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METHOD DEVELOPMENT OF AN ADAPTIVE AIR SAMPLING DEVICE FOR USE WITH PORTABLE GAS CHROMATOGRAPHY IN FIELD FORENSIC ANALYSES

presented by

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METHOD DEVELOPMENT OF AN ADAPTIVE AIR SAMPLING DEVICE FOR USE WITH PORTABLE GAS CHROMATOGRAPHY IN FIELD FORENSIC ANALYSES

By

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ABSTRACT

METHOD DEVELOPMENT OF AN ADAPTIVE AIR SAMPLING DEVICE FOR USE WITH PORTABLE GAS CHROMATOGRAPHY IN FIELD FORENSIC ANALYSES

By

Scott Alan Ramsey

The RVM Adaptive Air Sampler injection system, developed by RVM Scientific, Inc., has been evaluated as a potential improvement over conventional air sampling systems. This prototypical system utilizes both solid sorbent microtrap and solid phase microextraction (SPME) technology in a unique design. The primary air concentrator is a self-heating, SPME-coated nickel alloy wire contained in the lumen of two concentric tubes, creating a restrictive airspace. The secondary concentration stage incorporates a microtrap containing 10-mg of solid sorbent which provides rapid injection of the ensuing vapor plug into a GC for analyte separation and quantitation. The two-stage sorbent design enables dynamic, high-flow (4-5 L/min) air sampling which has not previously been investigated with SPME technology. Laboratory analysis of a 39-component, U.S. EPA compendium TO-14A gas mixture at concentrations of 0.5-150 ppbv (where ppbv = 1 part in 10^9 by volume) by the RVM injection system illustrated linearity with benchmark data in terms of sensitivity at low ppt(v) levels, detection limits, and desorption efficiency. The RVM Adaptive Air Sampler provided several advantages over a conventional air concentration system in terms of sampling flow rate, preconcentration time, and power consumption.

To Tessa, my beautiful and loving wife

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CHAPTER 1 – INTRODUCTION

1.1. Purpose of Research

With the advent of global and domestic terrorism within the last decade, there has risen a critical need to perform on-site and real-time air analyses for the detection of various volatile organic compounds (VOCs) which may be used in terrorist attacks. Although more expensive to produce and acquire, chemical warfare (CW) agents are a serious threat, but more readily available "toxic industrial materials" (TIMs) such as hydrogen cyanide and phosgene, mass-produced by many companies in the United States and internationally, are easier to obtain [1]. Released into the environment, TIMs have the potential to cause injury and irreparable, long-term health problems to large numbers of people. This situation necessitates the development of a portable, rapid air sampling system that will accurately assess volatile TIMs components which will provide crucial information to help enable law enforcement agents to execute a threat-specific response.

The detection of human remains, drugs, and explosives by police canines is also an important component of investigative law enforcement. Cases involving missing persons have been resolved by the ability of trained dogs to store a victim's distinct chemical signature, and track this specific odor to crime scene locations or buried remains. Canines have also been trained specifically to discern human scent on living persons and have been successful in matching criminal suspects to proffered scent evidence. Because there are no national

qualification standards for human scent-discriminating canines, scent detection is not currently accepted as evidence, although positive responses are generally accepted as probable cause by court systems [2]. It would therefore be beneficial for law enforcement to mechanically reproduce the canine's ability to extract and detect VOCs from air to determine target compounds and their respective concentrations. Rapid, *in situ* detection and analysis at this level requires the ability to extract volatile components from large volumes of air at high flow rates (L/min), assuring representative sampling in a minimal amount of time. This detection system could be integrated with a portable detection device (*i.e.* gas chromatography coupled with mass spectrometry, GC/MS) to be used with scent-discrimination canine teams in the field. During a search, the handler can utilize the detection device for providing confirmatory information of positive responses from canines at the specified area of interest (*i.e.* scent evidence or buried remains).

Improvements have been made in the miniaturization of the laboratory versions of the few commercial GC/MS systems available for field use, but they remain limited by substantial power consumption, and lengthy sampling times using headspace and/or low flow dynamics (mL/min). The extra time needed for sampling reduces to total number of samples that may be obtained over a given period, and this may be crucial in emergency situations. Field-portable GC/MS systems currently utilize in-house solid sorbent microtraps and/or valve loops that require long extraction times due to their low sample capacity. There are also no field-portable systems which currently have the ability to apply both preliminary

and confirmatory testing to an air sample, which could provide valuable court-defensible data. These shortcomings can be addressed by implementing an air sampling device that incorporates solvent-free extraction that minimizes sample preparation times and power consumption for efficient operation [3].

Solid-phase microextraction (SPME) coupled with laboratory GC/MS has been demonstrated to perform solvent-free extraction of volatiles from the headspace of forensic specimens including drugs and explosives, and shows potential in developing an understanding of the complicated process of canine odor detection [4]. SPME has proven to be useful in a wide variety of analytical applications, mainly due to its excellent sensitivity, cost effectiveness, and reproducible results. In its current syringe-based design, however, it remains limited by lengthy extraction times and requires bulky, power-thirsty thermal injection ports to passively heat and desorb analytes from the SPME fiber. Therefore most field sampling is performed via grab sampling using such materials as Tedlar bags, vacuated stainless steel canisters, charcoal strips, or desorption tubes, and analyzed in a laboratory setting.

This research project is part of a continuing endeavor to provide portable instrumentation for the Federal Bureau of Investigation (FBI) in the effort to perform rapid and reliable volatile chemical analyses in the field. The first phase of this project was the method development of the RVM low thermal mass (LTM) GC (RVM Scientific, Inc.) which proved to offer rapid (>100° C/min temperature ramps) yet highly controllable and reproducible chromatographic separations unmatched by conventional GC systems, operational at field-deployable size and

power [5, 6]. The subsequent phase of this project involves the development of a method which will characterize the RVM Adaptive Air Sampler air injection system as an effective alternative to headspace SPME and other forms of grab sampling used today. This system utilizes both SPME and solid phase extraction (SPE) technology in a design specific for sampling at high flow rates (L/min). Trace-level volatiles may be extracted from large volumes of air using only a fraction of the time required for traditional SPME headspace sampling, while retaining laboratory-level sensitivity. This extraction speed is representative of canine olfactory capabilities which is desired for rapid detection [7]. The air sampler requires no cryogen or extraneous solvents, making it amenable to field portability. The RVM Adaptive Air Sampler, coupled with proven LTM-GC technology, has the potential to provide rapid, cost-effective, and reproducible air sampling and analysis in the field while retaining laboratory-level performance.

To determine the system's capabilities and limitations, the RVM Adaptive Air Sampler was evaluated on a conventional Agilent 6890/5973 GC/MS laboratory system generally employed by many forensic and environmental laboratories. Comparative benchmark data was obtained using the Entech 7100 Air Concentrator coupled with a resistively heated LTM-GC column (installed on a retrofit oven door on the Agilent GC). Upon completion of baseline evaluation, the RVM Adaptive Air Sampler injection system was evaluated under similar conditions. A 39-component, U.S. EPA compendium method toxic organics (TO-14A) hydrocarbon gas mixture was analyzed under optimal extraction and desorption conditions using the laboratory Entech 7100 Air Concentrator system

for comparison against varying RVM experimental conditions. Performance of both systems was evaluated in terms of linear dynamic range, sensitivity, limits of detection, desorption efficiency, and power consumption.

1.2. Solvent-free Sample Preparation

The operating principle behind any sample preparation method is to partition analytes between the sample matrix and an extracting phase [8]. Ideal analytical separations, especially those performed in field situations, should be rapid with minimal sample loss, simple to perform, and cost effective. For sampling trace-level organic species in the field, a number of procedures can be applied. Presently, many analytical laboratories perform liquid-liquid extractions (LLE) such as the Soxlet method, requiring large volumes of solvent and 2-24 hours of sample preparation. Acceptable recoveries are obtainable from the procedure, but at the expense of hazardous air pollution from evaporated solvents and additional concentration procedures. This cumbersome and time-consuming process was the rate-determining step in the overall analytical process, and impractical for field implementation.

Solvent-*free* sample preparation methods have been introduced over the last three decades and have gained wide support from the scientific community for enabling more efficient, laboratory throughput by reduction of sample preparation times while retaining analyte sensitivity and selectivity. These methods are also the driving force behind field sample preparation. Solvent-free

extraction techniques are classified into three categories: gas phase, membrane, and solid sorbent extractions.

1.3 Gas Phase Extraction

1.3.1 Headspace Extraction

Static headspace (SHS) extraction is a widely used method for the recovery of volatiles. This method requires no solvents and little sample preparation, but may necessitate bulky instrumentation, depending on sample matrix type. For liquid matrices, the volatile components in a sample are allowed to equilibrate with the air above the sample (the headspace). The analytes must have a vapor pressure greater than or equivalent to the matrix for partitioning into the headspace. Equilibration of analytes between the matrix and headspace occurs after a period of time, by which a portion of the headspace can be sampled directly for on-column GC focusing or GC/MS analysis.

The SHS method can be applied to field samples, whereby a sampling instrument can "sniff" directly above the area in question. Sampling in this manner is rather low in sensitivity since trace-levels of analyte (ppb or sub-ppb) in a dynamic environment cannot be detected without being concentrated to remove interferences such as air and humidity. Lizzani-Cuvelier *et al* [9] illustrated that compound recoveries from olive oil by SHS were poor, even at various temperatures (40-110°C) and extraction exposure times (30-120 min.). Bicchi *et al* [10] tested the relative efficiencies of SHS and seven other solvent–free extraction techniques for 16 components found in Arabica coffee. It was

discovered that the SHS method extracted 1-2 orders of magnitude less than the average recovery for all other techniques.

Dynamic headspace methods are an improvement over static headspace methods and involve the addition of a gas purge of volatiles into a second trapping stage which concentrates the analyte for effective GC separation. In this "purge & trap" technique, air, nitrogen, or helium is forced through an aqueous sample matrix at ambient temperature, and the resulting effervescence removes volatile components from the sample which are collected in a cold (cryogenic) or sorbent trap. Unlike the SHS method, dynamic headspace extraction is an exhaustive approach which requires complete removal of analyte for quantitation, and thus realizes higher recoveries. U.S. Environmental Protection Agency (EPA) methods 601 and 624 utilize this proven method for quantitation of volatile petroleum contaminants in groundwater, and chlorinated pesticides in potable water, respectively. Le Pape *et al* [11] successfully isolated 16 volatiles of the red algae *Palmaria palmate* by crushing and diluting the seaweed for purge and trap dynamic headspace extraction, at recoveries comparable to simultaneous distillation-extraction (SDE), a popular yet cumbersome and artifact-producing method. Drawbacks to dynamic headspace extraction include long purge times (10-30 minutes per sample), contamination of sample transfer lines due to foaming from purging undiluted sample, and carryover signal from previous analyses.

1.3.2 Supercritical Fluid Extraction

The air pollution problems associated with the use of chlorinated organic solvents in liquid-liquid extraction (LLE) was addressed in the mid-1980s with the advent of supercritical fluid extraction (SFE). It was discovered that many semi-volatile organic compounds (SVOC) of analytical interest were soluble in certain solvents once the temperature and pressure exceeded the critical point of the solvent. The critical point is where the solvent is neither liquid nor gas, but a "dense gas" containing physical properties characteristic of both phases that favor higher extraction efficiencies. Supercritical fluid exhibits viscosity, surface tension, and diffusion properties comparable to a gas, enabling flow through pores of a sample and penetrates crevices of a material at a faster, more efficient rate than a liquid. It also favors the higher solubilizing power found in liquid matrices, adding solvating characteristics normally not found in a gaseous phase. Therefore contaminated soils, sludges, ash, and other material can be easily analyzed by SFE for the presence of SVOCs.

Many supercritical fluids are gases at ambient temperature and pressure (ATP). Recovery therefore becomes straightforward when compared to organic liquids, which must first be evaporated (*ergo* the pollution-related problems) to concentrate the analyte and thus contribute to lower recoveries. The supercritical fluid can be separated from the analyte by simply releasing the pressure. For volatiles analysis, the analyte stream can be bubbled through a suitable solvent for the analyte, which will dissolve in the small volume of solvent [12]. Using supercritical carbon dioxide as the solvent, Seitz *et al* [13] proved this

type of SFE/Purge & Trap procedure to be more effective in extracting 80 volatile compounds (C_3-C_6) from whole and ground grain samples than by purge & trap methods alone. Wong *et al* [14] showed that air toxicant extracts could be recovered from air sampling adsorbents by SFE without additional sample concentration steps. However, lower molecular weight volatiles, such as bromochloromethane ($<C_2$) were lost due to volatilization in the expanding CO_2 stream during decompression of the supercritical solvent. The implementation of SFE methods is preferred when conducting extractions of analytes of medium-to-low volatility, but do require extraneous concentration to ensure recovery of high-volatile components, such as C_1-C_2 halocarbons. For air analysis, SFE is best utilized in tandem with grab sampling by means of a portable adsorbent bed and a final purge and trap concentration method.

The only known portable supercritical fluid extractor has been developed [15] for the Federal Bureau of Investigation's Hazardous Materials Response Unit, for the extraction of hazardous materials from investigation sites. This device remains in the beta-testing stages, however, and requires lengthy extraction procedures and heavy CO_2 tanks which increase instrument weight.

1.4 Membrane Extraction

A faster, more portable alternative to gas phase extraction is the removal of volatiles through use of membrane material which can be directly coupled with GC or GC/MS for rapid, real-time monitoring. In membrane extraction, VOCs

selectively diffuse out of an air or water sample matrix through a hydrophobic polymer membrane into a nitrogen gas stripping phase. The polymer most associated with the removal of VOCs and SVOCs from air is a hollow-fiber membrane composed of silicone rubber [16]. It is more widely used than the sheet membrane predecessor because it offers a higher ratio of surface area to volume, which allows more efficient extraction [8]. Semi-volatile compounds may also be extracted with the use of liquid solvent streams, however at the expense of longer elution times and loss in sensitivity.

The stripping phase containing the extracted organics is directly interfaced with a GC or GC/MS, or is passed through an intermediate concentration stage such as a cryotrap or an adsorbent-filled trap. These traps are designed to further enrich volatiles and quickly desorb them as a vapor plug into the GC for a more efficient separation. Pawlizsyn *et al.* [17] showed that this membrane extraction with sorbent interface (MESI) approach provides a useful tool for real-time air monitoring of biogenic volatile organic compound (BVOC) emissions released by freshly cut branches from a *Eucalyptus dunnii* tree. Here, an automated sampling system was developed using a polydimethylsiloxane (PDMS) membrane coupled to a dual-sorbent trap containing Tenax solid sorbent and PDMS for trapping semi-volatiles and BVOC, respectively. It was demonstrated that BVOC concentrations diminished over a 24-hr sampling period, but semi-volatile emissions increased over the same period. It was observed that applying a higher stripping gas flow increases the extraction

efficiency of the membrane by enhancing analyte mass transfer between membrane and sorbent.

Hauser and Popp [16] optimized a method incorporating thermodesorption/GC with membrane extraction of VOCs from a water matrix. Detection limits for nine compounds had a range of 0.02-0.1 µg/L, and quantitative results corresponded well with those achieved with conventional headspace-GC/FID. The rate limiting factors for overall analysis however were a 30-minute enrichment time required for optimized system performance, and the decreasing extraction rates for volatiles whose boiling points approached 220°C. The method could not be used for the analysis of semi-volatile compounds, owing to slow diffusion across membrane boundaries.

1.5 Sorbent Extraction

1.5.1 Solid Phase Extraction

As opposed to liquid and gas phase extraction techniques, trace concentration from both air and water matrices can be more easily accomplished by trapping on a solid sorbent support to preconcentrate the analytes of interest to a concentration sufficient for analysis. Adsorbents commonly used for this method include charcoal, macroreticular porous polymers, polyurethane foams, bonded-phase materials, and ion-exchange resins [18]. Different sorbent materials are designed for the collection of specific organic chemicals based on the predominant functional group, polarity and/or molecular weight of the analyte. Some common characteristics of sorbent material include large sample capacity,

large breakthrough volume, and high affinity for non-polar organics coupled with its hydrophobicity toward water and humidity. Unlike traditional solvent extraction (LLE), solid phase extraction is simple to perform and requires less overall time than other methods, uses little or no solvent, and is relatively inexpensive.

Solid Phase Extraction from Water Matrices

The use of bonded-phase sorbents for the solvent extraction of semi-volatiles from water samples has gained wide acceptance as a valid environmental laboratory technique in the past two decades. Here, non-polar C_5 - C_{18} carbon chains are dispersed in a polymer coated on flat disks or contained in tube cartridges. In this method, an aqueous sample containing suspected SVOCs is passed through a SPE disk or cartridge in which the compounds of interest are retained on the polymer coating. Retention is driven by hydrophobic interactions from the net repulsion between solute and solvent (water), affinity for solute to the non-polar hydrocarbon phase on the SPE support, and selective polar interactions [18]. Using a small quantity of organic solvent, the analytes are flushed from the SPE support into a collection tube, and further concentrated by evaporating the solvent with a nitrogen gas stream to a quantity amenable for instrument detection. Enrichment factors of $10^3 - 10^7$ can be obtained by this method [18]. The procedure works well for exhaustive extraction (complete analyte removal) for quantifying SVOC in drinking water, which normally contains minimal amounts of interfering compounds. Recoveries are usually between 85-100%. However, waste water and aqueous biological

matrices may contain particulate matter (i.e. humic material) which can clog the sorbent material and diminish overall analyte recovery.

Although the use of solid phase extraction for liquid matrices has lessened the need for large amounts of solvent used in LLE, and actual extraction times are relatively short (< 1 hr), extensive preparation procedures increase the total extraction time and can require as much as 4 hours to perform up to eight simultaneous extractions using automated instrumentation. The SPE sorbent must be conditioned with solvent prior to use to remove any manufacturing contaminants. Conditioning may not remove all contaminants, such as bis-(ethylhexyl)-phthalate, a plasticizer found in manufacturing materials, which is also a target analyte for U.S. EPA method 625.2 (pesticides in drinking water). Extracts require drying with sodium sulfate to remove residual water. Depending on extract volume, the solvent may need to be evaporated further to achieve proper analyte concentration. The technique is limited to semi-volatile compounds with boiling temperatures substantially above that of the desorption solvent temperature [8].

Solid Phase Extraction from Air Matrices

The isolation and concentration of volatile organic compounds in air can be performed efficiently with solvent-free solid phase extraction. Because these high vapor pressure-organic species are normally encountered at the ppb and sub-ppb levels in the environment, preconcentration from a large sample size is required to achieve detectable levels. Traps made with solid sorbent materials mentioned are an effective means to accomplish this task. When an air stream

containing organics passes through a trap composed of a solid sorbent material at ambient temperature, the chemical vapors become adsorbed onto the support while air and humidity pass through, effectively concentrating VOCs over a given period of time. The VOCs are released from the sorbent by ballistic resistive heating of the trap as it is back-flushed with a carrier gas. The carrier gas injects this concentrated "plug" of chemical vapor onto the head of a GC column for chemical separation. The range of compounds to be studied usually includes molecules of varying volatility and polarity. Therefore the ideal sorbent would permit large breakthrough volumes for light gases while providing rapid quantitative desorption of larger molecules [19].

There is currently a wide variety of commercially available sorbent materials, each with its own affinity for certain chemical compounds. Traps can be constructed with single or multiple sorbencies, depending on the molecular weight and polarity of the compounds of interest. In the instance of multiple sorbents, beds are arranged in the trap in order of increasing sorption activity and decreasing mesh size from the sampling inlet. During the sampling phase of a purge and trap method, compounds of higher volatility and lower molecular weight pass through the larger mesh solid sorbents of the sorbent trap, but are trapped by succeeding smaller mesh beds. During desorption, the trap is backflushed by helium gas so higher molecular weight compounds do not come into contact with the strongest adsorbents [20]. Optimum desorption conditions will theoretically produce high analyte recoveries, sharp, chromatographed peaks, and accurate quantification with little to no carryover between runs.

The Microtrap: Extraction of Volatiles in Air

The efficiency of VOC trapping by solid sorbents has expanded their use in gas chromatography as miniaturized versions in portable instrumentation. These "microtraps" are produced by packing capillary or small-bore tubing with a solid adsorbent [21]. An on-line microtrap (OLMT) can effectively bypass the conventional GC injection port to make direct injections onto the GC capillary column. Trapped and concentrated organics are released by ballistic heating of the microtrap and swept onto the GC column by carrier gas. Due to small dimension and careful choice of adsorbents, microtraps have enabled the concentration and subsequent detection of analytes at the ppb and sub-ppb level from voluminous amounts of air without solvents or the need for cryogenic refocusing [22], a frequently incorporated procedure in laboratory air concentrators to aid in trapping lighter molecular weight VOCs and for removing moisture.

The implementation of the microtrap with gas chromatography has increased its use in on-site and near real-time monitoring of VOCs without the need of transporting gas samples to the laboratory for analysis [23]. Mitra *et al* [23] showed that a solid sorbent microtrap (L = 15 cm) coupled with a membrane extractor could effectively trap VOCs from catalytic incinerator exhaust over a wide linear dynamic range (sub-ppb to ppm levels), and maintain system response stability after 140 injections of a 1 ppm toluene standard (RSD 4%) at a 10 mL/min sampling rate. The microtrap was able to sample and desorb in 3-minute intervals, providing near-real-time and continuous chromatographic

analysis. Bassford *et al* [22] used a microtrap packed with three solid sorbents of 3-5 mg each to sample atmospheric halocarbons (oceanic and pollutant) in one-hour intervals continuously over a one month period. The analytical system was able to detect and quantitatively measure a wide range of halocarbons in 0.2 L air samples at concentrations as low as 0.1 ppt(v). The continual monitoring of the halocarbons in the field provided information on short-term fluctuations in concentration which could not otherwise be assessed by grab sampling, which requires transportation of samples to a laboratory for analysis and can cause halocarbon degradation if storage is required.

The use of solid sorbent materials for the extraction of VOCs has increased the versatility of air sampling protocol to the point where analysis can be performed in the field with use of portable gas chromatography or GC/MS. However, for complete desorption of captured vapor, the microtrap is limited to a small internal volume which can be rapidly heated to sufficient desorption temperatures in an amount of time short enough for tight vapor injections. This small volume severely limits the sampling flow rate to the mL/min range by which extraction can take place. Sampling with the microtrap therefore requires a long amount of time (10 min – 2 hrs per sample) to obtain representative analyte mass loading from a relatively large volume of air. Thus, sampling by microtrap alone may still be the limiting factor in performing air analysis in the field.

1.5.2 Solid Phase Microextraction

In 1987, Pawliszyn and Liu [24] discovered that several micrograms of chemicals of varying volatility could be easily desorbed from the chemically modified surface of a fused silica optical fiber by laser desorption for rapid GC injection. In a follow-up study in 1990, Pawliszyn and Arthur [25] created the technique of solid phase microextraction (SPME) by illustrating how a fused silica fiber, coated with stationary phase, could adsorb analytes from a liquid matrix and rapidly desorb them on-column via heated GC injection port . In the analysis, a 1-cm length fused silica fiber was coated with a polyimide stationary phase (171 ± 5 μm thickness), and placed in an aqueous sample inside a closed container. Analytes within the sample partitioned into the stationary phase during a two-minute exposure. The fiber was removed from the sample, and injected into a GC injection port via syringe which enabled rapid thermal desorption of analyte from the fiber, resulting in efficient, reproducible, on-column separations. Pawliszyn argued that SPME could retain the advantages of solid phase extraction (SPE); namely, the elimination of solvent and reduced analysis time over LLE methods, as well as surpass SPE extraction and desorption efficiencies by eliminating the need to perform exhaustive extractions to acquire quantitative analytical results. Solid phase microextraction, unlike SPE, only requires that the analyte establish equilibrium between sample matrix and stationary phase. The amount of time required to establish equilibrium depends on the diffusion properties and distribution constant of the analyte.

The successful implementation of SPME in water analysis broadened the scope of its use for other applications, including air analysis. In a preliminary study, a polydimethylsiloxane (PDMS) coating was used as the stationary phase on fused silica fiber to effectively capture atmospheric VOCs [26]. Pawliszyn in 1997 introduced the concept of extracting analyte from a dynamic airflow using SPME fibers [27]. He proved that a constant flow rate of gas mixture containing a stable concentration of analyte passing over a SPME fiber exhibited similar amounts of analyte loading for light volatiles (K ≤5000) to that of static headspace extraction over the same time period. Compounds in the headspace analysis with K ≥6000 required a doubling of the extraction time to reach equivalent loading observed with the dynamic flow analysis, since species with increasing molecular weight have decreasing rates of diffusion, where:

$$C_{air} = C_{fiber} / K \qquad (1)$$

K = analyte partition coefficient

C_{air} = concentration of analyte in air (in mg/m^3)

C_{fiber} = concentration of analyte on the SPME fiber (in mg/m^3)

Pawliszyn, using a known concentration of analyte on the SPME fiber, the known temperature, and rearranging equation (1) with the ideal gas law and Clausius-Clapeyron equations, derived the expression that determined the unknown concentration of an airborne analyte ($ppmv_{air}$):

$$ppm_{(v)air} = (C_{fiber}) \frac{R}{MWPV_f} \frac{T}{10^{((a/T)+b)}} \qquad (2)\ [27]$$

where:

R = ideal gas law constant

MW = analyte molecular weight

P = analyte vapor pressure at a known temperature T (in Kelvin)

V_f = volume of SPME fiber

$a = \frac{\Delta H^v}{2.303R}$, ΔH^v = analyte heat of vaporization

$b = \log\frac{RT}{\gamma P} - \frac{\Delta H^v}{2.303RT}$, γ = analyte activity coefficient in the fiber

Using equation (2), a battery of tests were performed to characterize calibration procedures for a VOC/SVOC gas mix using PDMS-coated SPME fibers of varying length and thickness. The results are summarized as follows:

- Upon normalization of SPME fiber lengths, interfiber analyte recovery precision was better than 9% RSD for 10 different fibers
- Intrafiber day-to-day reproducibility (n = 8) was < 9% RSD for all analytes tested
- Humidity in amounts < 95% relative humidity did not result in reduction of analyte mass loading
- Analytes with larger K values have lower limits of detection (LOD)
- Similar results were observed between SPME fiber sample loading at both laminar and turbulent flow rates

The last point indicates that the SPME method has the potential of incorporating flow rates up to the L/min maximum without compromising loading accuracy and reproducibility.

In 2003, Ciucanu *et al* [28] developed a microtrap design that incorporated SPME technology. Using a straight piece of wire (d = 0.1 mm) as support, a helical aluminum wire (d = 0.07 mm) coated with PDMS stationary phase was wrapped down the length of the straight wire at a constant pitch. The wires were then placed lengthwise in the lumen of an inert, stainless steel tube (80 mm x 0.75 mm i.d. x 0.95 mm o.d.). Desorption of the wire in the microtrap consisted of traditional resistive heating of the outer surface of the stainless steel tube, in which passive convection would internally heat the wires. Ciucanu claimed that this microtrap design increased the amount of time required to observe analyte breakthrough to ten times over that of a straight, thick-film SPME capillary trap with a similar amount and thickness of PDMS phase. It was theorized that analyte adsorption was aided by the helical design creating turbulence at low flow, increasing analyte mass transport from the air matrix to the surface of the stationary phase [28]. The experimental RVM Adaptive Air Sampler design implements a similar helical shape for the adsorbent to take advantage of turbulent flow, albeit higher flows (L/min) than the optimal 5 mL/min flow rate incorporated in the Ciucanu device.

1.6 Low Thermal Mass Gas Chromatography

A capillary gas chromatograph functions primarily to separate vaporized analyte mixtures by means of forcing them through a capillary tube whose inner walls have been coated with a polymer. This polymer is the stationary phase. The analyte vapor, moving through the column by a gaseous mobile phase, interacts with the stationary phase . The interactions are governed by analyte boiling point, vapor pressure, and molecular weight against the physical properties of the stationary phase. Since most chemical species each exhibit variations in these properties, some analytes will interact with the stationary phase more strongly than others. The analytes in the vaporized mixture can thus become separated from each other through the course of traversing the column. The analytes will emerge from the column at distinct times (retention times), and are then detected by means of various commercially available detector devices (FID, MS, etc.). By utilizing controlled temperature ramps to increase the temperature of the column during the chromatography, less volatile analyte becomes more volatile, eluting from the column earlier than if temperature was isothermal. Therefore the application of heat to the column decreases the overall analysis time, and is implemented in many GC methods used today.

Most conventional commercial benchtop GCs utilize large convection ovens to achieve stable temperatures for uniform column heating. However, their large thermal cavity and significant power consumption (> 1kW for a 0.5°C/min temperature ramp to 200°C) prohibits their use in field situations [5].

RVM Scientific, Inc. has created a GC design with reduced size and power requirements using proprietary technology [29]. This new lightweight, compact design (Figure 1.1) utilizes low thermal mass (LTM) technology which

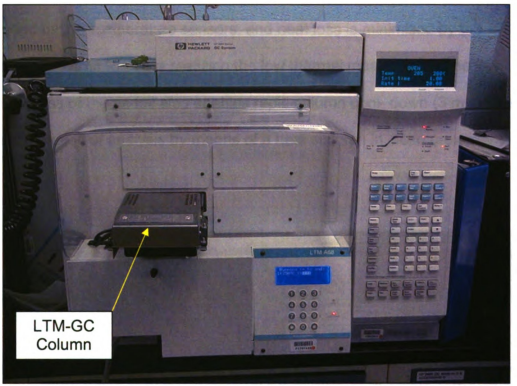

Figure 1.1. An RVM LTM A68 retrofit GC oven door and LTM GC column installed on an Agilent 6890 gas chromatograph

effectively replicates the function of a conventional GC oven, but at a fraction of power and space. Because the LTM-GC is highly efficient and small, it can incorporate fast temperature ramp rates and portability unachievable by conventional GC systems.

The concept design and ability of the LTM-GC has been previously discussed [5, 6]. The RVM device combines a commercially available GC capillary column with a ceramic filament-wrapped heating element [29]. These

ceramic filaments provide thin insulation and uniform heating up to 1200°C. Temperature sensors are also bundled with the GC column, and the assembly is tightly wound into a torus, which is then covered in tin foil (See Figure 1.2). The exchange of heat from the insulated heating element to the column is tightly controlled by the temperature sensors, and heat loss is minimized by the insulation of the tin foil, thus realizing the low thermal mass effect. The low thermal mass of the tin foil also enables rapid column cool- down (3 minutes) upon completion of analysis by means of a heat sink fan in close proximity to the column.

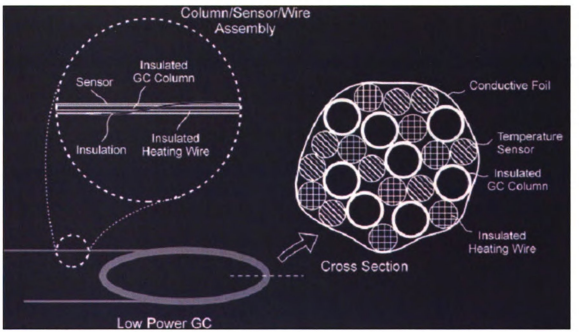

Figure 1.2. RVM Low thermal mass GC design. R. V. Mustacich, U.S. Patent 6,209,386, (2001).

The result of low thermal mass GC column technology is improved speed of analysis and sensitivity. An illustration contrasting conventional vs. low

thermal mass chromatography is shown in Figure 1.3. 1 µL injections of a 15-component aqueous alkane mixture were used as the test mix to observe differences in total run time and analyte peak height for an LTM-GC (90°C/min) vs. conventional GC (20°C/min) using capillary columns of similar dimension and stationary phase. It is observed that the LTM-GC offers peak resolution >1.5, one order of magnitude greater in peak height (higher analytical sensitivity), in 1/3 the total run time required in the conventional GC system operated at a maximum controllable temperature ramp rate.

LTM-GC technology is a proven method with much potential in the emerging field of near-real-time portable chemical detection devices. Combining LTM-GC with an adaptable front-end air preconcentration system with rapid sample extraction and injection capabilities could offer analytical advantages with many forensic applications, including canine scent tracking, clandestine lab sampling, and volatile chemicals monitoring for the Federal Bureau of Investigation and other law enforcement entities.

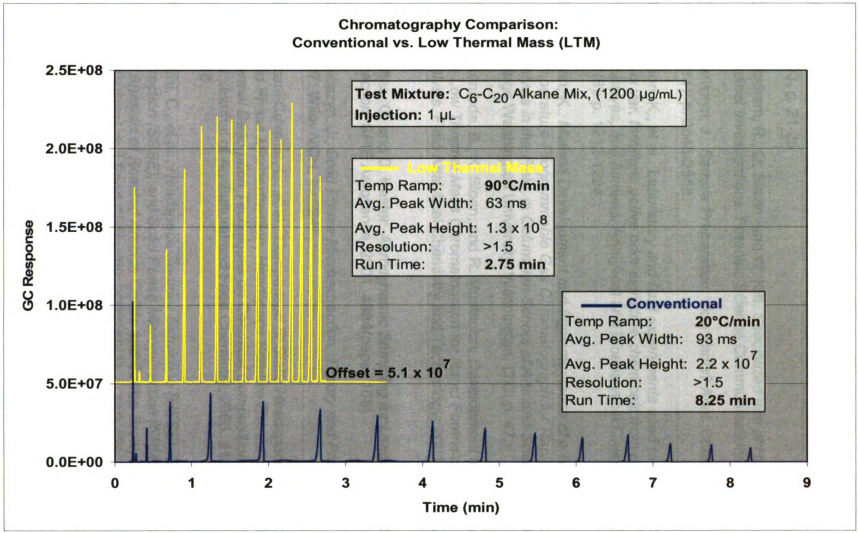

Figure 1.3. Chromatographic comparison of a 15-component alkane mix separated by conventional and low thermal mass GC capillary columns

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CHAPTER 2 – EXPERIMENTAL

2.1 Adaptive Air Sampler: HSA-SPME Element Design

In 2003, B.A. Eckenrode of the Federal Bureau of Investigation and R.V. Mustacich of RVM Scientific, Inc. developed a novel design utilizing solid phase microextraction (SPME) for trapping trace-levels of volatile and semi-volatile compounds from large volumes of air at high flow rates (L/min). Unlike the 10-mm length SPME-coated fibers traditionally employed in headspace syringes which use passive heating (via GC inlet) for desorption, the solid sorbent SPME phase is coated on a 100 mm-length (d = 0.127 mm) nickel alloy wire which can be self-heated by application of a small voltage. The alloy wire (Stablohm 675, California Fine Wire Co., Grover Beach, CA) is specifically manufactured to resist oxidation at higher temperatures to ensure thermal stability over the course of repeated flash heating. To ensure uniform desorption, the wire was calibrated for resistance by controlled heating in a laboratory oven. Using the temperature dependence of the resistance, both power and current were calculated as a function of temperature. From these measurements it was found that temperature dependence on current was independent of the length of wire with uniform diameter [1]. Technical data for the Stablohm 675 alloy wire is shown in Table 2.1. The high-surface area, SPME-coated wire, or "HSA-SPME element," is therefore capable of rapid, controllable desorption of adsorbed VOCs by means of a programmable current source, regardless of minor variations in the length of wire used. The nickel alloy can rapidly achieve proper desorption temperatures (200-400°C) at a rate of 4000°C/min from ambient temperature [1],

consuming considerably less power than most conventional air concentration systems.

Table 2.1. Technical data for the Stablohm 675 nickel alloy wire used in the HSA-SPME element

Electrical Properties	
Specific Resistance (Ohms/CMF)	675
Specific Resistivity (micro-ohms/cm)	112.22
Commercial Resistance Tolerance (<0.020)	5.00%
Temperature Coefficient of Resistance (ohms/ohm/°C {0 – 100°C}	0.00015
Thermal EMF vs. Copper	+0.002
Physical Properties	
Density (gm/cm^3)	8.247
Density (lbs/in^3)	0.298
Thermal Conductivity (watts/cm/°C)	0.132
Coefficient of Linear Expansion ($x\ 10^{-6}$ in/in °C)°C	14
Melting Point °C	1350
Melting Point °F	2462
Composition	
Nickel	60%
Chromium	16%
Iron	Balance
Miscellaneous	
Magnetic	Faint
Operating Temperature (°C)	900
Operating Temperature (°F)	1652

To provide optimum extraction efficiency under high flow rates, the air sampling device incorporating the HSA-SPME element requires a design (Figure 2.1) which will maximize contact between air flow and the HSA-SPME element

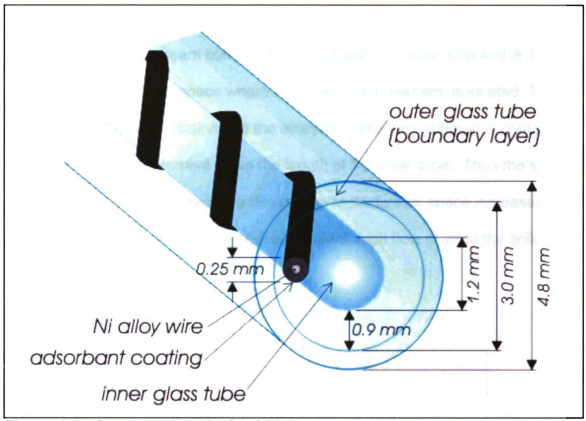

Figure 2.1. Cross-section of HSA-SPME element design

adsorbent coating. In this particular concept, the element is wound in helical fashion at a constant pitch down the outer surface of a 50 mm x 1.2 mm o.d. x 1.0 mm i.d. borosilicate glass tube which provides the element with inert physical support. The element termini are brazened to heating wire leads, with one lead running inside the length of the glass tube, so that both SPME contact leads terminate at the same end of the tube. The ends of the tube are then tightly plugged with silane-treated glass wool to minimize air flow through the lumen of this tube. The tube is then inserted into another borosilicate glass tube of larger diameter (78.5 mm x 4.8 mm o.d. x 3.0 mm i.d.), whereby the helical HSA-SPME element is contained in the annular space between the two tubes. A prototype of

this design is shown in Figure 2.2. During sampling, as air is forced into the 3-mm i.d. tube, the air stream comes into contact with the inner tube and is further restricted to the annular space where the HSA-SPME element is located. The air is forced into a helical rotation and the analytes come into continuous contact with the HSA-SPME element down the length of the inner tube. Thus the self-heated, helical SPME coated wire design in a restrictive air space increases mass transfer of volatile analyte from a turbulent, high flow of air to the solid sorbent.

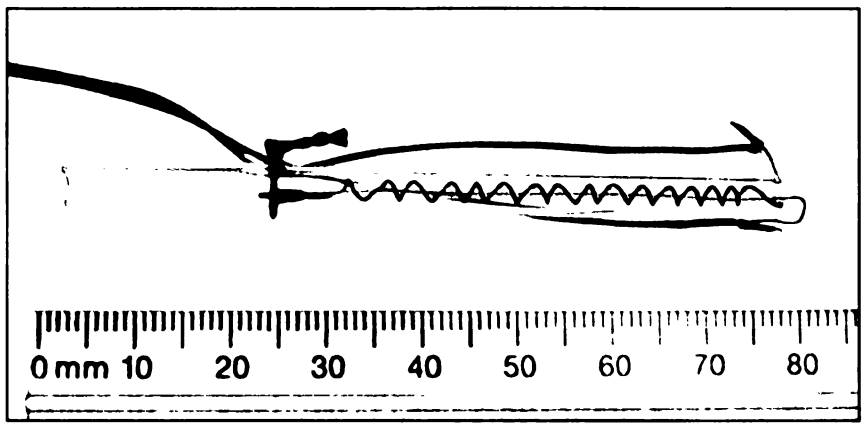

Figure 2.2. A prototype HSA-SPME Element

The rate of mass transfer is dictated by the size of the boundary layer of the SPME coating, which is essentially the area created by friction between the air flow and sorbent surface where analyte diffusion takes place (See Figures 2.1 & 2.3) [2]. Because sample flow through the HSA-SPME element is very high (4 L/min in this study), the boundary layer is reduced to an inconsequential size, so that mass transfer is essentially unlimited. Therefore, in a short, 1-minute

sampling period at a flow of 4L/min, a large, representative volume of air can be sampled to concentrate a qualitative amount of organic compound, and quickly then desorbed without the need of a bulky, high thermal mass injection port usually required for passive desorption of 10-mm SPME fibers .

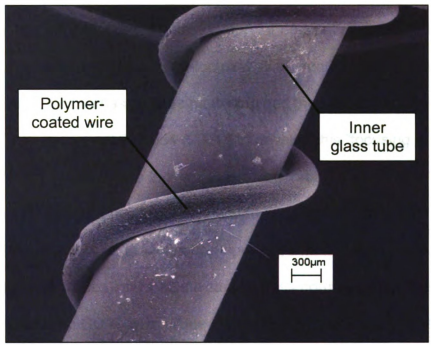

Figure 2.3. Scanning electron microscope (SEM) image of a Carboxen/PDMS HSA-SPME element at 1300X magnification (outer glass tube not shown)

The calculated HSA-SPME element surface area/ vapor volume ratio is 1:2.8. In comparison, the theoretical SPME surface area/ volume ratio of a typical syringe fiber (L = 10 mm, equivalent phase thickness of 65 µm) in the annular space of this tube is 1:41, and 1:376 for a headspace extraction in a 40mL glass vial. The relatively high surface area to vapor volume ratio for the HSA-SPME element should result in higher extraction efficiency than a syringe fiber by minimizing sample loss even at higher sampling flow rates (4-5 L/min).

Flow rates of this magnitude are possible in this particular design due to a low pressure drop across the relatively large-diameter, short-length tube.

2.2 Adaptive Air Sampler: Focusing Preconcentrator Design

The desorbed vapor volume from the HSA-SPME element is too large to be directly injected into a gas chromatograph for efficient chromatography; it must be further concentrated and re-focused by an intermediate sampling stage. RVM Scientific, Inc. and associates have obtained the patent [Mustacich and Richards, U.S. Patent # 6,223,584 (2001)] to develop this "focusing preconcentrator," (See Figure 2.4) which is an adsorbent-based microtrap integrated with a small valve [1]. The innovative design integrates the air sampling inlet directly with the microtrap opening, eliminating the requirement for extra valving and heated intermediate sample lines normally encountered in imbedded microtrap GC systems (See Figures 2.5 & 2.6). Therefore less wattage is required for valve and micro-pump operation, as well as for heating the microtrap and transfer line during injection.

The microtrap used in the focusing preconcentrator is composed of a 3.81 cm x 0.165 cm o.d. x 0.142 cm i.d stainless steel hypodermic needle tubing which contains 10 mg of solid sorbent material. The tubing is wrapped with thermally insulated heating wire which provides high-efficiency heating upon desorption/injection, controlled by two K-type thermocouples located at the heating wire termini. The microtrap is encased in stainless steel housing to retain low thermal mass during heating.

The microtrap carriage is composed of block aluminum which moves in one degree of freedom (forwards and backwards) by an actuator. The default mode of the actuator is in the sampling position, whereby the microtrap is fully

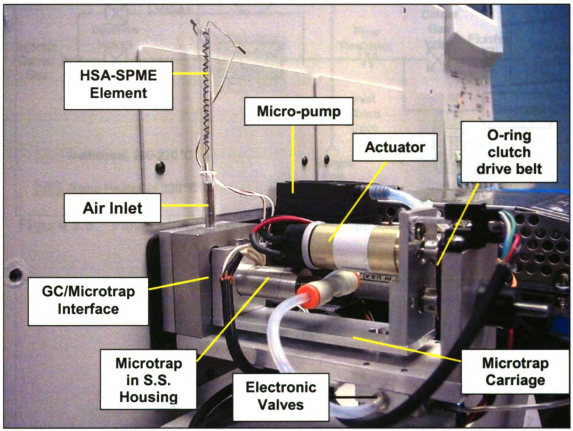

Figure 2.4. A first-generation focusing preconcentrator which integrates the HSA-SPME element with the microtrap

exposed to the air inlet. During sampling at ambient temperature, the micro pump creates a vacuum on the backside of the microtrap, which pulls air from the air inlet through the microtrap to effectively trap and concentrate organic vapor via solid sorbent. To begin an injection, the actuator turns a screw-fitted drive shaft by means of a simple o-ring, which moves the microtrap carriage into the Teflon-lined GC interface to effectively seat the opening of the microtrap onto

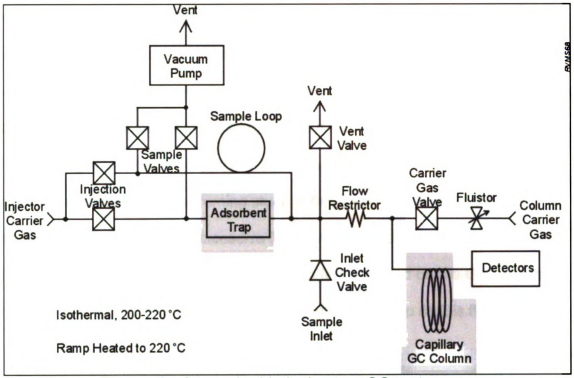

Figure 2.5. Flow path of an embedded microtrap GC system

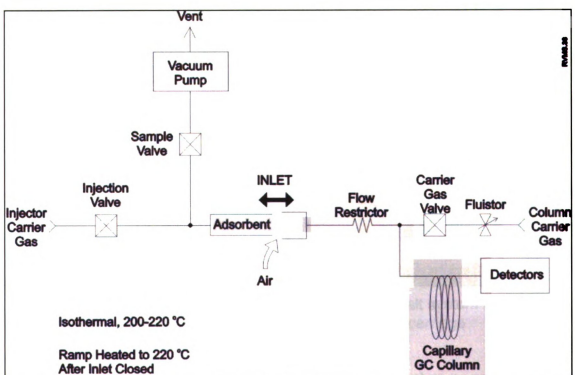

Figure 2.6. Flow path of a GC system with simple integration of microtrap (labeled "adsorbent") and air inlet

the GC transfer line opening. This movement also seals the microtrap opening from the air inlet. Placement of the actuator in-line with the microtrap allows movement in only one degree of freedom, reducing the possibility of incorrect seating of the microtrap onto the transfer line if the carriage succumbs to physical shock during transport. The clutch mechanism allows slippage of the o-ring to prevent the carriage from becoming stuck in the injection position if the actuator overdrives the carriage with excessive force. A close-up view of this mechanism is shown in Figure 2.7. Once the microtrap is firmly seated on the GC transfer line interface, helium carrier gas back-flushes the microtrap as it is flash-heated.

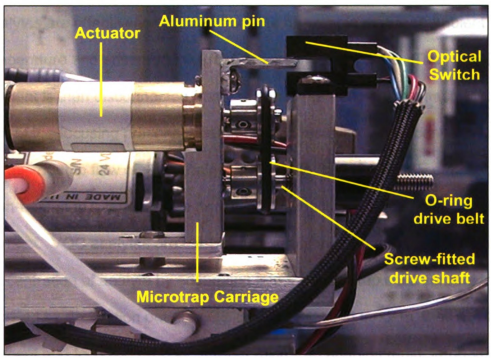

Figure 2.7. Close-up view of the O-ring clutch drive belt system for the RVM focusing preconcentrator microtrap carriage

The analytes are subsequently desorbed from the adsorbent as a vapor "plug," and injected into the heated, flow-restricted transfer line located inside the GC

interface plate and onto the head of the GC column for efficient separation. After injection, the actuator reverses to reposition the microtrap carriage for subsequent sampling, and terminates movement when an electronic optical switch detects an aluminum pin connected to the carriage.

The addition of the HSA-SPME element seated on the air inlet of the focusing preconcentrator comprises the dual-adsorbent, RVM Adaptive Air Sampler injection system (See Figure 2.4). For sampling, the HSA-SPME element can be detached from the focusing preconcentrator and attached to the outlet of a sampling pump, by which air can be pumped through the SPME tube at flow rates of up to 5 L/min using a portable air pump (See Figure 2.10). Analytes are effectively extracted from the air sample matrix at ambient temperature and adsorbed into the Carboxen/PDMS phase. The HSA-SPME element is then disconnected from the sampling pump and reattached to the air inlet of the focusing preconcentrator. During focusing preconcentrator sampling, the micropump flow of ~0.3 L/min is directed to the HSA-SPME element as it is flash-heated to a temperature necessary to effectively desorb analyte from the element. VOC analytes are carried via air inlet into the microtrap for a final concentration of analyte by adsorption into the microtrap solid sorbent material, followed by desorption onto the GC column. Used in tandem, the HSA-SPME element and focusing preconcentrator microtrap enables rapid, large-volume sampling at high flow rates necessary for field analysis. The dimensions (2.5" x 2.5" x 5") and weight (approx. 4 lbs) of the device is conducive for use with field-portable instrumentation.

2.3 Instrumentation

2.3.1 Benchmark Air Concentrator

The Entech 7100 Air Concentrator (Entech Instruments, Simi Valley, CA) was used as a benchmark for comparison with experimental results from the RVM Adaptive Air Sampler injection system. The baseline Entech 7100 houses three in-line cryogenic trapping modules designed specifically for the preconcentration of VOCs, including very light gases, from whole air samples in a laboratory setting. The first module consists of a thermally protected, 1/8" i.d. glass bead cryotrap with a temperature range of -180°C to 230°C and a 360°C/min ramp rate. The second module incorporates a 1/8" i.d. Tenax TA adsorbent cryotrap. Used in conjunction, these traps offer advanced H_2O and CO_2 management by effectively resisting adsorption of these interfering molecules [3]. The final trapping module comprises an internal megabore cryofocusing trap with a temperature range of -190°C to 100°C. During concentration, sample was heated via heated transfer line and extracted by modular adsorbent at the specified cryogenic temperature. Rapid heating of the module desorbed the vapor plug into the succeeding module held at cryogenic temperature. For on-column GC injection, the final module was back-flushed with helium while ballistically heated at a rate of 10,000°C/min from -190°C to a final temperature of 100°C, without overshoot. The Entech 7100 preconcentration system parameters are listed in Tables 2.2 and 2.3.

Table 2.2. Temperature parameters for the three trapping modules in the Entech 7100 Air Concentrator

Temperatures (deg C)			
Event	**Module 1: Glass Beads/ Cryogen**	**Module 2: Tenax TA/ Cryogen**	**Module 3: Megabore with Cryofocusing**
Concentration	-150	-50	-150
Preheat	20	---	---
Desorption	20	180	100
Bakeout	130 for 5 min	190	---

Table 2.3. Flow and volume parameters for trapping in the Entech 7100 Air Concentrator

Flows and Volumes			
Medium	**Preflush (sec)**	**Flow Rate (mL/min)**	**Volume (mL)**
Calibration	2	200	200
Standard	2	200	200
Sample	2	100	75
Purge Flush			

The instrument's mass flow controller was programmed to trap sampled air at its maximum rate of 200 mL/min, with continual flow adjustment capability. The Entech 7100 was controlled using a personal computer with Entech Instruments 7100/7000 Concentrator version 2.49-6 software.

2.3.2 Gas Chromatograph

An LTM A68 gas chromatograph (RVM Scientific, Inc.) was used to perform analyte separation. The LTM A68 housed a high-efficiency, low thermal mass GC capillary column capable of rapid, controllable temperature ramp rates (4000°C/min to 400°C) at low power which affords faster analytical run times over conventional benchtop GC ovens [4]. To enable mass spectrometric detection, the LTM A68 assembly was installed as a retrofit to the GC oven door of an Agilent 6890 series, model 1530A (serial #US000110032) gas chromatograph (See Figure 2.8). The Agilent GC oven was used primarily to control helium flow

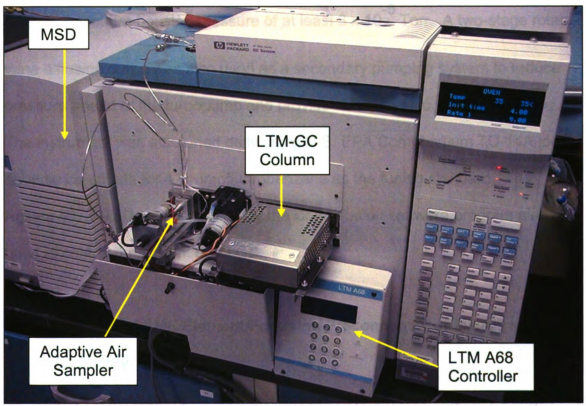

Figure 2.8. Installation of the RVM Adaptive Air Sampler on the LTM A68 retrofit oven door on the Agilent 6890 GC

by means of an electronic pressure control, and to heat transfer lines (210°C) of the respective preconcentrator systems to the LTM-GC, and from the LTM-GC to the mass selective detector situated adjacent to the Agilent GC (See Figure 2.8). The Agilent 6890 GC was controlled using a personal computer with Chemstation version B.01.00 software.

2.3.3 Mass Selective Detector

An Agilent 5973 mass selective detector (MSD), model G1099A (serial # US72821157) was used for identification and quantization of chromatographed analytes. The MSD system was equipped with a turbomolecular pump able to provide a vacuum-housing pressure of at least 3×10^{-5} Torr. A two-stage rotary-vane diffusion pump was also used as a secondary pumping system to reduce pressure ahead of the turbopump and provide an exhaust to the atmosphere. The instrument was autotuned daily using U.S. EPA Compendium TO-14A ion abundance criteria for 4-Bromofluorobenzene as the tuning standard. The Agilent 5973 MSD was controlled by the Chemstation software program also used to control the Agilent 6890 GC.

2.3.4 RVM HSA-SPME Element/Focusing Preconcentrator Microtrap Assembly

The RVM Adaptive Air Sampler injection system was originally designed for use in portable GC instrumentation; for experimental purposes, it was installed on the LTM A68 retrofit door (RVM Scientific, Inc.) which sits adjacent to

the LTM-GC column (Figure 2.8). The focusing preconcentrator transfer line was fitted through an insulated opening in the door, and connected to a three-way low dead volume tee (Valco, Inc.). The heated transfer outlet line from the Entech 7100 Preconcentrator was fastened to a second opening of this tee, enabling simultaneous connection of both preconcentrators to the LTM-GC column fitted on the LTM A68. To divert helium flow to the RVM Adaptive Air Sampler from the Agilent GC injection port during experimental injections, a 3-way tee was installed in the 1/16" stainless steel helium line leading to the 6890 GC injection port (See Figure 2.9). Helium carrier gas is diverted to the RVM focusing preconcentrator during injection by means of an electronic valve located on the microtrap carriage (See Figure 2.4).

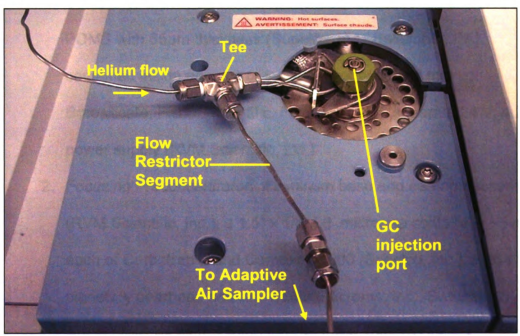

Figure 2.9. Installation of 1/16" 3-way tee; helium flows to the RVM Adaptive Air Sampler during preconcentrator injection.

The sorbents selected for this study were previously tested [5, 6] for effectiveness in trapping VOCs in air. The HSA-SPME element was coated with Carboxen dispersed in polydimethylsiloxane (PDMS) to a thickness of 65 µm, and the focusing preconcentrator microtrap was packed with ~5 mg each of 60/80 mesh Carbopack B and 60/80 mesh Carboxen 1000 (Supelco Inc., Bellefonte, PA). Sorbents were retained and separated by silane-treated glass wool (Supelco Inc.).

The RVM Adaptive Air Sampler consisted of the following major components and associated characteristics:

1. *HSA-SPME Element*: 100 mm (d = 0.127 mm) Stablohm 675 Nickel alloy wire (60% Ni, 16% Cr, bal Fe; California Fine Wire Company, Grover Beach, CA), coated with Carboxen dispersed in PDMS with 65µm thickness (Supelco, Inc., Bellefonte, PA), contained inside annulus of two glass tubes (1 & 3 mm i.d. Borosilicate, Fisher Scientific, Fair Lawn, NJ); separate 24 V, 4.2 A power supply (RVM Scientific, Inc.)
2. *Focusing Preconcentrator*: Aluminum base and carriage assembly (RVM Scientific, Inc.); a 1.5" x 1/8" i.d. microtrap containing ~5 mg each of Carbotrap B and Carboxen 1000 (Supelco, Inc.); a 264:1 planetary gearhead actuator motor (Micromo, Inc., Switzerland) which provides high holding torque; three solenoid valves (www.SMCUSA.com, model #SY114) for helium and air flow control; and a Knewberger micropump (www.KNF.com, model

#UNMP50KVD6) used for air sampling. Ceramic-insulated heating wires (RVM Scientific, Inc.) were used to heat the microtrap and transfer line; type K thermocouples were used for thermal control.

3. *Focusing Preconcentrator Temperature Controller*: mT-TC3 custom controller card (RVM Scientific, Inc.)
4. *Power Supply*: RVM Scientific, Inc. custom 24 V, 4.2 A, providing an average peak current (varying with heating rate) of 0.66 A.
5. *A/D Converter*: Model 203, 20-bit data acquisition with RS-232 connection (Lawson Labs, Inc., Malvern, PA)[7]

During the installation of the preconcentrators, the 6890 GC injector port and Agilent 5973 MS detector functions remained unchanged. Injection was controlled by the respective preconcentrator, while Chemstation software continued to control the gas flow, GC oven temperature, and detector functions. The RVM preconcentrator components were powered and controlled independently. The HSA-SPME element was heated by a separate, 24 V power supply. The focusing preconcentrator functions were controlled by the RVM A68 using a separate personal computer and DOS-based software written in C++ version 1.52 (See Appendix B).

2.3.5 GC Capillary Column

Laboratory chromatographic separations for the Entech baseline and RVM experimental studies were accomplished using a commercially available 30-m DB-5MS low thermal mass (LTM) capillary column (RVM Scientific, Inc.) The

leading column end was installed in the third port of the three-way low dead volume tee containing the terminal ends of both preconcentrator transfer lines previously described. The DB-5MS column had a nominal inner diameter of 250 µm and a stationary phase thickness of 0.25 µm.

2.3.6 Dynamic Gas Generator

Gas dilutions were performed using Kin-Tek Models 491M-B Precision Gas Standards Generator and DGB 491M Direct Gas Blending Module (La Marque, TX). The two modules used in tandem performed controlled, dynamic mixing of flowing gas streams of diluent air and component gas (TO-14A). Gas mix humidification was provided by the Kin-Tek model 491M HG Humidification Module. This module added moisture to the final mixture by controllable saturation of a portion of the dilution gas before addition to the mixture [8]. The resulting diluted, humidified outlet gas flow rate was monitored and verified by an ADM 3000 Flowmeter from J & W Scientific, Inc. (Folsom, CA). Relative humidity and temperature of dilution gas was measured using a Humidity Stick (SKC Inc., Eighty Four, PA). Final diluted gas samples were captured in 5 L Tedlar bags furnished by SKC, Inc.

2.3.7 Sampling Pump

To achieve sampling at high flow rates comparable to canine capabilities, a GILAIR-5 Portable Air Sampling Pump (Sensidyne/Gilian Inc., Clearwater, FL) was employed to sample Tedlar bags containing the gas dilutions. For sampling,

one end of the HSA-SPME element was attached to the outlet of the GILAIR-5 sample pump to capture VOCs from a Tedlar bag attached to the pump inlet (See Figure2.10).

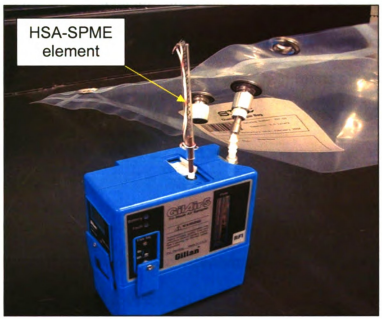

Figure 2.10. The Gilair-5® used in sampling Tedlar bags at 4 L/min into the HSA-SPME element

The pneumatic system of the GILAIR-5 contained a motor driven, dual piston pump, powered by a 6.0 Volt, 1.8 Ampere-hour Nickel Cadmium battery, capable of flows up to 5,000 scc/min. Unlike stainless steel air sampling canisters which must be evacuated before sampling, the use of Tedlar bags for gas dilutions permitted replication of actual field sampling protocol at standard atmospheric pressure.

2.3.8 Digital Multimeter

A Metex digital multimeter, model #M3860-M, was used to monitor power

consumption of the Entech and RVM Adaptive Sampler components during preconcentration events. Temperature measurements were performed with a thermocouple (Type K, Omega Engineering, Stamford, CT) connected to the multimeter. The multimeter was equipped with an RS-232 serial link and MultiView version 2.60 software to enable data collection with a personal computer [7]. Power readings were collected directly in terms of Watts (W) using an adapter rated at 13 amps and 120 AC volts.

2.4 Reagents

A U.S. EPA compendium Toxic Organics (EPA TO-14A) 39-component volatiles mix, each certified at 1 ppmv nominal concentration, was obtained from Restek Corp. (Bellefonte, PA). Table 2.4 lists the components of the gas mix, which ranges from light gases (e.g. Freons) to substituted benzenes. Table 2.4 also lists each component's respective molecular formula, expected retention time and molecular/qualifier ions to be quantitated during analysis. (Note: these retention times were obtained from U.S. EPA method TO-14A and represent analysis by conventional GC columns; they do not reflect shortened retention times from LTM-GC columns incorporated in this study). Ultra-pure air carrier gas furnished by Airgas (Radnor, PA) was used as the sample gas diluent. The Entech 7100 preconcentrator required liquid nitrogen and ultra high purity (99.999%) nitrogen gas obtained from Air Products (Allentown, PA) for cryofocusing purposes. All analytical separations were accomplished using GC grade helium (99.9995% purity) with built-in purifier (Air Products, Inc.).

Table 2.4. EPA TO-14A, 39-Component Gas Mixture (1 ppmv nominal each)

Target Analyte	Molecular Formula	Retention Time (min)	Ion/Abundance (amu/ % base peak)
1. Dichlorodifluoromethane*	CCl_2F_2	5.00	85/100 87/31
2. Chloromethane	CH_3Cl	5.34	50/100 52/34
3. Dichlorotetrafluoroethane*	$C_2Cl_2F_4$	5.46	85/100 135/56 87/33
4. Chloroethene	C_2H_5Cl	5.71	62/100 27/125 64/32
5. Bromomethane	CH_3Br	6.40	94/100 96/85
6. Chloroethane	C_2H_3Cl	6.67	64/100 29/140 27/140
7. Trichlorofluoromethane*	CCl_3F	7.59	101/100 103/67
8. 1,1-Dichloroethene	$C_2H_2Cl_2$	8.41	61/100 96/55 63/31
9. Methylene Chloride	CH_2Cl_2	8.64	49/100 84/65 86/45
10. Trichlorotrifluoroethane	$C_2Cl_3F_3$	8.71	151/100 101/140 103/90
11. 1,1-Dichloroethane	$C_2H_4Cl_2$	9.94	63/100 101/140 103/90
12. (Z)-1,2-Dichloroethane	$C_2H_4Cl_2$	10.73	61/100 96/60 98/44
13. Chloroform*	CH_3Cl	11.00	83/100 85/65 47/35

Table 2.4. (Cont'd.)

Target Analyte	Molecular Formula	Retention Time (min)	Ion/Abundance (amu/ % base peak)
14. 1,2-Dichloroethane	$C_2H_4Cl_2$	11.90	62/100 27/70 64/31
15. 1,1,1-Trichloroethane*	$C_2H_3Cl_3$	12.03	97/100 99/64 61/61
16. Carbon Tetrachloride*	CCl_4	12.51	117/100 199/97
17. Benzene*	C_6H_6	12.58	78/100 77/25 50/35
18. 1,2-Dichloropropane	$C_3H_6Cl_2$	13.39	63/100 41/90 62/70
19. Trichloroethylene*	C_2HCl_3	13.44	130/100 132/92 95/87
20. (Z)-1,3-Dichloropropene	$C_3H_4Cl_2$	14.38	75/100 39/70 77/30
21. (E)-1,3-Dichloropropene	$C_3H_4Cl_2$	14.99	75/100 39/70 77/30
22. 1,1,2-Trichloroethane	$C_2H_3Cl_3$	15.21	97/100 83/90 61/82
23. Toluene*	C_7H_8	15.46	91/100 92/57
24. 1,2-Dibromoethane	$C_2H_4Br_2$	16.27	107/100 109/96 27/115
25. Tetrachloroethylene*	C_2Cl_4	16.48	166/100 164/74 131/60

* Denotes most significant volatile chemicals detected at the surface of 1-yr old human burials

Table 2.4. (Cont'd.)

Target Analyte	Molecular Formula	Retention Time (min)	Ion/Abundance (amu/ % base peak)
26. Chlorobenzene	C_6H_5Cl	17.47	112/100 77/62 114/32
27. Ethylbenzene*	C_8H_{10}	17.75	91/100 106/28
28/29. *m,p*-Xylenes*	C_8H_{10}	18.02	91/100 106/40
30. Styrene*	C_8H_8	18.51	104/100 78/60 103/49
31. 1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	18.60	83/100 85/64
32. *o*-Xylene*	C_8H_{10}	18.61	91/100 106/40
33. 1,3,5-Trimethylbenzene	C_9H_{12}	20.19	105/100 120/42
34. 1,2,4-Trimethylbenzene	C_9H_{12}	20.70	105/100 120/42
35. 1,3-Dichlorobenzene	$C_6H_4Cl_2$	20.93	146/100 148/65 111/40
36. 1,4-Dichlorobenzene	$C_6H_4Cl_2$	21.01	146/100 148/65 111/40
37. 1,2-Dichlorobenzene	$C_6H_4Cl_2$	21.44	146/100 148/65 111/40
38. 1,2,4-Trichlorobenzene	C_9H_{12}	23.80	180/100 182/98 184/30
39. Hexachlorobutadiene	C_4Cl_6	24.23	225/100 227/66 223/60

* Denotes most significant volatile chemicals detected at the surface of 1-yr old human burials

2.5 Experimental Procedure

2.5.1 EPA TO-14A Gas Mix

A set of experiments were performed to develop a method to illustrate the functionality of the new tandem HSA-SPME element/microtrap design. A U.S. EPA method TO-14A gas was used as the test mix because although the this mix is normally used for environmental purposes, Vass *et al.* has demonstrated that approximately 14 of the 39 target compounds included in the TO-14A gas mix have also been identified as major components in decomposition of 1 year-old buried human remains [9]. These components are noted in Table 2.4. Thus the continued study of these specific compounds is relevant in law enforcement and forensic science initiatives.

The Entech 7100 Air Concentrator was used as a benchmark to provide a performance measurement against the experimental RVM Adaptive Air Sampler preconcentration system. Initial calibration of the Entech 7100 Preconcentrator was performed using a series of dilutions (0.5-32 ppbv, 60 ± 10% rel. humidity) of the TO-14A gas mixture to establish comparative sensitivity data to that of the performance of the RVM Adaptive Air Sampler. Each calibration point was performed in triplicate with corresponding responses averaged. A 13-minute preconcentration time was necessary for proper operation of the Entech 7100, which involved cryotrapping at ~150°C, a standard laboratory practice for the concentration of polar and non-polar light gases. The RVM Adaptive Air Sampler required considerably less concentration time than the Entech since the dual adsorbents trap at ambient temperature and does not use cryogen.

Although both systems are capable of trapping at flow rates of 200 mL/min, the additional HSA-SPME element on the front-end of the RVM permits trapping at higher flow rates of up to 5 L/min as well. Testing of the RVM Adaptive Air Sampler was accomplished using gas dilutions approximately equivalent to benchmark dilutions, as well as utilizing two contrasting flow rates: one calibration was performed with sampling at 0.3 L/min using only the focusing preconcentrator microtrap, and another at 4 L/min utilizing both the HSA-SPME element and focusing preconcentrator in tandem. The two flow rates represent laboratory and field sampling situations, respectively.

Evaluation of the RVM Adaptive Air Sampler involved a comparison study between the benchmark and HSA-SPME element/microtrap in tandem, as well as with the microtrap sans HSA-SPME element. Studies included desorption and extraction time profiles, analytical sensitivity, limits of detection and overall power consumption. Analyte recoveries from the three sampling modes were compared over 1-minute sampling times for each mode. Power consumption data was collected with the Metex multimeter during multiple analyses for both the benchmark and experimental concentrators. A quantitative method comparison between HSA-SPME element and benchmark systems was performed using uniform parameters, as well as a sampling flow rate of 0.2 L/min for both systems. These method parameters are listed in Table 2.5.

Table 2.5. LTM-GC/MS method parameters for the TO-14A experimental gas mix

AGILENT GC oven	
Temperature	210° C
LTM-GC TEMPERATURE PROGRAM	
Initial Temperature	30° C
Initial Hold Time	2.00 min
Temperature Rate 1	20° C/min
Intermediate Temperature 1	175° C
Hold Time	0.00 min
Temperature Rate 2	60° C/min
Final Temperature	210° C
Final Hold Time	0.00 min
INLET	
Mode	Splitless
Temperature	250°C
Carrier Gas	Helium
COLUMN PROGRAM	
Mode	Programmed Pressure
Initial Pressure	28.00 psi
Initial Hold Time	2.00 min
Pressure Rate 1	2.02 psi/min
Intermediate Pressure 1	38.11 psi
Hold Time	0.00 min
Pressure Rate 2	6.01 psi
Final Pressure 2	46.10 psi
Final Hold Time	0.00 min
Average Linear Velocity	53 cm/sec
MSD SETTINGS	
Acquisition Mode	Scan
Scan Range	29-180 m/z, 0-1.5 min 34-280 m/z, 1.5-11 min
Scan Rate	14.64 Hz, 0-1.5 min 10.13 Hz, 1.6-9.5 min
Threshold	150
Sampling (2^N)	n = 1
Solvent Delay	0.00 min
MS Quad Temperature	150°C
MS Source Temperature	230°C
MS Transfer Line Temperature	200°C

2.6 References

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7. Eckenrode, B., K. Sloan, and R. Mustacich, *Development and Evaluation of a Low Thermal Mass Chromatograph for Rapid Forensic GC/MS Analysis.* Field Analytical Chemistry and Technology, 2001. **5**(6): p. 288-301.

8. Kin-Tek Laboratories, I., *Model 491M-B Operation Manual*. 2001, Kin-Tek Labs: La Marque, TX. p. 1.

9. Vass, A., et al., *Decompositional Odor Analysis Database*. Journal of Forensic Sciences, 2004. **49**(4): p. 1-10.

CHAPTER 3 – RESULTS AND DISCUSSION

3.1 U.S. EPA Toxic Organics (TO-14A) Gas Mix

3.1.1 Baseline Gas Chromatograph

The TO-14A gas mixture was analyzed by the Entech 7100 benchmark air preconcentration system using the parameters listed in Table 2.5 to determine optimal air concentrator conditions for analyte quantitation. The baseline total ion chromatograph of the TO-14A components separated by the LTM-GC installed on the Agilent GC oven door is shown in Figure 3.1. Peak assignments were confirmed with the mass selective detector (mass spectra not shown). Total baseline analysis time for the 39-component mixture was 22 minutes, including 13 minutes for sampling and preconcentration, and 8 minutes for chromatographic separation. The average analyte peak width at half height (PWHH) was 0.83 seconds, with a peak tailing ratio of 1.0 (ratio of area right of peak center to area left of peak center, Gaussian = 1).

Analytes experiencing co-elution are shown in Table 3.1. Although MSD data acquisition was performed in scan mode, co-elution was of minimal consequence since chromatographic analysis was performed by quantitating the area of each analyte molecular and qualifier ion peak (listed in Table 2.4) rather than total ion chromatograms. Co-elution of *m*-Xylene and *p*-Xylene components required quantitation as a single peak, since these structural isomers exhibited identical molecular and qualifier ions, and could not be resolved based upon differences in the ion scan.

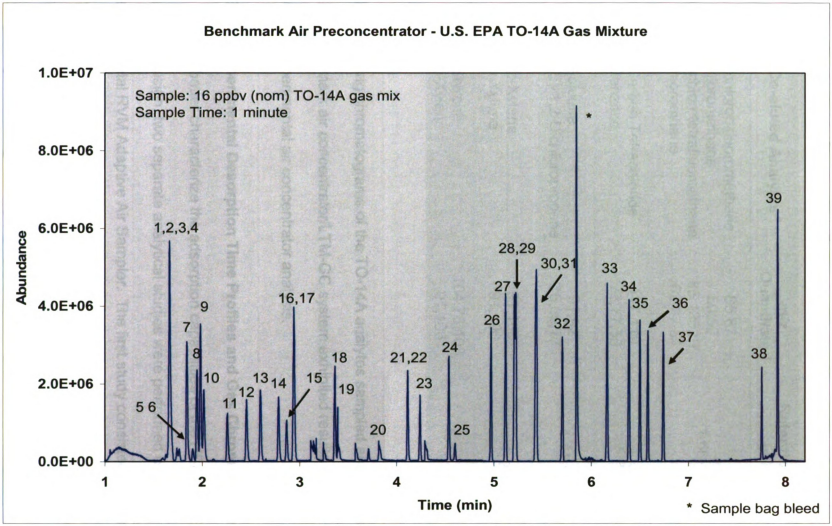

Figure 3.1. U.S. EPA Toxic Organics (TO-14A) volatiles gas mixture baseline chromatograph. See Table 2.4 for peak identification.

Table 3.1. Analytes exhibiting co-elution in the Entech baseline chromatograph

Co-eluted Analytes	m/z Quantitated	Retention Time (min)
1. Dichlorodifluoromethane	85,87	1.66-1.68
2. Chloromethane	50,52	
3. Dichlorotetrafluoroethane	85,135,87	
4. Chloroethane	62,27,64	
16. Carbon Tetrachloride	117,119	2.94
17. Benzene	78,77,50	
21. Toluene	91,92	4.11-4.13
22. (E)-1,2-Dichloropropene	75,39,77	
28. *m*-Xylene	91,106	5.21
29. *p*-Xylene	91,106	
30. Styrene	104,78,103	5.43-5.44
31. *o*-Xylene	91,106	

The resulting chromatograms of the TO-14A analytes sampled and separated by the benchmark air concentrator/LTM-GC system exhibited results acceptable to initiate experimental air concentrator analysis.

3.1.2 Experimental Desorption Time Profiles and Gas Chromatograms

To better characterize the adsorption capabilities of the HSA-SPME element design, two separate analytical studies were performed on the experimental RVM Adaptive Air Sampler. The first study consisted of 4 L/min gas sampling by the HSA-SPME element, followed by desorption onto the focusing preconcentrator microtrap. This contrasted with a second study performing 0.3 L/min gas sampling by the microtrap alone. Both studies

maintained 1-minute sampling times to replicate ideal, rapid sampling executed in field situations.

Desorption time tests for the HSA-SPME element and microtrap were required to optimize a number of variables, including quality of chromatographed analyte peaks, sorbent bleed, and total run time. Optimal desorption conditions would require a short analysis time (8-10 minutes, *including sampling*), with a minimal amount of sorbent bleed, followed by low analyte carryover on the SPME element and microtrap sorbents. Initial tests were performed on the lone microtrap to determine proper desorption time and temperature necessary to remove from the trap any analyte carryover. Once these parameters were established, they were used in the microtrap for desorption time tests for the HSA-SPME element to ensure that a majority of observed carryover and sorbent bleed came from the lone HSA-SPME element.

Microtrap Desorption Time Profile

In order to minimize sorbent bleed, it was found that the microtrap required relatively short desorption times (a few seconds) at maximum temperatures for the particular sorbent phase (330-385°C). Longer desorption times at lower temperatures failed to effectively reduce carryover, and the resulting peak tailing prevented accurate analyte quantitation. Using longer desorption times while increasing desorption temperature reduced carryover, however at the expense of increased sorbent bleed. A desorption temperature of 385°C sustained for 1.5 minutes caused complete sorbent breakdown in the microtrap, requiring replacement. It was determined that flash-heating the microtrap up to its highest

allowable temperature (330-385°C) for 10 seconds would offer comprehensive analyte desorption without sustaining a large amount of sorbent breakdown. Since the microtrap contained thermocouples within the heating wire coil, rapid and controllable temperature ramping was possible without overshoot (Figure 3.2).

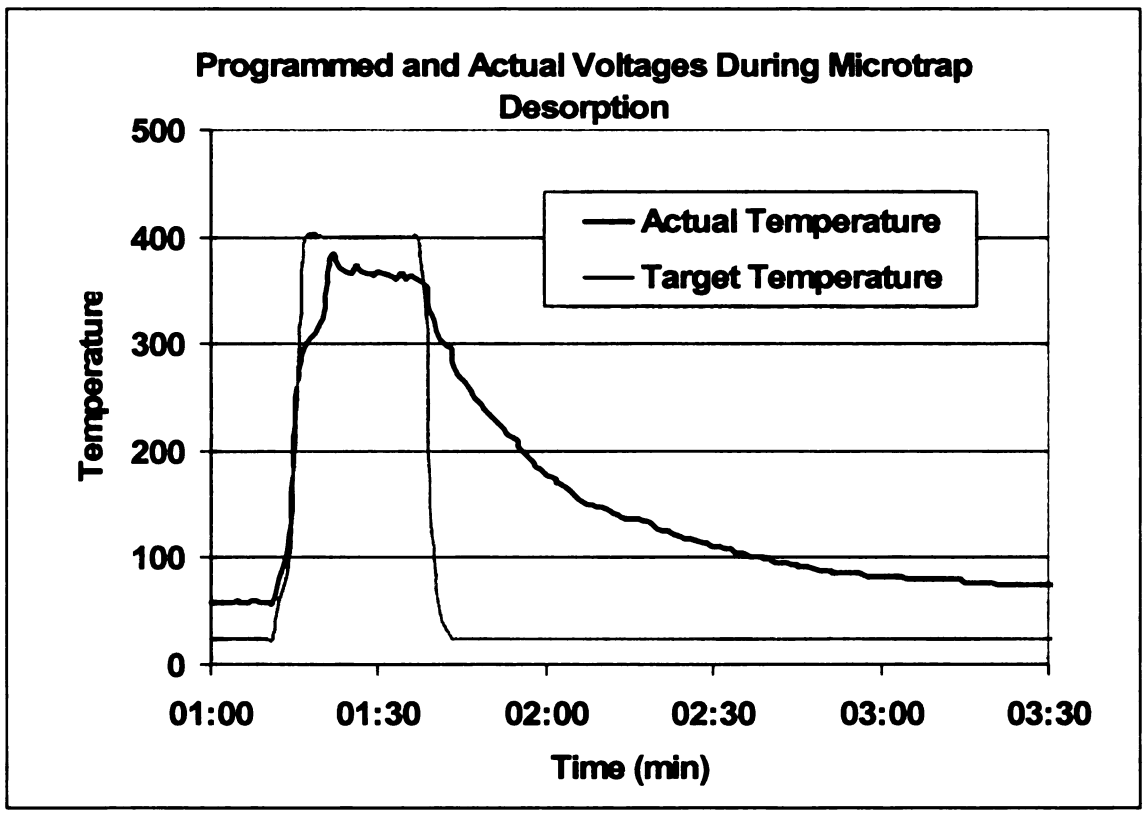

Figure 3.2. Diagram showing a 10-second temperature ramp typically observed during microtrap thermal desorption. The actual starting temperature is higher than the target temperature due to heat emanating from proximal heated GC components.

Chromatograms illustrating microtrap sample loading and the subsequent carryover blank at optimum conditions are shown in Figure 3.3. The top chromatograph displays 38 of the 39 components trapped, along with 2 bleed peaks and one sample bag remnant peak. Although large sorbent bleed peaks

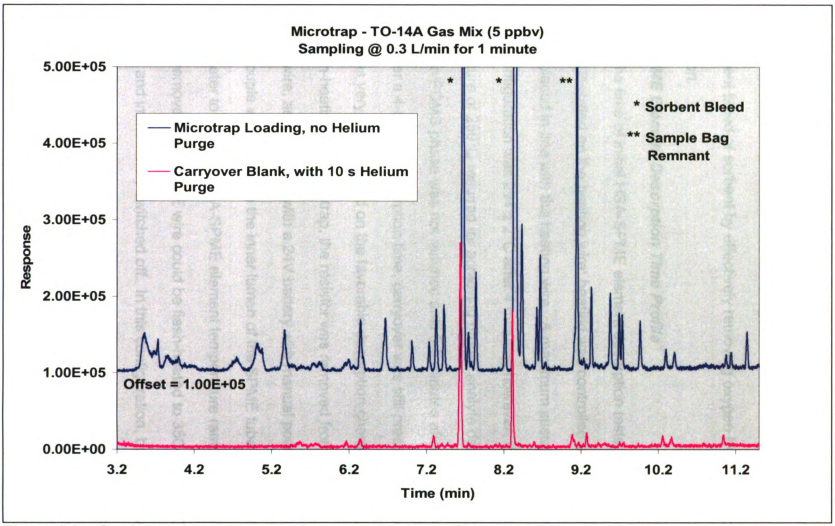

Figure 3.3. Overlayed chromatograms of gas sampling by the focusing preconcentrator microtrap and subsequent carryover blank. Desorption is ten seconds at a maximum temperature of 386°C.

are observed upon loading, they are significantly reduced in the carryover blank by the addition of a 10-second helium purge after microtrap sample loading but before thermal desorption. The helium purge decreases oxidation and subsequent bleed of sorbent by effectively removing oxygen from the trap before desorption.

HSA-SPME Element Desorption Time Profile

At the time of initial HSA-SPME element desorption tests, thermocouples were not installed on the heating wire; heating was controlled by an 18-ohm resistor placed in-line with the heating wire. A maximum sustained temperature in this configuration was 294 ± 2°C after 4 minutes; however, the minimum temperature of 250°C required for achieving proper analyte desorption from the Carboxen/PDMS phase was not reached until 0.5 minutes after thermal initiation. Even after a 4-minute desorption time, carryover was still present, and sorbent bleed was very high. Based on the favorable desorption characteristics observed with flash-heating the microtrap, the resistor was removed from the HSA-SPME heating wire, and replaced with a 24V battery with manual power switch. A thermocouple was added to the inner lumen of the SPME tube and connected to a multimeter to observe HSA-SPME element temperature ramps (°C). With the resistor removed, the SPME wire could be flash-heated to 350-400°C in 3-5 seconds and immediately switched off. In this configuration, both carryover and sorbent bleed remained minimal over successive trial runs. Figure 3.4 illustrates the desorption temperature profiles for the resistive and non-resistive power ramps. By driving off analyte from the solid sorbent materials by quick bursts of

heat, the desired run times were realized, and carryover was minimized.

Chromatograms contrasting optimal and non-optimal desorption times using the HSA-SPME element and microtrap in tandem are illustrated in Figure 3.5.

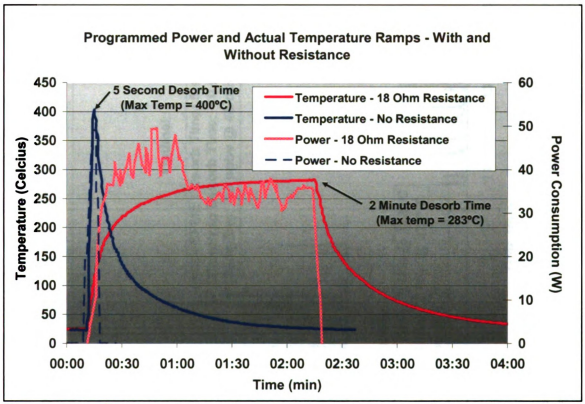

Figure 3.4. Diagram showing both resistive and non-resistive power ramps and their reflective temperature profile. Higher temperature is achieved in only a few seconds without resistance, thereby reducing overall analysis time by 2 minutes.

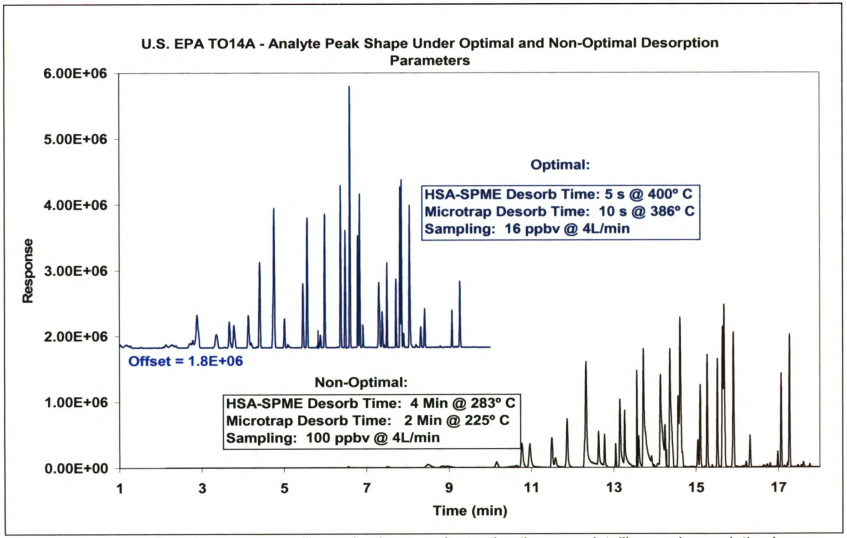

Figure 3.5. Contrasting chromatograms illustrating increased retention times, peak tailing, and convolution in non-optimal desorption conditions, vs. well-defined peaks in under optimal conditions

Optimized Experimental Gas Chromatograms

Under optimized desorption conditions for the HSA-SPME element and microtrap, total experimental analysis time, including a 1-minute gas sampling time followed by chromatographic separation and detection, was 9.5 minutes, with an average PWHH of 0.95 seconds and peak tailing ratio of 1.2 (See Figure 3.6). Of the 39 components in the TO-14A gas mixture, analytes chloromethane and chloroethene were not detected by the Agilent 5973 Mass Spectrometer when gas sampling was performed by the HSA-SPME element, and only chloromethane went undetected under lone microtrap sampling. These components are known to be poorly retained by the solid sorbents used in the microtrap [1]. Longer retention times (~1.5 minutes) observed by the experimental system relative to the benchmark system are due to the fact that mass spectra capture was initiated at the onset of experimental HSA-SPME desorption/microtrap sampling, prolonging retention by 1.16 minutes over the benchmark system, which remotely initiated MS capture only after a 13-minute sampling and preconcentration period.

Analytes from the experimental system experiencing co-elution are shown in Table 3.2. Despite the increased retention times, both experimental studies appeared to give acceptable peak widths and tailing comparable to that of the baseline system.

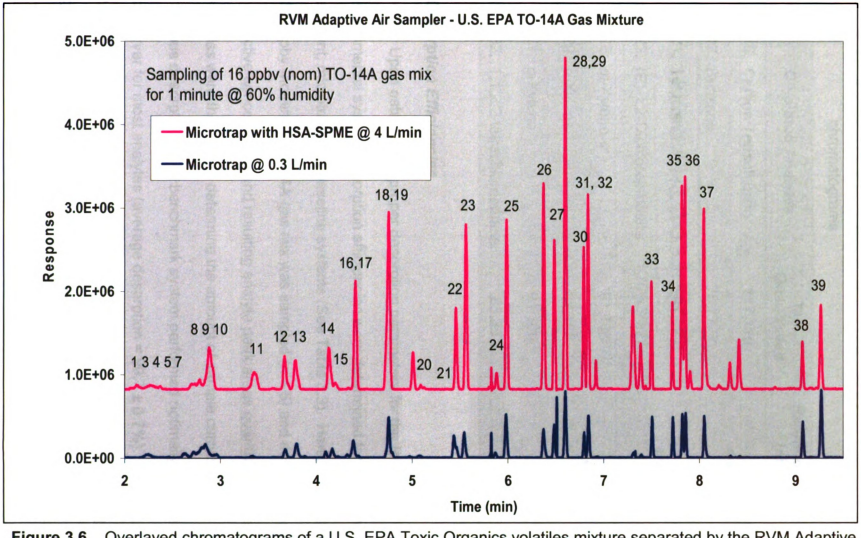

Figure 3.6. Overlayed chromatograms of a U.S. EPA Toxic Organics volatiles mixture separated by the RVM Adaptive Air Sampler experimental air concentration system. See Table 2.4 for peak identification.

Table 3.2. Analytes exhibiting co-elution in the RVM experimental chromatograms

Co-eluted Analytes	m/z Quantitated	Retention Time (min)
16. Carbon Tetrachloride	117,119	4.44
17. Benzene	78,77,50	
21. Toluene	91,92	4.75
22. (E)-1,2-Dichloropropene	75,39,77	
28. *m*-Xylene	91,106	6.60
29. *p*-Xylene	91,106	
31. *o*-Xylene	91,106	6.84
32. 1,1,2,2-tetrachloroethane	83,85	

Desorption Efficiencies

Upon establishing proper desorption parameters for the RVM experimental system, desorption efficiencies were determined for the HSA-SPME element, microtrap, and baseline systems (See Table 3.3). Here, a humidified, 100 ppbv (nominal) TO-14A gas mix was sampled (n = 5) and desorbed by the respective concentrator, and resulting analyte peak areas quantitated. Blank samples were then run to determine the amount of sample carryover from the previous desorption. The benchmark system performed optimally, with minimal carryover for most analytes (average desorption = 99.7 ± 0.7%). The RVM focusing preconcentrator microtrap had equivalent results (average desorption = 97.5 ± 2%). The average desorption for the HSA-SPME element

Table 3.3. Desorption efficiencies for benchmark and experimental air concentrators. 100 ppbv (nominal) TO-14A gas sampling performed @ 0.2 L/min (benchmark), 0.3 L/min (microtrap), and 4L /min (HSA-SPME element) ND = Not detected

Target Analyte	Boiling Point (°C)	Original Conc. ppb(v)	Benchmark (%)	% RSD (n=5)	Microtrap (%)	% RSD (n=5)	HSA-SPME (%)	% RSD (n=5)
Dichlorodifluoromethane	-29.8	97	100	0.0	100	0.2	94	4.7
Chloromethane	-24.2	100	100	0.1	ND	--	ND	--
Dichlorotetrafluoroethane	4.1	100	100	0.0	96	2.2	93	4.6
Chloroethane	-13.4	95	100	0.0	100	0.1	96	2.2
Bromomethane	3.6	94	100	0.0	92	1.3	91	9.3
Chloroethene	12.3	97	100	0.0	100	0.1	ND	--
Trichlorofluoromethane	23.7	96	100	0.0	96	1.3	95	5.6
1,1-Dichloroethene	31.7	98	100	0.0	98	0.6	96	0.8
Methylene Chloride	39.8	96	100	0.0	99	0.4	98	2.4
Trichlorotrifluoroethane	47.7	93	100	0.0	92	1.3	96	3.5
1,1-Dichloroethane	57.3	98	100	0.0	96	0.9	97	5.7
(Z)-1,2-Dichloroethane	60.3	98	100	0.0	99	0.6	98	1.4
Chloroform	61.7	99	100	0.0	97	0.8	97	1.7
1,2-Dichloroethane	83.5	101	100	0.0	98	0.6	97	1.0
1,1,1-Trichloroethane	74.1	99	100	0.0	96	0.9	96	0.5
Carbon Tetrachloride	76.5	96	100	0.0	100	0.4	99	2.3
Benzene	80.1	99	100	0.1	95	1.1	91	1.2
1,2-Dichloropropane	96.4	99	100	0.0	94	1.3	96	2.7

Table 3.3. Desorption efficiencies (Cont'd.)

Target Analyte	Boiling Point (°C)	Original Conc. ppb(v)	Benchmark (%)	% RSD (n=5)	Microtrap (%)	% RSD (n=5)	HSA-SPME (%)	% RSD (n=5)
Trichloroethylene	87	105	100	0.1	97	1.0	96	0.5
(Z)-1,3-Dichloropropene	104.3	85	100	0.0	100	0.1	99	0.1
(E)-1,3-Dichloropropene	112	66	100	0.1	98	1.4	91	9.0
1,1,2-Trichloroethane	113.8	103	100	0.0	96	0.9	95	0.9
Toluene	110.6	106	99	0.5	96	0.8	93	1.2
1,2-Dibromoethane	131.3	88	100	0.0	100	0.4	98	1.2
Tetrachloroethylene	121.1	107	100	0.1	94	0.9	93	1.2
Chlorobenzene	132	103	100	0.1	96	0.7	90	1.8
Ethylbenzene	136.2	102	100	0.1	98	0.5	92	1.6
m/p-Xylenes	139.1	102	100	0.2	99	0.2	92	1.4
Styrene	145.2	96	100	0.2	98	0.3	93	1.7
1,1,2,2-Tetrachloroethane	146.2	98	100	0.2	100	0.1	95	1.3
o-Xylene	144.4	102	100	0.1	99	0.6	92	1.5
1,3,5-Trimethylbenzene	164.7	100	100	0.2	100	0.2	94	1.3
1,2,4-Trimethylbenzene	169.3	99	99	0.1	99	0.2	94	1.2
1,3-Dichlorobenzene	173	86	99	0.1	98	0.3	88	2.6
1,4-Dichlorobenzene	180.5	96	99	0.1	99	0.2	88	3.3
1,2-Dichlorobenzene	174	93	99	0.3	98	0.4	87	3.5
1,2,4-Trichlorobenzene	213.5	95	97	0.6	97	0.8	79	11.6
Hexachlorobutadiene	186	98	97	0.9	99	0.3	82	7.2

however was 93.3 ± 4%, which was expected to be less than the average microtrap desorption efficiency since analyte must be further concentrated on the microtrap before final GC injection. Nevertheless, the experimental desorption efficiencies are found to be at acceptable levels based upon data from the literature [4].

3.1.3 Extraction Time Profiles

Having established proper desorption parameters for the RVM experimental system, it was necessary to determine the time required for the extraction process to reach equilibrium during high-flow sampling with the HSA-SPME element. Normally, 1-cm SPME fibers require long periods of time (5 minutes to 2 hours) for headspace extractions, and shorter times for agitated, or low-flow samples (5-10 minutes @ 4-5 ml/min). With a 10-cm length, helical HSA-SPME-coated wire under high flow (4 L/min), it is possible to load a much larger amount of analyte mass onto the fiber in a shorter amount of time. For this analysis, a humidified, 100 ppbv (nominal concentration) TO-14A gas mixture was sampled at 4 L/min by the HSA-SPME element for predetermined times, up to the one-minute sampling time threshold. Individual analyte responses were plotted against time to determine extraction time profiles (See Figure 3.7).

Since this particular study concentrates on a more qualitative approach towards fast field sampling, the focus was to determine the approximate amount of sample which could be loaded on to the SPME phase within a one-minute time interval. As can be observed in Figure 3.7, most of the early eluting light gases

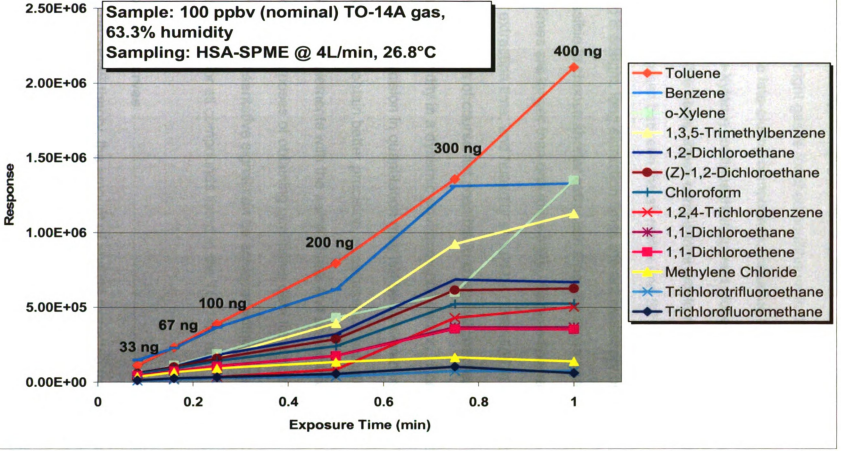

Figure 3.7. Representative selection of analyte extraction time profiles from a 100 ppbv (nom) TO-14A gas mix

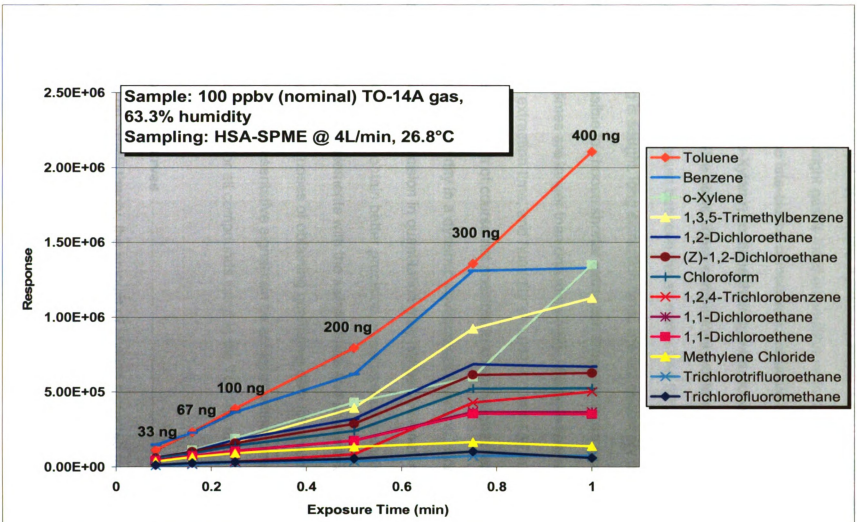

Figure 3.7. Representative selection of analyte extraction time profiles from a 100 ppbv (nom) TO-14A gas mix

reach equilibrium (noted by reaching a plateau) within 0.25-0.50 minutes. Medium-molecular weight gases reached equilibrium in 0.65-0.85 minutes. However, many of the late-eluting compounds, including the substituted benzenes (toluene, *o*-Xylene) continue their upward slope at the one-minute mark. On a quantitative basis, these compounds would require longer extraction times to reach equilibrium between the air matrix and SPME phase. Since rapid field sampling is sought, long extraction times are not necessary or desired. It is therefore possible to choose shorter extraction times for those analytes whose equilibration times are longer than one minute [2]. Sample flow rate, temperature, extraction time, and humidity should be controlled in order to obtain reproducible data. It is of course not possible to control slight changes in temperature and humidity in a dynamic environmental setting. For this reason, sample-to-sample precision in quantitation may not be achieved in HSA-SPME field applications. To obtain better precision, simultaneous sampling with multiple HSA-SPME elements with the same phase and phase thickness may be implemented. For purposes of obtaining qualitative data for a compound in rapid field sampling, a representative signal can be achieved within one minute for 100 ppbv concentrations for all compounds listed in the TO-14A mix.

3.1.4 Calibration Curves

Based on SPME theory, the amount of analyte extracted from the sample under set conditions should be directly proportional to the concentration of the analyte in the sample [2]. Therefore, plotting the analytical signal of the analyte

vs. the known concentration should produce a linear calibration curve. In this study, a 7-point calibration curve (0-32 ppbv nom, moisture added) was performed with both of the Entech benchmark and RVM experimental air concentrators. Again, sampling flow rates respective to the particular concentrator (0.2 L/min for the Entech, 0.3 L/min for the microtrap, and 4 L/min for the HSA-SPME element) were utilized, with extraction times remaining constant at one minute. Each calibration point was performed in triplicate with the ensuing responses averaged. The resulting analytical signals (*y*) at the respective concentration (*x*) were plotted by the least squares technique to obtain a line of linear regression using the equation $y = ax + b$, where *a* is the regression slope, and *b* is the y-Intercept (See Tables 3.4 and 3.5). Using the *y* residuals from each plot, the random errors were calculated for a and b at 95% confidence intervals [3].

Linear fit of the data was quantified in terms of the R^2 value, which represents the variance in *y* attributable to the variance in *x* [4]. The R^2 value is a measure of linear fit ranging from 0 to 1, with a perfect linear fit having an R^2 value of 1.000. The linear fit of the benchmark data and RVM preconcentrator data are also listed in tables 3.4 and 3.5. With exceptions of the undetected analytes chloromethane, chloroethene, and weakly retained bromomethane, comparison between the benchmark and experimental HSA-SPME element R^2 values indicate that the linear fit for a given analyte calibration curve was about the same (Table 3.4). The experimental focusing preconcentrator microtrap R^2

Table 3.4. Calibration curves for the Entech 7100 benchmark and the HSA-SPME element air concentrators with their respective correlation coefficients (R^2). All regression responses x 10^4.
ND = Not detected

	Benchmark			HSA-SPME element		
Target Analyte	**Slope**	**y-Intercept**	**R^2**	**Slope**	**y-Intercept**	**R^2**
Dichlorodifluoromethane	12 ± 1.2	-7 ± 18	0.9936	0.03 ± 0.03	0.4 ± 0.2	0.9609
Chloromethane	3.5 ± 0.6	3 ± 8	0.9821	ND	ND	ND
Dichlorotetrafluoroethane	1.1 ± 14	1 ± 200	0.9956	0.1 ± 0.05	0.1 ± 0.4	0.9944
Chloroethane	5.1 ± 0.9	3 ± 13	0.9908	0.5 ± 0.02	0 ± 0.3	0.9985
Bromomethane	1.6 ± 0.1	-1 ± 2	0.9957	0.04 ± 0.04	0.8 ± 0.5	0.6442
Chloroethene	1.6 ± 0.2	-1 ± 2	0.9917	ND	ND	ND
Trichlorofluoromethane	8.8 ± 0.5	4 ± 8	0.9970	0.5 ± 0.06	0.7 ± 0.8	0.9898
1,1-Dichloroethene	6.6 ± 0.4	-3 ± 5	0.9977	2.8 ± 0.2	3 ± 3	0.9953
Methylene Chloride	5.3 ± 0.5	-4 ± 8	0.9918	1.3 ± 0.4	5 ± 5	0.9397
Trichlorotrifluoroethane	4.5 ± 0.2	-1 ± 3	0.9983	0.4 ± 0	0.3 ± 0.5	0.9938
1,1-Dichloroethane	5.7 ± 0.6	0 ± 9	0.9937	0.9 ± 0.1	0.7 ± 2	0.9936
(Z)-1,2-Dichloroethane	5.9 ± 0.2	-3 ± 3	0.9992	3.8 ± 0.6	4 ± 10	0.9948
Chloroform	5.4 ± 0.4	-3 ± 6	0.9951	2.4 ± 0.2	2 ± 3	0.9959
1,2-Dichloroethane	3.7 ± 0.3	-3 ± 5	0.9934	3.7 ± 0.3	2 ± 4	0.9971

Table 3.4. (Cont'd.)

	Benchmark			HSA-SPME Element		
Target Analyte	**Slope**	**y-Intercept**	**R^2**	**Slope**	**y-Intercept**	**R^2**
1,1,1-Trichloroethane	4.4 ± 0.4	-3 ± 6	0.9927	3.0 ± 0.1	1 ± 2	0.9981
Carbon Tetrachloride	5.0 ± 0.4	-3 ± 5	0.9959	0.2 ± 0	0 ± 0.2	0.9972
Benzene	7.6 ± 0.7	-7 ± 10	0.9927	7.1 ± 0.7	17 ± 10	0.9959
1,2-Dichloropropane	2.8 ± 0.3	-2 ± 4	0.9912	1.9 ± 0.2	1 ± 2	0.9943
Trichloroethylene	3.5 ± 0.4	-3 ± 5	0.9902	4.5 ± 0.2	2 ± 3	0.9978
(Z)-1,3-Dichloropropene	1.1 ± 0.3	-2 ± 4	0.9584	0.2 ± 0.1	0.6 ± 0.8	0.9565
(E)-1,3-Dichloropropene	0.1 ± 0.1	1 ± 0.1	0.9960	0.1 ± 0.1	0.1 ± 0.2	0.9065
1,1,1-Trichloroethane	2.7 ± 0.2	-2 ± 3	0.9947	1.9 ± 0.1	0.4 ± 2	0.9975
Toluene	8.9 ± 0.8	-5 ± 11	0.9944	8.7 ± 0.8	11 ± 11	0.9939
1,2-Dibromoethane	2.0 ± 0.2	-1 ± 2	0.9952	0.7 ± 0.1	0.3 ± 0.6	0.9978
Tetrachloroethylene	4.5 ± 0.4	-4 ± 6	0.9933	4.2 ± 0.2	3 ± 3	0.9985
Chlorobenzene	6.8 ± 0.6	-4 ± 8	0.9945	7.5 ± 0.8	10 ± 12	0.9908
Ethylbenzene	12 ± 1.0	-7 ± 15	0.9942	7.1 ± 0.7	8 ± 9	0.9937
***m/p*-Xylenes**	17 ± 1.7	-6 ± 27	0.9924	12 ± 1.3	17 ± 18	0.9909
Styrene	6.6 ± 0.7	-5 ± 10	0.9922	5.2 ± 0.3	4 ± 4	0.9975
1,1,2,2-Tetrachloroethane	5.4 ± 0.4	-2 ± 6	0.9930	1.2 ± 0.1	1 ± 0.7	0.9974
o-Xylene	8.8 ± 0.8	-5 ± 12	0.9961	8 ± 0.3	3 ± 3	0.9979
1,3,5-Trimethylbenzene	9.1 ± 0.8	-4 ± 11	0.9947	5.8 ± 0.3	3 ± 2	0.9972

Table 3.4. (Cont'd.)

	Benchmark			HSA-SPME Element		
Target Analyte	**Slope**	**y-Intercept**	**R^2**	**Slope**	**y-Intercept**	**R^2**
1,2,4-Trimethylbenzene	8.5 ± 0.7	-4 ± 11	0.9946	3.5 ± 0.4	6 ± 6	0.9922
1,3-Dichlorobenzene	6.3 ± 0.6	-4 ± 9	0.9931	5.8 ± 0.5	9 ± 7	0.9950
1,4-Dichlorobenzene	6.0 ± 0.6	-3 ± 9	0.9921	5.7 ± 0.5	10 ± 7	0.9931
1,2-Dichlorobenzene	5.6 ± 0.5	-1 ± 7	0.9940	5.2 ± 0.5	9 ± 9	0.9897
1,2,4-Trichlorobenzene	2.5 ± 0.3	1 ± 4	0.9909	1.5 ± 0.1	0.6 ± 0.6	0.9994
Hexachlorobutadiene	2.7 ± 0.2	0 ± 2	0.9970	1.6 ± 0.1	-0.2 ± 0.7	0.9998

Table 3.5. Calibration curves for the focusing preconcentrator microtrap with correlation coefficients (R^2). All regression responses x 10^4
ND = Not Detected

Target Analyte	Slope	y-Intercept	R^2
Dichlorodifluoromethane	0.08 ± 0.01	0 ± 0.1	0.9933
Chloromethane	ND	ND	ND
Dichlorotetrafluoroethane	0.6 ± 0.08	-0.8 ± 1	0.9875
Chloroethane	0.2 ± 0.01	0 ± 0.1	0.9994
Bromomethane	0.04 ± 0.01	0.3 ± 0.2	0.9442
Chloroethene	0.2 ± 0.03	0.1 ± 0.4	0.9797
Trichlorofluoromethane	1.2 ± 0.1	-0.3 ± 0.8	0.9984
1,1-Dichloroethene	1.1 ± 0.02	-0.1 ± 0.3	0.9997
Methylene Chloride	0.8 ± 0.02	-0.01 ± 0.3	0.9994
Trichlorotrifluoroethane	0.8 ± 0.03	0.5 ± 0.5	0.9985
1,1-Dichloroethane	1.1 ± 0.05	0.2 ± 0.6	0.9987
(Z)-1,2-Dichloroethane	0.9 ± 0.04	0.2 ± 0.6	0.9983
Chloroform	1.2 ± 0.07	0.3 ± 0.9	0.9977
1,2-Dichloroethane	0.9 ± 0.03	0.1 ± 0.4	0.9994
1,1,1-Trichloroethane	0.8 ± 0.03	0.1 ± 0.4	0.9989
Carbon Tetrachloride	0.2 ± 0.01	-0.1 ± 0.1	0.9988
Benzene	1.8 ± 0.1	2 ± 1	0.9983
1,2-Dichloropropane	0.6 ± 0.05	0.5 ± 0.6	0.9957
Trichloroethylene	1.2 ± 0.1	0.9 ± 1	0.9959
(Z)-1,3-Dichloropropene	0.1 ± 0.02	0.2 ± 0.3	0.9698
(E)-1,3-Dichloropropene	0.02 ± 0	0.07 ± 0.1	0.9215
1,1,1-Trichloroethane	0.6 ± 0.05	0.5 ± 0.7	0.9949
Toluene	1.3 ± 1.0	1 ± 1	0.9975
1,2-Dibromoethane	0.4 ± 0.04	0.2 ± 0.6	0.9896
Tetrachloroethylene	1.1 ± 0.1	0.8 ± 1	0.9952

Table 3.5. (Cont'd.)

Target Analyte	Slope	y-Intercept	R^2
Chlorobenzene	1.4 ± 0.08	0.8 ± 1	0.9977
Ethylbenzene	1.9 ± 0.1	1 ± 1	0.9979
***m/p*-Xylenes**	3.1 ± 0.2	2 ± 3	0.9963
Styrene	1.1 ± 0.06	0.5 ± 0.8	0.9983
1,1,2,2-Tetrachloroethane	0.4 ± 0.04	0.4 ± 0.5	0.9947
***o*-Xylene**	1.5 ± 0.1	1.0 ± 2	0.9959
1,3,5-Trimethylbenzene	1.6 ± 0.2	2 ± 2	0.9916
1,2,4-Trimethylbenzene	1.5 ± 0.2	2 ± 2	0.9914
1,3-Dichlorobenzene	1.2 ± 0.1	1 ± 2	0.9905
1,4-Dichlorobenzene	1.3 ± 0.2	1 ± 2	0.9910
1,2-Dichlorobenzene	1.2 ± 0.1	1 ± 2	0.9899
1,2,4-Trichlorobenzene	0.8 ± 0.1	0.5 ± 1	0.9943
Hexachlorobutadiene	0.9 ± 0.1	0.9 ± 2	0.9930

values also had similar results when compared to the baseline system (Table 3.5).

The *a* term, or the slope in the linear regression equation, is also defined as the calibration sensitivity of the particular analyte, and can be used to compare relative sensitivities between methods [5]. It can be observed in Table 3.4 that the HSA-SPME element was less sensitive to the light gases (up to 1,1-Dichloroethene) than the benchmark system by 1-4 orders of magnitude. This may be attributed to the relatively high initial desorption temperature of 57°C detected in the microtrap (Figure 3.2), causing either a lack of initial uptake or premature desorption. This assumption seems valid since HSA-SPME slope

values for the first 11 analytes are more agreeable with microtrap values (Table 3.5), even though the theoretical analyte load on the HSA-SPME element was 13.3X higher than microtrap loading in the same 1-minute sampling time. For the mid- and late-eluting analytes, the HSA-SPME element adsorbed relatively similar amounts as the benchmark at given concentrations, although theoretical loading was 20X higher in the HSA-SPME system. This is to be expected since analyte adsorption by the HSA-SPME element is non-exhaustive and analyte breakthrough is large at higher sampling flow rates (4 L/min). Nevertheless, the HSA-SPME element samples a more representative volume of air in the same amount of time while retaining sensitivities observed with the benchmark, which uses near-exhaustive cryogenic sorption at lower sampling flow rates (0.2 L/min). The histogram in Figure 3.8 illustrates this point. The chart shows individual analyte load profiles (averaged triplicate runs) of a humidified, 16 ppbv (nominal conc.) TO-14A gas mixture performed by the benchmark and experimental systems. For each system, total sampling time was exactly one minute at respective system flow rates. Analyte loading of the light gases (compounds 1-11) by the benchmark system was more efficient due to cryogenic trapping than with either experimental system trapping at ambient temperature. However, in compounds 12-39, with the exception of carbon tetrachloride, the HSA-SPME element trapped relatively similar amounts of analyte as the benchmark system, but from ~20X the volume of air, without using cryogen. At this rate, the HSA-SPME element could realize qualitative signal from low and sub-ppb levels

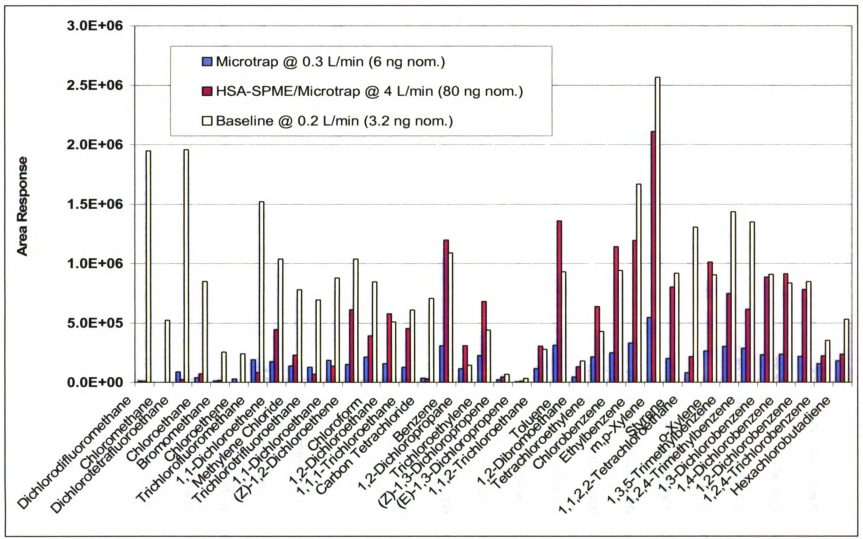

Figure 3.8. Comparison of 16 ppbv (nominal conc., moisture added) sample loading by benchmark and experimental air concentration systems

of analyte by concentrating from a large volume of air in the targeted time frame.

By plotting the linear regression of a particular analyte from each air concentrator on the same graph, a visual comparison can be made regarding sensitivity towards the analyte. Steep slopes are equivalent to higher sensitivity to a specific concentration of analyte versus flat slopes. Sensitivity comparison of the BTEX components (Benzene, Toluene, Ethylbenzene, and *o*-xylene) of the TO-14A gas mix is illustrated in Figure 3.9. Again, the HSA-SPME element illustrated sample uptake equivalent to the benchmark study at the lower (low and sub-ppb) concentrations, even though the HSA-SPME sampling flow rate was 20X faster than benchmark flow rates. As expected, the microtrap sensitivities were far less than both benchmark and HSA-SPME studies, since the non-cryogenic, exhaustive approach traps 0.33X and 13.3X less over a 1-minute period than these studies, respectively.

3.1.5 Limits of Detection

By definition, the limit of detection of an analyte is the minimum concentration required to give an instrument response which can be distinguished from the response given in a blank (no analyte present) at the same retention time [3]. The minimum concentration to give such a signal is equal to the blank signal, y_B, plus three standard deviations of the blank, s_B [3]:

$$y - y_B = 3s_B$$

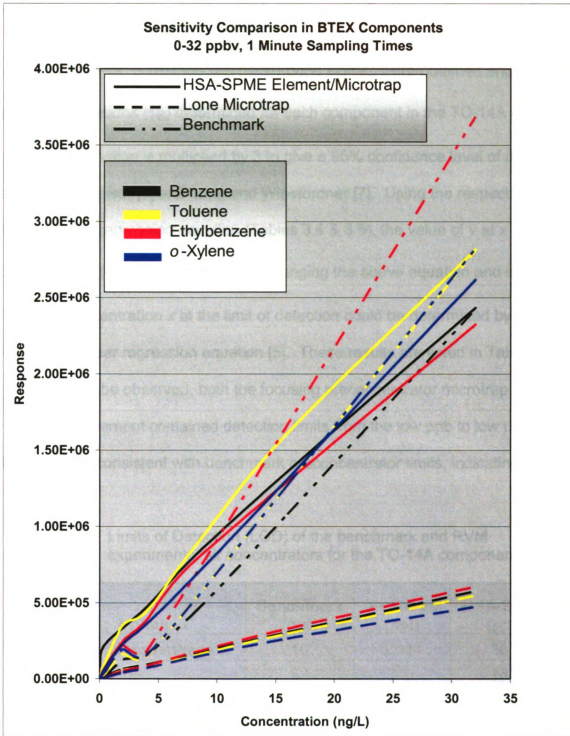

Figure 3.9. Calibration curves for the BTEX series in the TO-14A gas mixture. The HSA-SPME element has comparable sensitivities to that of the benchmark in identical 1-minute sampling time.

Based upon the published method [3] for determining the limit of detection (LOD) for each air concentration system, five pure air blanks were sampled, and upon LTM-GC analysis, corresponding background signals were obtained and standard deviations (s_B) determined for each component in the TO-14A gas mixture. This value is multiplied by 3 to give a 95% confidence level of detection, as noted by Kaiser [6] and Long and Winefordner [7]. Using the respective analyte linear regression equation (Tables 3.4 & 3.5), the value of y at $x = 0.0$ concentration (y_B) was acquired. Rearranging the above equation and solving for y, the concentration x at the limit of detection could be determined by solving for x in the linear regression equation [5]. These results are listed in Table 3.6.

As can be observed, both the focusing preconcentrator microtrap and HSA-SPME element contained detection limits from the low ppb to low ppt range. This range is consistent with benchmark preconcentrator limits, indicating that

Table 3.6. Limits of Detection (LOD) of the benchmark and RVM experimental air concentrators for the TO-14A components

Target Analyte	Benchmark (ppt)	Microtrap (ppt)	HSA-SPME (ppt)
Dichlorodifluoromethane	16	1,084	301
Chloromethane	53	ND	ND
Dichlorotetrafluoroethane	477	111	183
Chloroethane	2	184	22
Bromomethane	11	4106	9654
Chloroethene	13	1918	ND
Trichlorofluoromethane	16	63	1202
1,1-Dichloroethene	17	23	2815

Table 3.6. (Cont'd.)

Target Analyte	Benchmark (ppt)	Microtrap (ppt)	HSA-SPME (ppt)
Methylene Chloride	19	35	64
Trichlorotrifluoroethane	2	1281	1222
1,1-Dichloroethane	8	16	15
(Z)-1,2-Dichloroethane	17	13	203
Chloroform	5	15	459
1,2-Dichloroethane	5	21	337
1,1,1-Trichloroethane	3	37	723
Carbon Tetrachloride	17	21	21
Benzene	69	263	1405
1,2-Dichloropropane	27	132	631
Trichloroethylene	65	16	487
(Z)-1,3-Dichloropropene	11	192	129
(E)-1,3-Dichloropropene	162	1633	335
1,1,1-Trichloroethane	85	47	883
Toluene	466	234	148
1,2-Dibromoethane	39	43	84
Tetrachloroethylene	89	30	461
Chlorobenzene	119	17	133
Ethylbenzene	134	23	4
***m,p*-Xylene**	182	20	3
Styrene	153	11	9
1,1,2,2-Tetrachloroethane	132	37	8
***o*-Xylene**	123	6	4
1,3,5-Trimethylbenzene	171	19	4
1,2,4-Trimethylbenzene	167	19	6
1,3-Dichlorobenzene	188	11	72
1,4-Dichlorobenzene	144	8	40
1,2-Dichlorobenzene	247	14	42
1,2,4-Trichlorobenzene	1193	68	251
Hexachlorobutadiene	973	8	14

the experimental concentrators were able to achieve relatively low background noise for the particular analyte ions scanned. A comparison of these results to literature data [8] indicates that the benchmark and experimental air preconcentrators are both effective in detecting at low levels often encountered in large-volume sampling. The low-ppt values are also a consequence of the relatively small peak width values obtained by LTM column chromatography (See Figure 1.3). These values contribute to taller chromatographed peaks and subsequent increased analytical sensitivity (detector response) toward analyte.

In this investigation, calibration curves from the low ppt to low ppb range, coupled with the extraction profiles obtained in Figure 3.7, indicate a linear dynamic range of four orders of magnitude for TO-14A components #11-39 in Table 2.4.

3.1.6 Method Comparison

To determine whether the HSA-SPME method could be compared quantitatively to the EPA TO-14A method, sampling parameters were normalized to 0.2 L/min over a one-minute period for both HSA-SPME and benchmark systems. A Carboxen/PDMS HSA-SPME element with a 25 μm phase thickness was used to ensure desorption of the BTEX components at lower desorption temperatures of 250-285˚C.

Ten TO-14A gas samples were prepared in Tedlar bags such that nominal sample concentrations were 8, 16, 32, 40, 60, 80, 100, 120, and 140 ppb(v) except for *m/p*-xylenes, which were approximately twice these concentrations.

These gas samples were individually sampled by the benchmark concentration system at 0.2 L/min to produce nominal mass loading of 1.6, 3.2, 6.4, 8, 12, 16, 20, 24, and 28 ng, respectively. The sampling was repeated by the HSA-SPME element using the same concentrations and sampling flow rate to produce quantitatively similar mass loading. Benchmark and experimental calibration standards were composed at concentrations of 10, 20, 50, 100, and 150 ppb(v); the curves for all the BTEX components produced linear correlation coefficients greater than 0.99 Equally weighted regression lines were used to statistically compare the analytical techniques.

The data derived from the benchmark air concentration system were plotted on the *x*-axis (reference axis) of a regression graph, and responses from the HSA-SPME element were plotted on the *y*-axis. Each point on the graph thus represents one sample analyzed by the two methods. A regression plot for benzene is given in Figure 3.10. Perfect agreement between the methods for all samples would theoretically yield a slope and correlation coefficient of unity (1.0) and a *y*-intercept of zero [9]. The regression line parameters for each BTEX component with 95% confidence intervals [3] are listed in Table 3.7. From Table 3.7, it can be observed that there is strong correlation between the benchmark cryotrap method and the experimental HSA-SPME method.

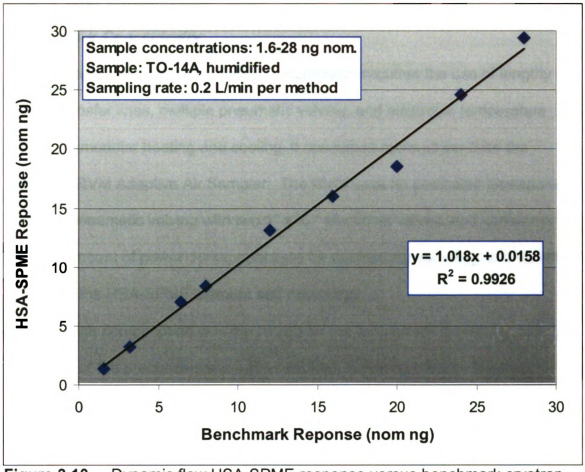

Figure 3.10. Dynamic flow HSA-SPME response versus benchmark cryotrap air concentration response for benzene in air.

Table 3.7. Regression line parameters for the BTEX components of the TO-14A gas mix. Method comparison of HSA-SPME element versus the benchmark cryotrap

Analyte	Regression Parameters: Benchmark System on x-axis		
	Slope	y-Intercept	Correlation (R^2)
Benzene	1.02 ± 0.078	0.016 ± 1.2	0.9926
Toluene	1.05 ± 0.104	-0.189 ± 1.6	0.9900
Ethylbenzene	1.05 ± 0.076	0.154 ± 1.2	0.9934
m/p-xylene	1.05 ± 0.076	0.257 ± 1.2	0.9935
o-xylene	1.04 ± 0.089	0.261 ± 1.3	0.9932

3.1.7 Power Consumption

Baseline Air Concentrator

Because the Entech 7100 Air Concentrator requires the use of lengthy heated transfer lines, multiple pneumatic valving, and electronic temperature control for modular heating and cooling, it consumes more power than the prototype RVM Adaptive Air Sampler. The RVM uses no dedicated heated lines, replaces pneumatic valving with two 1" x ¼ " electronic valves, and consumes a minimal amount of power during operation for micropump sampling and ballistic heating of the HSA-SPME element and microtrap.

Power consumption was measured for the benchmark Entech system for the length of the preconcentration (13 minutes), including transfer line heating and sampling events. Prior to initiating the preconcentration program, the instrument registered a standby power reading of 248 W with the transfer lines stabilized at 150°C. During preconcentration, power consumption was sporadic, with no defined power inclines or declines with specific preconcentration events, as shown in Figure 3.10. The benchmark system gave a maximum power reading of 712 W during the preconcentration program.

Experimental Air Concentrator

Power consumption for the RVM Adaptive Air Sampler prototype concentration system was recorded during preconcentration (micropump sampling/HSA-SPME desorption and microtrap desorption), for a total time of 1.16 minutes. The standby power reading before preconcentrator initiation was 10 W, which is primarily due to supplying power to the internal controller cards.

Maximum power observed during HSA-SPME element heating was 62 W, and 40 W for microtrap heating.

To give a more definitive estimate of total power consumption for *in situ* sampling and analysis, power readings for the RVM Adaptive Air Sampler and low thermal mass-GC (LTM-GC) were taken as a complete, stand-alone system to illustrate total power required for field portability. Other components required for a complete system are a laptop computer, an on- board detector device, and carrier gas peripherals (electronic pressure controls, carrier gas getters, etc.), all requiring a power source as well. Figure 3.10 shows the power consumption as a function of time for the RVM Adaptive Air Sampler followed by a 20C/min temperature ramp on the LTM-GC. The standby power observed was 52 W before preconcentration, which includes a 10 W standby amount from the RVM Adaptive Sampler. The difference confirms the LTM-GC standby reading of 42W observed by Sloan [4]. Upon preconcentrator initiation, power rose to a maximum amount of 101 W and 88 W for HSA-SPME element and microtrap ballistic heating, respectively. The average watts/min for the combined RVM prototype air concentrator/LTM-GC was 64, which represents 83% less power required to operate the lone baseline air concentrator at 375 W/min. The LTM-GC showed a maximum power reading of 101 W during the column temperature ramp. Power consumption profiles for the baseline and RVM Adaptive Sampler/LTM-GC systems are shown in Table 3.8. The total power consumption for the RVM Adaptive Air Sampler and LTM-GC devices during operation is equivalent to supplying power to a 75 W light bulb. At this rate, the experimental

system could theoretically perform a large number of analyses in the field utilizing a portable power source. At an average of 70 W with a 2.91 ampere load, the tandem RVM devices could theoretically operate for 3 hours [10] on an 18 amp-hour, 115 VAC portable power supply, providing up to 18 separate analyses using experimental GC parameters.

Table 3.8. Power consumption profiles for the benchmark Entech 7100 versus the coupled RVM Adaptive Air Sampler/LTM-GC systems

	Entech 7100	RVM / LTM-GC
Min Watts	90	43
Max Watts	712	101
Avg. Watts	346	71
Median Watts	343	72
Percent RSD	35	18
Total Power (W)	4875 in 13 min	759 in 11.3 min

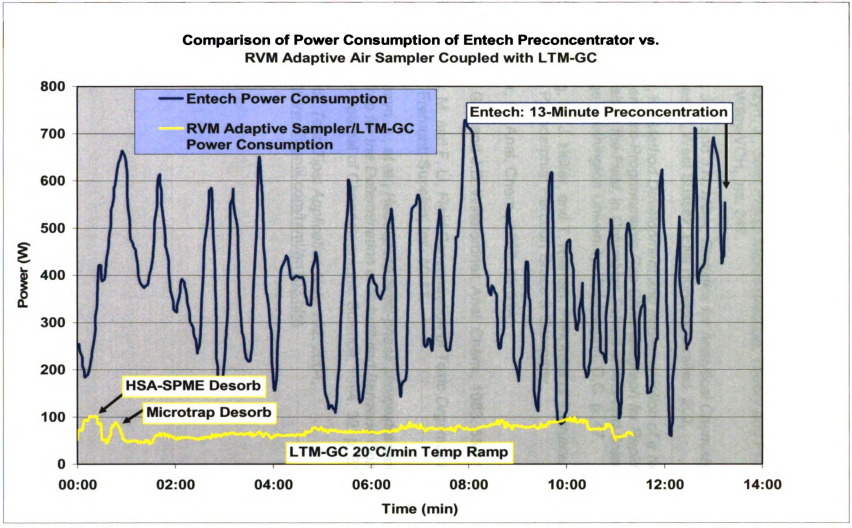

Figure 3.11. Total power consumption for Entech baseline and experimental RVM concentrator/LTM-GC temperature ramp. RVM Adaptive Air Sampler and LTM-GC power consumption is ideal for portability.

3.2 References

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CHAPTER 4 – CONCLUSIONS

Results from the analysis of the U.S. EPA TO-14A gas mixture indicate that the experimental high-surface area SPME element, combined with the focusing preconcentrator microtrap, provides performance similar to the Entech 7100 benchmark air concentration system for the BTEX components under low and high-flow sampling conditions at ambient temperature. For the majority of volatile organic compounds tested, linear dynamic range and desorption efficiencies were comparable to the benchmark system. While the benchmark system achieved lower limits of detection for the lighter molecular weight compounds, the lower limits found by the experimental system for the late-eluting compounds illustrates superior trapping efficiency for these compounds, even at 20 times the benchmark sampling flow rate. Therefore, sampling at a high flow rate while retaining high sensitivity enables a decrease in detection limits for these compounds.

The experimental air concentration system outperformed the benchmark system in preconcentration time and power consumption. Total sample and preconcentration time for the Entech 7100 required thirteen minutes to perform cryogenic trapping in three successive sorbent modules before final desorption and subsequent GC analysis. HSA-SPME element and microtrap preconcentration, including initial sampling, required 89% less time than the benchmark preconcentrator, theoretically enabling approximately 10X sample throughput over a 1-hr period using experimental parameters. Power consumption for the RVM Adaptive Air Sampler, coupled with the RVM LTM-GC,

required a maximum of 101 W during preconcentration and not more than 80 W for an entire chromatographic operation. The experimental system consumed seven times the power on average over the experimental system. Clearly, the RVM experimental system can provide representative field sampling in a relatively short amount of time, without large power requirements, or loss in sensitivity.

Future Work

Since HSA-SPME elements can be individually heated, the implementation of multiple elements in an array along the same flow path affords an adaptable front-end with sampling variation. By varying the SPME adsorbent coatings (e.g. polyacrylate and PDMS), detection of a broader range of compounds (SVOCs and VOCs) may be achieved, rather than using one type of adsorbent alone. In this arrangement, both preliminary and confirmatory analyses may be performed *from the same air sample*. Future extension of this project include testing SPME arrays by sampling compounds with a broader range of volatility in both controlled and open (field) environments.

Human scent detection and tracking by police canines has been successful in the field of forensic investigation, but canine training methods imposed in the United States have recently come under judicial scrutiny. Currently, there are standard procedures for training and certification, however there are no scientific studies that identify the chemical content of human scent "signatures," or respective concentrations upon which canines are responding. With the RVM Adaptive Air Sampler, it may be possible to sample at flow rates

and achieve detection levels comparable to canine olfactory systems to aid in forensic investigations in determining human scent chemical composition.

At the time of this writing, the RVM Adaptive Air Sampler and LTM-GC systems have been installed in a prototypical, portable GC, complete with on-board *micro* pulsed-discharge helium ionization detection (μPDHID). The next phase of this ongoing project is to develop methods that will optimize this detector, along with sampling and analytical methods for this novel, stand-alone system.

APPENDICES

APPENDIX A

GLOSSARY OF TERMS AND ABBREVIATIONS

analyte – a single component of mixture separated by gas chromatography

ballistic – rapid heating action

cm/sec – centimeters per second

carrier gas – a gas, usually diatomic, which carries sample analytes through the gas chromatograph

capillary column – a long marrow tube composed of glass silica that contains a stationary phase through which the mobile phase (carrier gas) is forced under pressure

chromatogram – a graphical record of chromatography containing a series of peaks which represent the detector response as a function of time

convolution – analyte peaks which are overlapped on a chromatograph

cryogen – liquid nitrogen; used to rapidly cool sorbent traps to effectively trap lighter volatile gases

deconvolution – the process of distinguishing individual peaks from multiple overlapped peaks

efficiency – relative ease of performance in terms of analyte separation, power consumption, and/or time

gas chromatograph – an instrument that uses a capillary column to separate mixtures on the basis of chemical interactions with a stationary phase and a mobile phase

GC – gas chromatograph or gas chromatography

HSA-SPME – high surface area-solid phase microextraction

K – partition coefficient for an analyte

L – liter

L/min – liters per minute

LOD – limit of detection [ppt(v)]

LTM-GC – low thermal mass gas chromatography

m – meter
mg – milligram (10^{-3} gram)

µm – micrometer (10^{-6} m)

mL – milliliter (10^{-3} L)

MS – mass spectrometry or mass spectrometer

MSD – mass selective detector

min – minute

Ohm – a unit of electrical resistance (Ω)

ppbv – parts per billion by volume

ppmv – parts per million by volume

pptv – parts per trillion by volume

precision – the agreement of results between repeated experiments

psi – pounds per square inch

quadrupole mass spectrometer – a scanning mass spectrometer that filters out ions based on mass as they are accelerated through the quadrupole area

RH – relative humidity

resolution – a quantitative measure of a column's ability to separate two analytes

retention time – the time required from the point of injection for the analyte to exit the column

RSD – relative standard deviation

sec – second

SPME – solid phase microextraction

SVOC – semi-volatile organic compound

temperature program – a series of time-based and controlled temperature changes applied to a GC column during separation

thermal mass – a measure of a material's ability to store energy in the form of heat

toroid – a closed-loop circular coil rotated about a second larger circular axis

V – volts

VOC – volatile organic compound

W – watts

APPENDIX B

Original software provided by RVM Scientific, Inc., to control the Adaptive Air Sampler system

```
//Door Preconcentrator.CPP  6/09/03

#include <stdio.h>
#include <math.h>
#include <dos.h>
#include <string.h>
#include <stdlib.h>
#include <time.h>
#include <conio.h>
#include <graph.h>
#include "pcl4c.h"
#include <ctype.h>
#undef tolower

#define DAC_enable 8
#define ON 1
#define OFF 0

unsigned char digital_out, PORT, gain, bipolar, bits_24, average, filter,
        polled, channel, char_count, dos_yscale, analog_out_a, analog_out_b,
        video = 1, term = 1, b[4], mode_reg_hi, mode_reg_mid, mode_reg_lo,
        c_mode, ch, cl, gain_prev;
int maxcnt=16383, digital_in (void), Seg, rate, num_ave, time_base_count,
counts_per_volt, time_base,
        wait_time, count_port, counter, wait_time_prev,
        ambient,iso_1_temp=60,iso_1_time=0,iso_2_temp=60,
        iso_2_time=90,sampling_time,trap_init,trap_desorb,trap_bake,trap_heatin
g_time,
        trap_update_freq,injection,bake_time,
        t_last=0, ramp_time,inj_delay=0, i=0, j, kbhit(void), v1, v2, v3, v4, inj_time,
samp_time;

float DAC_init,baud,f_time,data_rate, ramp_rate=60.0, time_per_update=0.1,
t=0, T_target,DAC_A, DAC_A_Init,
        DAC_A_Fin,datum,chromatogram_time, pressure, cvoltage, feedback;
static char LRxBuffer[128+16], LTxBuffer[128+16];
char far *LPtr,fname[13];
clock_t start;
char s1[15];
```

```
void Init_variables(void);
void Ready_com_port(void);
long Time_in_sec(void);
void Sign_on(void);
void delay_sec(int sec);
void delay(int ms);
void send_packet(unsigned char b1, unsigned char b2);
void wait_for_char(int nchar, int wait_in_sec);
void Set_DAC_voltage(char DAC, float voltage);
float RTD(float T);
void bit_8 (unsigned char action);
void bit_7 (unsigned char action);
void bit_6 (unsigned char action);
void bit_5 (unsigned char action);
void bit_4 (unsigned char action);
void bit_3 (unsigned char action);
void bit_2 (unsigned char action);
void bit_1 (unsigned char action);
void abort(void);
void DAC_Init(void);
void reposition(void);
void digital_in (unsigned char action);
void Init_A2D_mode(void);
void Calc_A2D_regs(void);
void DAC_Init(void);
void Set_A2D_mode(void);
//
// Main Program
//
void main(void)
{
        char s[20], c='y';
        int i, v1, v2, v3, v4;
        Init_variables();
        v1=0, v2=0, v3=0, v4=0;
        //Initialize RS232 port for communication with Lawson multi I/O board
        Ready_com_port();
        //Establish RS232 communication with Lawson board
        Sign_on();
        //Initialize analog outputs
        DAC_Init();
        DAC_init = RTD(20);
        bit_1(OFF);
        bit_2(OFF);
        bit_3(OFF);
        bit_4(OFF);
```

```
        bit_5(OFF);
        bit_6(OFF);
        bit_7(OFF);
        bit_8(OFF);
        //
        reposition();
        while (c != 'x')
        {
        _clearscreen(_GCLEARSCREEN);
        printf("Press (I) to move motor In\n");
        printf("Press (O) to move motor Out\n");
        printf("Press (P) to turn pump on and off\n");
        printf("Press (1) to open or close Valve 1\n");
        printf("Press (2) to open or close Valve 2\n");
        printf("Press (3) to open or close Valve 3\n");
        printf("Press (D) to desorb\n");
        printf("Press (S) to check status of optical switch\n");
        printf("Adjust motor in IN position and leave in OUT position before exiting
(X)\n");
                do c = tolower(getch());
                        while (c!='1' && c!='2' && c!='3' && c!='p' && c!='d' &&
c!='i' && c!='o' && c!='s' && c!='x');
                                switch (c)
                                {
                                        case 'i':
                                bit_6(ON);
                                delay_sec(1);
                                bit_6(OFF);
                                        break;
                                        case 'o':
                                        bit_5(ON);
                                delay_sec(1);
                                bit_5(OFF);
                                break;
                        case '1':
                        v1 = (v1 - 1);
                        v1 = abs(v1);
                        if (v1) bit_4(ON); else bit_4(OFF);
                        break;
                        case '2':
                        v2 = (v2 - 1);
                        v2 = abs(v2);
                        if (v2) bit_2(ON); else bit_2(OFF);
                        break;
                        case '3':
                        v3 = (v3 - 1);
```

```
                        v3 = abs(v3);
                        if (v3) bit_3(ON); else bit_3(OFF);
                        break;
                        case 'p':
                        v4 = (v4 - 1);
                        v4 = abs(v4);
                        if (v4) bit_7(ON); else bit_7(OFF);
                        break;
                        case 'd':
                                Set_DAC_voltage('A', 1);
                                        // turn on valves 2 and 3
                                        bit_2(ON);
                                        bit_3(ON);
                                        delay_sec(3);
                                        Set_DAC_voltage('A',0);
                                        bit_2(OFF);
                                        bit_3(OFF);
                                        break;
                                        case 's':
                                        if (digital_in()) printf("Valve is Closed");
else printf("Valve is Open");
                                        delay_sec(1);
                                        break;
                                }
        }
        c = 'y';
        while (c != 'x')
  {
                _clearscreen(_GCLEARSCREEN);
                printf("Injection Time: %d sec\n", inj_time);
                printf("Sample Time: %d sec\n",samp_time);
                printf("Change (T)ime to Inject\n");
                printf("      (S)ample time\n");
                printf("      Accept values, e(X)it menu, and start run\n");

                do c = tolower(getch());
                while (c!= 'x' && c!='t' && c!='s');

                switch (c)
                {
                        case 't':
                                printf("Injection Time = ");
                           scanf("%d",&inj_time);
                           break;
                        case 's':
                                printf("Sample Time = ");
```

```
                    scanf("%d",&samp_time);
                    break;
            }
        }
        // Starting new method for preconcentrator sampling
        //
        // here is where motor is repositioned
        printf("Repositioning motor\n");
        reposition();
        //
        // turn on valve 1 (sample valve)
        // simultaneously turn on pump - can use same digital channel in future
        _clearscreen(_GCLEARSCREEN);
        printf("\nNew Method Starting\n");
        printf("Turning on valve 1 and pump to sample\n");
        bit_4(ON); // valve 1
        bit_7(ON); // pump
        delay_sec(samp_time);
        // turn off valve 1 and pump
        bit_4(OFF);// valve 1
        bit_7(OFF);// pump
        //
        // Injection phase
        //
        // close motor, heat transfer line, heat preconcentrator for 2 seconds
        bit_6(ON);
delay_sec(3);
bit_6(OFF);
Set_DAC_voltage('A', 1);
delay_sec(3);
        // turn on valves 2 and 3
        bit_3(ON);
        bit_2(ON);
        printf("Injecting\n");

        // insert appropriate injection delay here
        delay_sec(inj_time);
        // turn off valves 2 and 3 to sample
        // here is where heating of transfer line and preconcentrator is turned off
        Set_DAC_voltage('A', 0);
        bit_3(OFF);
        bit_2(OFF);
        // Start LTM A68
        bit_8(ON);
        delay(100);
        bit_8(OFF);
```

```
        // Reposition motor
        //
        printf("Repositioning motor\n");
        reposition();
        //
        delay_sec(1);
        SioDone(PORT);                                  //Reset RS232 port
}
//  end of main program
//
void Init_variables()
{
        PORT = 0;    //com1 = 0, com2 = 1, etc.
        gain = 1;      //A/D gain in powers of 2
        bipolar = 1;   //polarity mode flag
        bits_24 = 1;   //A/D word length flag
        average = 0;   //A/D averaging of points as a power of 2
        filter = 2;    //A/D cutoff frequency as 4*10E(filter)
        polled = 1;    //polled mode flag
        rate = 10;     //A/D data rate in Hz
        num_ave = 1;   //parameter for wait_time calc
        baud = 0;      //parameter for wait_time calc
        channel = 0;   //analog input channel selection
//      wait_time = num_ave/rate + baud/rate + 2;   //wait time variable
        char_count = 3; //number of characters to transmit in Lawson I/O
        dos_yscale = 1; //A/D calibration flag
        f_time = 0.03;  //timing value
        time_base_count = 10000;  //DAC counter
        counts_per_volt = (int)ceil(time_base_count/5);  //DAC initialization
        time_base = 0;  //DAC initialization
        analog_out_a = 1;  //DAC port 'A' value
        analog_out_b = 2;  //DAC port 'B' value
        digital_out = 0;   //unsigned char for digital output
        inj_time = 5;  // injection time
        samp_time = 4;       // sample time
}

void Ready_com_port(void)
{
        char string[80];
        char buffer[1];

        //setup 128 byte receive buffer
        LPtr = (char far *)LRxBuffer;
        Seg = FP_SEG(LPtr) + ((FP_OFF(LPtr)+15)>>4);
        SioRxBuf(PORT,Seg,Size128);
```

```
        //setup 128 byte transmit buffer
        LPtr = (char far *)LTxBuffer;
        Seg = FP_SEG(LPtr) + ((FP_OFF(LPtr)+15)>>4);
        SioTxBuf(PORT,Seg,Size128);
        //set port parameters
        SioParms(PORT,NoParity,OneStopBit,WordLength8);
        //reset port for initial operation at 300 baud
        SioReset(PORT,Baud300);
        SioDTR(PORT,'S');
        SioRTS(PORT,'C');
        if (video) printf("\nRS232 initialized using COM%d @ 300
Baud\n",1+PORT);
   if (term)
   {
        strcpy(string,"RS232 initialized using COM");
        _itoa(1+PORT,buffer,10);
        strcat(string,buffer);
        strcat(string," @ 300 Baud");
        }
}

long Time_in_sec(void)
{
        time_t ltime;

        time(&ltime);
        return ltime;
}

void Sign_on(void)
{
        long time;
        int i,j;

        time = Time_in_sec();
        //Wake up Lawson multi I/O board
        while ((i != 3) && (Time_in_sec()-time < 5))
        {
                i = SioPutc(PORT,'\0');
                delay(200);                    //increased from 200 for laptop
                i = SioGetc(PORT,5);
        }
        if (video) printf("Lawson board output = %d\n",i);
        delay(200);
        //Send sign-on token
        SioPutc(PORT,0x88);
```

```
        delay(200);
        SioPutc(PORT,'\0');
        delay(200);
        SioGetc(PORT,0);
        //Lawson board should be ready to communicate at 9600 baud
        SioBaud(PORT,Baud9600);
        if (video)
        {
                printf("Echo test:\n");
                delay(200);
                for (i=1; i<11; i++)
                {
                        SioPutc(PORT,i);
                        delay(200);
                        j = SioGetc(PORT,0);
                        printf("%d %d\n",i,j);
                }
        }
        delay(200);
        SioPutc(PORT,'\0');
        //Initialize A/D converter
        Init_A2D_mode();
        send_packet(average,filter);
        if (polled) send_packet(0,1);
        else send_packet(0,0);
        delay(200);
        //Check to see if Lawson board correctly returns initialization values
        for (i=0; i<3; i++)
        {
                b[i] = SioGetc(PORT,1);
                delay(200);
        }
        if ((b[0] == mode_reg_hi) && (b[1] == mode_reg_mid) &&
           (b[2] == mode_reg_lo))
                if (video) printf("LOGGED ON AT 9600 BAUD IN POLLED
MODE\n");
        else if (video)
        {
                printf("PROBLEM LOGGING ON");
                exit(0);
        }
}

void send_packet(unsigned char b1,unsigned char b2)
{
        unsigned char check_sum;
```

```
        SioPutc(PORT,b1);
        SioPutc(PORT,b2);
        check_sum = (b1+b2) & 0xff;
        SioPutc(PORT,check_sum);
}

void DAC_Init(void)
{
        send_packet(5,64);              //set resolution to 14 bit
   Set_DAC_voltage('A',0);
   Set_DAC_voltage('B',0);
}

void wait_for_char(int nchar, int wait_in_sec)
{
        long start;

        start = Time_in_sec();
        while ((SioRxQue(PORT) != nchar) | (Time_in_sec()-start > wait_in_sec));
        if ((SioRxQue(PORT) != nchar) && video)
                printf("IO Error: not enough received characters");
}

void Set_DAC_voltage(char DAC, float voltage)
{
        float analog_duty_cycle;
        unsigned char anahigh,analow;

        if (voltage < 0) voltage = 0;
        if (voltage > 5) voltage = 5;
        analog_duty_cycle = (float)maxcnt*voltage/5;
        anahigh = (unsigned char)(analog_duty_cycle/256);
        analow = (unsigned char)(analog_duty_cycle-anahigh*256);
        send_packet(8,analow);              //set analog output low byte
        switch (DAC)                    //set high byte
        {
                case 'A': send_packet(9,anahigh & 0x7f); break;
                case 'B': send_packet(9,anahigh | 0x80);
        }
}

float RTD(float T)
{
        float x,Vref,Rf,R2,alpha,delta;

        Vref = 2.501;                       //V
```

```
        Rf = 13687;                     //gain resistor, ohms
        R2 = 9946;                      //ohms
        alpha = 0.00385;                  //Pt temperature coefficient
        delta = 1.5065;                  //Pt temperature coefficient
        x = Vref*Rf/R2*alpha*(T-delta*(T/100-1)*(T/100)); //Calendar-Van Dusen
//  Divide x by 2 to run TC3 board
        x = x/2;
        return x;
}

void bit_8 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0x7f ; break;
                case ON:  digital_out |= 0x80 ;
        }
        send_packet(2,digital_out);
}
void bit_7 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xbf; break;
                case ON:  digital_out |= 0x40;
        }
        send_packet(2,digital_out);
}
void bit_6 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xdf; break;
                case ON:  digital_out |= 0x20;
        }
        send_packet(2,digital_out);
}
void bit_5 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xef ; break;
                case ON:  digital_out |= 0x10 ;
        }
        send_packet(2,digital_out);
}
```

```
void bit_4 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xf7 ; break;
                case ON:  digital_out |= 0x08 ;
        }
        send_packet(2,digital_out);
}
void bit_3 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xfd ; break;
                case ON:  digital_out |= 0x02 ;
        }
        send_packet(2,digital_out);
}
void bit_2 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xfb ; break;
                case ON:  digital_out |= 0x04 ;
        }
        send_packet(2,digital_out);
}
void bit_1 (unsigned char action)
{
        switch (action)
        {
                case OFF: digital_out &= 0xfe ; break;
                case ON:  digital_out |= 0x01 ;
        }
        send_packet(2,digital_out);
}
int digital_in(void)
//
//      Optek optical switch on digital input RS 1
//
{
        send_packet(0x80,0x4c);
        wait_for_char(2,1);
        for (j=0; j<2; j++)
        {
                b[j] = SioGetc(PORT,1);
```

```
            delay(100);
        }
        if (b[0] != 0x80)
        {
            printf("digital input command token not returned\n");
            exit(0);
        }
        return (b[1] & 0x01);
}
//
void reposition (void)
{
        bit_5(ON);
        while(digital_in()==1);
        bit_5(OFF);
        bit_6(ON);
        while(digital_in()==0);
        bit_6(OFF);
}
void delay_sec(int sec)
{
        int i;
        for (i=0; i<sec; i++)  delay (1000);
}

void delay(int ms)
{
        int i,j,k;
        for (i=0; i<ms; i++)
           for (j=0; j<10; j++)
             for (k=0; k<5; k++);
}
void Init_A2D_mode(void)
{
        Calc_A2D_regs();
        send_packet(mode_reg_hi,mode_reg_mid);
        send_packet(mode_reg_lo,mode_reg_mid);
}
void Init_A2D(unsigned char channel)
{
        char string[80], j;
        int i, channel_prev;

        sprintf(string,"# Initializing A/D channel %d",channel);
        send_packet(0x01,channel*16 + DAC_enable);
        if (dos_yscale)
```

```
        {
                gain_prev = gain;
                channel_prev = channel;
                if (gain != 1)
                {
                        gain = 1;
                        Set_A2D_mode();
                }
        }
        channel = 7;
        wait_time_prev = wait_time;
        wait_time = wait_time + f_time + 2;
        //Do offset calc
        send_packet(0x82,16*channel + DAC_enable);
        wait_for_char(char_count+1,wait_time);
        for (i=1; i < char_count+2; i++) j = SioGetc(PORT,1);
        wait_time = wait_time_prev;
        channel = 6;
        wait_time_prev = wait_time;
        wait_time = wait_time + f_time + 2;
        //Do full scale cal
        send_packet(0x83,16*channel + DAC_enable);
        wait_for_char(char_count+1,wait_time);
        for (i=1; i < char_count+2; i++) j = SioGetc(PORT,1);
        wait_time = wait_time_prev;
        if (gain != gain_prev)
        {
                gain = gain_prev;
                Set_A2D_mode();
                channel = 7;
                wait_time_prev = wait_time;
                wait_time = wait_time + f_time + 2;
                if (video) printf("Repeating offset cal");
                //Do offset calc
                send_packet(0x82,16*channel + DAC_enable);
                wait_for_char(char_count+1,wait_time);
                for (i=0; i < char_count+1; i++) j = SioGetc(PORT,1);
                wait_time = wait_time_prev;
        }
        channel = channel_prev;
        send_packet(0x01,channel*16 + DAC_enable);
        delay(floor(f_time*6500)+1800);
        dos_yscale = 0;
}
void Set_A2D_mode(void)
{
```

```
        int j;

        send_packet(0x84,0);
        wait_for_char(1,wait_time);
        Calc_A2D_regs();
        send_packet(mode_reg_hi,mode_reg_mid);
        send_packet(mode_reg_lo,mode_reg_mid);
        delay(6500);
        //Check for proper token return after sending mode
        j = SioGetc(PORT,0);
        if ((j != 0x84) && video) printf("Wrong start token");
        for (j=0; j<3; j++)
        {
                b[j] = SioGetc(PORT,1);
                delay(3300);
        }
        if (((b[0] != mode_reg_hi) | (b[1] != mode_reg_mid) |
                (b[2] != mode_reg_lo)) && video) printf("PROBLEM SENDING A
MODE");
}
void Calc_A2D_regs(void)
{
        int mode_code, g;
        float AD_clock = 19531.25;
        int temp, standby = 0;

        rate = 10;
        //calc mode register data
        mode_code = (int)floor(AD_clock/rate);
        mode_reg_lo = mode_code & 0xff;
        mode_reg_mid = (mode_code & 0x700)/256;
        rate = floor(AD_clock/(((mode_reg_mid & 0x7)*256)+mode_reg_lo));
        if (video) printf("Calc rate to send: %d\n",rate);
        g = 0;
        temp = gain;
        while (temp != 1)
        {

                if (temp > 1) temp /= 2;
                g++;
        }
        //set gain and power down bits
        mode_reg_hi = g*4 | standby;
        if (!bipolar) mode_reg_mid += 16;  //unipolar
        if (bits_24) mode_reg_mid += 128;
}
```

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