu\text{m}^3$  of polymer volume of each of the test fibers for both the 100 and 1 ppm sample concentrations. From this comparison, it can be seen that HC (Ink Jet) and HC/PDMS (Dipped #1 and #2) fibers exhibited a significantly greater ( $p < 0.001$ ) uptake per  $\mu\text{m}^3$  of polymer volume than the commercial fibers. The  $\text{NM}_2\text{A}$  (Ink Jet) fiber also exhibited a significantly greater ( $p < 0.001$ ) DMMP uptake over all of the commercial fibers when polymer volume was taken into account. However, the  $\text{NM}_2\text{A}$  (Ink Jet) fiber performed much better at 100

ppm than at 1 ppm, which does not match the behavior of the other hydrogen bond acidic polymers.

Results from the expected and actual average advantage in DMMP uptake of the hydrogen bond acidic polymers versus the commercial PDMS (30µm) fiber are given in Table 4-5. Actual performance in DMMP uptake was calculated by comparing the total uptake per polymer volume ratios. At the 100 ppm concentration, none of the hydrogen bond acidic polymers matched the expected performance advantage. At the 1 ppm concentration, the amount of DMMP taken up by the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers was 42 and 79 times higher, respectively, than the commercial PDMS (30µm) fiber. As with the vapor phase sampling, these results support previous research by the NRL that found that the advantage in DMMP uptake of the hydrogen bond acidic polymers over commercial polymers tends to increase at lower concentrations.

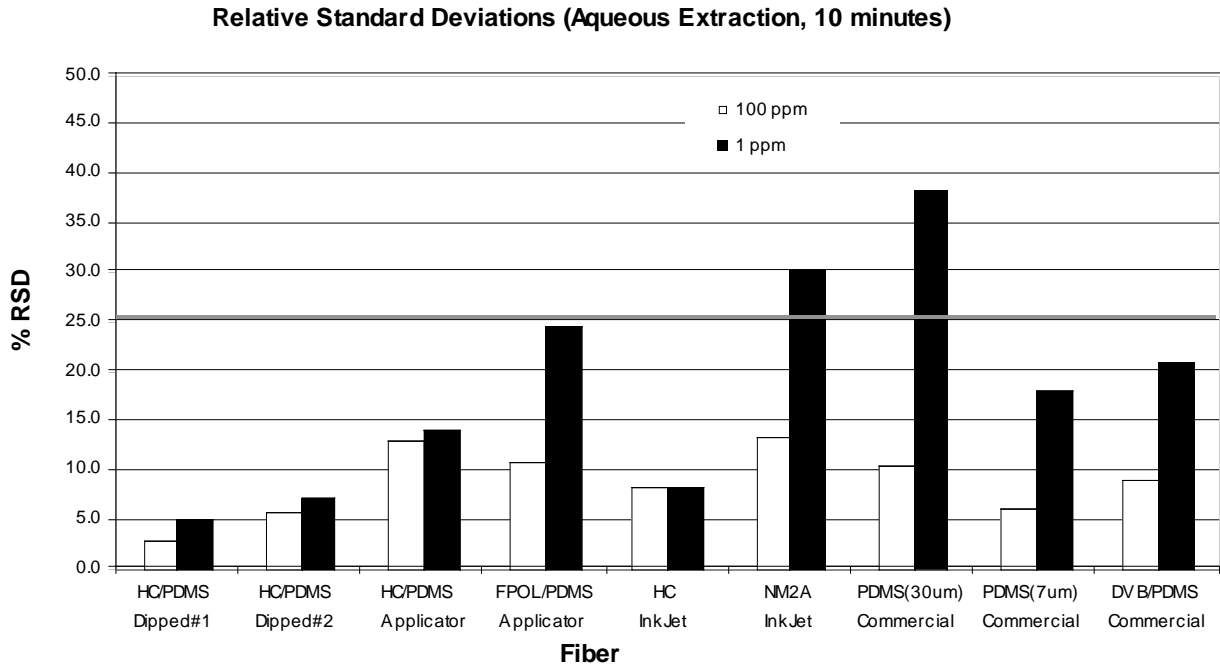
| <b>Expected and Actual Advantage in Analyte Uptake of Hydrogen Bond Acidic Polymers over PDMS for Aqueous Phase Sampling</b><br>(Comparison of Total Fiber Uptake Per Polymer Volume) |                           |  |              |
|---|---------------------------|--|--------------|
| <b>Fiber</b>  | <b>Expected Advantage</b> | <b>Actual Advantage for Sampling Concentration</b> |              |
|   |                           | <b>100 ppm</b>                                     | <b>1 ppm</b> |
| HC/PDMS<br>Dipped#1 and #2  | 10 fold                   | 2.7  | 42.4         |
| HC/PDMS<br>Applicator   | 10 fold                   | None   | None         |
| FPOL/PDMS<br>Applicator   | 1.5 fold                  | None   | None         |
| HC<br>Ink jet   | 20 fold                   | 6.1  | 78.9         |
| NM2A<br>Ink jet   | 10 fold                   | 3.6  | 3.6          |

**Table 4-5. Expected and Actual Advantage in DMMP Uptake for Aqueous Phase Extraction**

The smaller difference seen at the 100 ppm concentration could have been due to the dip coated and ink jet coated fibers reaching equilibrium sooner than the commercial fibers due to their lower polymer volumes. It is possible that while uptake for the dip coated and ink jet coated fibers was restricted due to reaching equilibrium quickly, the fibers with a larger polymer volume continued to take up DMMP. The poor results for the applicator coated fibers again indicate the possibility of thermal degradation during the curing process.

#### 4.3.2. Data Analysis

In order to demonstrate repeatability in the sampling results, RSDs for all aqueous phase sampling sets were calculated and are given in Figure 4-18. RSDs for all fibers



**Figure 4-18. Relative Standard Deviations for Aqueous Phase Sampling of DMMP**

were below 25% for the 100 ppm concentration. RSDs were higher for most of the fibers at the 1 ppm concentration with two fibers exceeding 25%. This suggests that reasonably repeatable results were achieved for all of the fibers at the 100 ppm concentration but, as the concentration was reduced to 1 ppm, some of the fibers may have been approaching their lower detection limits, resulting in higher RSDs. The RSDs for the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers, however, remained below 9% even at the 1 ppm concentration as these fibers continued to collect significantly higher amounts of DMMP than the other fibers.

Data tables for all aqueous phase extraction results are given in Appendix B. Statistical analysis of all data sets were performed using one-way ANOVA followed by Tukey HSD Post Hoc comparison and are provided in Appendix C.

## Conclusions and Recommendations

### 5. Conclusions

The focus of this research was to apply hydrogen bond acidic polymers to SPME. Three different methods of coating fused silica fibers with hydrogen bond acidic polymers were examined: dip coating, applicator coating and ink jet coating. Vapor and aqueous phase sampling of DMMP was accomplished to compare the uptake characteristics of hydrogen bond acidic coated SPME fibers to commercially manufactured SPME fibers. A summary of findings for each of the coating methods and each of the hydrogen bond acidic polymers is given in Table 5-1.

| Summary of Hydrogen Bond Acid Polymer Coatings |                 |                |                                       |                                       |
|--|-----------------|----------------|---------------------------------------|---------------------------------------|
| Fiber  | Uniform Coating | Bonded Coating | DMMP Uptake / Polymer Volume vs. PDMS | Notes                                 |
| HC/PDMS<br>Dipped#1 and #2                     | No              | Yes            | Very Good                             | Little control over coating thickness |
| HC/PDMS<br>Applicator                          | Yes             | Yes            | Poor                                  | Possible thermal damage to coating    |
| FPOL/PDMS<br>Applicator                        | No              | Yes            | Poor                                  | Possible thermal damage to coating    |
| HC<br>Ink Jet                                  | No              | No             | Very Good                             | Redistribution of coating             |
| NM2A<br>Ink Jet                                | No              | No             | Good                                  | Very thin coating                     |

**Table 5-1. Summary of Hydrogen Bond Acidic Polymer Coatings**

The dip coating method was able to produce coatings that were fully hardened and bonded to the fused silica fiber when used in a 50/50 mixture with PDMS. These fibers exhibited very good DMMP uptake performance versus PDMS, especially at trace concentrations in both air and water. Uptake for these fibers was not as high as the HC

(Ink Jet) fiber due to the addition of the adhesive PDMS polymer which bonds with some of the active absorptive sites on the HC molecules. There was difficulty in producing a uniform polymer thickness with the dip coating method. Further experimentation with different dipping solution concentrations and modified fiber dipping and smoothing techniques may be able to improve control over the thickness and uniformity of the polymer coating.

The applicator coating method gave significantly more control over the thickness of the polymer coating and was able to produce bonded fibers of uniform thickness. The HC polymer showed more promise as it bonded more effectively than the FPOL polymer. A high curing temperature most likely caused polymer degradation, limiting the effectiveness of these fibers. The applicator coating method may become an effective method for producing bonded uniform coatings if curing temperatures are held below 150° C.

The ink jet coating method was able to provide a significant amount of control over the thickness of the polymer coating, but was not able to produce fibers of uniform thickness. Fine tuning the ink jet coating parameters should be able to produce a more uniform coating. The HC (Ink Jet) fiber exhibited the best performance in DMMP uptake, but since it was not hardened or bonded to the fused silica fiber, redistribution and possible degradation of the coating was observed. The NM<sub>2</sub>A (Ink Jet) fiber exhibited only a slightly better performance over commercial PDMS but quantification of results was difficult due to the very limited volume of polymer on the fiber. The NM<sub>2</sub>A polymer coating did appear more stable than the HC possibly due to its higher molecular

weight and ability to internally crosslink. Ink jet coating with other higher molecular weight polymers may produce more stable coatings.

As demonstrated by this study, hydrogen bond acidic polymers can be coated onto SPME fibers through several different methods. Sampling of nerve agent simulant shows the increased sensitivity of these polymers over current commercially available fibers, especially at trace concentrations in both vapor and aqueous media. This study showed the ability of hydrogen bond acidic SPME fibers to detect DMMP simulant at concentrations below nerve agent IDLH levels using rapid 1 to 10 minute sampling times. Detection of DMMP was demonstrated at  $0.005 \text{ mg/m}^3$ , where the IDLH level for sarin is  $0.1 \text{ mg/m}^3$ . The use of hydrogen bond acidic polymers in conjunction with SPME may provide significantly enhanced nerve agent sampling and detection for field operations.

### **5.1. Study Limitations**

A limitation of this study was the fact that non-uniform polymer coatings required estimation of average polymer thickness. The use of fibers with significantly different polymer volumes also complicated direct comparison of analyte uptake between fibers. Another source of possible error is analyte losses to the test vial, syringe, or tedlar bag. Minor measurement errors may have occurred during preparation of standard solutions and injection of analyte into the test vials and tedlar bags. The use of a vapor standards generator may have been able to provide more accurate vapor concentrations. The limited availability of polymers also restricted the number of fibers that could be created and tested.

## 5.2. Additional Research

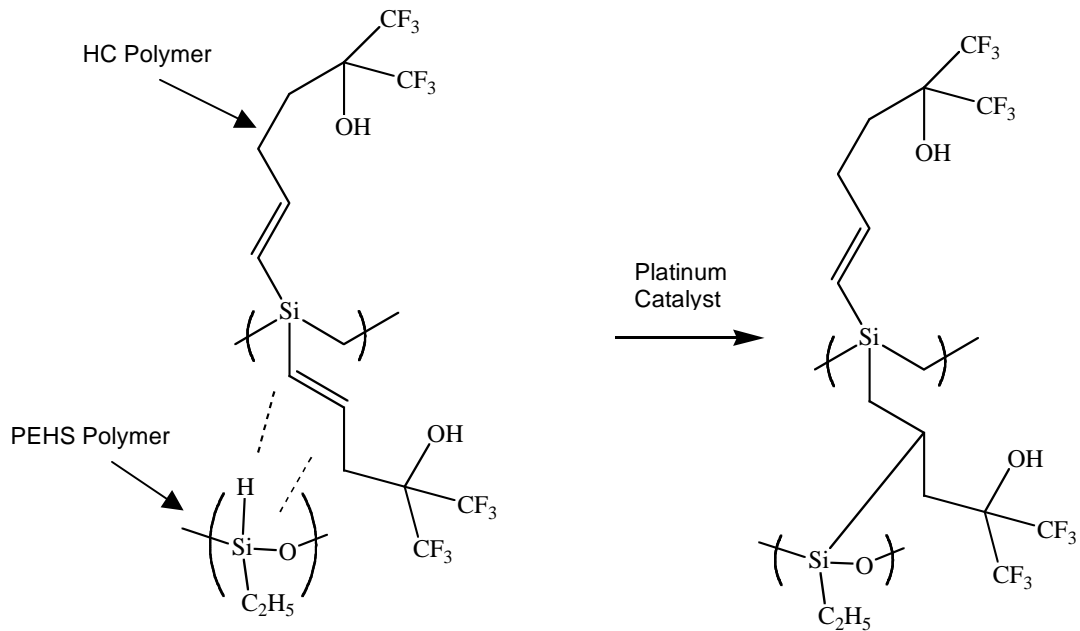
Hydrogen bond acidic polymers show great promise as a specialized polymer coating designed to adsorb trace levels of nerve agents in a field setting. Rapid field sampling may be greatly enhanced with the addition of these materials. This study was able to prove the concept but many more steps can be taken to optimize the hydrogen bond acidic SPME fibers and enhance their performance. Recommended follow-on research includes:

1. Applicator coating at a lower temperature: Reducing the curing temperature below 150° C during applicator coating may prevent polymer degradation and result in improved performance with a high quality coating. Successful modification of method parameters may result in the applicator coating method becoming a viable option for coating SPME fibers with hydrogen bond acidic polymers.
2. Optimization of ink jet coating parameters: Optimization of the ink jet coating parameters can be performed in order to consistently achieve a more uniform coating and an increased the ability to control the polymer thickness.
3. Varying the polymer mixture ratio: The 50/50 mixture of the HC polymer with PDMS produced a bonded and cured fiber coating. The percentage of PDMS may be able to be reduced to maximize the amount of HC in the mixture. An increased percentage of HC will result in a larger number of active –OH sites for analyte bonding and a higher sensitivity and selectivity. At the same time, the use of a higher



percentage of PDMS polymer with the lower viscosity FPOL polymer may result in better adherence of the polymer mixture to the fused silica fiber.

4. Polymer mixtures with PEHS: A poly-ethylhydrido siloxane (PEHS) polymer can be substituted for the adhesive PDMS polymer and mixed with the hydrogen bond acidic polymers. The PEHS has the advantage of having higher content of Si-H functional groups. These groups are used to crosslink the PEHS polymer and the hydrogen bond acidic polymer in the presence of the platinum catalyst. The PEHS should bind to the carbon chains of the HC polymer and not disturb the flouroalcohol groups needed for analyte uptake (Figure 5-1). This should increase crosslinking within the polymer mixture without sacrificing reaction sites on the HC molecules. In addition, it is possible that a smaller percentage of the PEHS would be needed to achieve the same amount of crosslinking provided by the PDMS.



**Figure 5-1. Reaction of PEHS with HC Polymer**

5. Coating with linear higher molecular weight polymers: The NRL has also developed linear hydrogen bond acidic polycarbosilane polymers that have higher molecular weights than the hyperbranched HC, NM<sub>2</sub>A, and FPOL polymers. These higher molecular weight polymers have the advantage of being significantly more viscous and should be easier to coat onto SPME fibers. They should also more readily crosslink and bind to the fused silica fiber. The use of these polymers may negate the need for adding a PDMS or PEHS polymer for additional crosslinking, allowing for an effective neat coating of the hydrogen bond acidic polymers.
  
6. Pre-treatment of fused silica fibers: Experimentation with a monomer primer can be conducted as a pretreatment for the uncoated fused silica fibers. Addition of the primer may provide a more favorable surface for attachment of the hydrogen bond acidic polymer and increase polymer binding.
  
7. Polymer uptake over time: The uptake of analyte over time for SPME fibers coated with hydrogen bond acidic polymers can be studied. Generating uptake curves over different sampling times will show the dynamics of analyte uptake over time and how long the fiber takes to reach equilibrium. This information will provide more comprehensive comparisons between different types of polymer coatings.
  
8. Limits of detection (LOD): This study has shown the effectiveness of hydrogen bond acidic polymers at a concentration of 0.005 mg/m<sup>3</sup>. Follow-on studies using a vapor

standards generator can test even lower concentrations in order to establish an LOD for these polymers and the GC/MS analytical method.

9. Live agent testing: This study has shown the effectiveness of these polymers using nerve agent simulants. Further study using live G-series agent should be conducted to confirm the findings presented here.

## Appendix A

### Ink Jet Coating Parameters

Ink jet coating using the HC and NM<sub>2</sub>A polymers was performed using a Jetlab II printing platform. The ink jet settings used in the creation of these fibers are provided below.

1. Ink jet coating settings for the HC (Ink Jet) fiber:

| <b>Parameter</b> | <b>Setting</b>     |
|------------------|--------------------|
| Burst Rate       | 25-200 drops/burst |
| Rise             | 3 $\mu$ s          |
| Dwell            | 30 $\mu$ s         |
| Fall             | 3 $\mu$ s          |
| Echo Dwell       | 60 $\mu$ s         |
| Final Rise       | 3 $\mu$ s          |
| Dwell Voltage    | 40 V               |
| Echo Voltage     | -40 V              |
| DC offset        | 0 V                |
| Pattern          |                    |
| x-direction      |                    |
| Bursts           | 50-100             |
| Burst separation | 110-220 microns    |
| Distance         | 11 mm              |
| y-direction      |                    |
| Bursts           | 2-3                |
| Burst separation | 83 microns         |
| Distance         | 0.125-0.250 mm     |
| Number of Passes | 8 (4 per side)     |

2. Ink jet coating settings for the NM<sub>2</sub>A (Ink Jet) fiber:

| <b>Parameter</b> | <b>Setting</b>  |
|------------------|-----------------|
| Burst Rate       | 50 drops/burst  |
| Rise             | 3 $\mu$ s       |
| Dwell            | 30 $\mu$ s      |
| Fall             | 3 $\mu$ s       |
| Echo Dwell       | 60 $\mu$ s      |
| Final Rise       | 3 $\mu$ s       |
| Dwell Voltage    | 40 V            |
| Echo Voltage     | -40 V           |
| DC offset        | 0 V             |
| Pattern          |                 |
| x-direction      |                 |
| Bursts           | 44              |
| Burst separation | 250 microns     |
| Distance         | 11 mm           |
| y-direction      |                 |
| Bursts           | 3               |
| Burst separation | 83 microns      |
| Distance         | 0.250 mm        |
| Number of Passes | 16 (8 per side) |

## Appendix B

### DMMP Uptake Data Tables

DMMP uptake data for both vapor and aqueous phase sampling are provided below.

#### 1. Vapor Phase Sampling

| <b>DMMP Uptake Data</b><br>(0.5 mg/m <sup>3</sup> , static air sampling, 10 minutes) |              |                         |      |   |                    |
|--|--------------|-------------------------|------|---|--------------------|
| Fiber  | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#2)  | 6            | 73888517                | 7.5  | 7451465                                 | 9.92               |
| HC/PDMS<br>(Dipped#1)  | 6            | 70969258                | 12.7 | 8781697                                 | 8.08               |
| HC/PDMS<br>(Applicator)  | 3            | 19314537                | 18.1 | 28451049                                | 0.68               |
| FPOL/PDMS<br>(Applicator)  | 3            | 9303526                 | 9.4  | 11875220                                | 0.78               |
| HC<br>(Ink Jet)  | 3            | 65202824                | 9.9  | 3284347                                 | 19.85              |
| NM2A<br>(Ink Jet)  | 3            | 4503001                 | 22.8 | 1065000                                 | 4.23               |
| PDMS<br>(30um)   | 6            | 29701210                | 8.3  | 14038992                                | 2.12               |
| PDMS<br>(7 um)   | 6            | 1907827                 | 5.3  | 3417268                                 | 0.56               |
| DVB/PDMS<br>(65um),  | 3            | 68695351                | 1.8  | 36579920                                | 1.88               |

| <b>DMMP Uptake Data</b><br>(0.05 mg/m <sup>3</sup> , static air sampling, 10 minutes) |              |                         |      |   |                    |
|---|--------------|-------------------------|------|---|--------------------|
| Fiber   | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#2)   | 3            | 7941034                 | 5.2  | 7451465                                 | 1.07               |
| HC/PDMS<br>(Dipped#1)   | 3            | 7529528                 | 9.3  | 8781697                                 | 0.86               |
| HC/PDMS<br>(Applicator)   | 3            | 1688715                 | 17.8 | 28451049                                | 0.06               |
| FPOL/PDMS<br>(Applicator)   | 3            | 989133                  | 12.1 | 11875220                                | 0.08               |
| HC<br>(Ink Jet)   | 3            | 5791004                 | 6.8  | 3284347                                 | 1.76               |
| NM2A<br>(Ink Jet)   | 3            | 891954                  | 19.7 | 1065000                                 | 0.84               |
| PDMS<br>(30um)  | 3            | 2614003                 | 18.7 | 14038992                                | 0.19               |
| PDMS<br>(7 um)  | 3            | 494269                  | 9.3  | 3417268                                 | 0.14               |
| DVB/PDMS<br>(65um),   | 3            | 6441191                 | 6.8  | 36579920                                | 0.18               |

| <b>DMMP Uptake Data</b><br>(0.005 mg/m <sup>3</sup> , static air sampling, 10 minutes) |              |                         |      |   |                    |
|--|--------------|-------------------------|------|---|--------------------|
| Fiber  | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#1)  | 3            | 1229887                 | 27.9 | 8781697                                 | 0.140              |
| HC<br>(Ink Jet)  | 3            | 472256                  | 7.3  | 3284347                                 | 0.144              |
| PDMS<br>(30um)   | 3            | 35614                   | 33.1 | 14038992                                | 0.003              |
| PDMS<br>(7 um)   | 3            | Not detected            | N/A  | 3417268                                 | N/A                |

| <b>DMMP Uptake Data</b><br>(0.005 mg/m <sup>3</sup> , static air sampling, 1 minutes) |              |                         |      |   |                    |
|---|--------------|-------------------------|------|---|--------------------|
| Fiber   | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#1)   | 3            | 682417                  | 12.8 | 8781697                                 | 0.08               |
| HC<br>(Ink Jet)   | 3            | 352213                  | 5.8  | 3284347                                 | 0.11               |
| PDMS<br>(30um)  | 3            | Not detected            | N/A  | 14038992                                | N/A                |
| PDMS<br>(7 um)  | 3            | Not detected            | N/A  | 3417268                                 | N/A                |

## 2. Aqueous Phase Sampling

| <b>DMMP Uptake Data</b><br>(100 ppm, direct immersion water sampling, 10 minutes) |              |                         |      |   |                    |
|---|--------------|-------------------------|------|---|--------------------|
| Fiber   | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#2)   | 3            | 12615821                | 3.0  | 7451465                                 | 1.69               |
| HC/PDMS<br>(Dipped#1)   | 3            | 12369074                | 5.8  | 8781697                                 | 1.41               |
| HC/PDMS<br>(Applicator)   | 3            | 4279002                 | 13.0 | 28451049                                | 0.15               |
| FPOL/PDMS<br>(Applicator)   | 3            | 4680873                 | 11.0 | 11875220                                | 0.39               |
| HC<br>(Ink Jet)   | 3            | 11594812                | 8.3  | 3284347                                 | 3.53               |
| NM2A<br>(Ink Jet)   | 3            | 2250010                 | 13.2 | 1065000                                 | 2.11               |
| PDMS<br>(30um)  | 3            | 8188440                 | 10.6 | 14038992                                | 0.58               |
| PDMS<br>(7 um)  | 3            | 3353670                 | 6.3  | 3417268                                 | 0.98               |
| DVB/PDMS<br>(65um),   | 3            | 8371008                 | 9.4  | 36579920                                | 0.23               |

| <b>DMMP Uptake Data</b>                              |              |                         |      |   |                    |
|--|--------------|-------------------------|------|---|--------------------|
| (1 ppm, direct immersion water sampling, 10 minutes) |              |                         |      |   |                    |
| Fiber  | # of Samples | Average GC/MS Peak Area | RSD  | Total Polymer Volume (um <sup>3</sup> ) | Peak Area / Volume |
| HC/PDMS<br>(Dipped#2)                                | 3            | 7941034                 | 5.2  | 7451465                                 | 1.07               |
| HC/PDMS<br>(Dipped#1)                                | 3            | 7767882                 | 7.2  | 8781697                                 | 0.88               |
| HC/PDMS<br>(Applicator)                              | 3            | 246134                  | 14.1 | 28451049                                | 0.01               |
| FPOL/PDMS<br>(Applicator)                            | 3            | 322056                  | 24.7 | 11875220                                | 0.03               |
| HC<br>(Ink Jet)                                      | 3            | 5957670                 | 8.2  | 3284347                                 | 1.81               |
| NM2A<br>(Ink Jet)                                    | 3            | 88420                   | 30.2 | 1065000                                 | 0.08               |
| PDMS<br>(30um)                                       | 3            | 322151                  | 38.4 | 14038992                                | 0.02               |
| PDMS<br>(7 um)                                       | 3            | 144521                  | 18.1 | 3417268                                 | 0.04               |
| DVB/PDMS<br>(65um),                                  | 3            | 424144                  | 20.8 | 36579920                                | 0.01               |



## Appendix C Statistical Comparisons

Statistical data comparing all sampling sets using one-way analysis of variance

(ANOVA) followed by Tukey HSD Post Hoc comparison tests are provided below.

### Total GC/MS Peak Area Comparisons (Vapor Phase, 0.5 mg/m<sup>3</sup>, 10 Minutes)

#### ANOVA

PeakArea

|                | Sum of Squares        | df | Mean Square          | F       | Sig. |
|----------------|-----------------------|----|----------------------|---------|------|
| Between Groups | 34254044046292840.000 | 8  | 4281755505786605.000 | 206.239 | .000 |
| Within Groups  | 622832595081963.000   | 30 | 20761086502732.120   |         |      |
| Total          | 34876876641374800.000 | 38 |                      |         |      |

#### Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error  | Sig. | 95% Confidence Interval |              |
|-----------|-----------|-----------------------|-------------|------|-------------------------|--------------|
|           |           |                       |             |      | Lower Bound             | Upper Bound  |
| PDMS30    | PDMS7     | 27793383.833(*)       | 2630658.124 | .000 | 19013562.01             | 36573205.65  |
|           | DVB/PDMS  | -38994140.500(*)      | 3221885.046 | .000 | -49747182.25            | -28241098.75 |
|           | HC/PDMS2  | -44187306.500(*)      | 2630658.124 | .000 | -52967128.32            | -35407484.68 |
|           | HC/PDMS3  | -41268047.333(*)      | 2630658.124 | .000 | -50047869.15            | -32488225.51 |
|           | HC/PDMS1  | 10386673.500          | 3221885.046 | .065 | -366368.25              | 21139715.25  |
|           | FPOL/PDMS | 20397684.833(*)       | 3221885.046 | .000 | 9644643.09              | 31150726.58  |
|           | HC        | -35501613.833(*)      | 3221885.046 | .000 | -46254655.58            | -24748572.09 |
|           | NMA       | 25198209.167(*)       | 3221885.046 | .000 | 14445167.42             | 35951250.91  |
| PDMS7     | PDMS30    | -27793383.833(*)      | 2630658.124 | .000 | -36573205.65            | -19013562.01 |
|           | DVB/PDMS  | -66787524.333(*)      | 3221885.046 | .000 | -77540566.08            | -56034482.59 |
|           | HC/PDMS2  | -71980690.333(*)      | 2630658.124 | .000 | -80760512.15            | -63200868.51 |
|           | HC/PDMS3  | -69061431.167(*)      | 2630658.124 | .000 | -77841252.99            | -60281609.35 |
|           | HC/PDMS1  | -17406710.333(*)      | 3221885.046 | .000 | -28159752.08            | -6653668.59  |
|           | FPOL/PDMS | -7395699.000          | 3221885.046 | .376 | -18148740.75            | 3357342.75   |
|           | HC        | -63294997.667(*)      | 3221885.046 | .000 | -74048039.41            | -52541955.92 |
|           | NMA       | -2595174.667          | 3221885.046 | .996 | -13348216.41            | 8157867.08   |
| DVB/PDMS  | PDMS30    | 38994140.500(*)       | 3221885.046 | .000 | 28241098.75             | 49747182.25  |
|           | PDMS7     | 66787524.333(*)       | 3221885.046 | .000 | 56034482.59             | 77540566.08  |
|           | HC/PDMS2  | -5193166.000          | 3221885.046 | .791 | -15946207.75            | 5559875.75   |
|           | HC/PDMS3  | -2273906.833          | 3221885.046 | .998 | -13026948.58            | 8479134.91   |
|           | HC/PDMS1  | 49380814.000(*)       | 3720312.398 | .000 | 36964270.90             | 61797357.10  |
|           | FPOL/PDMS | 59391825.333(*)       | 3720312.398 | .000 | 46975282.24             | 71808368.43  |
|           | HC        | 3492526.667           | 3720312.398 | .989 | -8924016.43             | 15909069.76  |
|           | NMA       | 64192349.667(*)       | 3720312.398 | .000 | 51775806.57             | 76608892.76  |
| HC/PDMS2  | PDMS30    | 44187306.500(*)       | 2630658.124 | .000 | 35407484.68             | 52967128.32  |
|           | PDMS7     | 71980690.333(*)       | 2630658.124 | .000 | 63200868.51             | 80760512.15  |
|           | DVB/PDMS  | 5193166.000           | 3221885.046 | .791 | -5559875.75             | 15946207.75  |
|           | HC/PDMS3  | 2919259.167           | 2630658.124 | .968 | -5860562.65             | 11699080.99  |
|           | HC/PDMS1  | 54573980.000(*)       | 3221885.046 | .000 | 43820938.25             | 65327021.75  |
|           | FPOL/PDMS | 64584991.333(*)       | 3221885.046 | .000 | 53831949.59             | 75338033.08  |
|           | HC        | 8685692.667           | 3221885.046 | .192 | -2067349.08             | 19438734.41  |
|           | NMA       | 69385515.667(*)       | 3221885.046 | .000 | 58632473.92             | 80138557.41  |
| HC/PDMS3  | PDMS30    | 41268047.333(*)       | 2630658.124 | .000 | 32488225.51             | 50047869.15  |
|           | PDMS7     | 69061431.167(*)       | 2630658.124 | .000 | 60281609.35             | 77841252.99  |
|           | DVB/PDMS  | 2273906.833           | 3221885.046 | .998 | -8479134.91             | 13026948.58  |

|           |           |                  |             |      |              |              |
|-----------|-----------|------------------|-------------|------|--------------|--------------|
|           | HC/PDMS2  | -2919259.167     | 2630658.124 | .968 | -11699080.99 | 5860562.65   |
|           | HC/PDMS1  | 51654720.833(*)  | 3221885.046 | .000 | 40901679.09  | 62407762.58  |
|           | FPOL/PDMS | 61665732.167(*)  | 3221885.046 | .000 | 50912690.42  | 72418773.91  |
|           | HC        | 5766433.500      | 3221885.046 | .688 | -4986608.25  | 16519475.25  |
|           | NMA       | 66466256.500(*)  | 3221885.046 | .000 | 55713214.75  | 77219298.25  |
| HC/PDMS1  | PDMS30    | -10386673.500    | 3221885.046 | .065 | -21139715.25 | 366368.25    |
|           | PDMS7     | 17406710.333(*)  | 3221885.046 | .000 | 6653668.59   | 28159752.08  |
|           | DVB/PDMS  | -49380814.000(*) | 3720312.398 | .000 | -61797357.10 | -36964270.90 |
|           | HC/PDMS2  | -54573980.000(*) | 3221885.046 | .000 | -65327021.75 | -43820938.25 |
|           | HC/PDMS3  | -51654720.833(*) | 3221885.046 | .000 | -62407762.58 | -40901679.09 |
|           | FPOL/PDMS | 10011011.333     | 3720312.398 | .194 | -2405531.76  | 22427554.43  |
|           | HC        | -45888287.333(*) | 3720312.398 | .000 | -58304830.43 | -33471744.24 |
|           | NMA       | 14811535.667(*)  | 3720312.398 | .010 | 2394992.57   | 27228078.76  |
| FPOL/PDMS | PDMS30    | -20397684.833(*) | 3221885.046 | .000 | -31150726.58 | -9644643.09  |
|           | PDMS7     | 7395699.000      | 3221885.046 | .376 | -3357342.75  | 18148740.75  |
|           | DVB/PDMS  | -59391825.333(*) | 3720312.398 | .000 | -71808368.43 | -46975282.24 |
|           | HC/PDMS2  | -64584991.333(*) | 3221885.046 | .000 | -75338033.08 | -53831949.59 |
|           | HC/PDMS3  | -61665732.167(*) | 3221885.046 | .000 | -72418773.91 | -50912690.42 |
|           | HC/PDMS1  | -10011011.333    | 3720312.398 | .194 | -22427554.43 | 2405531.76   |
|           | HC        | -55899298.667(*) | 3720312.398 | .000 | -68315841.76 | -43482755.57 |
|           | NMA       | 4800524.333      | 3720312.398 | .926 | -7616018.76  | 17217067.43  |
| HC        | PDMS30    | 35501613.833(*)  | 3221885.046 | .000 | 24748572.09  | 46254655.58  |
|           | PDMS7     | 63294997.667(*)  | 3221885.046 | .000 | 52541955.92  | 74048039.41  |
|           | DVB/PDMS  | -3492526.667     | 3720312.398 | .989 | -15909069.76 | 8924016.43   |
|           | HC/PDMS2  | -8685692.667     | 3221885.046 | .192 | -19438734.41 | 2067349.08   |
|           | HC/PDMS3  | -5766433.500     | 3221885.046 | .688 | -16519475.25 | 4986608.25   |
|           | HC/PDMS1  | 45888287.333(*)  | 3720312.398 | .000 | 33471744.24  | 58304830.43  |
|           | FPOL/PDMS | 55899298.667(*)  | 3720312.398 | .000 | 43482755.57  | 68315841.76  |
|           | NMA       | 60699823.000(*)  | 3720312.398 | .000 | 48283279.90  | 73116366.10  |
| NMA       | PDMS30    | -25198209.167(*) | 3221885.046 | .000 | -35951250.91 | -14445167.42 |
|           | PDMS7     | 2595174.667      | 3221885.046 | .996 | -8157867.08  | 13348216.41  |
|           | DVB/PDMS  | -64192349.667(*) | 3720312.398 | .000 | -76608892.76 | -51775806.57 |
|           | HC/PDMS2  | -69385515.667(*) | 3221885.046 | .000 | -80138557.41 | -58632473.92 |
|           | HC/PDMS3  | -66466256.500(*) | 3221885.046 | .000 | -77219298.25 | -55713214.75 |
|           | HC/PDMS1  | -14811535.667(*) | 3720312.398 | .010 | -27228078.76 | -2394992.57  |
|           | FPOL/PDMS | -4800524.333     | 3720312.398 | .926 | -17217067.43 | 7616018.76   |
|           | HC        | -60699823.000(*) | 3720312.398 | .000 | -73116366.10 | -48283279.90 |

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

## Peak Area Per Volume Comparisons (Vapor Phase, 0.5 mg/m<sup>3</sup>, 10 Minutes)

### ANOVA

PeakAreaPerVolume

|                | Sum of Squares | df | Mean Square | F       | Sig. |
|----------------|----------------|----|-------------|---------|------|
| Between Groups | 1169.183       | 8  | 146.148     | 264.225 | .000 |
| Within Groups  | 16.594         | 30 | .553        |         |      |
| Total          | 1185.776       | 38 |             |         |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|-------|-------------------------|-------------|
|           |           |                       |            |       | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | 1.5573333(*)          | .4293864   | .025  | .124256                 | 2.990411    |
|           | DVB/PDMS  | .2376500              | .5258888   | 1.000 | -1.517504               | 1.992804    |
|           | HC/PDMS2  | -7.8003667(*)         | .4293864   | .000  | -9.233444               | -6.367289   |
|           | HC/PDMS3  | -5.9658667(*)         | .4293864   | .000  | -7.398944               | -4.532789   |
|           | HC/PDMS1  | 1.4367500             | .5258888   | .179  | -.318404                | 3.191904    |
|           | FPOL/PDMS | 1.3322167             | .5258888   | .257  | -.422937                | 3.087371    |
|           | HC        | -17.7370167(*)        | .5258888   | .000  | -19.492171              | -15.981863  |
| PDMS7     | NMA       | -2.1125500(*)         | .5258888   | .010  | -3.867704               | -.357396    |
|           | PDMS30    | -1.5573333(*)         | .4293864   | .025  | -2.990411               | -.124256    |
|           | DVB/PDMS  | -1.3196833            | .5258888   | .267  | -3.074837               | .435471     |
|           | HC/PDMS2  | -9.3577000(*)         | .4293864   | .000  | -10.790777              | -7.924623   |

|           |           |                |          |       |            |            |
|-----------|-----------|----------------|----------|-------|------------|------------|
|           | HC/PDMS3  | -7.5232000(*)  | .4293864 | .000  | -8.956277  | -6.090123  |
|           | HC/PDMS1  | -.1205833      | .5258888 | 1.000 | -1.875737  | 1.634571   |
|           | FPOL/PDMS | -.2251167      | .5258888 | 1.000 | -1.980271  | 1.530037   |
|           | HC        | -19.2943500(*) | .5258888 | .000  | -21.049504 | -17.539196 |
|           | NMA       | -3.6698833(*)  | .5258888 | .000  | -5.425037  | -1.914729  |
| DVB/PDMS  | PDMS30    | -.2376500      | .5258888 | 1.000 | -1.992804  | 1.517504   |
|           | PDMS7     | 1.3196833      | .5258888 | .267  | -.435471   | 3.074837   |
|           | HC/PDMS2  | -8.0380167(*)  | .5258888 | .000  | -9.793171  | -6.282863  |
|           | HC/PDMS3  | -6.2035167(*)  | .5258888 | .000  | -7.958671  | -4.448363  |
|           | HC/PDMS1  | 1.1991000      | .6072441 | .571  | -.827577   | 3.225777   |
|           | FPOL/PDMS | 1.0945667      | .6072441 | .680  | -.932111   | 3.121244   |
|           | HC        | -17.9746667(*) | .6072441 | .000  | -20.001344 | -15.947989 |
|           | NMA       | -2.3502000(*)  | .6072441 | .014  | -4.376877  | -.323523   |
| HC/PDMS2  | PDMS30    | 7.8003667(*)   | .4293864 | .000  | 6.367289   | 9.233444   |
|           | PDMS7     | 9.3577000(*)   | .4293864 | .000  | 7.924623   | 10.790777  |
|           | DVB/PDMS  | 8.0380167(*)   | .5258888 | .000  | 6.282863   | 9.793171   |
|           | HC/PDMS3  | 1.8345000(*)   | .4293864 | .005  | .401423    | 3.267577   |
|           | HC/PDMS1  | 9.2371167(*)   | .5258888 | .000  | 7.481963   | 10.992271  |
|           | FPOL/PDMS | 9.1325833(*)   | .5258888 | .000  | 7.377429   | 10.887737  |
|           | HC        | -9.9366500(*)  | .5258888 | .000  | -11.691804 | -8.181496  |
|           | NMA       | 5.6878167(*)   | .5258888 | .000  | 3.932663   | 7.442971   |
| HC/PDMS3  | PDMS30    | 5.9658667(*)   | .4293864 | .000  | 4.532789   | 7.398944   |
|           | PDMS7     | 7.5232000(*)   | .4293864 | .000  | 6.090123   | 8.956277   |
|           | DVB/PDMS  | 6.2035167(*)   | .5258888 | .000  | 4.448363   | 7.958671   |
|           | HC/PDMS2  | -1.8345000(*)  | .4293864 | .005  | -3.267577  | -.401423   |
|           | HC/PDMS1  | 7.4026167(*)   | .5258888 | .000  | 5.647463   | 9.157771   |
|           | FPOL/PDMS | 7.2980833(*)   | .5258888 | .000  | 5.542929   | 9.053237   |
|           | HC        | -11.7711500(*) | .5258888 | .000  | -13.526304 | -10.015996 |
|           | NMA       | 3.8533167(*)   | .5258888 | .000  | 2.098163   | 5.608471   |
| HC/PDMS1  | PDMS30    | -1.4367500     | .5258888 | .179  | -3.191904  | .318404    |
|           | PDMS7     | .1205833       | .5258888 | 1.000 | -1.634571  | 1.875737   |
|           | DVB/PDMS  | -1.1991000     | .6072441 | .571  | -3.225777  | .827577    |
|           | HC/PDMS2  | -9.2371167(*)  | .5258888 | .000  | -10.992271 | -7.481963  |
|           | HC/PDMS3  | -7.4026167(*)  | .5258888 | .000  | -9.157771  | -5.647463  |
|           | FPOL/PDMS | -.1045333      | .6072441 | 1.000 | -2.131211  | 1.922144   |
|           | HC        | -19.1737667(*) | .6072441 | .000  | -21.200444 | -17.147089 |
|           | NMA       | -3.5493000(*)  | .6072441 | .000  | -5.575977  | -1.522623  |
| FPOL/PDMS | PDMS30    | -1.3322167     | .5258888 | .257  | -3.087371  | .422937    |
|           | PDMS7     | .2251167       | .5258888 | 1.000 | -1.530037  | 1.980271   |
|           | DVB/PDMS  | -1.0945667     | .6072441 | .680  | -3.121244  | .932111    |
|           | HC/PDMS2  | -9.1325833(*)  | .5258888 | .000  | -10.887737 | -7.377429  |
|           | HC/PDMS3  | -7.2980833(*)  | .5258888 | .000  | -9.053237  | -5.542929  |
|           | HC/PDMS1  | .1045333       | .6072441 | 1.000 | -1.922144  | 2.131211   |
|           | HC        | -19.0692333(*) | .6072441 | .000  | -21.095911 | -17.042556 |
|           | NMA       | -3.4447667(*)  | .6072441 | .000  | -5.471444  | -1.418089  |
| HC        | PDMS30    | 17.7370167(*)  | .5258888 | .000  | 15.981863  | 19.492171  |
|           | PDMS7     | 19.2943500(*)  | .5258888 | .000  | 17.539196  | 21.049504  |
|           | DVB/PDMS  | 17.9746667(*)  | .6072441 | .000  | 15.947989  | 20.001344  |
|           | HC/PDMS2  | 9.9366500(*)   | .5258888 | .000  | 8.181496   | 11.691804  |
|           | HC/PDMS3  | 11.7711500(*)  | .5258888 | .000  | 10.015996  | 13.526304  |
|           | HC/PDMS1  | 19.1737667(*)  | .6072441 | .000  | 17.147089  | 21.200444  |
|           | FPOL/PDMS | 19.0692333(*)  | .6072441 | .000  | 17.042556  | 21.095911  |
|           | NMA       | 15.6244667(*)  | .6072441 | .000  | 13.597789  | 17.651144  |
| NMA       | PDMS30    | 2.1125500(*)   | .5258888 | .010  | .357396    | 3.867704   |
|           | PDMS7     | 3.6698833(*)   | .5258888 | .000  | 1.914729   | 5.425037   |
|           | DVB/PDMS  | 2.3502000(*)   | .6072441 | .014  | .323523    | 4.376877   |
|           | HC/PDMS2  | -5.6878167(*)  | .5258888 | .000  | -7.442971  | -3.932663  |
|           | HC/PDMS3  | -3.8533167(*)  | .5258888 | .000  | -5.608471  | -2.098163  |
|           | HC/PDMS1  | 3.5493000(*)   | .6072441 | .000  | 1.522623   | 5.575977   |
|           | FPOL/PDMS | 3.4447667(*)   | .6072441 | .000  | 1.418089   | 5.471444   |
|           | HC        | -15.6244667(*) | .6072441 | .000  | -17.651144 | -13.597789 |

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

## Total GC/MS Peak Area Comparisons (Vapor Phase, 0.05 mg/m<sup>3</sup>, 10 Minutes)

### ANOVA

PeakArea

|                | Sum of Squares      | df | Mean Square        | F       | Sig. |
|----------------|---------------------|----|--------------------|---------|------|
| Between Groups | 287073006469922.100 | 8  | 35884125808740.260 | 131.125 | .000 |
| Within Groups  | 4925961484216.660   | 18 | 273664526900.926   |         |      |
| Total          | 291998967954138.800 | 26 |                    |         |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|------|-------------------------|-------------|
|           |           |                       |            |      | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | 2119733.333(*)        | 427133.490 | .003 | 623116.50               | 3616350.16  |
|           | DVB/PDMS  | -3827188.667(*)       | 427133.490 | .000 | -5323805.50             | -2330571.84 |
|           | HC/PDMS2  | -5976819.333(*)       | 427133.490 | .000 | -7473436.16             | -4480202.50 |
|           | HC/PDMS3  | -5632130.000(*)       | 427133.490 | .000 | -7128746.83             | -4135513.17 |
|           | HC        | -4935617.333(*)       | 427133.490 | .000 | -6432234.16             | -3439000.50 |
|           | HC/PDMS1  | 925288.000            | 427133.490 | .464 | -571328.83              | 2421904.83  |
|           | FPOL/PDMS | 1624870.000(*)        | 427133.490 | .028 | 128253.17               | 3121486.83  |
| PDMS7     | NMA       | 1722048.333(*)        | 427133.490 | .017 | 225431.50               | 3218665.16  |
|           | PDMS30    | -2119733.333(*)       | 427133.490 | .003 | -3616350.16             | -623116.50  |
|           | DVB/PDMS  | -5946922.000(*)       | 427133.490 | .000 | -7443538.83             | -4450305.17 |
|           | HC/PDMS2  | -8096552.667(*)       | 427133.490 | .000 | -9593169.50             | -6599935.84 |
|           | HC/PDMS3  | -7751863.333(*)       | 427133.490 | .000 | -9248480.16             | -6255246.50 |
|           | HC        | -7055350.667(*)       | 427133.490 | .000 | -8551967.50             | -5558733.84 |
|           | HC/PDMS1  | -1194445.333          | 427133.490 | .183 | -2691062.16             | 302171.50   |
| DVB/PDMS  | FPOL/PDMS | -494863.333           | 427133.490 | .956 | -1991480.16             | 1001753.50  |
|           | NMA       | -397685.000           | 427133.490 | .988 | -1894301.83             | 1098931.83  |
|           | PDMS30    | 3827188.667(*)        | 427133.490 | .000 | 2330571.84              | 5323805.50  |
|           | PDMS7     | 5946922.000(*)        | 427133.490 | .000 | 4450305.17              | 7443538.83  |
|           | HC/PDMS2  | -2149630.667(*)       | 427133.490 | .002 | -3646247.50             | -653013.84  |
|           | HC/PDMS3  | -1804941.333(*)       | 427133.490 | .012 | -3301558.16             | -308324.50  |
|           | HC        | -1108428.667          | 427133.490 | .254 | -2605045.50             | 388188.16   |
| HC/PDMS2  | HC/PDMS1  | 4752476.667(*)        | 427133.490 | .000 | 3255859.84              | 6249093.50  |
|           | FPOL/PDMS | 5452058.667(*)        | 427133.490 | .000 | 3955441.84              | 6948675.50  |
|           | NMA       | 5549237.000(*)        | 427133.490 | .000 | 4052620.17              | 7045853.83  |
|           | PDMS30    | 5976819.333(*)        | 427133.490 | .000 | 4480202.50              | 7473436.16  |
|           | PDMS7     | 8096552.667(*)        | 427133.490 | .000 | 6599935.84              | 9593169.50  |
|           | DVB/PDMS  | 2149630.667(*)        | 427133.490 | .002 | 653013.84               | 3646247.50  |
|           | HC/PDMS3  | 344689.333            | 427133.490 | .995 | -1151927.50             | 1841306.16  |
| HC/PDMS3  | HC        | 1041202.000           | 427133.490 | .322 | -455414.83              | 2537818.83  |
|           | HC/PDMS1  | 6902107.333(*)        | 427133.490 | .000 | 5405490.50              | 8398724.16  |
|           | FPOL/PDMS | 7601689.333(*)        | 427133.490 | .000 | 6105072.50              | 9098306.16  |
|           | NMA       | 7698867.667(*)        | 427133.490 | .000 | 6202250.84              | 9195484.50  |
|           | PDMS30    | 5632130.000(*)        | 427133.490 | .000 | 4135513.17              | 7128746.83  |
|           | PDMS7     | 7751863.333(*)        | 427133.490 | .000 | 6255246.50              | 9248480.16  |
|           | DVB/PDMS  | 1804941.333(*)        | 427133.490 | .012 | 308324.50               | 3301558.16  |
| HC        | HC/PDMS2  | -344689.333           | 427133.490 | .995 | -1841306.16             | 1151927.50  |
|           | HC        | 696512.667            | 427133.490 | .777 | -800104.16              | 2193129.50  |
|           | HC/PDMS1  | 6557418.000(*)        | 427133.490 | .000 | 5060801.17              | 8054034.83  |
|           | FPOL/PDMS | 7257000.000(*)        | 427133.490 | .000 | 5760383.17              | 8753616.83  |
|           | NMA       | 7354178.333(*)        | 427133.490 | .000 | 5857561.50              | 8850795.16  |
|           | PDMS30    | 4935617.333(*)        | 427133.490 | .000 | 3439000.50              | 6432234.16  |
|           | PDMS7     | 7055350.667(*)        | 427133.490 | .000 | 5558733.84              | 8551967.50  |
| HC/PDMS1  | DVB/PDMS  | 1108428.667           | 427133.490 | .254 | -388188.16              | 2605045.50  |
|           | HC/PDMS2  | -1041202.000          | 427133.490 | .322 | -2537818.83             | 455414.83   |
|           | HC/PDMS3  | -696512.667           | 427133.490 | .777 | -2193129.50             | 800104.16   |
|           | HC/PDMS1  | 5860905.333(*)        | 427133.490 | .000 | 4364288.50              | 7357522.16  |
|           | FPOL/PDMS | 6560487.333(*)        | 427133.490 | .000 | 5063870.50              | 8057104.16  |
|           | NMA       | 6657665.667(*)        | 427133.490 | .000 | 5161048.84              | 8154282.50  |
|           | PDMS30    | -925288.000           | 427133.490 | .464 | -2421904.83             | 571328.83   |
| HC/PDMS2  | PDMS7     | 1194445.333           | 427133.490 | .183 | -302171.50              | 2691062.16  |
|           | DVB/PDMS  | -4752476.667(*)       | 427133.490 | .000 | -6249093.50             | -3255859.84 |
|           | HC/PDMS2  | -6902107.333(*)       | 427133.490 | .000 | -8398724.16             | -5405490.50 |

|           |           |                 |            |       |             |             |
|-----------|-----------|-----------------|------------|-------|-------------|-------------|
|           | HC/PDMS3  | -6557418.000(*) | 427133.490 | .000  | -8054034.83 | -5060801.17 |
|           | HC        | -5860905.333(*) | 427133.490 | .000  | -7357522.16 | -4364288.50 |
|           | FPOL/PDMS | 699582.000      | 427133.490 | .773  | -797034.83  | 2196198.83  |
|           | NMA       | 796760.333      | 427133.490 | .643  | -699856.50  | 2293377.16  |
| FPOL/PDMS | PDMS30    | -1624870.000(*) | 427133.490 | .028  | -3121486.83 | -128253.17  |
|           | PDMS7     | 494863.333      | 427133.490 | .956  | -1001753.50 | 1991480.16  |
|           | DVB/PDMS  | -5452058.667(*) | 427133.490 | .000  | -6948675.50 | -3955441.84 |
|           | HC/PDMS2  | -7601689.333(*) | 427133.490 | .000  | -9098306.16 | -6105072.50 |
|           | HC/PDMS3  | -7257000.000(*) | 427133.490 | .000  | -8753616.83 | -5760383.17 |
|           | HC        | -6560487.333(*) | 427133.490 | .000  | -8057104.16 | -5063870.50 |
|           | HC/PDMS1  | -699582.000     | 427133.490 | .773  | -2196198.83 | 797034.83   |
| NMA       | NMA       | 97178.333       | 427133.490 | 1.000 | -1399438.50 | 1593795.16  |
|           | PDMS30    | -1722048.333(*) | 427133.490 | .017  | -3218665.16 | -225431.50  |
|           | PDMS7     | 397685.000      | 427133.490 | .988  | -1098931.83 | 1894301.83  |
|           | DVB/PDMS  | -5549237.000(*) | 427133.490 | .000  | -7045853.83 | -4052620.17 |
|           | HC/PDMS2  | -7698867.667(*) | 427133.490 | .000  | -9195484.50 | -6202250.84 |
|           | HC/PDMS3  | -7354178.333(*) | 427133.490 | .000  | -8850795.16 | -5857561.50 |
|           | HC        | -6657665.667(*) | 427133.490 | .000  | -8154282.50 | -5161048.84 |
|           | HC/PDMS1  | -796760.333     | 427133.490 | .643  | -2293377.16 | 699856.50   |
|           | FPOL/PDMS | -97178.333      | 427133.490 | 1.000 | -1593795.16 | 1399438.50  |

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

### Peak Area Per Volume Comparisons (Vapor Phase, 0.05 mg/m<sup>3</sup>, 10 Minutes)

#### ANOVA

PeakAreaPerVolume

|                | Sum of Squares | df | Mean Square | F       | Sig. |
|----------------|----------------|----|-------------|---------|------|
| Between Groups | 13.365         | 8  | 1.671       | 118.469 | .000 |
| Within Groups  | .254           | 18 | .014        |         |      |
| Total          | 13.618         | 26 |             |         |      |

#### Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|-------|-------------------------|-------------|
|           |           |                       |            |       | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | .0415667              | .0969585   | 1.000 | -.298162                | .381296     |
|           | DVB/PDMS  | .0101000              | .0969585   | 1.000 | -.329629                | .349829     |
|           | HC/PDMS2  | -.9667000(*)          | .0969585   | .000  | -1.306429               | -.626971    |
|           | HC/PDMS3  | -.7528333(*)          | .0969585   | .000  | -1.092562               | -.413104    |
|           | HC        | -2.1125000(*)         | .0969585   | .000  | -2.452229               | -1.772771   |
|           | HC/PDMS1  | .1268333              | .0969585   | .916  | -.212896                | .466562     |
|           | FPOL/PDMS | .1029333              | .0969585   | .973  | -.236796                | .442662     |
|           | NMA       | -.6513333(*)          | .0969585   | .000  | -.991062                | -.311604    |
| PDMS7     | PDMS30    | -.0415667             | .0969585   | 1.000 | -.381296                | .298162     |
|           | DVB/PDMS  | -.0314667             | .0969585   | 1.000 | -.371196                | .308262     |
|           | HC/PDMS2  | -1.0082667(*)         | .0969585   | .000  | -1.347996               | -.668538    |
|           | HC/PDMS3  | -.7944000(*)          | .0969585   | .000  | -1.134129               | -.454671    |
|           | HC        | -2.1540667(*)         | .0969585   | .000  | -2.493796               | -1.814338   |
|           | HC/PDMS1  | .0852667              | .0969585   | .991  | -.254462                | .424996     |
|           | FPOL/PDMS | .0613667              | .0969585   | .999  | -.278362                | .401096     |
|           | NMA       | -.6929000(*)          | .0969585   | .000  | -1.032629               | -.353171    |
| DVB/PDMS  | PDMS30    | -.0101000             | .0969585   | 1.000 | -.349829                | .329629     |
|           | PDMS7     | .0314667              | .0969585   | 1.000 | -.308262                | .371196     |
|           | HC/PDMS2  | -.9768000(*)          | .0969585   | .000  | -1.316529               | -.637071    |
|           | HC/PDMS3  | -.7629333(*)          | .0969585   | .000  | -1.102662               | -.423204    |
|           | HC        | -2.1226000(*)         | .0969585   | .000  | -2.462329               | -1.782871   |
|           | HC/PDMS1  | .1167333              | .0969585   | .945  | -.222996                | .456462     |
|           | FPOL/PDMS | .0928333              | .0969585   | .985  | -.246896                | .432562     |
|           | NMA       | -.6614333(*)          | .0969585   | .000  | -1.001162               | -.321704    |
| HC/PDMS2  | PDMS30    | .9667000(*)           | .0969585   | .000  | .626971                 | 1.306429    |
|           | PDMS7     | 1.0082667(*)          | .0969585   | .000  | .668538                 | 1.347996    |
|           | DVB/PDMS  | .9768000(*)           | .0969585   | .000  | .637071                 | 1.316529    |
|           | HC/PDMS3  | .2138667              | .0969585   | .442  | -.125862                | .553596     |
|           | HC        | -1.1458000(*)         | .0969585   | .000  | -1.485529               | -.806071    |

|           |             |               |          |         |           |           |
|-----------|-------------|---------------|----------|---------|-----------|-----------|
| HC/PDMS3  | HC/PDMS1    | 1.0935333(*)  | .0969585 | .000    | .753804   | 1.433262  |
|           | FPOL/PDMS   | 1.0696333(*)  | .0969585 | .000    | .729904   | 1.409362  |
|           | NMA         | .3153667      | .0969585 | .081    | -.024362  | .655096   |
|           | PDMS30      | .7528333(*)   | .0969585 | .000    | .413104   | 1.092562  |
|           | PDMS7       | .7944000(*)   | .0969585 | .000    | .454671   | 1.134129  |
|           | DVB/PDMS    | .7629333(*)   | .0969585 | .000    | .423204   | 1.102662  |
|           | HC/PDMS2    | -.2138667     | .0969585 | .442    | -.553596  | -.125862  |
| HC        | HC          | -1.3596667(*) | .0969585 | .000    | -1.699396 | -1.019938 |
|           | HC/PDMS1    | .8796667(*)   | .0969585 | .000    | .539938   | 1.219396  |
|           | FPOL/PDMS   | .8557667(*)   | .0969585 | .000    | .516038   | 1.195496  |
|           | NMA         | .1015000      | .0969585 | .975    | -.238229  | .441229   |
|           | PDMS30      | 2.1125000(*)  | .0969585 | .000    | 1.772771  | 2.452229  |
|           | PDMS7       | 2.1540667(*)  | .0969585 | .000    | 1.814338  | 2.493796  |
|           | DVB/PDMS    | 2.1226000(*)  | .0969585 | .000    | 1.782871  | 2.462329  |
| HC/PDMS1  | HC/PDMS2    | 1.1458000(*)  | .0969585 | .000    | .806071   | 1.485529  |
|           | HC/PDMS3    | 1.3596667(*)  | .0969585 | .000    | 1.019938  | 1.699396  |
|           | HC/PDMS1    | 2.2393333(*)  | .0969585 | .000    | 1.899604  | 2.579062  |
|           | FPOL/PDMS   | 2.2154333(*)  | .0969585 | .000    | 1.875704  | 2.555162  |
|           | NMA         | 1.4611667(*)  | .0969585 | .000    | 1.121438  | 1.800896  |
|           | PDMS30      | -.1268333     | .0969585 | .916    | -.466562  | .212896   |
|           | PDMS7       | -.0852667     | .0969585 | .991    | -.424996  | .254462   |
| FPOL/PDMS | DVB/PDMS    | -.1167333     | .0969585 | .945    | -.456462  | .222996   |
|           | HC/PDMS2    | -1.0935333(*) | .0969585 | .000    | -1.433262 | -.753804  |
|           | HC/PDMS3    | -.8796667(*)  | .0969585 | .000    | -1.219396 | -.539938  |
|           | HC          | -2.2393333(*) | .0969585 | .000    | -2.579062 | -1.899604 |
|           | FPOL/PDMS   | -.0239000     | .0969585 | 1.000   | -.363629  | .315829   |
|           | NMA         | -.7781667(*)  | .0969585 | .000    | -1.117896 | -.438438  |
|           | PDMS30      | -.1029333     | .0969585 | .973    | -.442662  | .236796   |
| NMA       | PDMS7       | -.0613667     | .0969585 | .999    | -.401096  | .278362   |
|           | DVB/PDMS    | -.0928333     | .0969585 | .985    | -.432562  | .246896   |
|           | HC/PDMS2    | -1.0696333(*) | .0969585 | .000    | -1.409362 | -.729904  |
|           | HC/PDMS3    | -.8557667(*)  | .0969585 | .000    | -1.195496 | -.516038  |
|           | HC          | -2.2154333(*) | .0969585 | .000    | -2.555162 | -1.875704 |
|           | HC/PDMS1    | .0239000      | .0969585 | 1.000   | -.315829  | .363629   |
|           | NMA         | -.7542667(*)  | .0969585 | .000    | -1.093996 | -.414538  |
| NMA       | PDMS30      | .6513333(*)   | .0969585 | .000    | .311604   | .991062   |
|           | PDMS7       | .6929000(*)   | .0969585 | .000    | .353171   | 1.032629  |
|           | DVB/PDMS    | .6614333(*)   | .0969585 | .000    | .321704   | 1.001162  |
|           | HC/PDMS2    | -.3153667     | .0969585 | .081    | -.655096  | .024362   |
|           | HC/PDMS3    | -.1015000     | .0969585 | .975    | -.441229  | .238229   |
|           | HC          | -1.4611667(*) | .0969585 | .000    | -1.800896 | -1.121438 |
|           | HC/PDMS1    | .7781667(*)   | .0969585 | .000    | .438438   | 1.117896  |
| FPOL/PDMS | .7542667(*) | .0969585      | .000     | .414538 | 1.093996  |           |

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

## Total GC/MS Peak Area Comparisons (Vapor Phase, 0.005 mg/m<sup>3</sup>, 10 Minutes)

### ANOVA

PeakArea

|                | Sum of Squares    | df | Mean Square       | F      | Sig. |
|----------------|-------------------|----|-------------------|--------|------|
| Between Groups | 2190951569393.556 | 2  | 1095475784696.778 | 27.680 | .001 |
| Within Groups  | 237455809288.000  | 6  | 39575968214.667   |        |      |
| Total          | 2428407378681.555 | 8  |                   |        |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|------|-------------------------|-------------|
|           |           |                       |            |      | Lower Bound             | Upper Bound |
| PDMS30    | HC/PDMS2  | -1194273.667(*)       | 162431.459 | .001 | -1692657.99             | -695889.35  |
|           | HC        | -436642.000           | 162431.459 | .080 | -935026.32              | 61742.32    |
| HC/PDMS2  | PDMS30    | 1194273.667(*)        | 162431.459 | .001 | 695889.35               | 1692657.99  |
|           | HC        | 757631.667(*)         | 162431.459 | .008 | 259247.35               | 1256015.99  |
| HC        | PDMS30    | 436642.000            | 162431.459 | .080 | -61742.32               | 935026.32   |
|           | HC/PDMS2  | -757631.667(*)        | 162431.459 | .008 | -1256015.99             | -259247.35  |

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

## Peak Area Per Volume Comparisons (Vapor Phase, 0.005 mg/m<sup>3</sup>, 10 Minutes)

### ANOVA

PeakAreaPerVolume

|                | Sum of Squares | df | Mean Square | F      | Sig. |
|----------------|----------------|----|-------------|--------|------|
| Between Groups | .047           | 2  | .023        | 31.561 | .001 |
| Within Groups  | .004           | 6  | .001        |        |      |
| Total          | .051           | 8  |             |        |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|------|-------------------------|-------------|
|           |           |                       |            |      | Lower Bound             | Upper Bound |
| PDMS30    | HC/PDMS2  | -.1625333(*)          | .0222366   | .001 | -.230761                | -.094305    |
|           | HC        | -.1412333(*)          | .0222366   | .002 | -.209461                | -.073005    |
| HC/PDMS2  | PDMS30    | .1625333(*)           | .0222366   | .001 | .094305                 | .230761     |
|           | HC        | .0213000              | .0222366   | .627 | -.046928                | .089528     |
| HC        | PDMS30    | .1412333(*)           | .0222366   | .002 | .073005                 | .209461     |
|           | HC/PDMS2  | -.0213000             | .0222366   | .627 | -.089528                | .046928     |

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

## Total GC/MS Peak Area Comparisons (Aqueous Phase, 100 ppm, 10 Minutes)

### ANOVA

PeakArea

|                | Sum of Squares      | df | Mean Square        | F       | Sig. |
|----------------|---------------------|----|--------------------|---------|------|
| Between Groups | 392855357967250.700 | 8  | 49106919745906.300 | 121.488 | .000 |
| Within Groups  | 7275809252534.000   | 18 | 404211625140.778   |         |      |
| Total          | 400131167219784.700 | 26 |                    |         |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|-------|-------------------------|-------------|
|           |           |                       |            |       | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | 4834769.667(*)        | 519109.253 | .000  | 3015882.45              | 6653656.89  |
|           | DVB/PDMS  | -182568.333           | 519109.253 | 1.000 | -2001455.55             | 1636318.89  |
|           | HC/PDMS2  | -4427381.333(*)       | 519109.253 | .000  | -6246268.55             | -2608494.11 |
|           | HC/PDMS3  | -4180634.333(*)       | 519109.253 | .000  | -5999521.55             | -2361747.11 |
|           | HC/PDMS1  | 3909438.333(*)        | 519109.253 | .000  | 2090551.11              | 5728325.55  |
|           | FPOL/PDMS | 3507567.000(*)        | 519109.253 | .000  | 1688679.78              | 5326454.22  |
|           | HC        | -3406372.000(*)       | 519109.253 | .000  | -5225259.22             | -1587484.78 |
|           | NMA       | 5938429.667(*)        | 519109.253 | .000  | 4119542.45              | 7757316.89  |
|           | PDMS7     | -4834769.667(*)       | 519109.253 | .000  | -6653656.89             | -3015882.45 |
|           | DVB/PDMS  | -5017338.000(*)       | 519109.253 | .000  | -6836225.22             | -3198450.78 |
| PDMS7     | HC/PDMS2  | -9262151.000(*)       | 519109.253 | .000  | -11081038.22            | -7443263.78 |
|           | HC/PDMS3  | -9015404.000(*)       | 519109.253 | .000  | -10834291.22            | -7196516.78 |
|           | HC/PDMS1  | -925331.333           | 519109.253 | .692  | -2744218.55             | 893555.89   |
|           | FPOL/PDMS | -1327202.667          | 519109.253 | .270  | -3146089.89             | 491684.55   |
|           | HC        | -8241141.667(*)       | 519109.253 | .000  | -10060028.89            | -6422254.45 |
|           | NMA       | 1103660.000           | 519109.253 | .487  | -715227.22              | 2922547.22  |
|           | DVB/PDMS  | 182568.333            | 519109.253 | 1.000 | -1636318.89             | 2001455.55  |
|           | PDMS30    | 5017338.000(*)        | 519109.253 | .000  | 3198450.78              | 6836225.22  |
|           | HC/PDMS2  | -4244813.000(*)       | 519109.253 | .000  | -6063700.22             | -2425925.78 |
|           | HC/PDMS3  | -3998066.000(*)       | 519109.253 | .000  | -5816953.22             | -2179178.78 |
| DVB/PDMS  | HC/PDMS1  | 4092006.667(*)        | 519109.253 | .000  | 2273119.45              | 5910893.89  |
|           | FPOL/PDMS | 3690135.333(*)        | 519109.253 | .000  | 1871248.11              | 5509022.55  |
|           | HC        | -3223803.667(*)       | 519109.253 | .000  | -5042690.89             | -1404916.45 |
|           | NMA       | 6120998.000(*)        | 519109.253 | .000  | 4302110.78              | 7939885.22  |
|           | HC/PDMS30 | 4427381.333(*)        | 519109.253 | .000  | 2608494.11              | 6246268.55  |
|           | PDMS7     | 9262151.000(*)        | 519109.253 | .000  | 7443263.78              | 11081038.22 |
|           | DVB/PDMS  | 4244813.000(*)        | 519109.253 | .000  | 2425925.78              | 6063700.22  |
|           | HC/PDMS3  | 246747.000            | 519109.253 | 1.000 | -1572140.22             | 2065634.22  |

|           |           |                  |            |       |              |             |
|-----------|-----------|------------------|------------|-------|--------------|-------------|
|           | HC/PDMS1  | 8336819.667(*)   | 519109.253 | .000  | 6517932.45   | 10155706.89 |
|           | FPOL/PDMS | 7934948.333(*)   | 519109.253 | .000  | 6116061.11   | 9753835.55  |
|           | HC        | 1021009.333      | 519109.253 | .582  | -797877.89   | 2839896.55  |
|           | NMA       | 10365811.000(*)  | 519109.253 | .000  | 8546923.78   | 12184698.22 |
| HC/PDMS3  | PDMS30    | 4180634.333(*)   | 519109.253 | .000  | 2361747.11   | 5999521.55  |
|           | PDMS7     | 9015404.000(*)   | 519109.253 | .000  | 7196516.78   | 10834291.22 |
|           | DVB/PDMS  | 3998066.000(*)   | 519109.253 | .000  | 2179178.78   | 5816953.22  |
|           | HC/PDMS2  | -246747.000      | 519109.253 | 1.000 | -2065634.22  | 1572140.22  |
|           | HC/PDMS1  | 8090072.667(*)   | 519109.253 | .000  | 6271185.45   | 9908959.89  |
|           | FPOL/PDMS | 7688201.333(*)   | 519109.253 | .000  | 5869314.11   | 9507088.55  |
|           | HC        | 774262.333       | 519109.253 | .846  | -1044624.89  | 2593149.55  |
|           | NMA       | 10119064.000(*)  | 519109.253 | .000  | 8300176.78   | 11937951.22 |
| HC/PDMS1  | PDMS30    | -3909438.333(*)  | 519109.253 | .000  | -5728325.55  | -2090551.11 |
|           | PDMS7     | 925331.333       | 519109.253 | .692  | -893555.89   | 2744218.55  |
|           | DVB/PDMS  | -4092006.667(*)  | 519109.253 | .000  | -5910893.89  | -2273119.45 |
|           | HC/PDMS2  | -8336819.667(*)  | 519109.253 | .000  | -10155706.89 | -6517932.45 |
|           | HC/PDMS3  | -8090072.667(*)  | 519109.253 | .000  | -9908959.89  | -6271185.45 |
|           | FPOL/PDMS | -401871.333      | 519109.253 | .996  | -2220758.55  | 1417015.89  |
|           | HC        | -7315810.333(*)  | 519109.253 | .000  | -9134697.55  | -5496923.11 |
|           | NMA       | 2028991.333(*)   | 519109.253 | .022  | 210104.11    | 3847878.55  |
| FPOL/PDMS | PDMS30    | -3507567.000(*)  | 519109.253 | .000  | -5326454.22  | -1688679.78 |
|           | PDMS7     | 1327202.667      | 519109.253 | .270  | -491684.55   | 3146089.89  |
|           | DVB/PDMS  | -3690135.333(*)  | 519109.253 | .000  | -5509022.55  | -1871248.11 |
|           | HC/PDMS2  | -7934948.333(*)  | 519109.253 | .000  | -9753835.55  | -6116061.11 |
|           | HC/PDMS3  | -7688201.333(*)  | 519109.253 | .000  | -9507088.55  | -5869314.11 |
|           | HC/PDMS1  | 401871.333       | 519109.253 | .996  | -1417015.89  | 2220758.55  |
|           | HC        | -6913939.000(*)  | 519109.253 | .000  | -8732826.22  | -5095051.78 |
|           | NMA       | 2430862.667(*)   | 519109.253 | .005  | 611975.45    | 4249749.89  |
| HC        | PDMS30    | 3406372.000(*)   | 519109.253 | .000  | 1587484.78   | 5225259.22  |
|           | PDMS7     | 8241141.667(*)   | 519109.253 | .000  | 6422254.45   | 10060028.89 |
|           | DVB/PDMS  | 3223803.667(*)   | 519109.253 | .000  | 1404916.45   | 5042690.89  |
|           | HC/PDMS2  | -1021009.333     | 519109.253 | .582  | -2839896.55  | 797877.89   |
|           | HC/PDMS3  | -774262.333      | 519109.253 | .846  | -2593149.55  | 1044624.89  |
|           | HC/PDMS1  | 7315810.333(*)   | 519109.253 | .000  | 5496923.11   | 9134697.55  |
|           | FPOL/PDMS | 6913939.000(*)   | 519109.253 | .000  | 5095051.78   | 8732826.22  |
|           | NMA       | 9344801.667(*)   | 519109.253 | .000  | 7525914.45   | 11163688.89 |
| NMA       | PDMS30    | -5938429.667(*)  | 519109.253 | .000  | -7757316.89  | -4119542.45 |
|           | PDMS7     | -1103660.000     | 519109.253 | .487  | -2922547.22  | 715227.22   |
|           | DVB/PDMS  | -6120998.000(*)  | 519109.253 | .000  | -7939885.22  | -4302110.78 |
|           | HC/PDMS2  | -10365811.000(*) | 519109.253 | .000  | -12184698.22 | -8546923.78 |
|           | HC/PDMS3  | -10119064.000(*) | 519109.253 | .000  | -11937951.22 | -8300176.78 |
|           | HC/PDMS1  | -2028991.333(*)  | 519109.253 | .022  | -3847878.55  | -210104.11  |
|           | FPOL/PDMS | -2430862.667(*)  | 519109.253 | .005  | -4249749.89  | -611975.45  |
|           | HC        | -9344801.667(*)  | 519109.253 | .000  | -11163688.89 | -7525914.45 |

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

## Peak Area Per Volume Comparisons (Aqueous Phase, 100 ppm, 10 Minutes)

### ANOVA

PeakAreaPerVolume

|                | Sum of Squares | df | Mean Square | F       | Sig. |
|----------------|----------------|----|-------------|---------|------|
| Between Groups | 28.991         | 8  | 3.624       | 178.933 | .000 |
| Within Groups  | .365           | 18 | .020        |         |      |
| Total          | 29.355         | 26 |             |         |      |

### Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|------|-------------------------|-------------|
|           |           |                       |            |      | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | -.3981000             | .1161964   | .058 | -.805236                | .009036     |
|           | DVB/PDMS  | .3544333              | .1161964   | .118 | -.052703                | .761570     |
|           | HC/PDMS2  | -1.1098000(*)         | .1161964   | .000 | -1.516936               | -.702664    |
|           | HC/PDMS3  | -.8252667(*)          | .1161964   | .000 | -1.232403               | -.418130    |
|           | HC/PDMS1  | .4328667(*)           | .1161964   | .032 | .025730                 | .840003     |



|           |           |               |          |      |           |           |
|-----------|-----------|---------------|----------|------|-----------|-----------|
|           | FPOL/PDMS | .1891000      | .1161964 | .779 | -.218036  | .596236   |
|           | HC        | -2.9470667(*) | .1161964 | .000 | -3.354203 | -2.539930 |
|           | NMA       | -1.5294333(*) | .1161964 | .000 | -1.936570 | -1.122297 |
| PDMS7     | PDMS30    | .3981000      | .1161964 | .058 | -.009036  | .805236   |
|           | DVB/PDMS  | .7525333(*)   | .1161964 | .000 | .345397   | 1.159670  |
|           | HC/PDMS2  | -.7117000(*)  | .1161964 | .000 | -1.118836 | -.304564  |
|           | HC/PDMS3  | -.4271667(*)  | .1161964 | .036 | -.834303  | -.020030  |
|           | HC/PDMS1  | .8309667(*)   | .1161964 | .000 | .423830   | 1.238103  |
|           | FPOL/PDMS | .5872000(*)   | .1161964 | .002 | .180064   | .994336   |
|           | HC        | -2.5489667(*) | .1161964 | .000 | -2.956103 | -2.141830 |
|           | NMA       | -1.1313333(*) | .1161964 | .000 | -1.538470 | -.724197  |
| DVB/PDMS  | PDMS30    | -.3544333     | .1161964 | .118 | -.761570  | .052703   |
|           | PDMS7     | -.7525333(*)  | .1161964 | .000 | -1.159670 | -.345397  |
|           | HC/PDMS2  | -1.4642333(*) | .1161964 | .000 | -1.871370 | -1.057097 |
|           | HC/PDMS3  | -1.1797000(*) | .1161964 | .000 | -1.586836 | -.772564  |
|           | HC/PDMS1  | .0784333      | .1161964 | .999 | -.328703  | .485570   |
|           | FPOL/PDMS | -.1653333     | .1161964 | .875 | -.572470  | .241803   |
|           | HC        | -3.3015000(*) | .1161964 | .000 | -3.708636 | -2.894364 |
|           | NMA       | -1.8838667(*) | .1161964 | .000 | -2.291003 | -1.476730 |
| HC/PDMS2  | PDMS30    | 1.1098000(*)  | .1161964 | .000 | .702664   | 1.516936  |
|           | PDMS7     | .7117000(*)   | .1161964 | .000 | .304564   | 1.118836  |
|           | DVB/PDMS  | 1.4642333(*)  | .1161964 | .000 | 1.057097  | 1.871370  |
|           | HC/PDMS3  | .2845333      | .1161964 | .317 | -.122603  | .691670   |
|           | HC/PDMS1  | 1.5426667(*)  | .1161964 | .000 | 1.135530  | 1.949803  |
|           | FPOL/PDMS | 1.2989000(*)  | .1161964 | .000 | .891764   | 1.706036  |
|           | HC        | -1.8372667(*) | .1161964 | .000 | -2.244403 | -1.430130 |
|           | NMA       | -.4196333(*)  | .1161964 | .040 | -.826770  | -.012497  |
| HC/PDMS3  | PDMS30    | .8252667(*)   | .1161964 | .000 | .418130   | 1.232403  |
|           | PDMS7     | .4271667(*)   | .1161964 | .036 | .020030   | .834303   |
|           | DVB/PDMS  | 1.1797000(*)  | .1161964 | .000 | .772564   | 1.586836  |
|           | HC/PDMS2  | -.2845333     | .1161964 | .317 | -.691670  | .122603   |
|           | HC/PDMS1  | 1.2581333(*)  | .1161964 | .000 | .850997   | 1.665270  |
|           | FPOL/PDMS | 1.0143667(*)  | .1161964 | .000 | .607230   | 1.421503  |
|           | HC        | -2.1218000(*) | .1161964 | .000 | -2.528936 | -1.714664 |
|           | NMA       | -.7041667(*)  | .1161964 | .000 | -1.111303 | -.297030  |
| HC/PDMS1  | PDMS30    | -.4328667(*)  | .1161964 | .032 | -.840003  | -.025730  |
|           | PDMS7     | -.8309667(*)  | .1161964 | .000 | -1.238103 | -.423830  |
|           | DVB/PDMS  | -.0784333     | .1161964 | .999 | -.485570  | .328703   |
|           | HC/PDMS2  | -1.5426667(*) | .1161964 | .000 | -1.949803 | -1.135530 |
|           | HC/PDMS3  | -1.2581333(*) | .1161964 | .000 | -1.665270 | -.850997  |
|           | FPOL/PDMS | -.2437667     | .1161964 | .503 | -.650903  | .163370   |
|           | HC        | -3.3799333(*) | .1161964 | .000 | -3.787070 | -2.972797 |
|           | NMA       | -1.9623000(*) | .1161964 | .000 | -2.369436 | -1.555164 |
| FPOL/PDMS | PDMS30    | -.1891000     | .1161964 | .779 | -.596236  | .218036   |
|           | PDMS7     | -.5872000(*)  | .1161964 | .002 | -.994336  | -.180064  |
|           | DVB/PDMS  | .1653333      | .1161964 | .875 | -.241803  | .572470   |
|           | HC/PDMS2  | -1.2989000(*) | .1161964 | .000 | -1.706036 | -.891764  |
|           | HC/PDMS3  | -1.0143667(*) | .1161964 | .000 | -1.421503 | -.607230  |
|           | HC/PDMS1  | .2437667      | .1161964 | .503 | -.163370  | .650903   |
|           | HC        | -3.1361667(*) | .1161964 | .000 | -3.543303 | -2.729030 |
|           | NMA       | -1.7185333(*) | .1161964 | .000 | -2.125670 | -1.311397 |
| HC        | PDMS30    | 2.9470667(*)  | .1161964 | .000 | 2.539930  | 3.354203  |
|           | PDMS7     | 2.5489667(*)  | .1161964 | .000 | 2.141830  | 2.956103  |
|           | DVB/PDMS  | 3.3015000(*)  | .1161964 | .000 | 2.894364  | 3.708636  |
|           | HC/PDMS2  | 1.8372667(*)  | .1161964 | .000 | 1.430130  | 2.244403  |
|           | HC/PDMS3  | 2.1218000(*)  | .1161964 | .000 | 1.714664  | 2.528936  |
|           | HC/PDMS1  | 3.3799333(*)  | .1161964 | .000 | 2.972797  | 3.787070  |
|           | FPOL/PDMS | 3.1361667(*)  | .1161964 | .000 | 2.729030  | 3.543303  |
|           | NMA       | 1.4176333(*)  | .1161964 | .000 | 1.010497  | 1.824770  |
| NMA       | PDMS30    | 1.5294333(*)  | .1161964 | .000 | 1.122297  | 1.936570  |
|           | PDMS7     | 1.1313333(*)  | .1161964 | .000 | .724197   | 1.538470  |
|           | DVB/PDMS  | 1.8838667(*)  | .1161964 | .000 | 1.476730  | 2.291003  |
|           | HC/PDMS2  | .4196333(*)   | .1161964 | .040 | .012497   | .826770   |
|           | HC/PDMS3  | .7041667(*)   | .1161964 | .000 | .297030   | 1.111303  |
|           | HC/PDMS1  | 1.9623000(*)  | .1161964 | .000 | 1.555164  | 2.369436  |
|           | FPOL/PDMS | 1.7185333(*)  | .1161964 | .000 | 1.311397  | 2.125670  |
|           | HC        | -1.4176333(*) | .1161964 | .000 | -1.824770 | -1.010497 |

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

**Total GC/MS Peak Area Comparisons (Aqueous Phase, 1.0 ppm, 10 Minutes)**

**ANOVA**

PeakArea

|                | Sum of Squares      | df | Mean Square        | F       | Sig. |
|----------------|---------------------|----|--------------------|---------|------|
| Between Groups | 298481487143147.600 | 8  | 37310185892893.450 | 445.504 | .000 |
| Within Groups  | 1507467095970.667   | 18 | 83748171998.370    |         |      |
| Total          | 299988954239118.300 | 26 |                    |         |      |

**Post Hoc Multiple Comparisons**

Dependent Variable: PeakArea

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|-------|-------------------------|-------------|
|           |           |                       |            |       | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | 177630.333            | 236288.203 | .997  | -650290.94              | 1005551.60  |
|           | DVB/PDMS  | -101993.333           | 236288.203 | 1.000 | -929914.60              | 725927.94   |
|           | HC/PDMS2  | -7618882.667(*)       | 236288.203 | .000  | -8446803.94             | -6790961.40 |
|           | HC/PDMS3  | -7445731.333(*)       | 236288.203 | .000  | -8273652.60             | -6617810.06 |
|           | HC/PDMS1  | 76017.333             | 236288.203 | 1.000 | -751903.94              | 903938.60   |
|           | FPOL/PDMS | 95.000                | 236288.203 | 1.000 | -827826.27              | 828016.27   |
|           | HC        | -5635519.333(*)       | 236288.203 | .000  | -6463440.60             | -4807598.06 |
| PDMS7     | NMA       | 233731.333            | 236288.203 | .982  | -594189.94              | 1061652.60  |
|           | PDMS30    | -177630.333           | 236288.203 | .997  | -1005551.60             | 650290.94   |
|           | DVB/PDMS  | -279623.667           | 236288.203 | .950  | -1107544.94             | 548297.60   |
|           | HC/PDMS2  | -7796513.000(*)       | 236288.203 | .000  | -8624434.27             | -6968591.73 |
|           | HC/PDMS3  | -7623361.667(*)       | 236288.203 | .000  | -8451282.94             | -6795440.40 |
|           | HC/PDMS1  | -101613.000           | 236288.203 | 1.000 | -929534.27              | 726308.27   |
|           | FPOL/PDMS | -177535.333           | 236288.203 | .997  | -1005456.60             | 650385.94   |
| DVB/PDMS  | HC        | -5813149.667(*)       | 236288.203 | .000  | -6641070.94             | -4985228.40 |
|           | NMA       | 56101.000             | 236288.203 | 1.000 | -771820.27              | 884022.27   |
|           | PDMS30    | 101993.333            | 236288.203 | 1.000 | -725927.94              | 929914.60   |
|           | PDMS7     | 279623.667            | 236288.203 | .950  | -548297.60              | 1107544.94  |
|           | HC/PDMS2  | -7516889.333(*)       | 236288.203 | .000  | -8344810.60             | -6688968.06 |
|           | HC/PDMS3  | -7343738.000(*)       | 236288.203 | .000  | -8171659.27             | -6515816.73 |
|           | HC/PDMS1  | 178010.667            | 236288.203 | .997  | -649910.60              | 1005931.94  |
| HC/PDMS2  | FPOL/PDMS | 102088.333            | 236288.203 | 1.000 | -725832.94              | 930009.60   |
|           | HC        | -5533526.000(*)       | 236288.203 | .000  | -6361447.27             | -4705604.73 |
|           | NMA       | 335724.667            | 236288.203 | .876  | -492196.60              | 1163645.94  |
|           | PDMS30    | 7618882.667(*)        | 236288.203 | .000  | 6790961.40              | 8446803.94  |
|           | PDMS7     | 7796513.000(*)        | 236288.203 | .000  | 6968591.73              | 8624434.27  |
|           | DVB/PDMS  | 7516889.333(*)        | 236288.203 | .000  | 6688968.06              | 8344810.60  |
|           | HC/PDMS3  | 173151.333            | 236288.203 | .997  | -654769.94              | 1001072.60  |
| HC/PDMS3  | HC/PDMS1  | 7694900.000(*)        | 236288.203 | .000  | 6866978.73              | 8522821.27  |
|           | FPOL/PDMS | 7618977.667(*)        | 236288.203 | .000  | 6791056.40              | 8446898.94  |
|           | HC        | 1983363.333(*)        | 236288.203 | .000  | 1155442.06              | 2811284.60  |
|           | NMA       | 7852614.000(*)        | 236288.203 | .000  | 7024692.73              | 8680535.27  |
|           | PDMS30    | 7445731.333(*)        | 236288.203 | .000  | 6617810.06              | 8273652.60  |
|           | PDMS7     | 7623361.667(*)        | 236288.203 | .000  | 6795440.40              | 8451282.94  |
|           | DVB/PDMS  | 7343738.000(*)        | 236288.203 | .000  | 6515816.73              | 8171659.27  |
| HC/PDMS1  | HC/PDMS2  | -173151.333           | 236288.203 | .997  | -1001072.60             | 654769.94   |
|           | HC/PDMS1  | 7521748.667(*)        | 236288.203 | .000  | 6693827.40              | 8349669.94  |
|           | FPOL/PDMS | 7445826.333(*)        | 236288.203 | .000  | 6617905.06              | 8273747.60  |
|           | HC        | 1810212.000(*)        | 236288.203 | .000  | 982290.73               | 2638133.27  |
|           | NMA       | 7679462.667(*)        | 236288.203 | .000  | 6851541.40              | 8507383.94  |
|           | PDMS30    | -76017.333            | 236288.203 | 1.000 | -903938.60              | 751903.94   |
|           | PDMS7     | 101613.000            | 236288.203 | 1.000 | -726308.27              | 929534.27   |
| FPOL/PDMS | DVB/PDMS  | -178010.667           | 236288.203 | .997  | -1005931.94             | 649910.60   |
|           | HC/PDMS2  | -7694900.000(*)       | 236288.203 | .000  | -8522821.27             | -6866978.73 |
|           | HC/PDMS3  | -7521748.667(*)       | 236288.203 | .000  | -8349669.94             | -6693827.40 |
|           | FPOL/PDMS | -75922.333            | 236288.203 | 1.000 | -903843.60              | 751998.94   |
|           | HC        | -5711536.667(*)       | 236288.203 | .000  | -6539457.94             | -4883615.40 |
|           | NMA       | 157714.000            | 236288.203 | .999  | -670207.27              | 985635.27   |
|           | PDMS30    | -95.000               | 236288.203 | 1.000 | -828016.27              | 827826.27   |
| HC/PDMS2  | PDMS7     | 177535.333            | 236288.203 | .997  | -650385.94              | 1005456.60  |
|           | DVB/PDMS  | -102088.333           | 236288.203 | 1.000 | -930009.60              | 725832.94   |
|           | HC/PDMS2  | -7618977.667(*)       | 236288.203 | .000  | -8446898.94             | -6791056.40 |

|     |           |                 |            |       |             |             |
|-----|-----------|-----------------|------------|-------|-------------|-------------|
|     | HC/PDMS3  | -7445826.333(*) | 236288.203 | .000  | -8273747.60 | -6617905.06 |
|     | HC/PDMS1  | 75922.333       | 236288.203 | 1.000 | -751998.94  | 903843.60   |
|     | HC        | -5635614.333(*) | 236288.203 | .000  | -6463535.60 | -4807693.06 |
|     | NMA       | 233636.333      | 236288.203 | .982  | -594284.94  | 1061557.60  |
| HC  | PDMS30    | 5635519.333(*)  | 236288.203 | .000  | 4807598.06  | 6463440.60  |
|     | PDMS7     | 5813149.667(*)  | 236288.203 | .000  | 4985228.40  | 6641070.94  |
|     | DVB/PDMS  | 5533526.000(*)  | 236288.203 | .000  | 4705604.73  | 6361447.27  |
|     | HC/PDMS2  | -1983363.333(*) | 236288.203 | .000  | -2811284.60 | -1155442.06 |
|     | HC/PDMS3  | -1810212.000(*) | 236288.203 | .000  | -2638133.27 | -982290.73  |
|     | HC/PDMS1  | 5711536.667(*)  | 236288.203 | .000  | 4883615.40  | 6539457.94  |
|     | FPOL/PDMS | 5635614.333(*)  | 236288.203 | .000  | 4807693.06  | 6463535.60  |
|     | NMA       | 5869250.667(*)  | 236288.203 | .000  | 5041329.40  | 6697171.94  |
| NMA | PDMS30    | -233731.333     | 236288.203 | .982  | -1061652.60 | 594189.94   |
|     | PDMS7     | -56101.000      | 236288.203 | 1.000 | -884022.27  | 771820.27   |
|     | DVB/PDMS  | -335724.667     | 236288.203 | .876  | -1163645.94 | 492196.60   |
|     | HC/PDMS2  | -7852614.000(*) | 236288.203 | .000  | -8680535.27 | -7024692.73 |
|     | HC/PDMS3  | -7679462.667(*) | 236288.203 | .000  | -8507383.94 | -6851541.40 |
|     | HC/PDMS1  | -157714.000     | 236288.203 | .999  | -985635.27  | 670207.27   |
|     | FPOL/PDMS | -233636.333     | 236288.203 | .982  | -1061557.60 | 594284.94   |
|     | HC        | -5869250.667(*) | 236288.203 | .000  | -6697171.94 | -5041329.40 |

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

## Peak Area Per Volume Comparisons (Aqueous Phase, 1.0 ppm, 10 Minutes)

### ANOVA

PeakAreaPerVolume

|                | Sum of Squares | df | Mean Square | F       | Sig. |
|----------------|----------------|----|-------------|---------|------|
| Between Groups | 10.430         | 8  | 1.304       | 391.706 | .000 |
| Within Groups  | .060           | 18 | .003        |         |      |
| Total          | 10.489         | 26 |             |         |      |

### Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

| (I) Fiber | (J) Fiber | Mean Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval |             |
|-----------|-----------|-----------------------|------------|-------|-------------------------|-------------|
|           |           |                       |            |       | Lower Bound             | Upper Bound |
| PDMS30    | PDMS7     | -.0193333             | .0471045   | 1.000 | -.184381                | .145714     |
|           | DVB/PDMS  | .0113333              | .0471045   | 1.000 | -.153714                | .176381     |
|           | HC/PDMS2  | -1.0427667(*)         | .0471045   | .000  | -1.207814               | -.877719    |
|           | HC/PDMS3  | -.8616333(*)          | .0471045   | .000  | -1.026681               | -.696586    |
|           | HC/PDMS1  | .0142667              | .0471045   | 1.000 | -.150781                | .179314     |
|           | FPOL/PDMS | -.0042000             | .0471045   | 1.000 | -.169248                | .160848     |
|           | HC        | -1.7910333(*)         | .0471045   | .000  | -1.956081               | -1.625986   |
|           | NMA       | -.0601000             | .0471045   | .926  | -.225148                | .104948     |
| PDMS7     | PDMS30    | .0193333              | .0471045   | 1.000 | -.145714                | .184381     |
|           | DVB/PDMS  | .0306667              | .0471045   | .999  | -.134381                | .195714     |
|           | HC/PDMS2  | -1.0234333(*)         | .0471045   | .000  | -1.188481               | -.858386    |
|           | HC/PDMS3  | -.8423000(*)          | .0471045   | .000  | -1.007348               | -.677252    |
|           | HC/PDMS1  | .0336000              | .0471045   | .998  | -.131448                | .198648     |
|           | FPOL/PDMS | .0151333              | .0471045   | 1.000 | -.149914                | .180181     |
|           | HC        | -1.7717000(*)         | .0471045   | .000  | -1.936748               | -1.606652   |
|           | NMA       | -.0407667             | .0471045   | .992  | -.205814                | .124281     |
| DVB/PDMS  | PDMS30    | -.0113333             | .0471045   | 1.000 | -.176381                | .153714     |
|           | PDMS7     | -.0306667             | .0471045   | .999  | -.195714                | .134381     |
|           | HC/PDMS2  | -1.0541000(*)         | .0471045   | .000  | -1.219148               | -.889052    |
|           | HC/PDMS3  | -.8729667(*)          | .0471045   | .000  | -1.038014               | -.707919    |
|           | HC/PDMS1  | .0029333              | .0471045   | 1.000 | -.162114                | .167981     |
|           | FPOL/PDMS | -.0155333             | .0471045   | 1.000 | -.180581                | .149514     |
|           | HC        | -1.8023667(*)         | .0471045   | .000  | -1.967414               | -1.637319   |
|           | NMA       | -.0714333             | .0471045   | .834  | -.236481                | .093614     |
| HC/PDMS2  | PDMS30    | 1.0427667(*)          | .0471045   | .000  | .877719                 | 1.207814    |
|           | PDMS7     | 1.0234333(*)          | .0471045   | .000  | .858386                 | 1.188481    |
|           | DVB/PDMS  | 1.0541000(*)          | .0471045   | .000  | .889052                 | 1.219148    |
|           | HC/PDMS3  | .1811333(*)           | .0471045   | .025  | .016086                 | .346181     |
|           | HC/PDMS1  | 1.0570333(*)          | .0471045   | .000  | .891986                 | 1.222081    |

|           |           |               |          |       |           |           |
|-----------|-----------|---------------|----------|-------|-----------|-----------|
|           | FPOL/PDMS | 1.0385667(*)  | .0471045 | .000  | .873519   | 1.203614  |
|           | HC        | -.7482667(*)  | .0471045 | .000  | -.913314  | -.583219  |
|           | NMA       | .9826667(*)   | .0471045 | .000  | .817619   | 1.147714  |
| HC/PDMS3  | PDMS30    | .8616333(*)   | .0471045 | .000  | .696586   | 1.026681  |
|           | PDMS7     | .8423000(*)   | .0471045 | .000  | .677252   | 1.007348  |
|           | DVB/PDMS  | .8729667(*)   | .0471045 | .000  | .707919   | 1.038014  |
|           | HC/PDMS2  | -.1811333(*)  | .0471045 | .025  | -.346181  | -.016086  |
|           | HC/PDMS1  | .8759000(*)   | .0471045 | .000  | .710852   | 1.040948  |
|           | FPOL/PDMS | .8574333(*)   | .0471045 | .000  | .692386   | 1.022481  |
|           | HC        | -.9294000(*)  | .0471045 | .000  | -1.094448 | -.764352  |
|           | NMA       | .8015333(*)   | .0471045 | .000  | .636486   | .966581   |
| HC/PDMS1  | PDMS30    | -.0142667     | .0471045 | 1.000 | -.179314  | .150781   |
|           | PDMS7     | -.0336000     | .0471045 | .998  | -.198648  | .131448   |
|           | DVB/PDMS  | -.0029333     | .0471045 | 1.000 | -.167981  | .162114   |
|           | HC/PDMS2  | -1.0570333(*) | .0471045 | .000  | -1.222081 | -.891986  |
|           | HC/PDMS3  | -.8759000(*)  | .0471045 | .000  | -1.040948 | -.710852  |
|           | FPOL/PDMS | -.0184667     | .0471045 | 1.000 | -.183514  | .146581   |
|           | HC        | -1.8053000(*) | .0471045 | .000  | -1.970348 | -1.640252 |
|           | NMA       | -.0743667     | .0471045 | .804  | -.239414  | .090681   |
| FPOL/PDMS | PDMS30    | .0042000      | .0471045 | 1.000 | -.160848  | .169248   |
|           | PDMS7     | -.0151333     | .0471045 | 1.000 | -.180181  | .149914   |
|           | DVB/PDMS  | .0155333      | .0471045 | 1.000 | -.149514  | .180581   |
|           | HC/PDMS2  | -1.0385667(*) | .0471045 | .000  | -1.203614 | -.873519  |
|           | HC/PDMS3  | -.8574333(*)  | .0471045 | .000  | -1.022481 | -.692386  |
|           | HC/PDMS1  | .0184667      | .0471045 | 1.000 | -.146581  | .183514   |
|           | HC        | -1.7868333(*) | .0471045 | .000  | -1.951881 | -1.621786 |
|           | NMA       | -.0559000     | .0471045 | .949  | -.220948  | .109148   |
| HC        | PDMS30    | 1.7910333(*)  | .0471045 | .000  | 1.625986  | 1.956081  |
|           | PDMS7     | 1.7717000(*)  | .0471045 | .000  | 1.606652  | 1.936748  |
|           | DVB/PDMS  | 1.8023667(*)  | .0471045 | .000  | 1.637319  | 1.967414  |
|           | HC/PDMS2  | .7482667(*)   | .0471045 | .000  | .583219   | .913314   |
|           | HC/PDMS3  | .9294000(*)   | .0471045 | .000  | .764352   | 1.094448  |
|           | HC/PDMS1  | 1.8053000(*)  | .0471045 | .000  | 1.640252  | 1.970348  |
|           | FPOL/PDMS | 1.7868333(*)  | .0471045 | .000  | 1.621786  | 1.951881  |
|           | NMA       | 1.7309333(*)  | .0471045 | .000  | 1.565886  | 1.895981  |
| NMA       | PDMS30    | .0601000      | .0471045 | .926  | -.104948  | .225148   |
|           | PDMS7     | .0407667      | .0471045 | .992  | -.124281  | .205814   |
|           | DVB/PDMS  | .0714333      | .0471045 | .834  | -.093614  | .236481   |
|           | HC/PDMS2  | -.9826667(*)  | .0471045 | .000  | -1.147714 | -.817619  |
|           | HC/PDMS3  | -.8015333(*)  | .0471045 | .000  | -.966581  | -.636486  |
|           | HC/PDMS1  | .0743667      | .0471045 | .804  | -.090681  | .239414   |
|           | FPOL/PDMS | .0559000      | .0471045 | .949  | -.109148  | .220948   |
|           | HC        | -1.7309333(*) | .0471045 | .000  | -1.895981 | -1.565886 |

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

## Comparisons of Dip Coated Fiber Sampling 8-Day Repeat Sampling

### (VaporPhase, 1.0 ppm, 10 Minutes)

#### ANOVA

PeakAreaPerVolume

|                | Sum of Squares          | df | Mean Square        | F    | Sig. |
|----------------|-------------------------|----|--------------------|------|------|
| Between Groups | 1171611908200<br>8.390  | 1  | 11716119082008.390 | .283 | .606 |
| Within Groups  | 4139560764839<br>93.300 | 10 | 41395607648399.330 |      |      |
| Total          | 4256721955660<br>01.600 | 11 |                    |      |      |

## Bibliography

- Bryant, C.K. Uniformed Services University of the Health Sciences Thesis: "Chemical Agent Identification Using Field-Based Attenuated Total Reflectance Infrared Detection and Solid Phase Microextraction", June 2006.
- Department of the Army. Memorandum, Subject: "Implementation Guidance Policy for Airborne Exposure Limits for GB, GA, GD, GF, VX, H, HD, and HT". 18 June 2004.
- Grate, Jay W.; Patrash, Samuel J.; Kaganove, Steven N. "Hydrogen Bond Acidic Polymers for Surface Acoustic Wave Vapor Sensors and Arrays". *Analytical Chemistry*, 1999, 71, 5: 1033-1040.
- Harvey, S.D.; Nelson, D.A; Wright, B.W.; Grate, J.W. "Selective Stationary Phase for Solid-Phase Microextraction Analysis of Sarin (GB)". *Journal of Chromatography*, 2002, 954: 217-225.
- Hauser, Eric J.; Simonson, Duane L.; Stepnowski, Jennifer L.; Ross, Stuart K.; Stepnowski, Stanley V.; McGill, R. Andrew. "Design of Hydrogen Bond Acidic Polycarbosilanes for Chemical Sensor Applications." *Polymer Preprints*, 2004, 45(1): 541-542.
- Hook, Gary L.; Kimm, Gregory; Koch, David; Savage, Paul B; Ding, Bangwei; Smith, Philip A. "Detection of VX Contamination in Soil Through Solid-Phase Microextraction Sampling and Gas Chromatography/Mass Spectrometry of the VX Degradation Product Bis(diisopropylaminoethyl)disulfide. *Journal of Chromatography*, 2003, 992: 1-9.
- Hook, Gary L; Kimm Gregory; Betsinger, Geoffrey; Savage, Paul B.; Swift, Austin; Logan, Tom; Smith, Philip A. "Solid Phase Microextraction Sampling and Gas Chromatography/Mass Spectrometry for Field Detection of the Chemical Warfare Agent O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)." *Journal of Separation Science*, 2003, 26: 1091-1096.
- Hook, Gary L.; Jackson Lapage, Carmela; Miller, Stephen I; Smith, Philip A. "Dynamic Solid-Phase Microextraction for Sampling of Airborne Sarin with Gas Chromatography-Mass Spectrometry for Rapid Field Detection and Quantification". *Journal of Separation Science*, 2004, 27: 1017-1022.
- Kimm, Gregory L.; Hook, Gary L.; Smith, Philip A. "Application of Headspace Solid-Phase Microextraction and Gas Chromatography-Mass Spectrometry for Detection of the Chemical Warfare Agent Bis(2-chloroethyl)sulfide in Soil. *Journal of Chromatography*, 2002, 971: 185-191.

- Lakso, H.-A. and Ng, W.F. "Determination of Chemical Warfare Agents in Natural Water Samples by Solid Phase Microextraction." *Analytical Chemistry*, 1997, 69: 1866-1872.
- McCafferty, R.R. and Lennarson, P.J. "Common Chemical Agent Threats" *Neurosurgery*, 2002, 12, 3.
- Naval Research Laboratory (NRL). SPME-Polymer Meeting: 13 Feb 2006. U.S. Naval Research Laboratory, Washington D.C.
- Pawliszyn, J. Solid Phase Microextraction Theory and Practice. New York, Wiley-VCH Inc., 1997.
- Pawliszyn, J. Applications of Solid Phase Microextraction. Hertfordshire, Royal Society of Chemistry, 1999.
- Schneider, J. F.; Bopari, A. S.; Reed, L. L "Screening for Sarin in Air and Water by Solid Phase Microextraction - Gas Chromatography - Mass Spectrometry." *Journal of Chromatographic Science*, 1999, 39: 420-424.
- Smith, Philip A.; Jackson Lepage, Carmela R.; Koch, David; Wyatt, Haley D.M.; Hook, Gary L.; Betsinger, Geoffrey; Erickson, Richard P.; Eckenrode, Brian A. "Detection of Gas Phase Chemical Warfare Agents Using Field-Portable Gas Chromatography-Mass Spectrometry Systems: Instrument and Sampling Strategy Considerations". *Trends in Analytical Chemistry*, 2004, 23, 4: 296.
- Sun, Y. and Ong, K. Detection Technologies for Chemical Warfare Agents. Boca Raton, CRC Press, 2005. 16-20.
- U.S. Department of State. Bureau of International Security and Nonproliferation. "Combating WMD Terrorism: WMD Terrorism Risk", 2006, <http://www.state.gov/t/isn/c16585.htm>.

## **Curriculum Vitae**

Capt Stephen L. Boglarski graduated from Rensselaer Polytechnic Institute in 1996 with a Bachelor of Science in Environmental Engineering. He served as a Chief, Industrial Hygiene Element at Vandenberg AFB from 1997-1999 where he supported space and missile launch operations for the Western Range and managed the health risk assessment and surveillance program affecting over 300 workplaces and over 3500 workers and. While stationed at Osan AB from 1999-2000 he served as OIC, Occupational and Environmental Readiness and as Base Radiation Safety Officer. From 2001-2005, he served as Chief, Bioenvironmental Engineering at Hanscom AFB and was recognized as the U.S. Air Force Company Grade Bioenvironmental Engineer of the Year for 2001. In 2005, he entered the Graduate School of Biomedical Sciences and Public Health, Uniformed Services University. Upon graduation in Jun 2006, he will be assigned as Chief, Bioenvironmental Engineering at Ellsworth AFB.