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4301 JONES BRIDGE ROAD
BETHESDA, MARYLAND 20814-4799

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Title of Thesis: Influence of Geometry on a High Surface Area-Solid Phase
Microextraction Sampler for Chemical Vapor Collection

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

Thesis and Abstract Approval:

Chairman: Lt Col Peter T. LaPuma, PhD

Date

LCDR Greg Cook, PhD

Date

Brian A. Eckenrode, PhD

Date

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

ABSTRACT

Title:

INFLUENCE OF GEOMETRY ON A HIGH SURFACE AREA-SOLID PHASE MICROEXTRACTION SAMPLER FOR CHEMICAL VAPOR COLLECTION

Robbie L. Wheeler, Master of Science in Public Health, 2007

Directed By: Peter LaPuma, Lt Col, USAF
Assistant Professor, Department of Preventive Medicine and Biometrics

The High Surface Area Solid Phase Microextraction (HSA-SPME) device is an internally heated sampling device designed for high-volume, trace level air sampling. This study compared the analyte extraction and durability of five different HSA-SPME geometric configurations at two sample flow rates. Each HSA-SPME configuration was tested for its ability to extract a 10 ppb_v 39-component gas mixture and thermally desorb into an analytical instrument. Differences in analyte recovery between the five HSA-SPME geometries were not significant. The lower sample flow rate (0.1 Lpm) yielded higher analyte recoveries compared to the higher flow rate of 4 Lpm ($P < 0.001$) given a fixed volume of air sampled. However, the higher flow rate exhibited 30-fold higher extraction efficiency in terms of mass per unit time, which is more beneficial for instrumentation and decision making when sampling speed is of the essence. Although some physical degradation occurred, the devices' ability to collect analytes did not appreciably decline after 100 desorption cycles.

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MICROEXTRACTION SAMPLER FOR CHEMICAL VAPOR COLLECTION

By

Robbie L. Wheeler

Thesis submitted to the Faculty of the Preventive Medicine and Biometrics Graduate
Program of the Uniformed Services University of the Health Sciences in partial
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Dedication

- To my wife, Suzanne, for her support and patience during this endeavor.
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1 Introduction

1.1 Background

The ability to rapidly detect and identify volatile and semi-volatile organic chemicals (VOCs and SVOCs) in field settings can contribute greatly to health protection in a variety of military and civilian situations. Specifically, the ability to detect chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) at concentrations low enough to protect human health, during an emergency response, is extremely important. An on-scene commander must be able to contain a situation while minimizing adverse health effects during wartime, terrorist actions or accidental chemical release.

Law enforcement can also benefit from the development of improved field-portable VOCs and SVOCs detection methods. Currently, canines are used to detect narcotics and explosives, locate missing persons, find buried cadavers, and match individuals to proffered scent evidence. (Lorenzo, Wan et al. 2003) Analytical instrumentation can provide confirmation of canine evidence, strengthen the value of the evidence in court, or be used as a stand-alone evidence collection method. (Ramsey 2004).

Several technologies are currently used to detect VOCs and SVOCs in the field: colorimetric, electrochemical, ion mobility spectrometry (IMS), photoionization and infrared spectrometry. The major limitations of their use include:

- a) inability to selectively detect chemicals at low concentrations,
- b) propensity toward false positive results,
- c) susceptibility to interference from non-target chemicals,
- d) logistics for power requirements and consumables,
- e) slow response times (tens of minutes (min) or more).

Limitations also exist for the use of canines in law enforcement:

- a) recent challenges to admissibility in court,
- b) limited availability of properly trained canines,

- c) associated costs of training, care and maintenance,
- d) canines can be “mis-led” by handlers,
- e) do not always possess the desire to work.

One of the most significant limitations of air sampling in a field environment is the sample preparation. To detect at low concentrations, analytes are typically extracted from the air onto a sampling media (i.e. charcoal tube). For analysis, the analytes are extracted from the sample media, which frequently involves use of solvents. The solvents often pose environmental and occupational hazards and they may mask the analytes of interest. (Pawliszyn 2003) Sample preparation can also be time intensive, consuming up to 80% of total analysis time. (Vas and Vekey 2004) Thus, a solvent-free method of sample collection and preparation is desirable for field use.

One instrument used to overcome the aforementioned detection technology limitations is a field-portable gas chromatograph/mass spectrometer (GC/MS). A GC consists of a small diameter tubular column used to separate chemicals in a mixture. The inner surface of the column is coated with a stationary phase that interacts with some molecules more than others. As a volume of sample is carried through the column by a moving gas phase, chemicals in a mixture are partitioned into individual components. Each component enters into the MS and is identified based on its unique fragmentation pattern. Energy is transferred to the analyte, which breaks the molecule into a repeatable pattern of ion fragments, which constitutes a mass spectrum. A computer compares the mass spectrum to a mass spectral library like a fingerprint. (McMaster and McMaster, 1997) A GC/MS can reduce false positives (caused by interferences) and detect most VOCs and SVOCs at concentrations low enough to protect human health. (Eckenrode 2001) While the portability of GC/MS instruments is improving, a GC/MS requires

considerable operating expertise and presents design challenges for quality, high-speed, field-portability.

Solid-phase microextraction (SPME), introduced in 1989, has expanded the usefulness of GC/MS in the field. SPME devices consist of a “solid-phase” polymer material coated on an 80 – 125 μm diameter silica fiber. (Vas and Vekey 2004) The coating both adsorbs and absorbs analytes for delivery to an analytical instrument. (Pawliszyn 2000) The coated fiber is usually housed in a protective syringe and is exposed to air or a liquid only during sampling. The coating concentrates analytes and allows sample collection from locations not accessible to a full-sized GC/MS (Pawliszyn 1997). Analytes are transferred from a SPME device to a GC/MS by inserting the device into a heated GC injection port. Carrier gas flows over the fiber and carries the analytes to the GC. SPME devices combine sampling, extraction, concentration, and sample introduction into a single, solvent-free step that is faster and often more sensitive than other sampling methods. (Vas and Vekey 2004)

Commercial SPME sampling devices are 1 cm in length and are commonly used to collect samples from static or low velocity gas flows. Ramsey, et al (Ramsey 2004; McDonald 2006) investigated the advantages of employing High-Surface Area SPME (HSA-SPME) device over commercial SPME devices. The HSA-SPME design consists of applying the coating onto a 10 cm long nickel-alloy wire (254 μm diameter) rather than a 1 cm long silica fiber, giving the HSA-SPME device approximately ten times more surface area than commercial SPME devices. The coated wire is helically wrapped around a glass tube, which is then placed within a larger glass tube. The sample air is drawn across the coated wire in the annular space between the glass tubes. The annular

space also allows HSA-SPME device to collect dynamic samples (i.e. pulling air across the HSA-SPME fiber with a pump) with high velocity gas streams (0.1 – 10 liters per minute (Lpm)). The annular space reduces the sample to coating volume ratio and the helical sorbent is designed to induce turbulent sample flow across the sorbent surface. The design is expected to increase the HSA-SPME device's ability to detect analytes at lower concentrations; however, this has not been tested extensively.

Ramsey, et al (2004) demonstrated that HSA-SPME was ten times more efficient at extracting and desorbing analytes from air than commercial SPME and “yielded 1-2 orders of magnitude lower detection limit” for a short list of target compounds: benzene, toluene, ethyl benzene, and m-, p-, and o-xylene (BTEX). The HSA-SPME device's nickel-alloy wire core enables use of resistive heating for desorption of analytes; the benefits of this design over commercial SPME include faster sample results and improved GC/MS performance. (Ramsey 2004, McDonald 2006)

1.2 Research Question and Specific Aims

Is the analyte uptake of an HSA-SPME device influenced by geometry or is the improvement in analyte uptake of HSA-SPME over commercial SPME solely a result of increased sorbent surface area?

1. Evaluate methods for measuring desorption temperatures of the HSA-SPME device.
2. Develop an HSA-SPME desorption protocol to minimize analyte retention and damage to the HSA-SPME device coating while maximizing desorption of captured analytes.
3. Test the durability of the HSA-SPME device under 270°C and 310°C desorption temperatures.

4. Compare the total analyte uptake results for five HSA-SPME geometries at 0.1 and 4 Lpm to determine if different geometry influences uptake.

2. Literature Review

The following chapter will provide insight into field detection research, the SPME technique, efforts to improve SPME, and the development of HSA-SPME. Fluid flow characterization and mass transfer across geometries similar to the HSA-SPME device will also be discussed.

2.1 Field Instrumentation

The need to detect and identify volatile airborne chemicals in field settings has long been recognized. The initial efforts to detect chemicals during WWI involved soldiers, trained to smell chemical agents and visual colorimetric reagents, designed to detect specific (CWAs). Subsequent efforts toward chemical detection focused on improving colorimetric methods, although more advanced methods such as IMS began to become more prevalent as chemical detection technologies matured. (Sun 2005)

One of the most powerful technologies for detection and identification of VOCs and SVOCs in the field has been the field portable GC/MS. These new instruments are based on the same GC/MS technology used in laboratories. A 1995 study compared performance characteristics and data obtained using a field-portable GC/MS to analyze air samples collected on charcoal tubes versus sending samples collected on charcoal tubes to an off-site, Environmental Protection Agency (EPA) laboratory. Results were on the same order of magnitude range between the two methods, with on-site results being available much more quickly (hours vs. days). (Schuetz 1995) In 2004, a Viking 573 field-portable GC/MS (Bruker Daltonics, Billerica, MA), and a man-portable HAPSITE® GC/MS (Inficon, Syracuse, NY) instrument were used to identify and detect four different CWAs. This study found that while both instruments could detect and identify

the target chemicals, the field-portable GC/MS was able to accomplish this in 20% of the time, and with improved chromatographic resolution. (Smith 2004) The California EPA recently certified the HAPSITE® as capable of measuring VOCs in the lab and field, with recommended applications for: (a) long term monitoring of chlorinated hydrocarbons in air, soil, and water, (b) detection of TICs released during industrial accidents, and (c) on-site analysis to speed clean up activities. (2004)

The use of GC/MS in a field setting includes use in an austere jungle setting to identify components of a haze on the island of Borneo, and monitoring of CWAs during demilitarization and military reconnaissance tests. In these situations, the Viking 572 field portable GC/MS provided rapid identification and a high degree of certainty. (Eckenrode 2001)

2.2 Solid Phase Microextraction

2.2.1 History

SPME was originally developed to extract analytes from a liquid matrix. Extraction was completed by direct immersion into the sample or by headspace collection above the sample. Chemists later observed that samples could also be acquired from a gaseous matrix. For static SPME sampling, extraction is generally considered complete when the analyte reaches an equilibrium condition between the sample matrix and the sorbent; further sampling time does not increase the amount of analyte on the sorbent. (Pawliszyn 1997) Because the amount of analyte extracted by the fiber at equilibrium is proportional to the analyte concentration in the air, equilibrium sampling with SPME has been widely used for quantitation. Three different calibration methods have been successfully used in quantitative SPME sampling: calibration curves using known standards, the use of

characteristics of the analytes (i.e. distribution coefficients) to calculate concentrations, and non-equilibrium methods based on diffusion theory. (Ouyang 2006) Development of non-equilibrium models for quantitation of analytes using SPME allows for a shorter sampling time. (Ai 1997) The interest in SPME as a sampling technique has become popular as evidenced by the number of scientific papers concerning SPME. There were 50 articles during 1990-1995 and nearly 400 articles in 2002 alone. (Vas and Vekey 2004)

2.2.2 Commercial SPME Design

In commercially available SPME devices (Sigma-Aldrich, St. Louis, Mo) the 1 – 2 cm fused silica fiber is attached to a needle assembly. The silica fiber is coated with a polymer, which serves as the extracting phase. This fiber assembly is contained inside a protective housing that resembles a syringe (see Figure 2-1). The coated fiber remains in the protective housing until sampling. The fiber is extended outside the septum piercing needle for a discrete period of time. The fiber is then retracted and transferred to a GC/MS or other instrument for analysis. Typically, desorption of analytes from the coating is accomplished thermally in the heated injection inlet of the GC. (Vas and Vekey 2004).

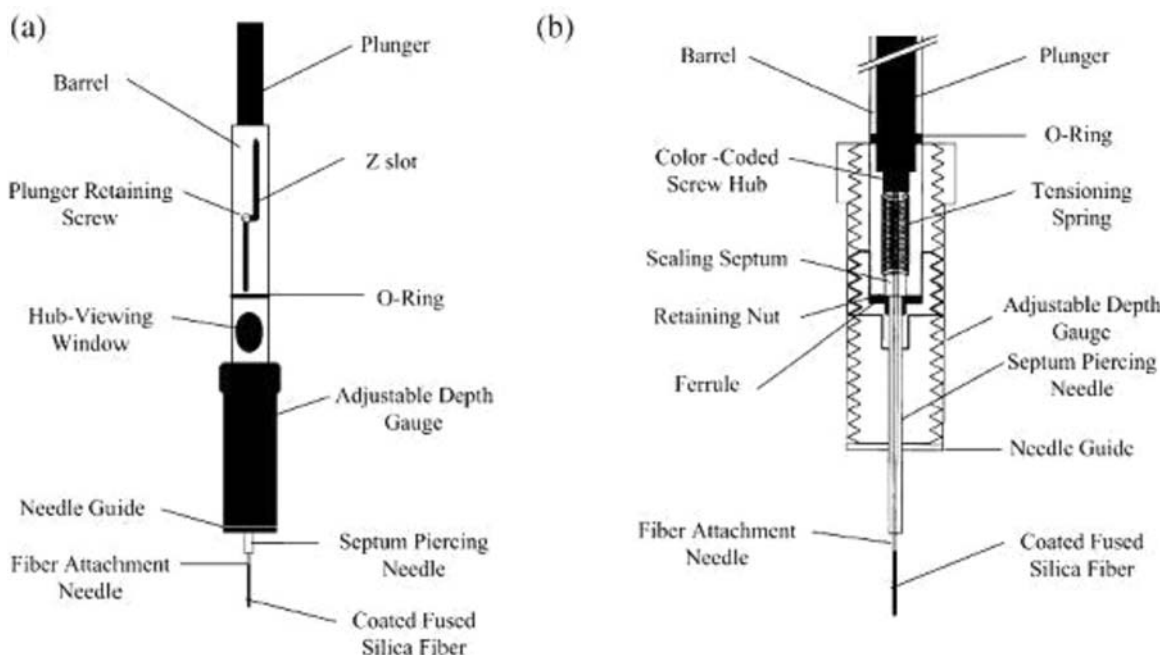


Figure 2-1: (a) SPME Fiber Holder (b) Fiber Assembly (Supelco Data Sheet 1998)

SPME has been used in many applications. Researchers have applied SPME to indoor air quality monitoring (Koziel 1999; Li, Santilli et al. 2001; Koziel 2002; Hippelein 2006), personnel monitoring for time weighted average exposures (Martos and Pawliszyn 1999; Smith, Kluchinsky et al. 2002; Isetun, Nilsson et al. 2004), and disaster response during an aircraft crash into a large building (Hook 2002). Chemical warfare agent detection with SPME has been accomplished using both GC/MS (Hook, Kimm et al. 2003; Hook, Jackson Lepage et al. 2004) and IMS technology. (Rearden 2005) Further applications of SPME include fields such as environmental monitoring, analysis of food chemistry, analysis of wines, and even in-vivo monitoring of pharmaceuticals. (Vas and Vekey 2004) SPME with IMS has also been suggested for other VOC classes such as narcotics, explosives, and environmental pollutants. (Liu 2006)

Commercial SPME devices are manufactured using a proprietary coating process. Polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA),

Carboxen (CAR) and Carbowax (CW), as well as combinations of these coatings, comprise the commercially available coating materials. (Dietz, Sanz et al. 2006) SPME coatings can be divided into two classes: homogenous polymers and polymers embedded with porous solid particles (i.e. Carboxen). The most commonly used coating, PDMS, is a homogenous polymer with an affinity for non-polar analytes. (Vas and Vekey 2004)

While the kinetics of analyte absorption or adsorption by PDMS is well understood and numerous air sampling methods for PDMS SPME fibers have been developed, Carboxen/PDMS is not as well characterized as PDMS; however, it has been proven that Carboxen/PDMS has higher sensitivity for extracting VOCs than PDMS. (Kozziel, Jia et al. 2000) Carboxen/PDMS has been shown to be subject to competitive sorption. Competitive sorption is a phenomenon that results in lower affinity compounds being displaced with higher affinity compounds on the carbon microparticles. This competitive sorption phenomenon makes quantitation using embedded solid coatings difficult. (Tuduri 2001) The use of short sampling times was found to mitigate the competitive sorption effect. (Tuduri 2002) A key parameter in SPME sampling is the choice of sorbent coating. The use of coatings with different polarities and different mechanisms of extraction (adsorption or absorption) will dictate the SPME device's affinity for a particular analyte.

2.2.3 Efforts to Improve SPME

Researchers have tested various new coatings to optimize selectivity or sensitivity for certain applications beyond the capabilities provided by commercially available coatings. A 2006 review revealed seven different coating processes are currently being used in research studies to produce SPME fibers in-house. The review found that many in-house

fibers suffer from inconsistent coating application methods. Coating materials other than those which are commercially available have shown potential to enhance selectivity and sensitivity for target analytes. (Dietz, Sanz et al. 2006) A study of four coating materials found that prototype coatings displayed increased sensitivity toward nerve agent simulants compared to commercially available coatings. (Boglarski 2006) The continued expansion of research into custom coating materials will further increase the versatility of SPME sampling for field use.

Another area of focus has been to improve the sorptive characteristics of the coating. A temperature gap was achieved through a device that heated the sample matrix while simultaneously using CO₂ to cool the SPME fiber. This approach increased the coating/sample partition coefficient between the coating and the sample matrix, and by allowing the sample matrix to be heated, increased the release of analytes, while avoiding a decrease in sample uptake by the SPME fiber which would correspond to increased fiber temperatures. Limits of detection in 0.3 to 3 picogram/gram range were obtained. (Ghiasvand, Hosseinzadeh et al. 2006)

Other efforts to improve SPME have focused on increasing the surface area of the sorptive surface. In one experiment, researchers coated glass fibers with C-18-bonded silica particles then glued 15 of the coated fibers together for a sorbent-phase surface area 250 times greater than a 100 µm PDMS coated SPME fiber. Using a modified SPME holder, the “multifiber” was desorbed into the inlet of a GC/MS, where the adsorption rate of the porous multifiber was 10 times greater than a commercial PDMS SPME fiber. (Xia 2001) In another experiment, 1 cm x 1 cm and 1 cm x 2 cm sheets of thin PDMS membrane, with surface areas ~20 and ~40 times greater than a 100 µm PDMS coated

SPME fiber, resulted in higher extraction rates (direct and headspace) of polycyclic aromatic hydrocarbons than a commercial 100 μm PDMS coated SPME fiber. The membranes were attached to a thin, deactivated stainless steel rod, in a configuration similar to a flag on a flagpole, during sampling. The membranes were then rolled around the steel rod for removal from the sample and for injection into the GC. The membrane devices produced higher extraction efficiency and sensitivity without sacrificing analysis time. (Bruheim, Liu et al. 2003)

2.2.4 SPME Dynamic Air Sampling

Dynamic air sampling with SPME has certain advantages. For equilibrium extraction sampling, the time to reach equilibrium can be shortened by flowing sample air across the SPME fiber. (Ouyang 2006) Dynamic SPME sampling can be beneficial when using sorbent coatings such as Carboxen/PDMS, which have high sensitivity to VOCs, but require long equilibration times. (Tuduri 2001) Dynamic air sampling with SPME fibers has been evaluated under non-equilibrium conditions. (Augusto, Koziel et al. 2001; Tuduri 2001; Tuduri 2002; Isetun, Nilsson et al. 2004) Dynamic air sampling with SPME fibers can obtain trace level quantitation of analytes with very short sample times. (Bartelt 1999)

In 1999, a model was developed for quantitation of volatiles in air prior to full equilibration. (Bartlett 1999) Bartlett's model was later expanded to cover a wider range of airflow rates. One notable finding was that, while extraction efficiency decreased with faster flow rates, the total mass of analyte collected during a given sample period was actually greater with faster flow, due to the faster equilibration. (Bartelt and Zilkowski 2000)

Dynamic air sampling with SPME fibers has resulted in reduced sampling time by two to three orders of magnitude compared to the National Institute of Occupational Safety and Health (NIOSH) sampling method for aromatic VOCs. Detection limits between the dynamic SPME and NIOSH sampling methods were in the low parts per billion by volume range. (Koziel 1999; Augusto, Koziel et al. 2001) In addition, the feasibility of non-equilibrium SPME sampling for time-weighted average occupational exposures was demonstrated. (Koziel 1999) A study of dynamic SPME sampling of organophosphate triesters revealed that the analyte uptake rate as a function of sample air flow appeared to level off above 7 cm/sec, indicating that increasing flow rates beyond this speed could be used to shorten sample times without sacrificing sensitivity. (Isetun, Nilsson et al. 2004) The coupling of dynamic SPME sampling with field instrumentation was tested in 2004, when a field GC/MS system was used with dynamic SPME to detect and quantify the chemical warfare agent sarin. (Hook, Jackson Lepage et al. 2004)

2.3 New SPME Device Designs

To improve performance, various SPME designs have been studied besides the commercial type fiber. Ciucanu fabricated a coiled SPME device by wrapping a 0.07 mm diameter chromium-aluminum alloy wire around another wire of the same diameter at a constant pitch. The center wire was removed and the remaining wire coil was cut to 10-15 mm in length and dip-coated with a PDMS. The coil was placed inside a 0.60 mm outer-diameter stainless steel tube, which was used to pierce the septum of the sample vial and the GC injector port. Samples were collected in the headspace above an agitated liquid solution, which would result in air movement perpendicular to the axis of the helix. Desorption was achieved by heating the metal tube housing the PDMS coated coil.

Ciucanu reported improved performance in the form of reduced extraction times and desorption times. Improvements were credited to a reduction in the boundary layer due to turbulent helical flow induced by the coil. (Ciucanu 2002) The idea of a coiled SPME was next used for continuous sampling of VOCs as part of a trap system. A 0.07 mm wire was coiled around a 1.0 mm straight wire, and then the coil was removed and coated as before, resulting in a coil with a larger diameter than in the 2002 study. The SPME coil was placed axially inside a 0.75 mm inner-diameter silicosteel tube, which was then resistively flash-heated to desorb analytes from the coil into a GC/MS system. In this experiment, the sample gas flow was parallel to the axis of the helix. The helical trap was used for on-line monitoring of four VOCs from a fume hood, and for monitoring VOCs in diesel exhaust, with good chromatographic results and lower limit of detection in the picogram per cubic meter range. (Ciucanu, Caprita et al. 2003)

Ciucanu's 2002 observations of improved performance with the coiled SPME design were disputed in 2003 by Bruheim, et al. Bruheim's group, from the University of Waterloo, rejected Ciucanu's claims of a ten-fold decrease in equilibration time using the helical SPME device, based on their own experiments and on the theories of mass transfer in SPME. The Waterloo group contended that the airflow around Ciucanu's helical device would not induce helical turbulent flow, and in fact their experiments showed an effective shielding of adjacent loops of the coil, reducing effectiveness. The Waterloo group also questioned the coating-application technique used by Ciucanu, stating that the dip-coating technique used to make the spiral SPME did not produce consistent results. (Bruheim, Lord et al. 2003) Ciucanu defended the validity of his data and contended that the observations made in Bruheim's comments were invalid, because

the Waterloo researchers had been unable to reproduce his device correctly in their attempts to replicate his results. (Ciucanu 2003)

The Federal Bureau of Investigation (FBI) Counterterrorism and Forensic Science Research Unit (CFSRU) detailed efforts to develop an “adaptive sampling approach” (Eckenrode 2002) for VOCs, designed for high volume air sampling with a small footprint and minimal power consumption. The HSA-SPME device was engineered and constructed as part of this project, to be integrated with a microtrap preconcentrator and a Low-Thermal Mass GC/MS column. (Mustacich 2003)

Figure 2-2 is a computer generated cross section of an HSA-SPME device. The ends of the Carboxen/PDMS coated, nickel alloy wire are soldered to lead wires. One of the lead wires is placed inside the center of the smaller glass tube to minimize airflow in this space. Sample air is drawn through the annular space between the glass tubes, making HSA-SPME sampling dynamic. This helical design in an annular space reduces the ratio of sample volume to coating surface area and should theoretically provide a continuous airflow with maximum contact and therefore, uptake, down the length of the HSA-SPME device. (Mustacich 2003)

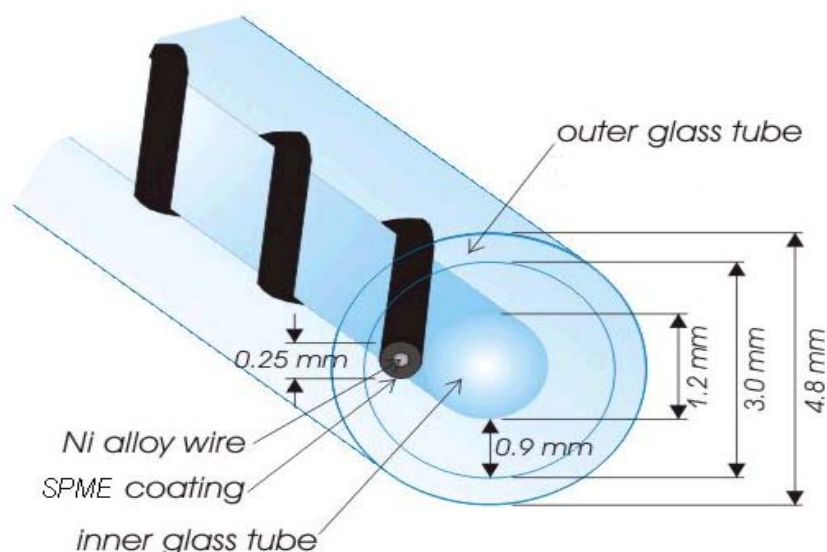


Figure 2-2: Cross-section of HSA-SPME Device (Ramsey 2004)

The use of StablohmTM wire as the substrate for the coating allows rapid resistive heating of the HSA-SPME device with relatively low power. The coiled design allows an increased absorptive surface area in a relatively small space. Electron microscopic analysis of the HSA-SPME revealed little contact between the wire and the inner glass tube, so almost the full wire is available for absorption. (Ramsey 2004) The initial experiments with the HSA-SPME devices achieved an increase of approximately 300% in GC/MS peak area for gasoline analytes, demonstrating the HSA-SPME devices' potential for sampling high volumes of trace volatile compounds in air. (Mustacich 2003)

Further method development and characterization of the HSA-SPME prototype devices were conducted in 2004. Using a Carboxen/PDMS HSA-SPME device (65 μm coating thickness) the analyte uptake of the HSA-SPME device was compared to a commercial Carboxen/PDMS SPME fiber of the same coating thickness under static and dynamic conditions. (see Figure 2-3) In addition, the lower limit of detection with HSA-SPME was 1-2 orders of magnitude lower than dynamic sampling using commercial

SPME fibers and 1-4 orders of magnitude lower than static sampling in the headspace.

(Ramsey 2004)

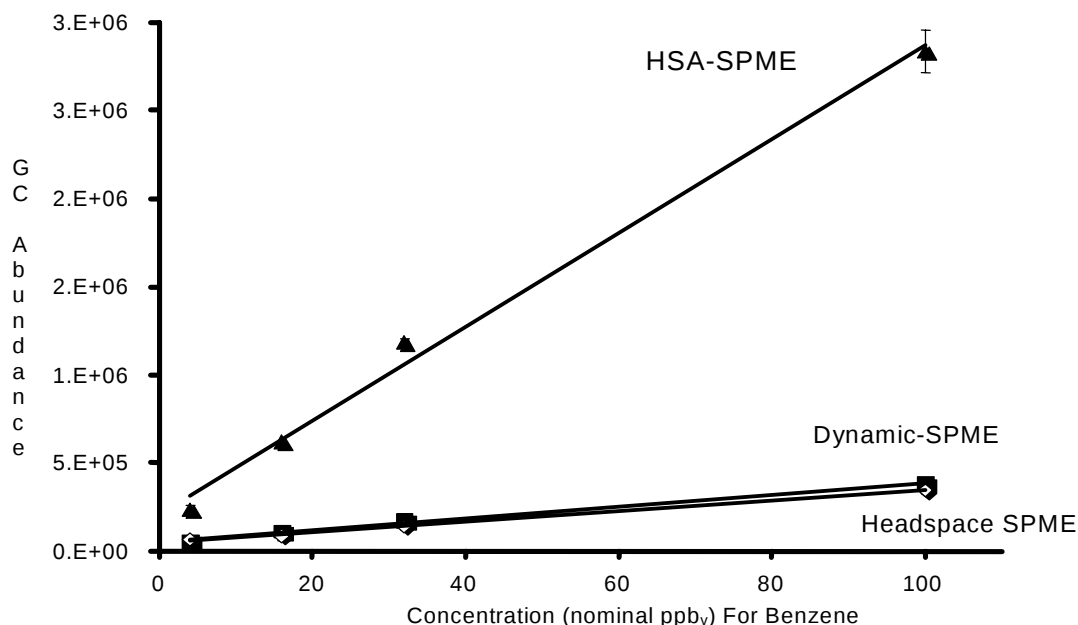


Figure 2-3: HSA-SPME with Static and Dynamic SPME Comparison (Ramsey, 2007)

Subsequent research with the HSA-SPME device focused on extraction efficiency and total analyte extraction using various sample flow rates. Sample gas was drawn through an HSA-SPME device and then the HSA-SPME was desorbed into an Entech 7100 pre-concentrator. In addition to evaluating the collection and desorption efficiencies of the HSA-SPME devices, the McDonald (2006) study considered the durability of the devices and examined the performance of several coatings under sampling conditions. The McDonald (2006) study found that physical damage (white discoloration, cracking, and flaking) to the HSA-SPME coating began to appear more rapidly as desorption times exceeded 2 seconds. At a 2 second desorption, the

Carboxen/PDMS coated HSA-SPME devices effectively extracted analytes for 75 desorption cycles. (McDonald 2006)

Carboxen/PDMS was found to be the most suitable coating for the HSA-SPME device. (McDonald 2006) At sampling flow rates above 1.5 Lpm, the PDMS-only coating was stripped from the wire, while the Carboxen/PDMS coating was able to withstand sample flow rates up to 10 Lpm. The Carboxen/PDMS coating was found to desorb 93% of trapped analytes when heated for 2 seconds, while the HSA-SPME device with PDMS-only coating desorbed 52% of trapped analytes under the same conditions. This combination of durability and ability to desorb trapped analytes made Carboxen/PDMS superior to other HSA-SPME coatings examined. (McDonald 2006)

Examination of the effect of sampling flow rate on the HSA-SPME devices' performance indicated that there are two competing factors to consider when sampling; analyte recovery (termed "extraction efficiency" in this study), and total volume sampled. When sampling a fixed volume of a fixed concentration, analyte recovery was greater at a sampling flow rate of 0.1 Lpm than at a flow rate of 10 Lpm. Therefore, when sampling a fixed volume of air where rapid sampling is not a priority, it is more effective to sample at a lower flow rate. If one wishes to rapidly sample a given volume (as is commonly the case for field detection instruments), a faster flow rate will provide more total analyte collected per unit time. This is due to the lower analyte recovery being offset by the much higher volume of sample that the HSA-SPME device is exposed to during a unit of time. (McDonald 2006)

2.4 Gas Flow and Mass Transfer

While there are no detailed studies of the flow of a gas across a design such as the HSA-SPME, there are some techniques that can be used to visualize flow in such cases. For example, research conducted with membrane filtration gives some indication of the flow characteristics of a fluid in geometries similar to the HSA-SPME device.

A 1994 study examined the use of inserts, or “baffles” for increasing mass transfer of permeate (or permeate “flux”) through the wall of a tubular mineral filter. Three designs: (1) no baffle, (2) a rod baffle (a straight rod along the axis of the cylindrical membrane), and (3) a helical baffle (a central rod wrapped with a coil of wire, shown in Figure 2-4), which is similar to the HSA-SPME device design, tested here. The permeate flux was observed to increase with the helical baffle, and as the number of turns of the helix increased beyond an optimum point, the amount of increase slowed. Slowing of beyond the optimum was explained by observing that as the distance between coils decreases, the geometry begins to approach that of a rod-shaped insert rather than a helix. Flow visualization of the helical baffle revealed three components to the liquid flow: a tangential component in the annular space between the coils and the outer membrane surface; a rotational component that followed the shape of the helix and was the main part of the flow; and a small reverse flow component that moved opposite the main flow near the surface of the rod on the downstream side of the coils. There were no “dead-spots” or stagnant regions observed when velocity ranged from approximately 6400 mm/min to 14,500 mm/min. (Gupta 1995)



Main Types of Flow

- perimeter component
- helical component
- reverse flow

Figure 2-4: Flow Along a Helical Baffle (Gupta 1995)

3 Methodology

This chapter describes the methods used to answer the research question and specific aims identified in Chapter 1. The primary objective was to determine if analyte uptake by the HSA-SPME device was influenced by the geometry of the device. A test plan was developed to evaluate five HSA-SPME device designs. Known concentrations and volumes of a 39-compound gas mixture were generated in Tedlar™ bags and exhausted through the HSA-SPME devices using an air sampling pump. The HSA-SPME devices were integrated with a GC/MS instrument, desorbed via resistive heating, and analyzed to determine the device response. Two variables, desorption efficiency and device durability, of the HSA-SPME devices were evaluated.

3.1 HSA-SPME Devices

The original geometry HSA-SPME device consists of a 100 mm long, 0.254 mm diameter nickel alloy wire (Stablohm 675, California Fine Wire Co., Grover Beach, CA) coated with a 65 µm layer of Carboxen/PDMS using a proprietary process (Supelco, Bellefonte, PA), and wrapped at a constant pitch around a borosilicate glass tube (50 mm x 1.2 mm outer diameter (o.d.) x 1.0 mm interior diameter(i.d.)) (Fisher Scientific, Fairlawn, NJ), with 2.2 mm distance between wire coils. The nickel alloy wire is formulated to resist oxidation when heated and ensure repeatable heating over repeated

heating cycles. This assembly is inserted into a larger borosilicate glass tube (78.5 mm x 4.8 mm o.d. x 3.0 mm i.d.), forming an annular space between tubes, with the coated wire coils located in the annular space.

The HSA-SPME geometries for this experiment were based on modifications of an original geometry HSA-SPME device with the total surface area of the Carboxen/PDMS coating held constant between devices. Except for the hand-coiling process and use of different borosilicate glass tube diameters (as shown in Table 3-1) and lengths (as needed to accommodate wire length), all manufacturing processes and materials were identical between geometries. Table 3-1 lists the geometric parameters of the HSA-SPME designs used for this experiment. All five geometries are shown in Figure 3-1.

HSA-SPME Design	Inner Tube		Outer Tube		Distance Between Coils (mm)
	Inner Diameter (mm)	Outer Diameter (mm)	Inner Diameter (mm)	Outer Diameter (mm)	
Original	1.0	1.2	3.0	4.8	2.2
Larger Inner Diameter	1.4	1.6	3.0	4.8	2.2
Loose Coil	1.0	1.2	3.0	4.8	4.4
Tight Coil	1.0	1.2	3.0	4.8	1.1
Straight	N/A	N/A	3.0	4.8	N/A

Table 3-1: Five Experimental HSA-SPME Device Geometries

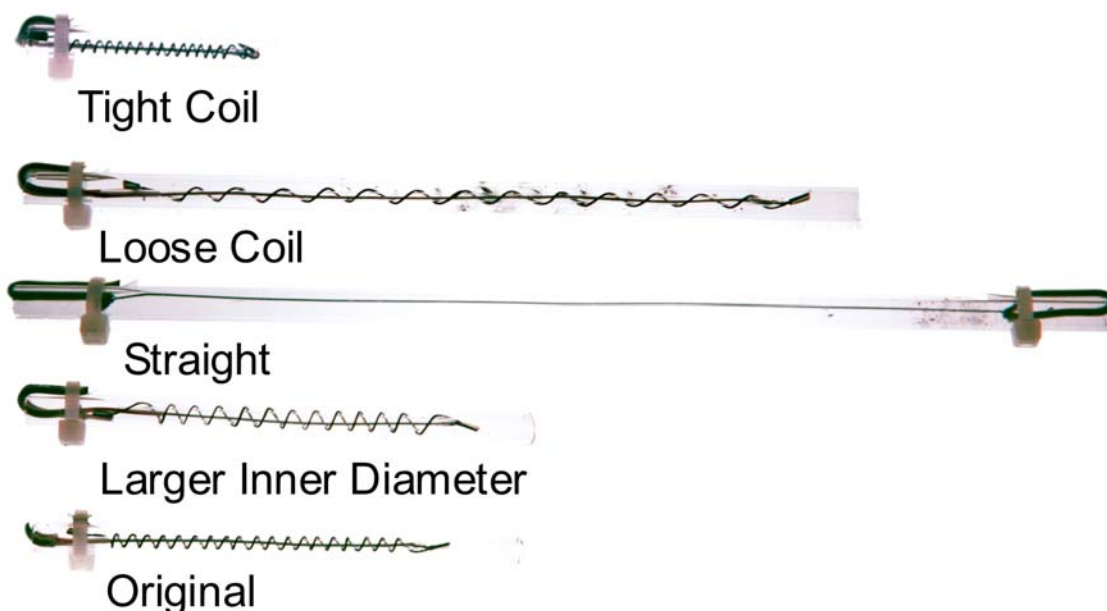


Figure 3-1: Five Experimental HSA-SPME Device Geometries

3.2 HSA-SPME Desorption Temperature Control

To ensure optimal desorption of analytes from the HSA-SPME devices, procedures were implemented to achieve repeatable resistive heating of the devices. Sigma Aldrich (St. Louis, Mo.) recommends that desorption for commercial Carboxen/PDMS SPME fibers be conducted at temperatures between 250°C - 300°C, not to exceed 310°C. (Supelco Data Sheet 1999). Desorption temperatures set outside this range may result in incomplete desorption of captured analytes (i.e. too low) or damage to the Carboxen/PDMS coating (i.e. too high).

Resistive heating of the HSA-SPME devices was accomplished by applying electrical current to the wire for a specified time while 200 mL/min of helium (He) flowed across the HSA-SPME. Alternating current was applied to the HSA-SPME device through a solid-state timer (4310-8-B-1, Artisan Controls, Parsippany, NJ) operating in single-shot mode with two one-mega ohm timing resistors in series to

achieve a consistent eight second resistive heating current (see Figure 3-2). A magnetic low voltage dimmer (P.N. 6613-PL, Leviton Mfg. Co., Little Neck, NY) was placed in-line to control amperage, then a transformer (Model BHU160400, Jameco Electronics, Belmont, CA) reduced the voltage from 120 Volts to 16 Volts alternating current (VAC), with a 3860-M electrical multimeter (Metex Corporation, Seoul, Korea) used to monitor amperage during desorption.

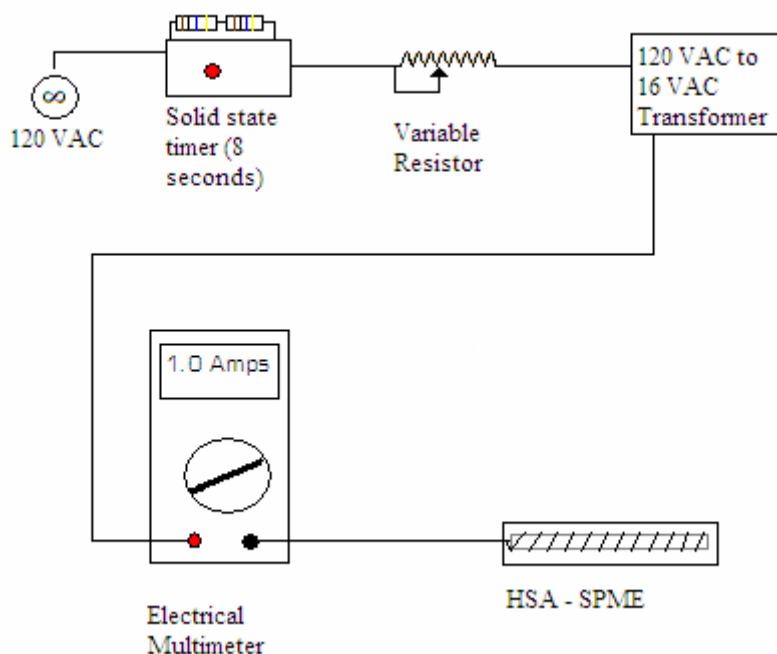


Figure 3-2: Resistive Heating Power Source and Timer

Because the thickness of the Carboxen/PDMS coating is not negligible, the temperature differential between the interface of the wire and the coating and the outer surface of the coating (the gas stream) was calculated to determine if temperature near the wire would damage the coating prior to the outer surface of the coating. The temperature of the interface of the wire and coating (T_i) was calculated using Equation 3-1.

$$T_i = \frac{\dot{g}r_1^2}{2k_{Car/PDMS}} \ln \frac{r_2}{r_1} + T_s \quad \text{Equation (3-1)}$$

Where

T_i = Temperature at interface of wire and coating, °C

T_s = Temperature at outer surface of coating, °C

$k_{Car/PDMS}$ = Thermal conductivity of Carboxen/PDMS, W/m*°C

$\dot{g}$ = constant rate of heat generation, W/m³

r_1 = radius of wire, meters

r_2 = radius from centerline of wire to outer coating surface (Çengel 2003)

Assumptions:

$T_s = 300^\circ\text{C}$

$k_{Car/PDMS} \sim 6000 \text{ W/m}^\circ\text{C}$ [approximated by amorphous carbon] (Shirey 2006)

$r_1 = 0.0000635 \text{ meters}$

$r_2 = 0.00125 \text{ meters}$

wire length = 0.1 meters

maximum current = 4 amperes (based on limits of transformer)

maximum voltage = 16 volts (based on limits of transformer)

These values were substituted into Equation 3-1, and the equation was solved for T_i :

$$T_i = \frac{3208136 * 0.0000635^2}{2 * 6000} \ln \frac{0.00125}{0.0000635} + 300^\circ\text{C}$$

$$T_i = 300^\circ\text{C}$$

T_i was equivalent to T_s out to five decimal places, demonstrating nominal temperature difference between the inner and outer surfaces of the Carboxen/PDMS coating.

Three methods were tested to determine the best method to measure the desorption temperatures of the HSA-SPME devices. First, temperatures were measured by establishing a relationship between resistance, amperage, and temperature for the nickel alloy wire (the “indirect method”). Second, a thermocouple was inserted into the annular space of the HSA-SPME during desorption (the “thermocouple method”). Third, a thermal imaging video system was used to measure temperatures (the “thermal imaging method”).

The indirect method, used in the initial HSA-SPME study to measure desorption temperature (Mustacich 2003), was based on the thermal and resistive properties of the nickel alloy wires. The resistance to temperature of a 0.254mm diameter Alumel® wire (Omega Engineering, Stamford, CT) was calibrated in a laboratory oven, and then a series of amperages were applied to the Alumel wire. At each amperage level, voltage was measured, allowing calculation of the resistance and current, which in turn yielded the temperature and power dissipated per unit length. Since two wires of equal diameter dissipating the same power per unit length and having the same surface area should have the same temperature, the Alumel wire information was then applied to the nickel alloy wire. Measurement of the current and voltage could then provide an in-situ indirect measurement of wire temperature.

The thermocouple method used to measure desorption temperature consisted of inserting a small thermocouple into the annular space of the HSA-SPME device. This method of measuring temperature during desorption had been used previously. (Ramsey 2004; McDonald 2006)

The thermal imaging method used an infrared thermal imaging video system (Avio TVS 8500, Nippon Avionics, Tokyo, Japan). The thermal imaging system, capable of 0.025°C resolution, was set to automatically detect the hottest point on the surface of the HSA-SPME and this setting was recorded for temperature measurement.

Because the outer borosilicate glass tube of the HSA-SPME was between the thermal imaging system and the nickel-alloy wire of interest, a correction factor was employed to account for the attenuation of infrared energy by the outer tube. While common (silicon dioxide) glass interferes with infrared imaging, the borosilicate glass

allowed the infrared energy to be monitored by the thermal imaging system, with an attenuation factor. The attenuation factor was determined by measuring the temperature of HSA-SPME coils at set amperages with and without the outer borosilicate glass tube. By comparing the results at each amperage setting, a relationship between the surface temperature of the Carboxen/PDMS and the temperature recorded by the thermal imaging system through the outer borosilicate glass was established. This allowed estimation of the desorption temperature via remote measurement with the thermal imaging system. Data tables for temperatures with and without the borosilicate glass are provided in Appendix A.

3.3 Sample Preparation

The EPA compendium Toxic Organics (TO-14) mixture of 39 volatile compounds (Restek Corp, Bellefonte, PA) was selected as the analytes for this study (see Table 3-2). The 39-compound mixture represented a diverse range of chemical properties (molecular weights, boiling points, etc.) and contained common analytes for environmental sampling and analysis. The molecular weights and boiling points for several of the larger compounds in this mixture offered a comparison to the molecular weights and boiling points of some CWAs, narcotics and explosives.

Compound		Molecular Weight	Boiling Point (°C)	*Density (g/mL)	CAS Number
1	Dichlorodifluoromethane	121	-29	1.329	75-71-8
2	Methyl Chloride	51	-24	1.780	74-87-3
3	Vinyl Chloride	63	-14	2.210	75-01-4
4	Bromomethane	95	-16	1.732	74-83-9
5	1,2-dichlorotetrafluoroethane	171	3	1.455	76-14-2
6	Ethyl Chloride	64	12	0.890	75-00-3
7	Trichlorofluoromethane	137	24	1.477	75-69-4
8	1,1-dichloroethene	96	31	1.218	75-35-4
9	Methylene Chloride	85	40	1.318	75-09-2
10	1,1,2-trichlorotrifluoroethane	186	48	1.564	76-13-1
11	1,1-dichloroethane	99	57	1.168	75-34-3
12	cis-1,2-dichloroethylene	97	60	1.265	156-59-2
13	Chloroform	119	61	1.480	67-66-3
14	1,2-dichloroethane	99	84	1.246	107-06-2
15	1,1,1-trichloroethane	133	74	1.330	71-55-6
16	Carbon Tetrachloride	154	77	1.583	56-23-5
17	Benzene	78	80	0.873	71-43-2
18	1,2-dichloropropane	113	96	1.150	78-87-5
19	Trichloroethylene	131	87	1.458	79-01-6
20	Cis-1,3-dichloropropene	111	104	1.217	10061-01-5
21	Trans-1,3-dichloropropene	110	111	1.224	10061-02-6
22	Toluene	92	111	0.865	108-88-3
23	1,1,2-trichloroethane	133	114	1.435	79-00-5
24	Tetrachloroethylene	166	121	1.613	127-18-4
25	1,2-dibromoethane	186	131	2.180	106-93-4
26	Chlorobenzene	113	132	1.101	108-90-7
27	Ethylbenzene	106	136	0.865	100-41-4
28	p-Xylene	106	138	0.858	106-42-3
29	m-Xylene	106	139	0.861	108-38-3
30	Styrene	104	145	0.900	100-42-5
31	o-Xylene	106	144	0.876	95-47-6
32	1,1,2,2-tetrachloroethane	168	146	1.587	79-34-5
33	1,3,5-trimethylbenzene	120	165	0.860	108-67-8
34	1,2,4-trimethylbenzene	120	169	0.872	95-63-6
35	m-Dichlorobenzene	146	173	1.290	541-73-1
36	p-Dichlorobenzene	147	174	1.250	106-46-7
37	o-Dichlorobenzene	147	180	1.299	95-50-1
38	1,2,4-trichlorobenzene	181	213	1.450	120-82-1
39	Hexachloro-1,3-butadiene	261	215	1.550	87-68-3

Table 3-2: Chemical Properties of the 39-Compound Mixture (SAX 1984; NIOSH 1994; CRC 1995) * Density at 25°C

The 1 ppm_v 39-compound mixture was diluted to specific concentrations using a Kin-Tek 491M-B Precision Gas Standard Generator and DGB 491-M Direct Gas Blending Module (Kin-tek Laboratories, LaMarque, TX), nitrogen gas (99.99% pure, Airgas, Radnor, PA), and 5-Liter TedlarTM sample bags (SKC 231-05A, SKC, Eighty Four, PA). The 39-compound mixture was diluted 1:99 with nitrogen through the gas standard generator to create a 10 ppb_v concentration. The Kin-Tek gas standard generator mixed the two gases simultaneously. All sample bags were triple purged with nitrogen and then triple purged with the 10 ppb_v 39-compound mixture to minimize potential losses to the sample bags. The dilution flow rates from the gas generator for both gases were verified with a digital flow meter (J & W ADM3000 Intelligent Flow meter, Agilent Technologies, Santa Clara, CA).

3.4 Analytical Instruments

Analyses of the HSA-SPME devices were performed on a laboratory-grade Agilent 6890N GC with a 5973 quadrupole MS detector (Agilent Technologies, Wilmington, DE). The GC oven was retrofitted with a resistively heated DB-5MS, 30 m x 0.25 mm ID x 0.25 µm phase column (RVM Scientific, Santa Barbara, CA). GC grade helium (Airgas, Radnor, PA) was used as the carrier gas and set at 20 psi. The injector, injector transfer lines, and oven were set at 200°C, with the MS transfer line set at 215°C. Electron impact ionization (70 eV) was used and mass spectra were collected over the range of 50 - 350 m/z (mass to charge ratio). Sample retention characteristics and mass spectra were stored and analyzed using Agilent Chemstation software (Version D.00.00.38).

An Entech 7100A Air Preconcentrator (Entech Instruments, Simi Valley, CA) was coupled to the GC/MS to collect and concentrate air samples desorbed from the HSA-SPME devices because the GC/MS could not effectively analyze the collected air samples. The Entech 7100A, a triple stage concentrator, is capable of concentrating VOCs from air sample volumes up to 2000 mL. The first stage (Module 1) uses a thermally protected glass bead cryotrap, the second stage (Module 2) uses a TenaxTM TA adsorbent cryotrap, and the third stage (Module 3) uses an internal megabore cold trap focuser to concentrate the air sample. Liquid nitrogen (Airgas, Radnor, PA) was used as the cryogenic coolant, and nitrogen gas (99.99% pure, Airgas, Radnor, PA) was used as the purge/sweep gas. The preconcentrator's modules were all heated to 190°C for 15 min while being purged with nitrogen each day prior to sampling, to remove any residual compounds.

3.5 Experimental Methods

3.5.1 Calibrating Air Sampling Pumps

Gilair-5 air sampling pumps (Sensidyne, Clearwater, FL) were used to collect air samples with the HSA-SPME devices and to pump helium across the HSA-SPME device during conditioning and thermal desorption cycles. A low flow module (Sensidyne, Clearwater, FL) was added to the air sampling pumps when flow rates of less than 750 mL/min were needed. The air sampling pumps were calibrated daily using a Bios DC-Lite Primary Flow Meter (Brandt Instruments, Prairieville, LA). All sampling pump connections were made with TygonTM clear tubing (St. Gobain Plastics, Paris, France).

3.5.2 HSA-SPME Preparation

Prior to initial use, each HSA-SPME device was conditioned to remove any background chemical contaminants that may have become absorbed or adsorbed in the coating. The devices were resistively heated, as previously described, to the recommended conditioning temperature of 300°C (Supelco Data Sheet 1999) for 15 min. During conditioning, helium from a 10-Liter Tedlar™ bag (SKC, Eighty Four, PA) was pumped across the HSA-SPME at 200 mL/min. If a device had not been conditioned within one week prior to being used for an experiment, the device was reconditioned to minimize background chemical contamination.

For each sample, the air sampling pump was set to 0.1 Lpm or 4 Lpm, based on the flow rate desired. The HSA-SPME device was connected in-line between the outlet of the 5-Liter Tedlar™ bag containing 10 ppb_v of the 39 analytes in a balance of nitrogen and the inlet of the air sampling pump, using Tygon tubing. The air pump was turned on the appropriate interval required to sample 0.667 liters which was either 10 seconds at 4 Lpm or 6 min 42 seconds at 0.1 Lpm. The pump was then turned off, the valve on the bag was closed, and the HSA-SPME device was disconnected and transferred to the preconcentrator for desorption.

3.5.3 Analytical Instrument Analysis

3.5.3.1 Sample Analysis

The HSA-SPME device was connected to the preconcentrator inlet, with a 10-Liter Tedlar™ bag of helium connected to the inlet of the HSA-SPME device to provide carrier gas for the desorbed analytes and to prevent the preconcentrator from capturing ambient air contaminants. The multi-trap method of the Entech 7100A flow rate to load

the first trap was 200 mL/min, and the air volume was held at 500 mL, for a 2.5 min sample time. The HSA-SPME device was resistively heated for eight seconds starting at 30 seconds into the 2.5 min sample period. The preconcentrator trapped and isolated the analytes using multiple trapping modules and automatically purged the analytes into the GC/MS for separation and analysis. In addition, the preconcentration steps removed water vapor from the sample. The operating parameters for the Entech 7100A preconcentrator and the Agilent GC/MS system are listed in Table 3-3.

Entech 7100A Air Preconcentrator		
Component		Setting
Inlet Line		120°C
Internal Valve		150°C
Transfer Line		150°C
Module #1 (glass bead)	Trap	-150°C
	Preheat	50°C
	Desorb	70°C
	Bake	180°C
Module #2 (Tenax™ TA)	Trap	-50°C
	Preheat	160°C
	Desorb	180°C
	Bake	190°C
Module #3 (liquid N ₂ only)	Trap	-160°C
	Desorb	130°C
	Transfer Time	2 min
Total Time:		15 min ± 2
Agilent GC/MS		
Component		Setting
Injector Temp		200°C
Injector Transfer Line		200°C
Oven		200°C
MS Transfer Line		215°C
Column Head Pressure		20 psi
LTM-GC Column		
Component		Setting
Starting Temp		35°C (2 min hold)
Ramp Rate		15°C/min
Final Temp		200°C (2 min hold)
Total Time:		15 min

Table 3-3: Entech 7100 and Agilent GC/MS Parameters

3.5.3.2 Analyte Carryover

To determine the amount of analyte remaining on the HSA-SPME device after a desorption cycle, the HSA-SPME was left connected to the preconcentrator and another eight second desorption cycle was triggered immediately following the conclusion of the previous GC/MS analysis.

3.5.3.3 Thermal Desorption Cycle

To test durability, the HSA-SPME device was subjected to a thermal desorption cycle without GC/MS analysis. The HSA-SPME device was disconnected from the preconcentrator and connected to an air pump which was set to 200 mL/min of helium across the HSA-SPME. The flow rate of 200 mL/min was selected to simulate the sample flow rate drawn in by the Entech preconcentrator during sample collection. The HSA-SPME was then resistively heated to replicate the thermal desorption that the HSA-SPME would have undergone if a GC/MS analysis had been performed. This thermal desorption cycle was also intended to eliminate carryover of analytes into subsequent GC/MS analyses.

3.6 HSA-SPME Desorption Temperature Protocol Development

A desorption temperature protocol method was developed to minimize the analyte retention and damage to the HSA-SPME device coating while achieving maximum analyte removal. First, a temperature to amperage relationship was established for each HSA-SPME device when heated for eight seconds. This relationship was established by setting the variable resistor to low amperage (approximately 1.0 amperes) and resistively heating the HSA-SPME device. The measured temperature was corrected for attenuation by the borosilicate glass and was recorded, and then the process was repeated at slightly

higher amperage. The incremental increase of amperage enabled establishment of 3-4 data points to develop a linear relationship, while avoiding a risk of heating an HSA-SPME above 310°C, the recommended maximum temperature for Carboxen/PDMS coating. (Supelco Data Sheet 1999)

Two target desorption temperatures were selected, 270°C and 310°C. The variable resistor was set to provide amperage calculated to produce the desired desorption temperature, using a “reference” HSA-SPME device to enable setting the amperage without heating the experimental HSA-SPME device to desorption temperatures (or inadvertently higher) while setting the amperage. An original geometry HSA-SPME (2.2 mm/coil) was conditioned, then loaded with 10 ppb_v of the 39 analytes in nitrogen mixture for 10 seconds at 4 Lpm. The HSA-SPME was desorbed (270°C) into the preconcentrator for GC/MS analysis. Without disconnecting from the preconcentrator, the HSA-SPME was then desorbed again into the preconcentrator for GC/MS analysis to evaluate carryover, or the presence and amounts of target analytes remaining on the HSA-SPME after the first desorption. The device was disconnected from the preconcentrator and thermally desorbed twice more, before collecting a subsequent air sample for analysis. Thus, in the first five desorptions, the HSA-SPME was loaded with analyte and desorbed for GC/MS analysis twice (#1 and #5), desorbed without analyte loading to check for retention once (#2), and thermally desorbed without GC/MS analysis twice (#3 and #4). Subsequently, samples of the 39-compound mixture were sampled and desorbed for GC/MS analysis on the 10th, 15th, 20th, 30th, 40th, 50th, 60th, 70th, 80th, 90th, and 100th cycles. The HSA-SPME was desorbed without sample to evaluate analyte retention on the 51st and 91st cycles, and all other cycles up to 100 were thermal

desorption cycles with no analyte loading or GC/MS analysis. This procedure was repeated for a second original geometry HSA-SPME device at the higher target desorption temperature (310°C) and 110 total desorption cycles. Figures 3-3 and 3-4 display the series of desorptions for each of the two original geometry HSA-SPME devices tested for specific aim #2.

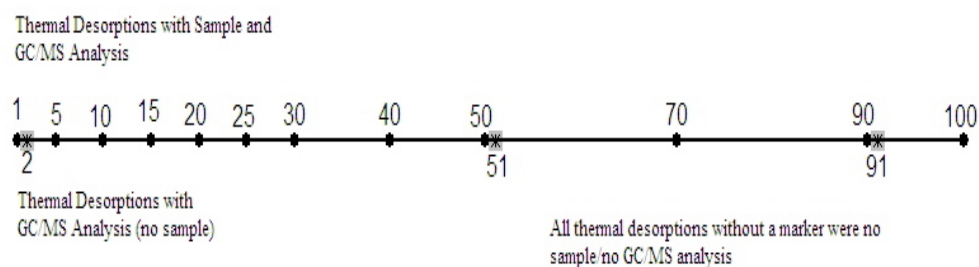


Figure 3-3: Desorption Series for HSA-SPME Durability Test, 270°C

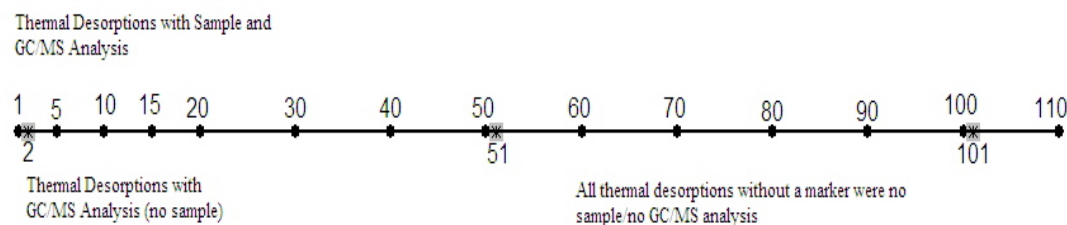


Figure 3-4: Desorption Series for HSA-SPME Durability Test, 310°C

After each thermal desorption, the HSA-SPME device was visually inspected for signs of physical degradation.

3.7 Comparison of HSA-SPME geometries at two flow rates

For each of the five experimental geometry designs (original, larger inner diameter, tight coils, loose coils, and straight) two HSA-SPME devices were tested. Each device was tested at two sample flow rates (0.1 Lpm and 4 Lpm) to determine if the difference in analyte recovery and extraction efficiency (defined as mass recovered per unit time) collected between flow rates was affected by the geometry of the HSA-SPME sampler.

The procedure for each device was to first condition the HSA-SPME. The device was then exposed to 10 ppb_v of the 39-compound mixture in nitrogen for six minutes and 42 seconds at 0.1 Lpm, for a total sample volume of 667 milliliters. The HSA-SPME was desorbed into the GC/MS for analysis. A subsequent desorption was performed to evaluate the extent of retention. The device was then exposed to the 39-compound mixture for 10 seconds at 4 Lpm, and desorbed for analysis and retention as before. Next, the device was again loaded with 667 mL of 100 ppb_v of the 39-compound mixture at 0.1 Lpm and desorbed into the GC/MS for analysis, then underwent a thermal desorption cycle to minimize carryover. After the thermal desorption cycle, the device was loaded with 667 mL of 100 ppb_v of the 39-compound mixture at 4 Lpm and desorbed into the GC/MS for analysis, then underwent another thermal desorption cycle to minimize retention. The process of sampling at 0.1 Lpm and analyzing, then thermally desorbing, then sampling at 4 Lpm and analyzing, was repeated, giving a final tally of three samples at each flow rate for each device, plus one carryover check for each flow rate for each device. Table 3-4 summarizes the process.

Desorption #	Sample Flow (Lpm)	Sample Time (min:sec)	Sample Volume (mL)	GC/MS Analysis (Y/N)
1	0.1	6:42	667	Y
2	N/A	N/A	N/A	Y
3	4	0:10	667	Y
4	N/A	N/A	N/A	Y
5	0.1	6:42	667	Y
6	N/A	N/A	N/A	N
7	4	0:10	667	Y
8	N/A	N/A	N/A	N
9	0.1	6:42	667	Y
10	N/A	N/A	N/A	N
11	4	0:10	667	Y

Table 3-4: Desorption Series for HSA-SPME Geometry Comparison

By following the same order of sampling and desorptions, the influence of confounding factors such as analyte carryover or degradation of the coating were minimized, since they should be the same for all geometries, and would therefore not skew any comparisons between the HSA-SPME geometries.

4 Results

4.1 HSA-SPME/Analytical Instrument Integration

While not the focus of this research, the integration of the HSA-SPME devices with the preconcentrator and GC/MS instruments is noteworthy. The analyte gas mixture used in these experiments contained 39 components, in a balance of nitrogen. While all 39 analytes were detected when the gas mixture was injected directly into the preconcentrator, four of the analytes could not be detected when any Carboxen/PDMS HSA-SPME device was used to collect the sample for desorption. Three of the four chemicals had low boiling points (dichlorodifluoromethane, -29°C ; methyl chloride, -12°C ; vinyl chloride, -14°C). The fourth, m-xylene, was not detected in any of the experiments and was likely not discernable from p-xylene, which has almost identical properties. The fact that these chemicals could not be detected by the HSA-SPME devices in this study is a function of the Carboxen/PDMS coating. The use of a different HSA-SPME coating and/or GC column would be expected to improve detection of these analytes.

4.2 HSA-SPME Desorption Temperatures

Evaluation of the three different methods for measuring desorption temperatures indicated that the thermal imaging method was preferable.

4.2.1 Indirect Method

The indirect method was found to provide inconsistent results, likely attributable to the difficulty in measuring the low resistances ($< 5\ \Omega$) and lower changes in resistance as temperature changed. Additionally, this method assumed that temperature was uniform

along the length of the nickel-alloy wire, which was not the case for geometries other than the straight geometry.

4.2.2 Thermocouple Method

Tests showed that positioning of the 0.13mm diameter, type-K thermocouple (Omega Engineering, Stamford, CT) was difficult, and inconsistent thermocouple placement resulted in readings with poor repeatability. Depending on where the thermocouple junction was placed in the annular space (i.e. proximity to coils, near inlet or outlet of HSA-SPME), temperature readings varied by up to 100°C. Furthermore, damage to the coating could result if the thermocouple touched the HSA-SPME coil.

4.2.3 Thermal Imaging Method

Based on the repeatability of observed temperature readings and the ease of use, the thermal imaging video system was selected as the method for determining HSA-SPME device desorption temperatures in this study. The thermal imaging system also allowed evaluation of the temperature along the entire HSA-SPME, enabling examination of differences in desorption temperature along the length of the coil.

Although the nickel-alloy wire dissipated heat equally along its length, the transfer of heat between adjacent coils, as well as the convective transfer of heat to the helium gas as it flowed past the HSA-SPME coils, resulted in non-uniform temperature distributions along the surface of the HSA-SPME coils. Coils near the middle of the HSA-SPME were radiatively heated by adjacent coils, resulting in higher temperatures near the center of the HSA-SPME. Figure 4-1, a screen capture from the TVS 8500 thermal imaging system, displays the variation in the temperature with the darker area in the center of the HSA-SPME at a higher temperature.

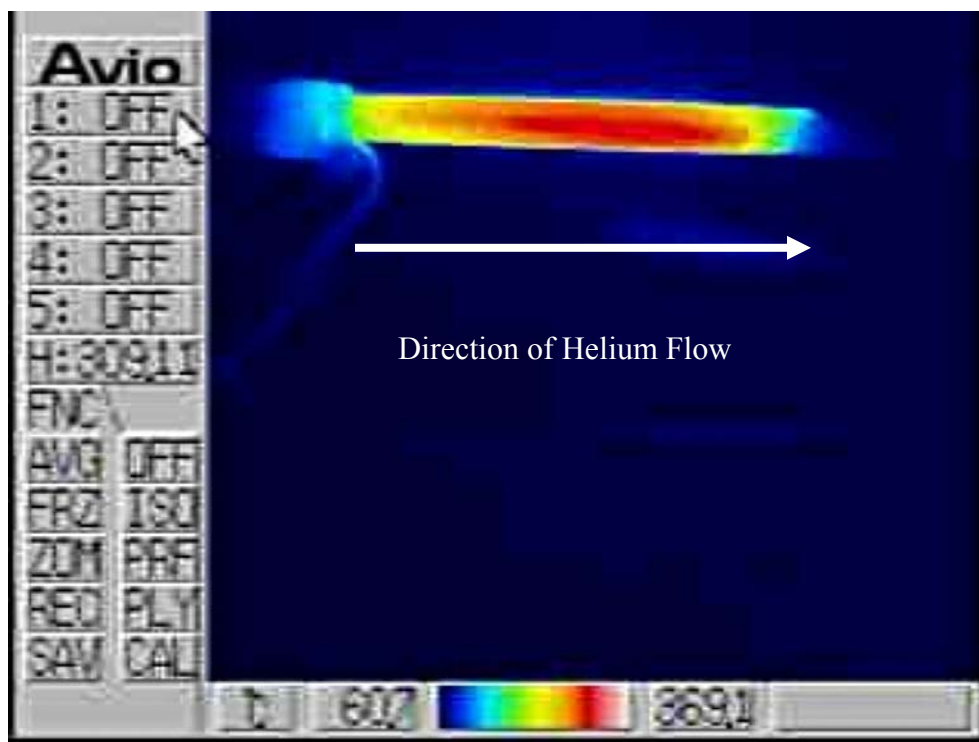


Figure 4-1: Infrared Image of HSA-SPME Heating

The convective transfer of heat from the “upstream” coils to the helium flow resulted in higher observed temperatures toward the outlet end of the HSA-SPME. Figure 4-2 shows that temperatures along the length of an original-design HSA-SPME coil are highest near the center and are slightly higher at the flow outlet than at the flow inlet. As seen in figure 4-2, the temperature profile remains consistent as amperage is increased. Because temperatures observed using the thermal imaging system varied by as much as 65°C along the length of the coil during a given desorption, it is likely that some portions of the HSA-SPME coil, particularly near the inlet, did not reach adequate desorption temperatures.

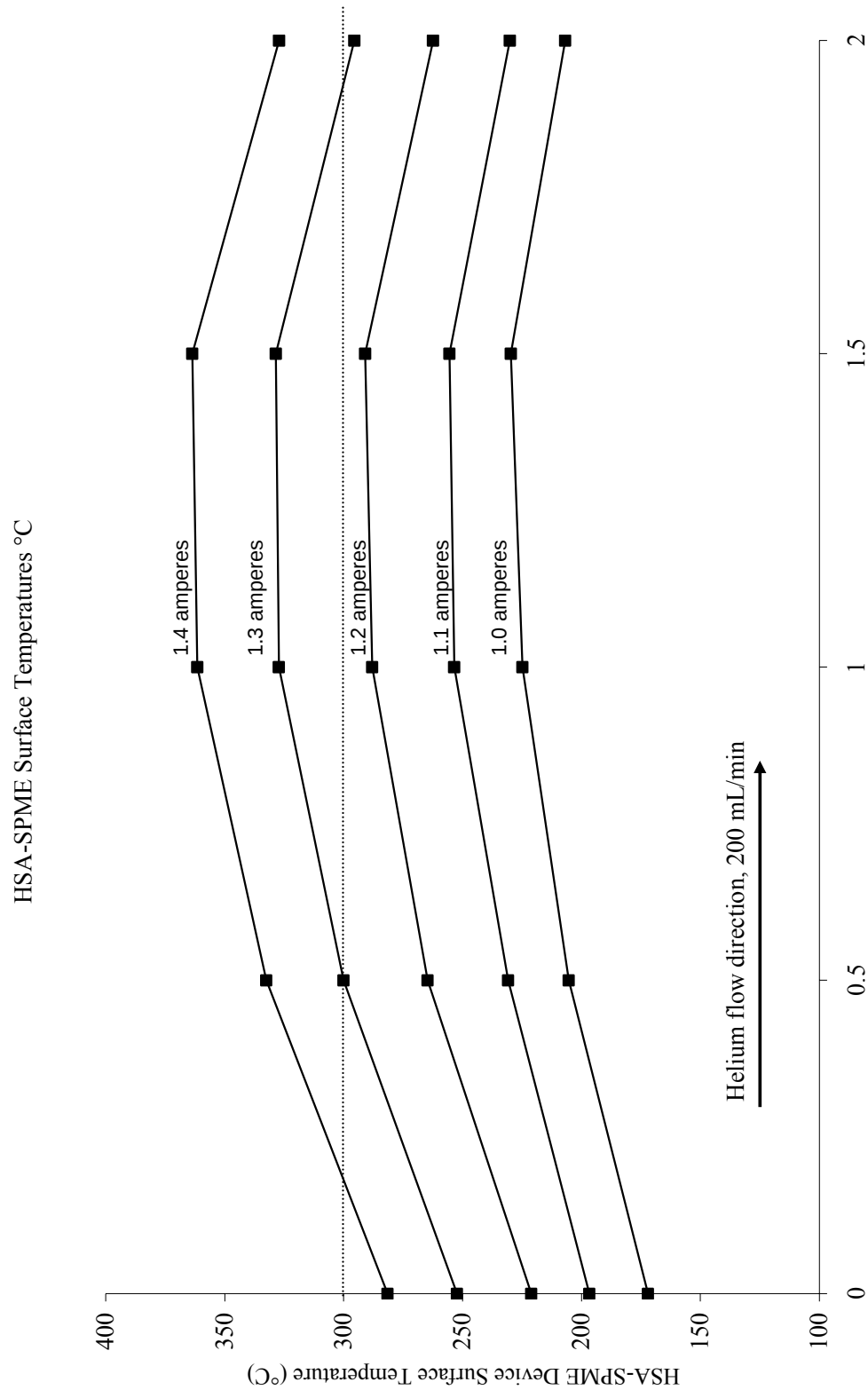


Figure 4-2: Desorption Temperatures Along Surface of Original Geometry HSA-SPME Coil

4.3 HSA-SPME Desorption Method Development

Two original geometry HSA-SPME devices were tested through 100 desorption cycles to assess polymer durability and analyte carryover. For the 1st device, the amperage controller was set to provide amperage that was correlated to a target desorption temperature of 270°C at the hottest point. For the 2nd device, the target desorption temperature was 310°C at the hottest point.

4.3.1 Analyte Carryover

Figure 4-3 illustrates the 270°C desorption GC/MS response for 10 selected analytes at 10 ppb_v. GC/MS response was measured at the 1st, 2nd, 50th, 51st, 90th, and 91st desorptions to test for analyte carryover as well as polymer performance through 91 desorptions. Analytes with lower boiling points (24° - 77°C range) experienced little carryover (averages of 2 to 9%). The analytes with medium (87° - 136°C) and higher (138° - 215°C) boiling points ranged from 0 to 17%, except for toluene, where 55% carryover was observed in the 2nd desorption cycle. The high toluene abundance and carryover seen in the 1st and 2nd desorptions of Figure 4-3 are not seen elsewhere, and may be an anomaly, resulting from contamination in the ambient air of the laboratory during this experiment.

Analyte Carryover for 270°C Desorption

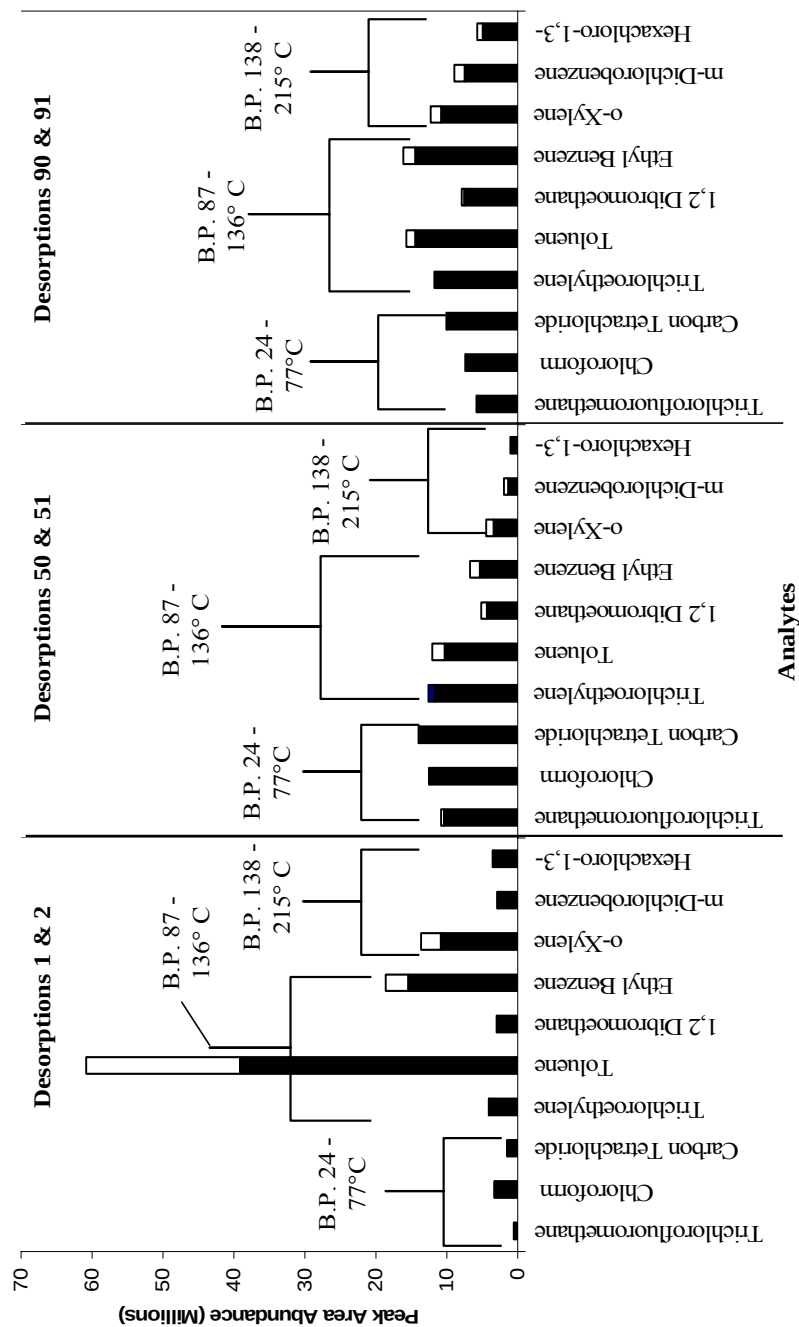


Figure 4-3: 270°C Desorption Series Analyte Carryover After Initial Desorption

Note: Black bar represents GC/MS peak area abundance at initial desorption. While bar represents subsequent desorption to test for analyte carryover

For the 2nd desorption series, the mean desorption temperature, measured at the hottest point on the HSA-SPME device was 311°C with a standard deviation of 24°C. Desorption temperatures were not recorded for the 270°C target temperature experiments. The analyte carryover and desorption efficiency through 101 desorptions are depicted in Figure 4-4. Inadvertently, the temperature of the first desorption was 380°C, resulting in higher peak area abundances and less carryover than was observed in the 270°C desorption. Results on subsequent carryover checks varied; but overall, there was no pattern of reduced performance observed from 1 to 100 desorptions.

Much of the variability in this study is likely attributed to inconsistent desorption temperature control. Although desorption temperature relative standard deviations (RSDs) for the geometry portion of the experiment averaged 5% (range 2-10%), the corresponding temperature fluctuations (average standard deviation of 12°C) from one desorption to another were large enough to have effected desorption of analytes.

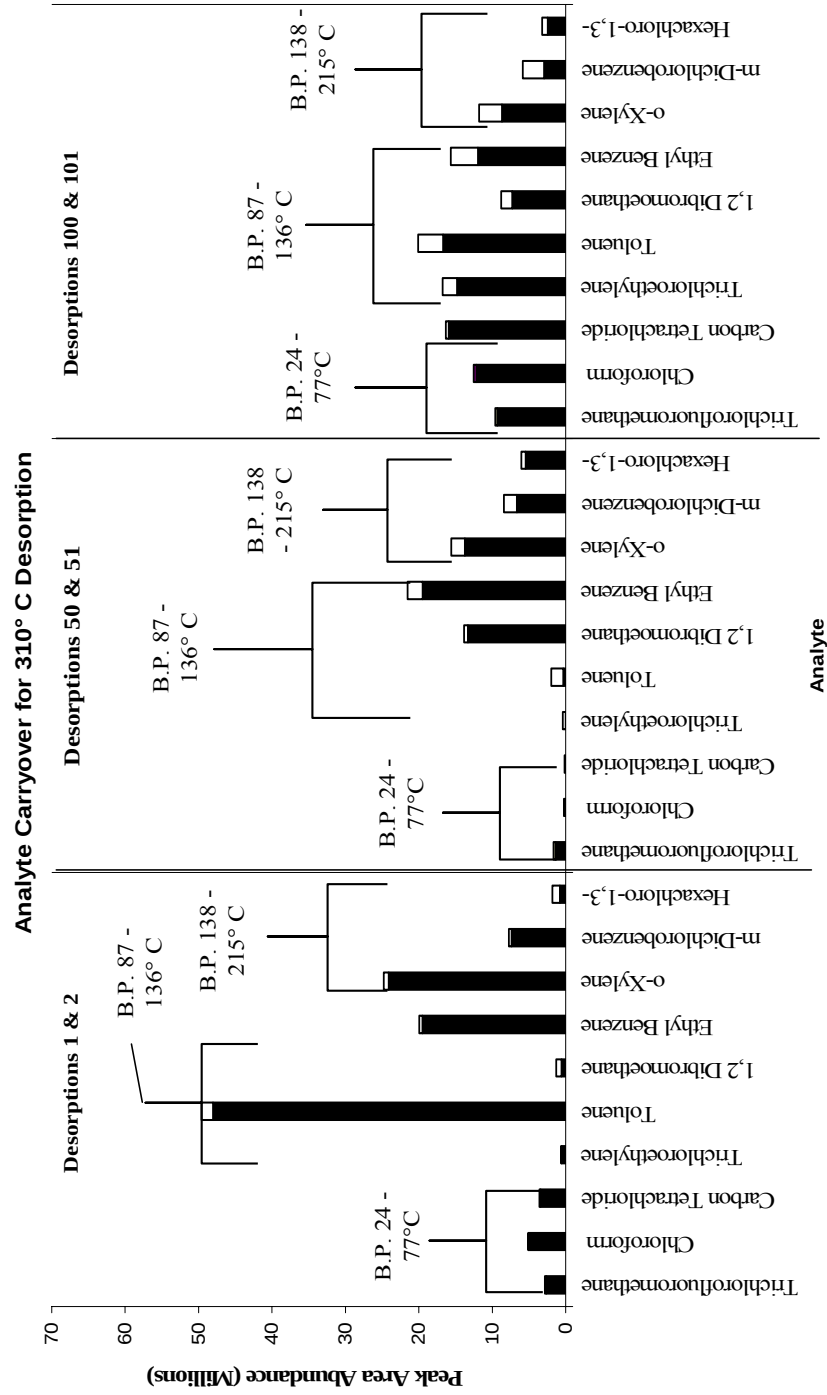


Figure 4-4: 310°C Desorption Series Analyte Carryover After Initial Desorption

Note: Lower black bar represents GC/MS peak area abundance at the initial desorption. White upper bar represents the subsequent desorption to test for analyte carryover

4.3.2 HSA-SPME Durability

To further assess the performance of the HSA-SPME, the original geometry HSA-SPME was evaluated during the 270°C and 310°C series of thermal desorptions. GC/MS peak area abundance for all compounds was summed and compared. The results for the 270°C series are shown in Figure 4-5. While the results varied there does not appear to be a drop in GC/MS peak area abundance after repeated thermal desorption cycles. This indicates that at the analyte concentration studied, the useful life of the HSA-SPME under these desorption conditions could exceed 100 desorptions.

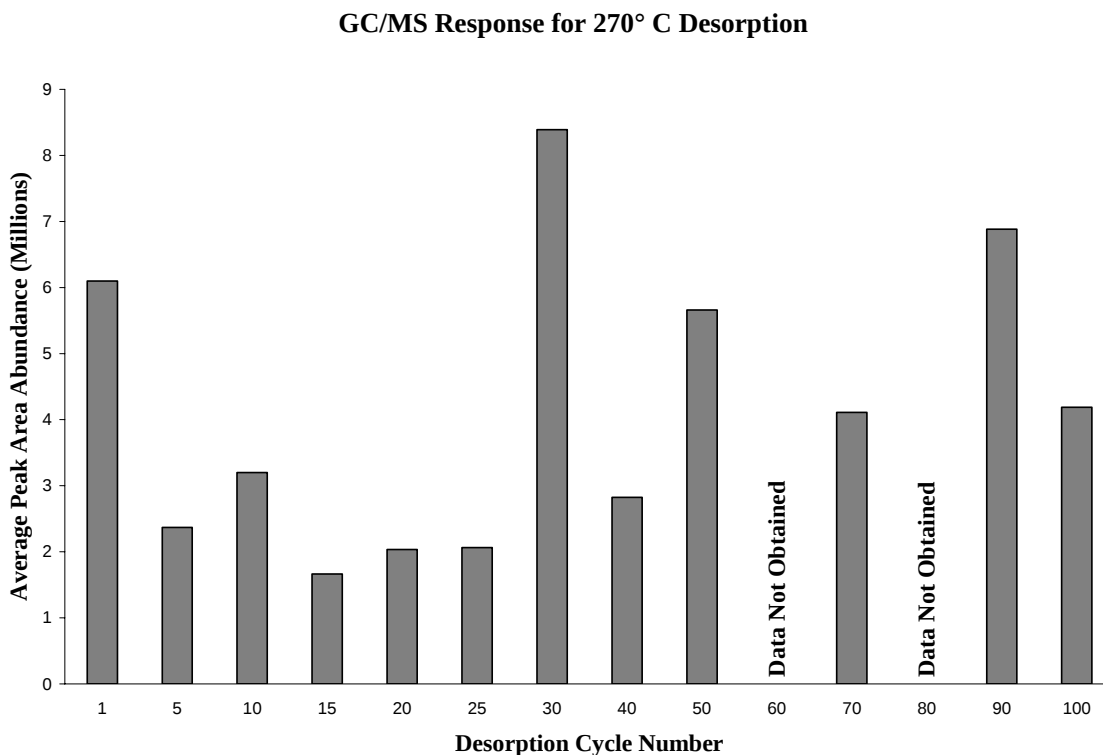


Figure 4-5: Analyte Extraction for 270°C Desorption Series

Figure 4-6 illustrates the 310°C desorption series results. As mentioned previously, the first desorption of this series (380°C) was much higher than the target temperature.

This was due to the imprecision of the procedure for setting initial amperage using the reference device. The temperature for each desorption (except #100 due to thermal imager malfunction) is displayed. The high variability of desorption temperatures (280° - 380°C) is shown in Figure 4-6. As in Figure 4-5, in Figure 4-6 the average peak area does not degrade with repeated thermal desorptions through 110 desorptions. Overall GC/MS peak areas at the 310°C target desorption temperature are higher than the 270°C desorptions, with lower carryover as seen in Figure 4-4.

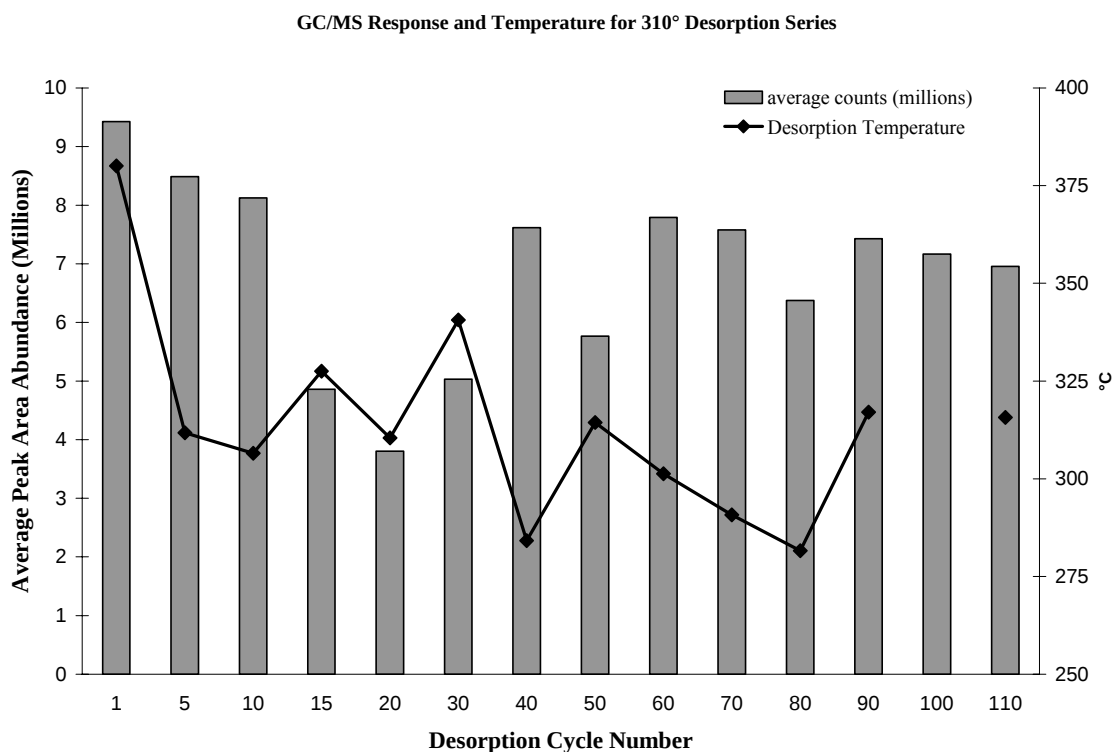


Figure 4-6: Analyte Extraction for 310°C Desorption Series

The physical appearance of the Carboxen/PDMS polymer was visually inspected after each thermal desorption. The physical degradation commonly appears grey-to-white, with an ashen appearance instead of the smoother black appearance of a new coating. Occasionally, degradation to the HSA-SPME coating manifests as physical

removal or flaking of the coating, which will expose the nickel-alloy wire. The removed Carboxen/PDMS coating is either carried away by the helium gas, or adheres as residue on the inner surface of the larger borosilicate tube.

The visual examination of the HSA-SPME device during the 270°C desorption series revealed degradation of the physical appearance of the device. After the 50th cycle, the HSA-SPME began to have visible particles of black material, presumably Carboxen/PDMS, adhered to the inner surface of the larger borosilicate tube. The surface of the HSA-SPME began to display a gray, ashen appearance on portions of some coils, and missing coating from other coils by the 60th cycle. The presence of the black particles on the inner surface of the glass, as well as more gray appearance increased with subsequent cycles. The graying of the coating occurred first on the down-stream side of the coils (the hotter area).

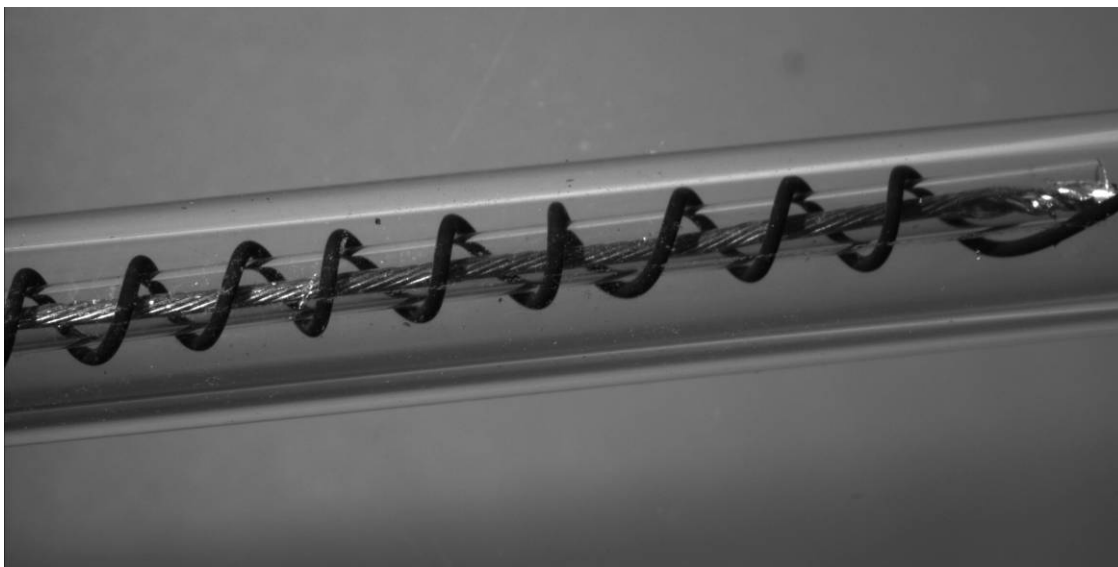


Figure 4-7: HSA-SPME Device Before Any Desorptions

Figure 4-7 shows the physical appearance of the coils of an HSA-SPME after conditioning but before desorption, while Figure 4-8 displays the appearance of the HSA-SPME after 100 cycles with a target temperature of 270°C.

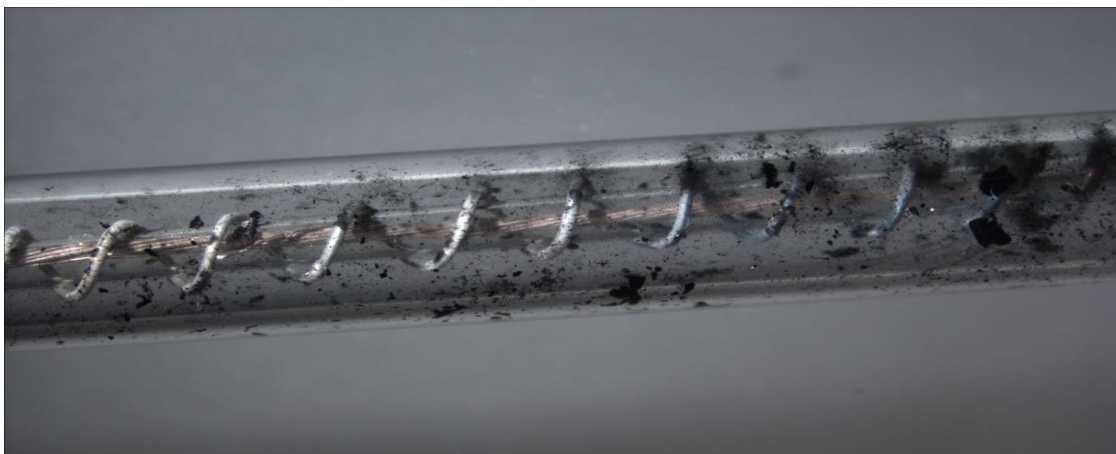


Figure 4-8: 270°C Desorption Series HSA-SPME Device After 100 Desorptions

The HSA-SPME device used during higher target temperature desorption series was subjected to a much higher temperature (380°C) than the target temperature for the 270°C desorption series or the desorption temperatures for the remainder of the 310°C series. The HSA-SPME device in the 310°C desorption series began to show visual signs of physical degradation earlier than the HSA-SPME at 270°C, with the initial appearance of black particles on the inner glass surface, graying of the coating, and missing coating occurring at the 15th cycle. By the 50th cycle, an estimated 50% of the Carboxen/PDMS coating had turned gray, with about four of 18 coils stripped of coating. By the 110th cycle, the HSA-SPME had approximately four coils (the outermost two on each end) that appeared to still have black coating on them, while the remaining coils had either been stripped of coating, or the remaining coating had turned gray.

4.5 HSA-SPME Analyte Uptake Comparisons

4.5.1 Repeatability of Analyses

To evaluate variability, the RSD of peak area abundance data for each chemical was calculated for each geometry/flow rate combination. The RSDs of all chemicals were then averaged for each HSA-SPME device geometry/flow rate combination. None of the HSA-SPME geometries tested in this research achieved an average peak area abundance RSD below 25%. Overall, the tight coil HSA-SPME geometry had the lowest RSD values (42% at 0.1 Lpm and 60% at 4 Lpm). The relatively high RSDs likely resulted from a combination of inconsistent desorption temperatures (both spatially along the length of the coil and overall due to variations in applied amperage). There were also differences between each HSA-SPME device as a result of the manufacturing method. A table of RSDs for the results of each geometry/flow rate combination can be found in Appendix B.

4.5.2 Comparison of Sampling Flow Rates

4.5.2.1 Analyte Recovery

Evaluation of analyte recovery for the two air sampling flow rates showed an advantage to the 0.1 Lpm sample rate in most cases. In Figure 4-9, data points above 0 on the y-axis indicate greater analyte uptake at 0.1 Lpm, points below indicate greater uptake at 4 Lpm. As the figure illustrates, when sampling a fixed volume, the lower flow rate provides higher analyte recovery for most situations.

Statistical analysis of the results supports the advantage of the 0.1 Lpm sampling flow rate *for collection of a fixed sample volume*. The geometric mean was used, in a one-way ANOVA test because of the non-normal distribution of data. The geometric

mean peak area abundance for the 0.1 Lpm samples (2.5 million counts) was significantly greater ($p < 0.001$) than for the 4 Lpm samples (1.4 million counts).

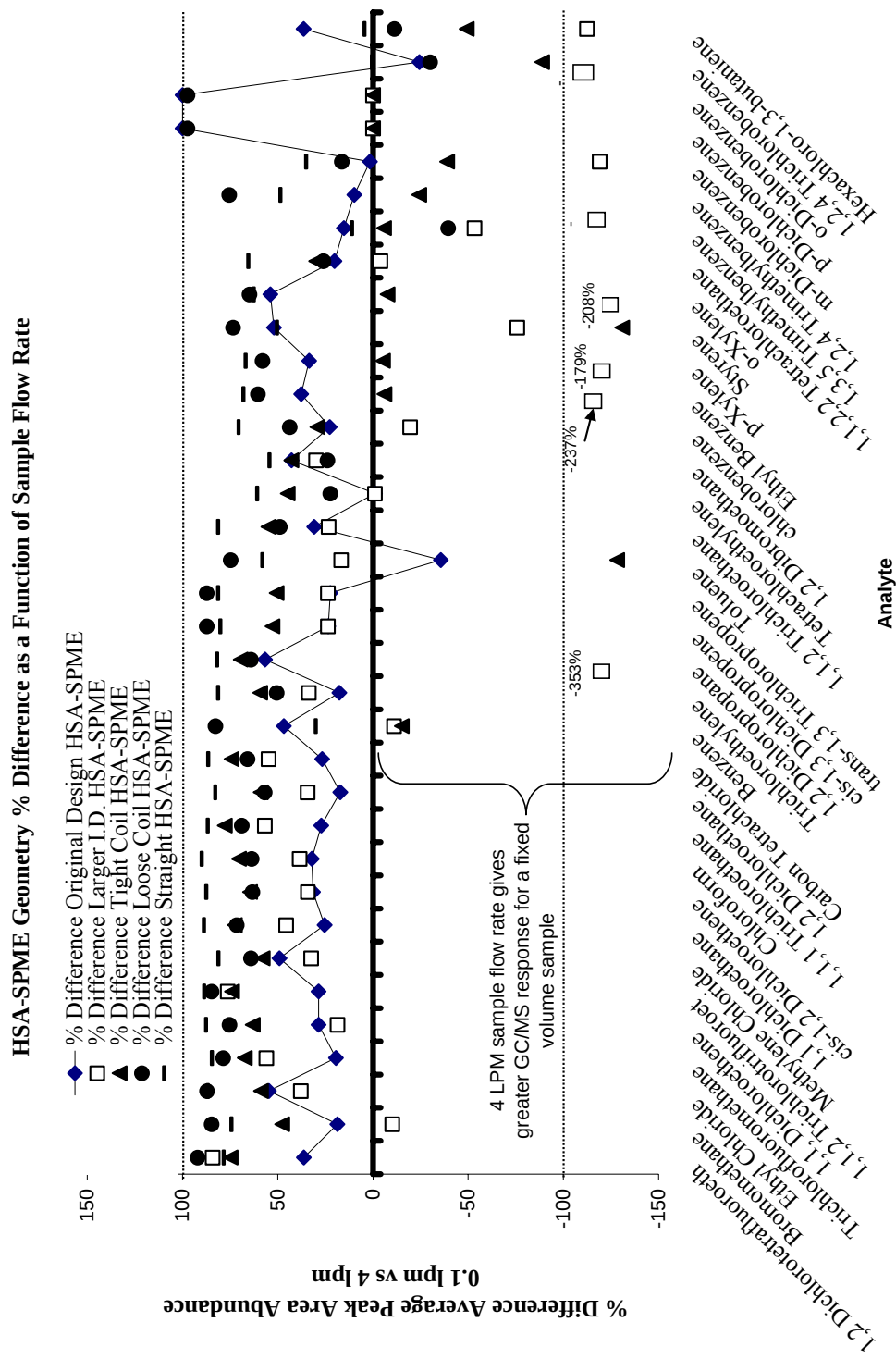


Figure 4-9: Comparison of GC/MS Response 0.1 Lpm vs. 4 Lpm for a 667 mL sample of 39-component mixture at 10 ppb_v

4.5.2.2 Extraction Efficiency

Although analyte recovery indicates an advantage to lower sampling flow rates when sampling a fixed volume at a fixed concentration consideration of extraction efficiency (mass extracted per unit time) is more applicable to field sampling, where rapid sampling times are desirable, and sampling volume is often not fixed.

One-way ANOVA analysis of the geometric mean of the mass collected per unit time showed a statistically significant ($p < 0.000$) higher extraction efficiency at the 4 Lpm sample flow rate over the 0.1 Lpm sample flow rate. Figure 4-10 illustrates the larger extraction efficiency (by an order of magnitude) measured at 4 Lpm than at 0.1 Lpm for all five HSA-SPME geometries. Thus, when the goal is to sample a fixed concentration from a given volume as rapidly as possible, sampling at the higher flow rate will yield more analyte mass extracted onto the HSA-SPME device than will lower sampling flow rates.

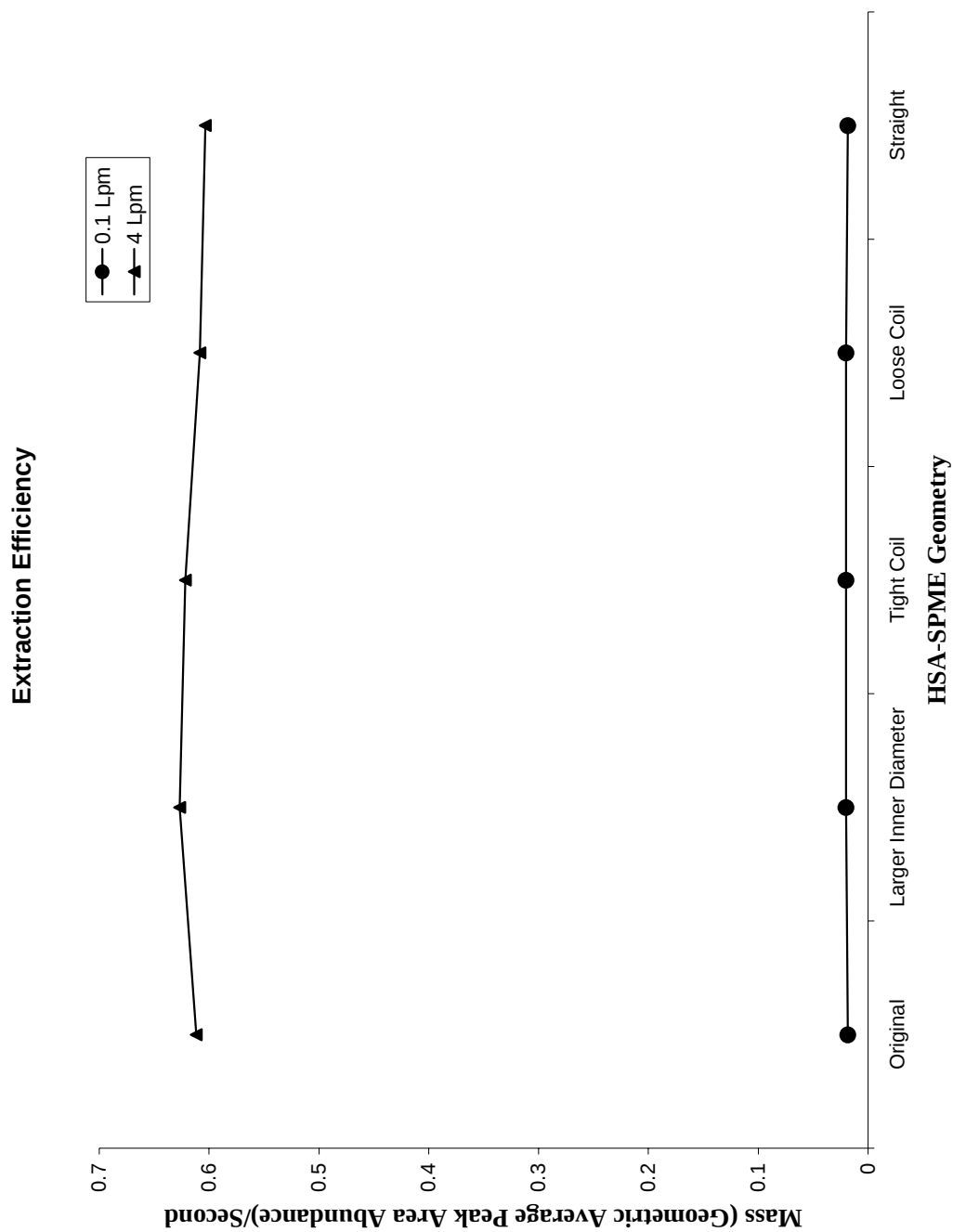


Figure 4-10: Extraction Efficiency Comparison for 5 Geometries at 2 Flow Rates

4.5.3 Comparison of HSA-SPME Geometries

Comparison of the HSA-SPME geometries was considered for each flow rate.

Figure 4-10 compares the average (arithmetic) analyte uptake for all five geometries at both flow rates. Although the average peak area abundance appears to be greater for some geometries, consideration of the error bars (1 standard deviation) highlights the variability in the HSA-SPME GC/MS results. When this variability is taken into account, differences between geometries are generally not significant.

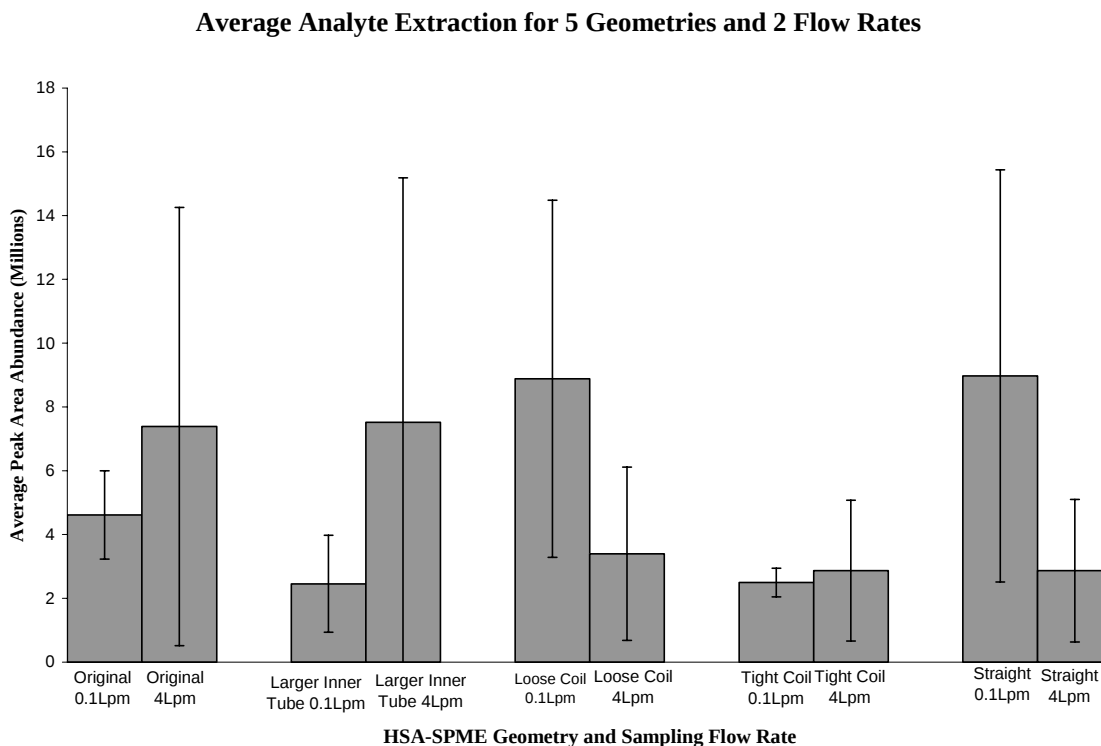


Figure 4-11: Average Analyte Extraction for 5 Geometries at 2 Flow Rates

Statistical analysis does not reveal a significant difference between the geometries.

A univariate analysis of variance reveals no significant difference between either geometry ($p < 0.893$) or the combination of geometry and flowrate ($P < 0.119$).

Comparing the geometries within the two flow rates using ANOVA comparisons of the

lognormal data shows no significant difference between geometries within the 0.1 Lpm sample flow rate ($P < 0.234$) or the 4 Lpm sample flow rate ($P < 0.601$).

5 Discussion and Conclusions

5.1 HSA-SPME Air Sampling Device

The main objective of this research was to determine if the analyte uptake per unit time of an HSA-SPME device was influenced by geometry or was the improvement in analyte uptake of HSA-SPME over commercial SPME solely a result of increased sorbent surface area. The performance characteristics of the devices were evaluated for their durability after repeated desorption cycles, their ability to extract analytes from a mix of 39 compounds under two different flow rates, and their ability to desorb captured analytes into a detector. Analyte extraction from a fixed volume was evaluated for sample flow rates of 0.1 Lpm and 4 Lpm for all five HSA-SPME geometry configurations.

The lower flow rate resulted in a statistically significantly higher analyte recovery for all geometries. This is expected, because the lower flow rate gives a longer contact time between the Carboxen/PDMS coating and the sample mixture, resulting in more analyte diffusing to the coating. Comparison of the five geometries showed no significant difference between the analyte recovery for the different geometries.

The higher sample flow rate resulted in a statistically significant extraction efficiency for all five HSA-SPME device geometries. Since extraction efficiency measures performance of the sampling device under constraints likely to encountered by a field sampler (i.e. sampling a large volume of air as quickly as possible), this result indicates that field sampling using the HSA-SPME device should be conducted at as high a flow rate as constraints (sampling pump strength, environmental conditions) allow.

Evaluation of the durability of the HSA-SPME devices was based on desorptions at targeted temperatures of 270° and 310°C. The HSA-SPME devices under both conditions showed signs of extensive physical degradation after 100 desorptions, with the onset of physical degradation coming earlier at the higher targeted desorption temperature. The overall ability of the HSA-SPMEs to extract and desorb analytes did not appear to undergo similar degradation, as overall analyte extraction did not appear to decrease, even after 100 desorptions. Physical degradation of the Carboxen/PDMS may not be related to the ability of the HSA-SPME to extract and desorb analytes.

5.2 Application

The HSA-SPME device has been shown able to detect analytes at a level lower than commercial SPME for dynamic sampling of trace level VOCs in air. (Ramsey 2004) In addition, the HSA-SPME is internally heated, thus potentially reducing the power requirements for field use over commercial SPME. HSA-SPME could be integrated into field instruments to allow military personnel and emergency responders to rapidly detect trace levels of chemical warfare agents and TICs in situations where expediency and sensitivity are critical. HSA-SPME could also be applied to law enforcement and security operations, detecting targets such as human remains, narcotics, and explosives. The fact that no significant difference between the analyte capture abilities of the different geometries tested in this study suggests that developers of the HSA-SPME to focus on improvement of other aspects of the design. These might include selection of HSA-SPME geometries that are more easily manufactured, require less power to thermally desorb, or are more compact and thus more easily integrated into a small, field-use instrument.

5.3 Study Limitations

Manufacturing of the HSA-SPME devices: The HSA-SPME devices were individually manufactured by hand, resulting in an unquantified degree of variability between devices of supposedly similar geometry. In addition, only two HSA-SPME devices of each geometry (except the original geometry) were available for testing; this limited number hindered evaluation of the consistency of HSA-SPME analyte uptake between devices of the same geometry.

Control of the desorption temperatures: The variations in desorption temperatures, both along the surface of each device as well as between different devices, is believed to have introduced a large degree of variability to the experiments.

5.4 Future Research

Ongoing improvement to the HSA-SPME concept will allow greater understanding of the abilities and limitations of the HSA-SPME. This will, in turn, enable eventual integration of the HSA-SPME into a reliable, field-portable instrument.

1. HSA-SPME Desorption Temperature Control: Develop a method to precisely control repeatable desorption temperatures to fully optimize the potential of HSA-SPME.

Temperature control would allow the use of various sorbent coatings, effective desorption of analytes, greater useable life cycle of each device, and eventual use of HSA-SPME for quantification as well as detection.

2. Flow Characterization: Perform flow visualization techniques or flow modeling for the HSA-SPME devices. Assessment of whether the flow is turbulent or laminar will facilitate a more thorough understanding of the kinetics of the mass transfer to and from the sorbent coating, and will be important in efforts to use HSA-SPME for analyte

quantification. In addition, flow characterization to quantify pressure loss through an HSA-SPME will be needed to optimize sampling pump selection.

3. Alternative HSA-SPME Coatings: Variations in the composition and characteristics of HSA-SPME coating may yield desirable results. In addition to coating materials other than Carboxen/PDMS, variations in coating thickness could be examined.

4. HSA-SPME for Quantification of Analytes: Although Carboxen/PDMS is not considered the optimal coating for quantification of analytes, HSA-SPME with other sorbent coatings and repeatable desorption temperatures could be used to quantify analytes.

Appendix A Thermal Imaging Data

Data used to determine attenuation of temperature measurements listed below.

Observed Temperature Through Glass, °C	Observed Temperature, No Glass, °C
142	194
149	215
169	236
174	219
179	250
195	261
197	254
218	299
225	290
236	316
245	328
249	316
257	350
265	363
271	354
283	383

Table A-1: Observed Temperatures With and Without Outer Borosilicate Glass

Observed Temperatures Through Glass vs. No Glass

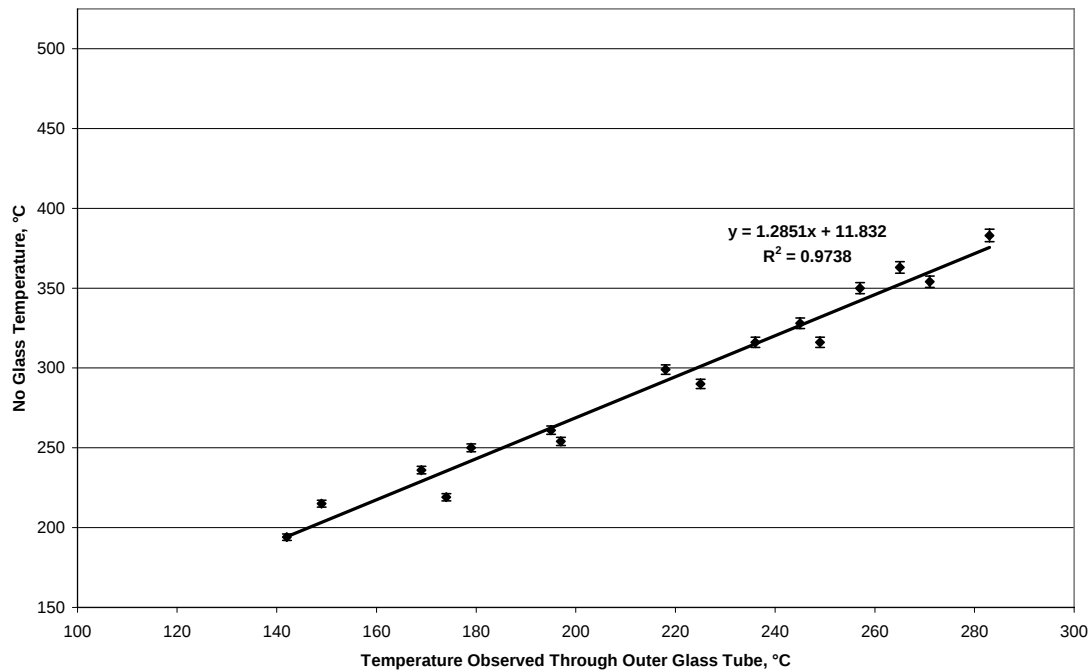


Figure A-1: Observed Temperature With Glass vs. Without Glass

Appendix B

Relative Standard Deviations

Chemical	0.1 LPM Sample Flowrate						4 LPM Sample Flowrate				
	Initial Design 0.1LPM	Larger Inner Tube 0.1LPM	Loose Coil 0.1LPM	Tight Coil 0.1LPM	Straight 0.1LPM		Initial Design 4LPM	Larger Inner Tube 4LPM	Loose Coil 4LPM	Tight Coil 4LPM	Straight 4LPM
1,2 Dichlorotetrafluoroe	58	50	80	175	208		172	71	160	90	141
Bromomethane	63	45	111	21	104		98	159	80	96	88
Ethyl Chloride	199	60	231	50	118		171	108	90	49	67
Trichlorofluoromethane	79	47	51	22	115		114	44	52	22	75
1,1, Dichloroethene	79	69	49	47	95		105	69	57	48	57
1,1,2 Trichlorotrifluoroe	79	56	75	69	98		104	55	84	52	79
Methylene Chloride	53	49	64	72	101		79	77	86	29	67
1,1 Dichloroethane	86	52	44	67	92		122	44	77	27	45
cis-1,2 Dichloroethene	83	44	42	40	88		129	34	57	29	50
Chloroform	80	39	45	37	86		108	34	63	37	77
1,1,1 Trichloroethane	88	42	41	40	81		132	26	74	33	69
1,2 Dichloroethane	75	40	37	36	78		95	30	57	34	70
Carbon Tetrachloride	87	60	56	35	79		127	41	78	19	69
Benzene	166	68	124	33	101		155	83	75	70	135
Trichloroethylene	75	40	40	35	77		82	35	57	20	74
1,2 Dichloropropane	101	37	47	38	86		97	211	62	50	52
cis-1,3 Dichloropropene	62	40	185	39	83		82	34	61	14	53
trans-1,3 Trichloroprop	61	40	185	37	81		81	34	61	11	57
Toluene	55	82	115	29	69		162	83	33	141	90
1,1,2 Trichloroethane	52	40	32	38	85		77	32	62	9	69
Tetrachloroethylene	49	23	21	29	54		66	50	27	36	57
1,2 Dibromoethane	56	32	58	34	60		72	42	65	14	74
chlorobenzene	53	41	50	35	72		67	61	21	27	62
Ethyl Benzene	92	21	105	31	69		103	180	27	71	58
p-Xylene	87	17	109	29	68		106	164	31	59	66
Styrene	166	37	198	30	82		143	103	83	138	90
o-Xylene	133	17	106	29	66		100	167	33	65	60
1,1,2,2 Tetrachloroetha	64	32	82	33	79		75	22	33	21	81
1,3,5 Trimethylbenzene	31	51	103	29	62		19	28	83	32	57
1,2,4 Trimethylbenzene	70	28	123	27	84		87	126	50	40	53
m-Dichlorobenzene	56	35	116	34	59		64	76	68	47	66
p-Dichlorobenzene	245		245					245	245	245	
o-Dichlorobenzene	245		245					245	245	245	
1,2,4 Trichlorobenzene	57	63	93	45	51		75	84	87	76	68
Hexachloro-1,3-butanic	56	36	61	31	76		25	95	27	97	84
Average RSD	90	43	96	42	85		100	86	73	60	71

Table B-1: Peak Area Abundance (millions) Relative Standard Deviations

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Curriculum Vitae

Captain Robbie L. Wheeler graduated from the University of Minnesota in 1997 with a Bachelor's of Mechanical Engineering Degree. During college, he worked as a quality control technician at 3M in Woodbury, MN, and as a Test Engineering Intern at TEAM Industries of Bagley, MN. Upon graduation, he joined the United States Air Force, where he served as a Bioenvironmental Engineering Technician at Minot Air Force Base until receiving his commission as a Bioenvironmental Engineer in 1999. Capt Wheeler's military service has included Bioenvironmental Engineering positions at Holloman Air Force Base, NM, Kunsan Air Base, Korea, and Offutt Air Force Base, Nebraska. He served as the Readiness Flight Chief and then the Base Bioenvironmental Engineer at Lajes Air Base, Portugal. In 2003, he was the Preventative Aerospace Medicine Team Chief at Thumrait Air Base, Oman, during OPERATIONS ENDURING FREEDOM and IRAQI FREEDOM. He was a Distinguished Graduate from both Officer's Training School and Squadron Officer's School. In 2005, Captain Wheeler entered the Graduate School of Biomedical Sciences and Public Health, Uniformed Services University. Upon graduation in June 2007, he will be assigned to the Operations Sustainment Branch of the Air Force's Ranges and Airspace Division at the Pentagon.