SANDIA REPORT

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Real-time Discriminatory Sensors for Water Contamination Events: LDRD 52595 Final Report

Curtis D. Mowry, Alex Robinson, Steven K. Showalter, Patrick R. Lewis, Douglas R. Adkins, David R. Wheeler, Gregory Shelmidine, Kimberly Carrejo, Shawn M. Dirk, Andrew M. Goodin, W. Clayton Chambers, Theodore T. Borek III, and Adriane N. Irwin

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Abstract

The gas-phase μChemLab™ developed by Sandia can detect volatile organics and semi-volatiles organics via gas phase sampling. The goal of this three year Laboratory Directed Research and Development (LDRD) project was to adapt the components and concepts used by the μChemLab™ system towards the analysis of water-borne chemicals of current concern. In essence, interfacing the gas-phase μChemLab™ with water to bring the significant prior investment of Sandia and the advantages of microfabrication and portable analysis to a whole new world of important analytes. These include both chemical weapons agents and their hydrolysis products and disinfection by-products such as Trihalomethanes (THMs) and haloacetic acids (HAAs). THMs and HAAs are currently regulated by EPA due to health issues, yet water utilities do not have rapid on-site methods of detection that would allow them to adjust their processes quickly; protecting consumers, meeting water quality standards, and obeying regulations more easily and with greater confidence. This report documents the results, unique hardware and devices, and methods designed during the project toward the goal stated above. It also presents and discusses the portable field system to measure THMs developed in the course of this project.

Acknowledgments
The authors would like to acknowledge additional contributors to this work through its three year course. The data in this report would not exist without this diverse and talented team. It includes: Dan Trudell, James Barnett, Jennifer Ellison, Stephen Howell, Kim S. Rawlinson, Rameen Hadizadeh, Patrick Fletcher, and David Mullhollen. In addition the investment area management of Wayne Einfeld and Ray Finley was invaluable in keeping the research relevant toward "real-world" customers.

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Executive Summary

Sandia National Laboratories has developed a portable system for the detection of the trihalomethane group (THMs) of disinfection byproducts. This system provides a small footprint, low cost, sensitive, and quickly deployable water sensor. The self contained system weighs less than 32 pounds, occupies a carry-on luggage sized case, and performs THM analysis in less than four minutes. The technique of purge and trap (P&T) is performed on a water sample followed by isothermal gas chromatography. A three sensor surface acoustic wave (SAW) detector array, which provides a set of three responses for additional confidence, detects the THMs. An inexpensive programmable integrated circuit (PIC) processor handles heating, timing, valve control and data collection functions for the system. Plotting and analysis are performed with a portable computer. While the system has been assembled, it has not been field tested and its detection limits still must be quantified.

Current methods of organic sample collection/analysis are costly, slow and useful primarily for imposition of fines, not for protection of the consumers. Rapid, on-site detection is not available for THMs at this time, yet mitigation steps need to be performed immediately following detection of contaminates or high THMs in the water system, not days or weeks after sample collection. Sensors identifying specific contaminants would allow water system operators options to address the problem by suspending water flow in the parts of the system where contamination has been detected. Real time identification of the contaminant(s) would be helpful in determining effective mitigation methods and procedures as well as providing timely notification to the water utility customers.

Sandia's detection system is meant to fill the need for a rapid, portable, and sensitive low cost analysis. The system and components are described in this report, along with results, unique hardware and devices, and methods designed during the project. One goal of this three year Laboratory Directed Research and Development (LDRD) project was to adapt the components and concepts used by the μChemLab™ system towards the analysis of water-borne chemicals of current concern. Results toward the collection and analysis of additional analytes using μChemLab™-type components and methods are also presented.

Acronyms and Abbreviations

AWWA	American Water Works Association
CWA	chemical weapons agents
COTS	commercial off the shelf
cm	centimeters
DOE	Department of Energy
DMMP	dimethyl methyl phosphonate
DPBs	disinfection byproducts
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
i.d.	internal diameter
mL	milliliter
MS	mass spectrometry
ng	nanogram
ppm	parts per million
ppb	parts per billion
PC	preconcentrator
PIC	programmable integrated circuit
P&T	purge and trap
THM	trihalomethane
THMs	trihalomethanes

1.0 Introduction

This report documents the results, methods, and field system developed through a three year Laboratory Directed Research and Development (LDRD) project. One goal of this LDRD project was to adapt the components and concepts used by the μChemLab™ system towards the analysis of water-borne chemicals of current concern. In essence, interfacing the gas-phase μChemLab™ with water. A second goal of the project was to develop a portable system for the measurement of trihalomethanes (THMs) in water. Both of these goals required leveraging the significant past prior investments of Sandia in μChemLab™ technology and utilizing the advantages of microfabrication for portable analysis.

The μChemLab™ utilizes microfabricated components to achieve general laboratory concepts of collection, separation, and detection. It is a gas-phase analytical system and therefore has targeted gas-phase analytes such as chemical weapons agents and toxic industrial chemicals. The results of this project, by developing technology to bring water-borne chemicals to μChemLab™-style portable analysis, open up a whole new field of capabilities.

The project has ties to DOE's National Security Mission in that pure, clean, unadulterated water is necessary for the safety and security of the citizens of the United States. The technology developed here and based upon advances made here will protect the national security infrastructure by allowing accelerated detection of disinfection byproducts and hydrolysis products of chemical weapons agents. They will also decrease the required time to identify/corroborate possible terrorist acts and thereby increase the security of water, a vital national resource.

The results of this project will be of interest to the nation's water utilities, enforcement agencies, the Environmental Protection Agency (EPA) and other regulatory agencies, and others who require rapid field knowledge of their water supply. THMs and HAAs are currently regulated by EPA due to health issues, yet water utilities do not have rapid on-site methods of detection that would allow them to adjust their processes quickly; protecting consumers, meeting water quality standards, and obeying regulations more easily and with greater confidence.

Results are presented on microfabricated components used to collect (extract) chemicals out of water, derivatize haloacetic acids (HAAs) for enhanced analysis and detection, and the technology enabling the field system developed for THM detection. This report documents the results, unique hardware and devices, and methods designed during the project toward the goal stated above. It also presents and discusses the portable field system to measure THMs developed in the course of this project.

2.0 Background

What are Trihalomethanes (THMs?)

THMs are chlorine and/or bromine (or other halogen) containing chemicals created as a byproduct of the disinfection chemicals used by water utilities. Disinfectants are required to control microbial contaminants. THMs are therefore also referred to as disinfection byproducts (DBPs), and are regulated along with other DBPs by the Unite States Environmental Protection Agency (EPA). The basic chemical structures of the most common THMs are shown in Figure 1, and are more specifically named (left to right) chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

Figure 1: The most common THMs found in treated water.

Not just an issue in the United States, THMs have been found for example at levels from less than 10 parts per billion (ppb) to greater than 80 ppb in tap water and drinking water in Thailand[1]. EPA specifies that water utilities report detected levels of THMs to their customers on a regular basis, and is in the process of implementing additional rules to regulate Total Trihalomethanes (TTHM) at a maximum allowable annual average level of 80 ppm, down from 100 ppb. In addition, utilities will be required to survey (and measure) their system infrastructure to determine where increased THM levels are detected.

How are THMs formed?

The disinfectant chemicals used by water utilities react with naturally occurring organic and inorganic matter in water to generate THMs. The general chemical reaction is shown in Equation 1. Bromine is found naturally in water and at higher levels near ocean sources.

Equation 1: Formation of halogenated disinfection byproducts (NOM=natural organic matter).

$$HOCl^{-} + Br^{-} + NOM \rightarrow \text{Halogenated DPBs}$$

Methods of Detection

There are standard laboratory methods for the detection of THMs. These methods also specify procedures for the collection of samples and data quality objectives. Two certified analytical methods are the American Water Works Association (AWWA) method 6200 and EPA method 524.2. Both of these methods perform purge and trap (P&T) for collection and concentration of samples, gas

chromatography (GC) for separation, and mass spectrometry (MS) for detection. Minimum detectable levels for the AWWA method are less than 0.2 ppb for both chloroform and bromoform.

A general comparison between the certified methods and the field system developed in this project is shown Figure 2. Further discussion of the field system components is presented in the Results and Discussion section of this document.

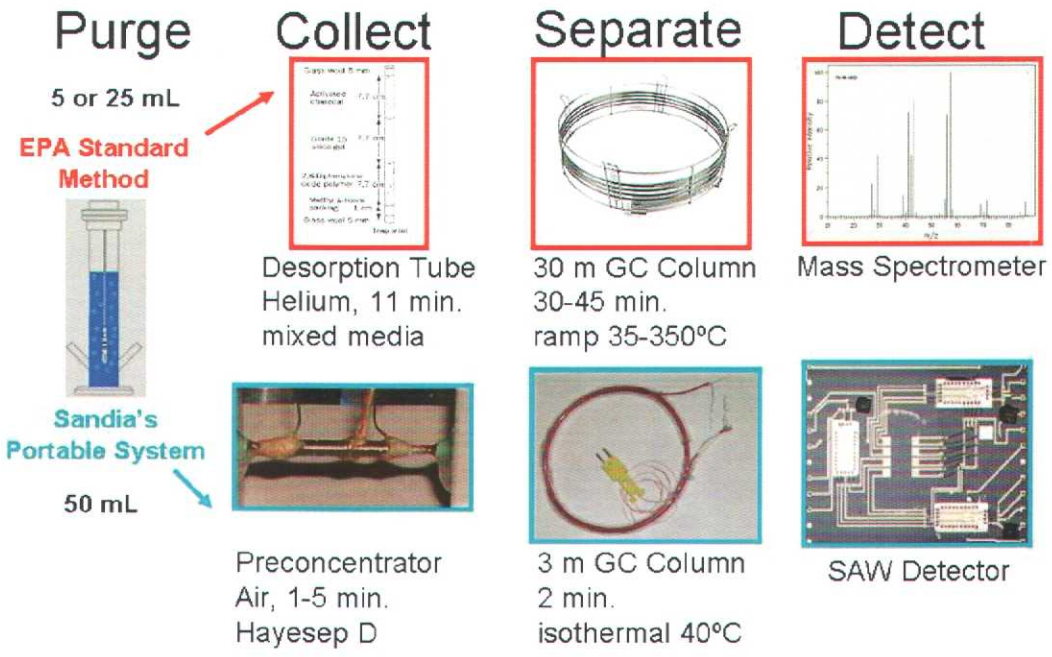


Figure 2: Comparison between certified laboratory and field system methods and components.

Chromatography of THMs

As with any gas-phase analyte, there are a host of conditions, including GC column phases, which can be used to separate and resolve the analyte of interest. Separation is used to increase the confidence in the measurement, and reduce interferants. A general survey of the literature shown in Table 1 illustrates the variety of phase materials used. Phase stability, durability, and resolution are all determining factors in choosing a column for field analysis.

Table 1: Chromatography columns used for the separation of THMs.

Name	Chemical	Method
Carbowax	polyethelyene glycol	THM SPME
OV-1	polydimethlysiloxane	THM SPME
DB-5	5%-Phenyl-95%-dimethyl polysiloxane	THM separation
SP-1000	PEG- acid modified	THM separation
DB-624	6% Cyanopropyl-phenyl 94% dimethyl polysiloxane	volatiles
DB-1701	14% Cyanopropyl-phenyl 86% dimethyl polysiloxane	HAA separation
DB-210	50% trifluoropropyl 50% dimethyl polysiloxane	HAA separation

Other applications/interest of this work

The field system developed here should also be of interest to the pharmaceutical industry, as water quality and VOC control and monitoring are important. Other industries that must use process water (semiconductors, power generation), as well as water system modeling studies can benefit from field monitoring.

Preconcentrator Technologies Background

Other investigators have tested carbon-based preconcentrators as injection/trapping for GC. These studies are important as they show the flexibility and benefits from temperature programming, stop flow, and conditioning of a preconcentration device[2]. The same investigators have shown the benefits of microfabrication for PCs and the use of packed-bed microfabricated PC's., packed with Carbopack X for VOCs[3].

Other Compounds of interest

These include water contaminants that can be purged from water, and are important as a hazardous chemical or due to taste and odor concerns. Examples include Methyl Tertiary Butyl Ether (MTBE, CAS#1634-04-4), the gasoline additive that leaks from storage tanks and has been found in well water. The odor threshold of neat MTBE is reported as between 0.1 to 0.3 ppm. Another compound of interest from the perspective of field analysis is 1,4-dichlorobutane (CAS#110-56-5) which has been used as an internal standard for the determination of method efficiency.

3.0 Experimental Details

Samples and Reagents

Adsorbents

General information, including breakthrough volumes of various adsorbents for a wide variety of volatile analytes can be found on the world wide web[4].

Carboxen 569

Carboxen 569 is a carbon molecular sieve adsorbent resin designed for small chlorinated and other molecules. It has a large mesh size which minimizes the backpressure in the desorption tubes and also has a low affinity for water, and a temperature limit of 400°C.

Tenax™ TA

Tenax™ is a porous polymer resin based on 2.6-diphenylene oxide. It has been specifically designed for the trapping of volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrices. Due to its low affinity for water, Tenax™ TA is especially useful for the purging and trapping of volatiles from high moisture content samples including the analysis of volatile organic compounds in water. It is important that no oxygen be permitted to enter the Tenax™ TA material when it is at elevated temperatures. The temperature limit is 350 °C

Hayesep D

Hayesep D is a high purity divinylbenzene polymer, and is normally used for the separation of light gases rather than as a preconcentrator material.

Table 2: Hayesep D physical information from VICI Metronics.

Polymer	Max operating temp	Surface area $m^2/gram$	Tapped bulk density *gram/cc*	Composition	Polarity
D	290°C	795	0.3311	DVB*	1

Permeation tubes

Some permeation tubes were purchased from Kin-Tek (La Marque, TX). The following section lists permeation tubes and related information.

Table 3: Permeation tube information.

Chemical name	Part no. information	vendor
Chloroform	SRT-004.00-4012/30	Kin-Tek #35209
Chlorodibromomethane	hrt-010.00-4102/30	Kin-Tek #35213
trichloromethane	dynacal size 1.5cm part no. 110-015-4202 type std. 60ng/min/cm +/- 10% at 50C	Vici Metronics (Santa Clara, CA)
bromoform	hrt-007.50-4096/30	Kin-Tek #35212
Bromodichloromethane	hrt-001.00-4103/30	Kin-Tek #35215
carbon tetrachloride	dynacal size 6.3cm part no. 100-063-4203 type H.E., 200ng/min/cm +/- 15% at 50C	Vici Metronics (Santa Clara, CA)
1,1,1 trichloroethane	dynacal size 13.7cm part no. 100-137-4207 type H.E., 80 ng/min/cm +/- 15% at 50C	Vici Metronics (Santa Clara, CA)
trichloroethylene	dynacal size 11.0 cm part no. 110-110-4303 type std., 97 ng/min/cm +/- 10% at 50C	Vici Metronics (Santa Clara, CA)

Table 4: THM permeation tube data, calibrated by Kin-Tek.

Compound	Permeation (ng/min)	K_0	Notes
chloroform	47 @ 30C	0.188	max 40C
chlorodibromo-methane	134 @ 30C	0.108	max 40C
bromoform	33 @ 30C	0.089	max 40C
bromodichloro-methane	57 @ 30C	0.137	max 40C

The following Equation is used to calculate the concentration of a known flow past a permeation tube.

Equation 2: Equation for calculating concentration for calibrated permeation tubes.

$$\text{rate (ppm)} = (K_0 * \text{ng/min})/\text{Flow cc/min. @STP}$$

Flow System

For the delivery of known concentrations of vapor, the flow of Brooks mass flow controllers is calibrated using a Gilibrator flowmeter. For measurements of GC flow or PC loading flow, Alltech flow meters model 5700 were used.

Table 5: Flow Rates for Unit A1 (Brooks 5850E 205ccm, SN 3050/01)

SCCM Indicated	Measured w/ Gilibrator (SN 104790-L)			Average
5	6.77	6.91	6.75	6.81
10	13.55	13.63	13.48	13.55
15	20.30	20.27	20.32	20.30
20	27.07	27.16	27.11	27.11

Table 6: Flow Rates for Unit A2 (Brooks 5850 205 ccm, SN 6846/2)

SCCM Indicated	Measured w/ Gilibrator (SN 104790-L)			Average
5	6.72	6.76	6.79	6.76
10	13.44	13.47	13.53	13.48
15	20.04	20.01	20.00	20.02
20	26.82	26.83	26.91	26.85

Sparging Experiments

Helium and air sparging experiments were performed on a flow test stand as shown in Figure 3 and the photo in Figure 4. Desorption tubes were commercially obtained and contained Tenax TA adsorbent. Analysis was performed on either a Perkin Elmer ATD 400 thermal desorber or on the unit shown Figure 5.

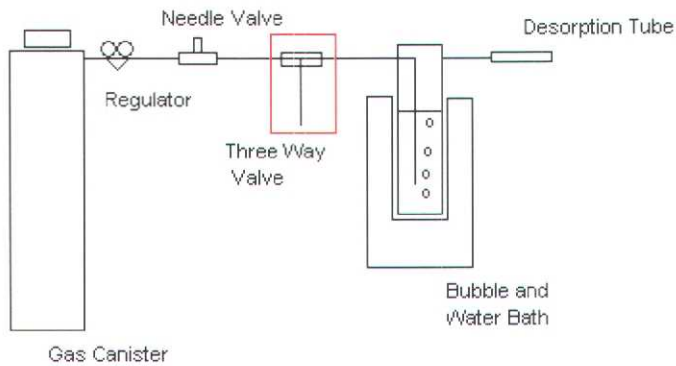


Figure 3: Schematic of sparging test setup.

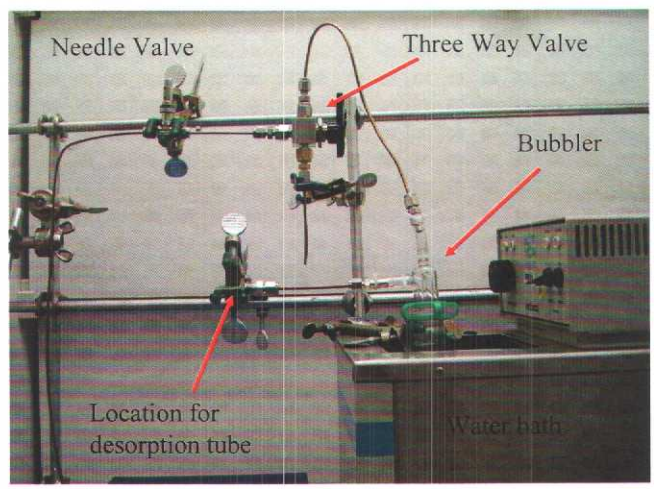


Figure 4: Photo of sparging test setup.

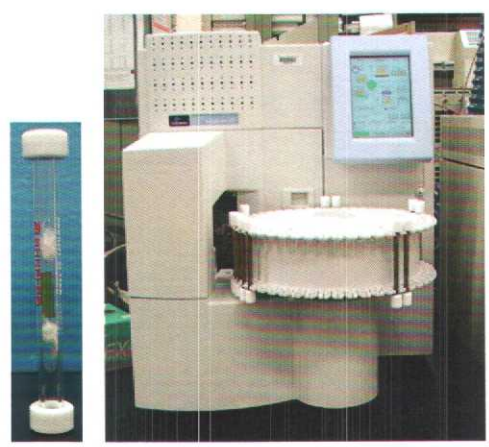


Figure 5: Calibration tube and thermal desorption autosampler.

Automated SPME Injection Interface

The automated SPME injection interface is shown below, and consisted of a commercial SPME needle and a commercial motor controller to control timing of the motor drives. These drives actuate to either inject or retract the needle.

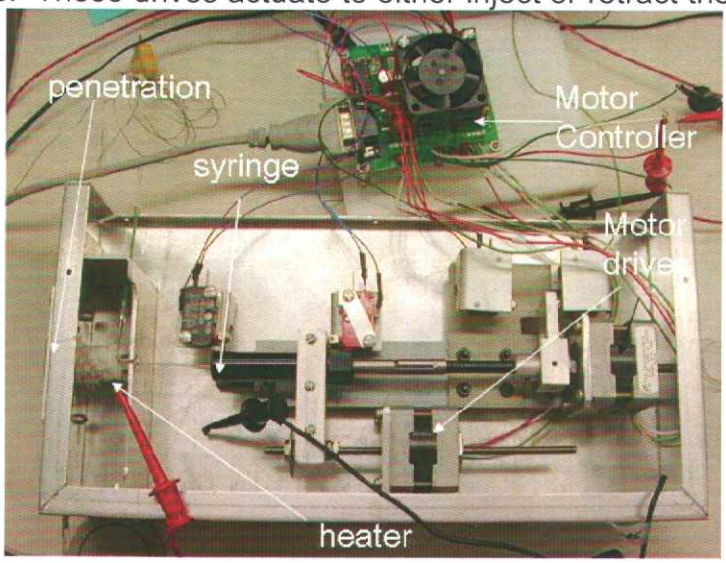


Figure 6: Photo of automated SPME injection interface.

Solid Phase Extraction Column (SPEC)

The extraction column consists of a microfabricated silicon column (indicated by square) with attached capillaries to transport either liquid or gas. Loading is shown on the left below, where pressurizing the vessel drives liquid through the column. On the right is shown the procedure for desorbing from the SPEC and to a secondary planar preconcentrator for refocusing. The SPEC can also be desorbed directly towards a detector.

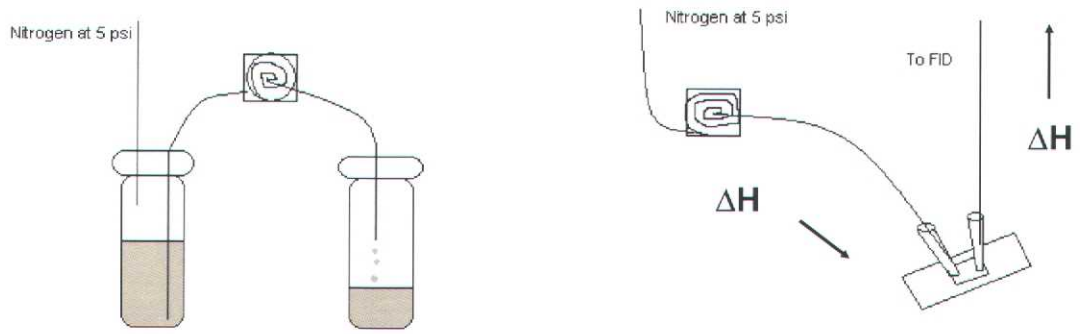


Figure 7: Schematic of microfabricated solid phase extraction column during loading and desorption with secondary refocusing.

Preconcetrators

Preconcentrators used during the course of the project are shown in the following figures. They are presented roughly in chronological order.

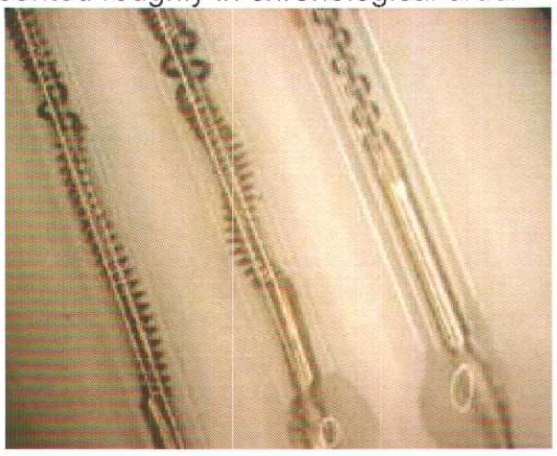


Figure 8: Photo of ohmic bead PCs.

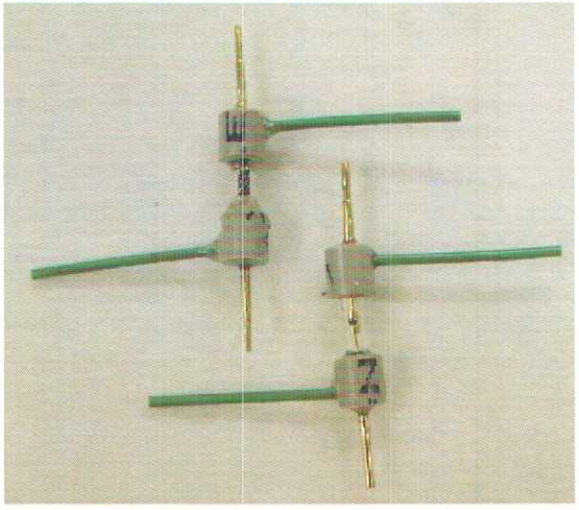


Figure 9: Photo of ohmic bead PC with PEEK flow connections (green).

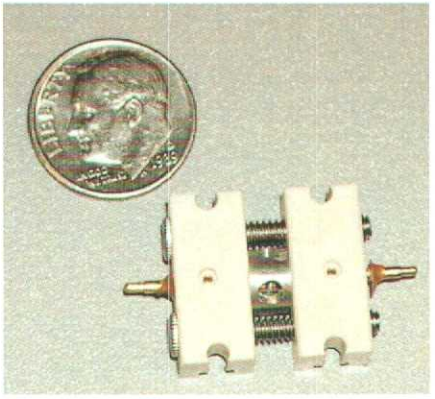


Figure 10: Photo of "cannonball" PC in field box flow fixture.

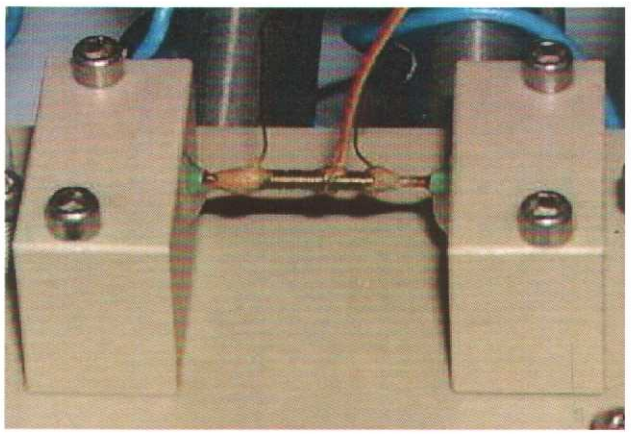


Figure 11: Photo of tubular nichrome-wrapped PC mounted in field box.

Tubular nichrome wrapped PCs as shown in Figure 11 were assembled using the following components and procedure. A section of commercial stainless steel tubing (.0285 ID, .0355 OD Part #:HTX-20X-36) Small Parts, Inc., is passivated with 1,1,1,3,3,3-hexamethyldisilazane. Sintered steel wool is cut and rolled into .04 OD spheres and treated with 1,1,1,3,3,3-hexamethyldisilazane to fabricate small retainer plugs. One side of the coiled device to which the first capillary tube will be epoxied is referred to as "end-a".

The general procedure is as follows:
1. Stablohm 650 Nickel Chromium resistance wire (7.863 Ohms/ft), California Wire Company, is wrapped around the "tube" for 1cm of length and secured at both ends with Epotek H74 Epoxy (Epoxy Technology, Inc.). A K-type precision fine wire thermocouple insulated with Teflon (Omega Engineering, Inc. Stamford, CT, part # PL2005/08) is affixed at the midpoint (against the coil) with Epotek H74 Epoxy.
2. A plug is placed immediately inside the coiled "tube" at "end-A".
3. A 1cm section of Megabore capillary (non-polar fused silica .53mm, Supelco P#2-5771) is mounted into "end-A" and epoxied with Epotek H74.
4. Vacuum is applied to "end-A" and Hayesep-D (Supelco, Bellefonte, PA) is collected into the "tube" until it is visibly full. Using a section of megabore capillary, insert capillary into the open end and remove 2mm of Haysep-D (to make room for the plug and capillary attachment).
5. Place "plug" inside the open end, and epoxy a 1cm section of Megabore capillary (as above on "end-a").
6. Attach a K-type thermocouple connector to the unbeaded end of the wires (red being -, yellow being +).

Chromatography

The commercial capillary column used in the field system is a 3 meter, 0.25 micron internal diameter (i.d.), db-624 phase commercial column from Restek. The column has been enclosed in a fiberglass insulative sleeve (red) along with a

nichrome wire. The column is coiled and contained in large-bore plastic tubing for support. A thermocouple is inserted between the coils of the column.

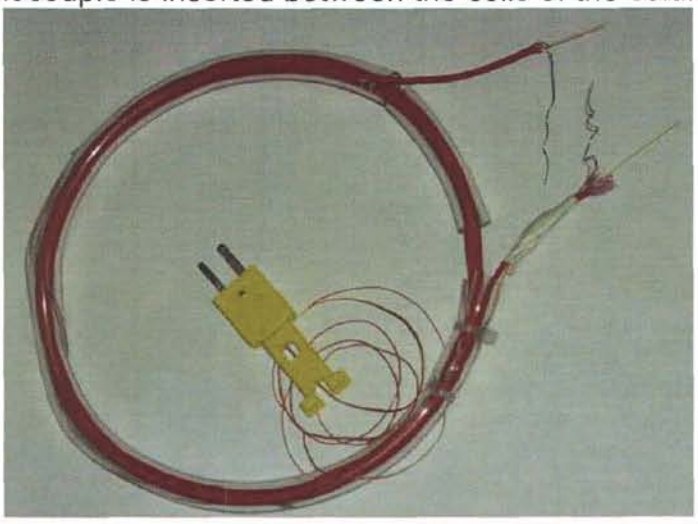


Figure 12: Photo of commercial column prepared for field system.

The packed microcolumn was packed with commercial particles of 1701 phase. Packing is achieved by using a light vacuum to pull particles through the channel. Vibrating the column is advantageous and speeds the process.

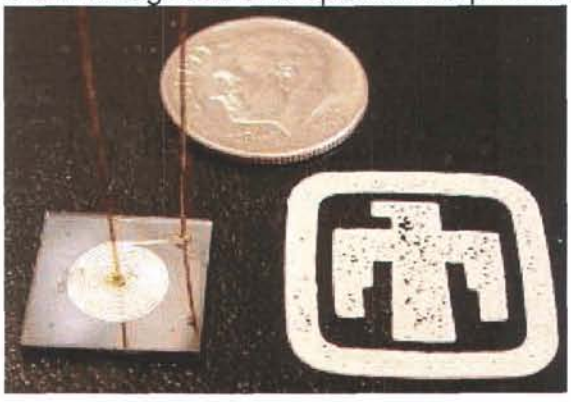


Figure 13: Photo of packed microGC column.

Surface Acoustic Wave (SAW) Detection

A wide variety of SAW devices were used during the course of this work. The specific devices are listed below by their designator, followed by the coatings on each delay line.

120903C - DKAP, BSP3, PECH
RH063 - DKAP, ADMT, tenax
RH271C8 - DKAP, ADMET, modified tenax
RH32L3 – PPP (polyphenylene), DKAP, Tenax
RH31H5 - all three channels w/ DKAP
RH45E5 - DKAP, "A",-PPP

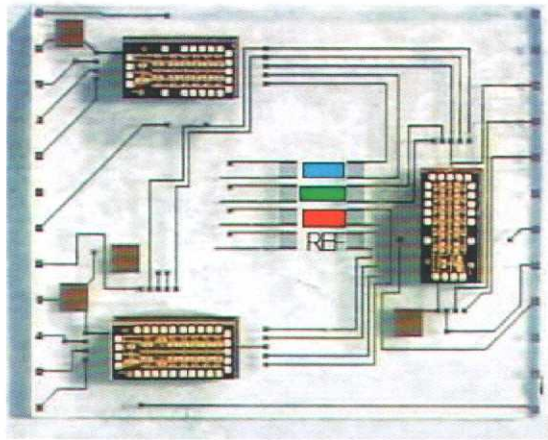


Figure 14: Photo of SAW device, with delay lines indicated by colored rectangles.

SAW coatings

All of our coatings are polar. The structures of several are shown in the following figure. Abbreviations are as follows: DKAP – modified fluorinated polyol, BSP3 – fluorinated polyol, PECH – polyepichlorohydrin, ADMT – admet, PPP – polyphenylated phenylene.

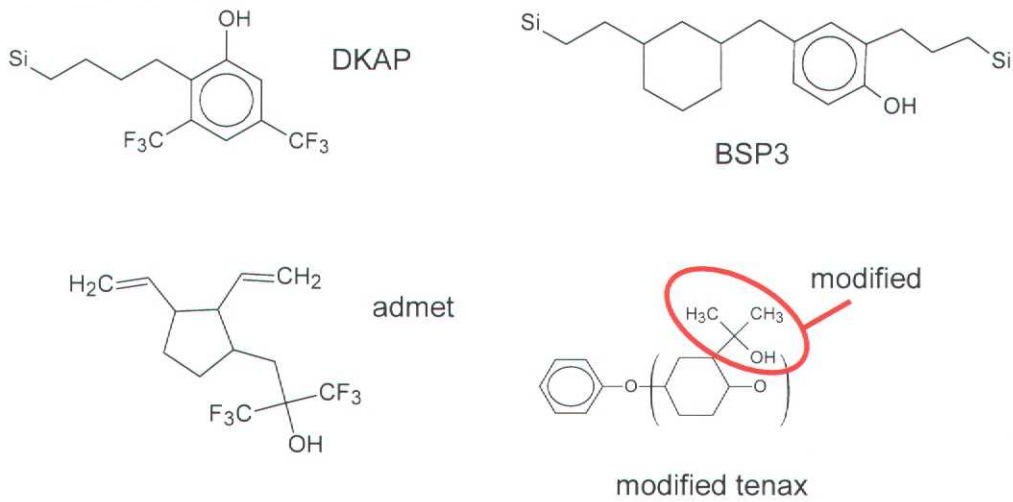


Figure 15: Structures of SAW coatings - DKAP, BSP3, ADMET, and Modified Tenax.

SAW Dither Optimization

The following procedure was used to determine the optimal dither setting to maximize response.

data collection:

chloroform D tube, 40C oven, 0% dilution flow

collect data, record conditions/filenames onto excel worksheet "saw comparison.xls"

(file located in "newSAW_data" on S805547 computer, shortcut is on desktop)

2 runs at each dither setting:

convert data files:

convert all *ch1, *ch2, *ch3 files to *.CGM using Galactic (Thermo Electron) "grams a/l" program

start grams, "file" menu, "import/export"

use the file converter option: ascii x,y (non-even spacing)

change baselines:

use Galactic "grams a/l" program

"applications menu", "offset correction"

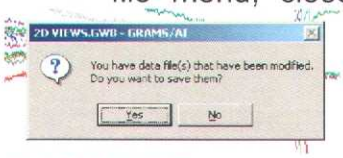
click near start of peak

"apply"

"ok"

with menu "add new, replace, cancel" – choose replace

"file" menu, "close traces", "close all traces", on menu



choose "yes"

Laboratory Demo Unit Details

A laboratory test stand for component testing was used for PC and SAW performance testing. It uses a visual basic control program to interface with an HP34970A unit that performs switching and power output. Further details are given in the Results and Discussion section.

Field Unit Details

Circuits were designed in-house and printed circuit boards fabricated off-site. The overall schematic of the components is shown in the following figure. The volume of the metal water vessel is 68mL to the top.

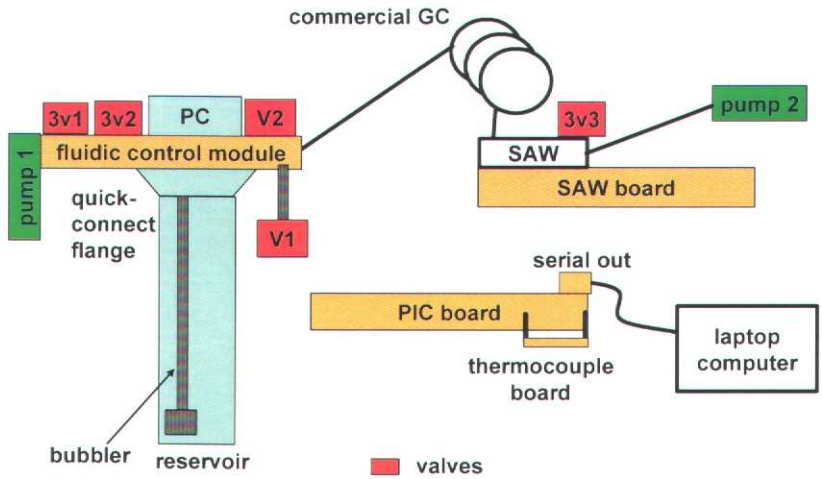


Figure 16: Schematic of fluidics and circuit boards for field system.

A commercial programmable integrated circuit (PIC) controls the timing functions of the valves, pumps, and heating events. The PIC also performs the data output, which is in the form of a simple ASCII string.

To display the data an in-house developed Labview program (National Instruments) is used, while another COTS software (Grams AI, Thermo Electron Corp.) is used to display and calibrate the signals.

4.0 Results and Discussion

Results are presented in the following sequence – advanced technologies or concepts, components required for collection, separation, and detection, the benchtop system, and finally the field system.

4.1 Solid Phase Extraction Column

This unique concept uses a microfabricated GC column as an extraction device. Water is flowed through the column, analytes are adsorbed into the column coating (normally the stationary phase when used as a GC column), and the column is heated to drive the chemicals out of the coating and to the detector. The concept utilizes the inherent low power advantage of the device. This method would be useful for semi-volatile compounds that could not be purged or sparged out of the water. An example extraction for three chemical weapons agent simulants (three individual tests) is shown in Figure 17. This would be considered a collection and injection technique. While the width of the peaks suggests that this would not be an adequate injection technique, it does demonstrate the feasibility of the concept.

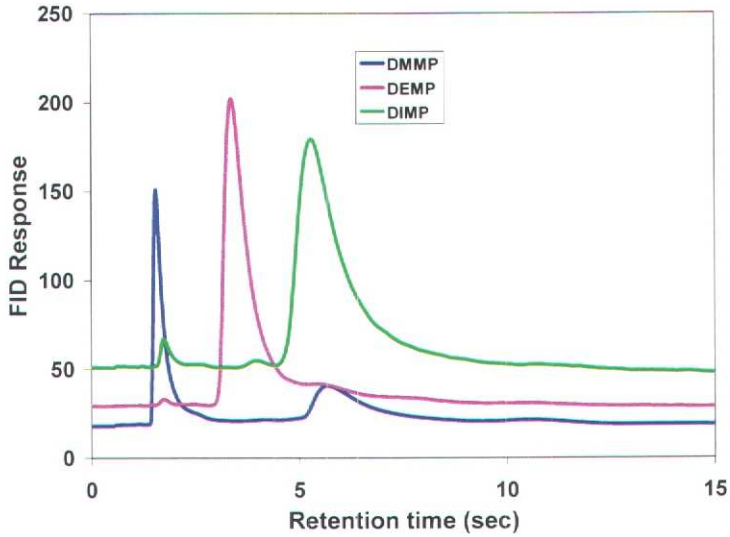


Figure 17: Solid phase extraction column collection and desorption of chemical weapons simulants in water.

The peak broadness indicates that a secondary focusing of the gas phase analytes would be needed to provide a narrow injection pulse (beneficial to resolution and detection limits). Such a collection, desorption, and secondary collection was performed as described in the Experimental section, and the resulting data is plotted in Figure 18. While there are many experimental parameters left to optimize, this data shows that the concept is sound. The size and low power advantages of these devices would allow this concept to be implemented in a field system. The field system goals for this project targeted more volatile compounds, and therefore this concept was not further developed.

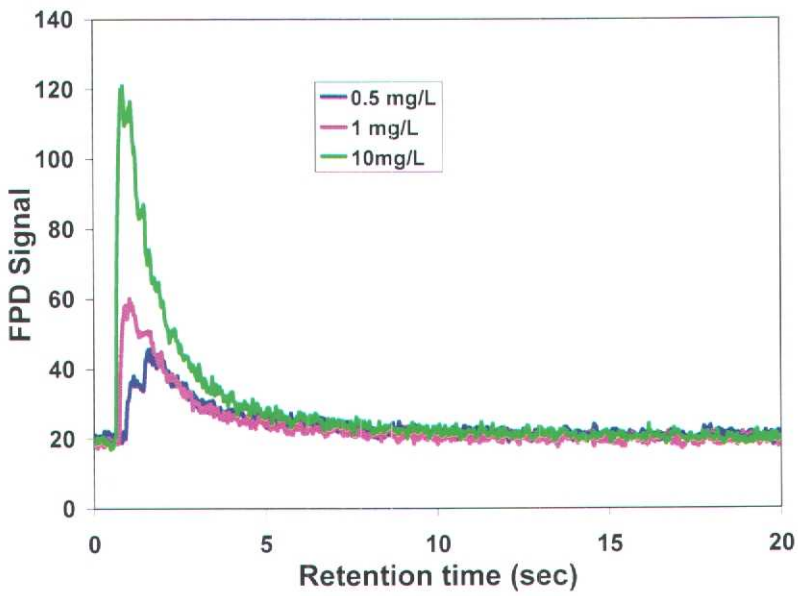


Figure 18: Desorption of DMMP simulants collected on planar preconentrator following extraction and desorption from SPEC column.

4.6 Trap, Tag, Release for Haloacetic Acids

Another class of regulated DBPs is the haloacetic acids (HAAs). Again, these are less volatile and were not the focus for the field system developed. Nonetheless, they are important compounds and because they are acids, which typically have tailing unsymmetrical peaks, they are difficult to analyze by chromatography. The solution in the laboratory and standard methods is to derivatize them to a less polar and more volatile derivative. This concept is difficult to achieve in a field analysis. A concept termed "trap, tag, and release" was adapted here toward the field analysis of HAAs. In addition, the embodiment here again utilizes the low power advantages of microfabricated devices. The concept is illustrated in Figure 19.

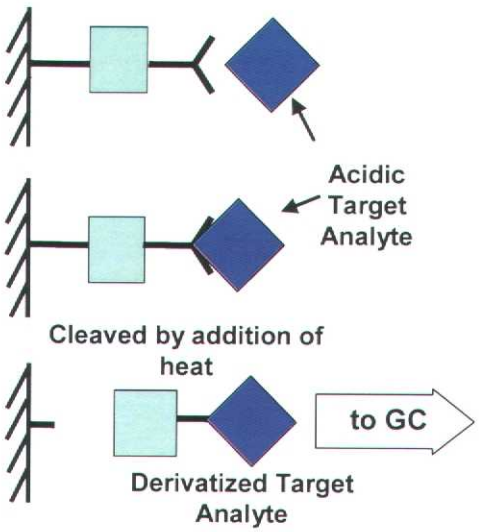


Figure 19: General schematic of trap, tag, and release concept.

A reactive stationary phase traps the incoming analyte; the application of heat releases the analyte in a derivatized form. The specific concept tested here, with chemical structures, is shown in Figure 20. The sawtooth line at the bottom of the figure represents the wall of the column.

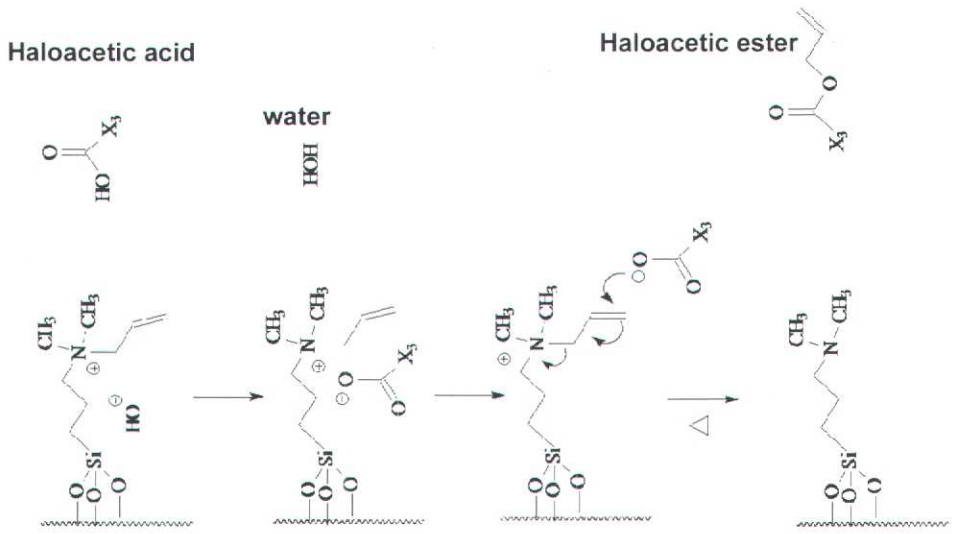


Figure 20: Chemical structure illustration of trap, tag, and release concept.

The liquid phase is removed for the final step so that the derivatized product is released into the gas phase. The proof-of-principal tests performed here used this material and acetic acid as the analyte. The resulting reaction should produce a bound acid complex that can be thermally decomposed to form an allyl acetate. To test the release properties, the system was analyzed via thermal gravimetric analysis. Plotting the change in mass versus temperature (Figure 21) demonstrates the progress of the release of derivatized product. The bulk of the reaction occurs between 175 and 250°C. This range is well within the capabilities of the microfabricated devices already in use for other portable analysis systems.

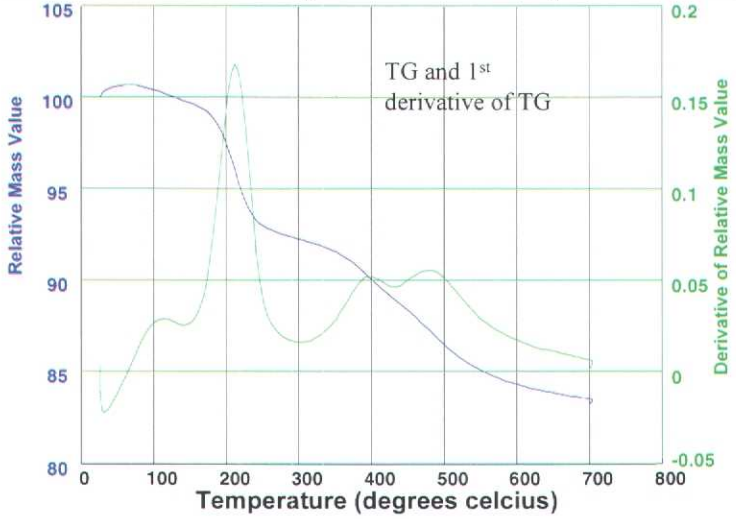


Figure 21: Thermogravimetric analysis (mass change versus temperature) of trap, tag, and release material reacted with acetic acid.

The products of the thermal reaction shown in Figure 21 were also analyzed by infrared (IR) spectroscopy. A summary of that data is shown in Figure 22 in a chromatogram representation. Individual analysis of the IR data shows that an acetate-containing species is responsible for the large peak at 200°C. As the

product expected was allyl acetate, this convincing evidence that the trap, tag, and release concept worked as designed.

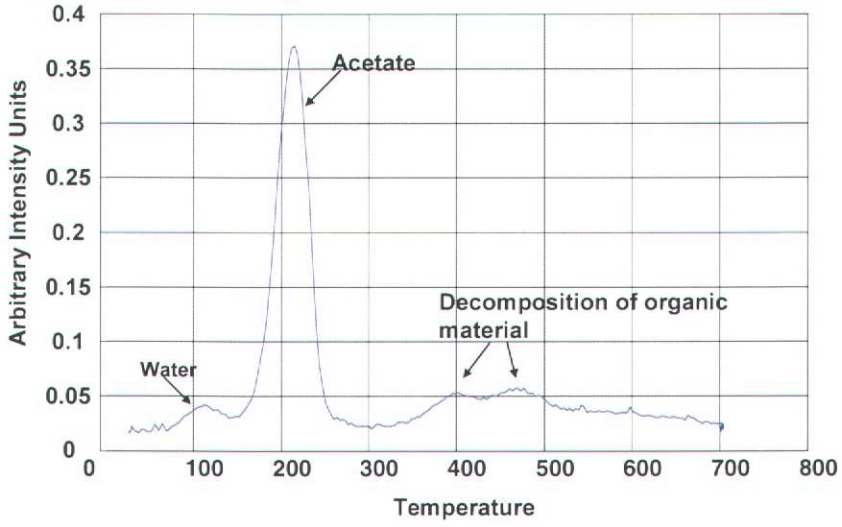


Figure 22: Plot of total infrared absorbance intensity versus temperature of trap, tag, release material reacted with acetic acid to produce allyl acetate.

4.1 Sample Sparging

For the analysis of THMs, laboratory methods purge them out of the liquid media and into the gas phase using helium. This is convenient in the lab, where helium is readily available, and strict data quality objectives are easily met. Helium is not necessarily convenient for a portable analysis system, and therefore experiments were performed to determine if an air purge would be as efficient as helium.

EPA methods specify an 11 minute helium purge, and Figure 23 shows the mass spectral peaks obtained for equivalently spiked samples purged with helium and air. Results of these tests suggest that air is only 51% as effective at sparging chloroform than helium, correcting for flow and using a nominal 40 cc/min flow.

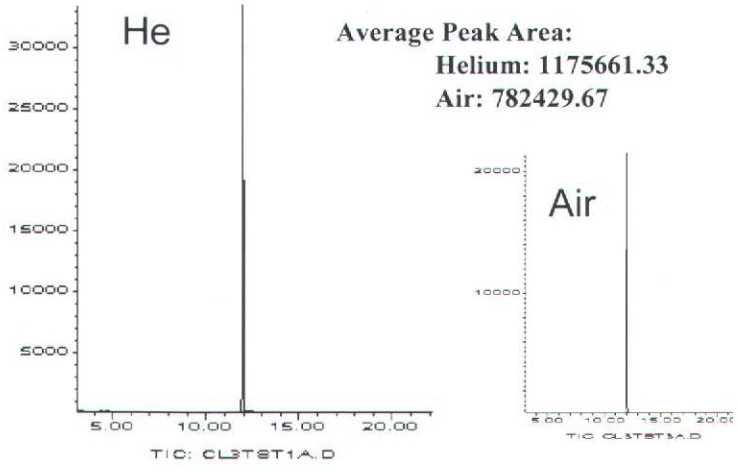


Figure 23: Comparison of chloroform peak areas, helium and air purging 11 minutes.

Additional tests were performed to determine the extraction efficiency versus time, as an 11 minute purge might not be practical in the field. A purge time of 1 minute was only 29% as effective as 11 minutes for chloroform (a reduction was expected).

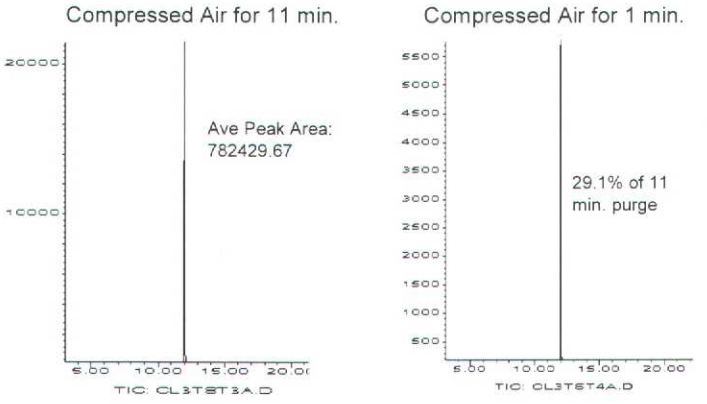


Figure 24: Comparison of chloroform purging efficiency, air for 11 or 1 minute.

Other testing compared the purging efficiency for all four target THMs either using a glass vessel or a stainless steel vessel that had been surface treated to deactivate the surface. This data is not presented here, but there was no difference between vessels.

The percentage of THMs removed over time for two different (1000 and 300 ng in 25 mL) spiked concentration levels was similar. This data (plotted in Figure 25 and Figure 26) is qualitative because the calculation assumes that 100% of the material was extracted by 15 minutes. A metal reservoir was desired for robustness.

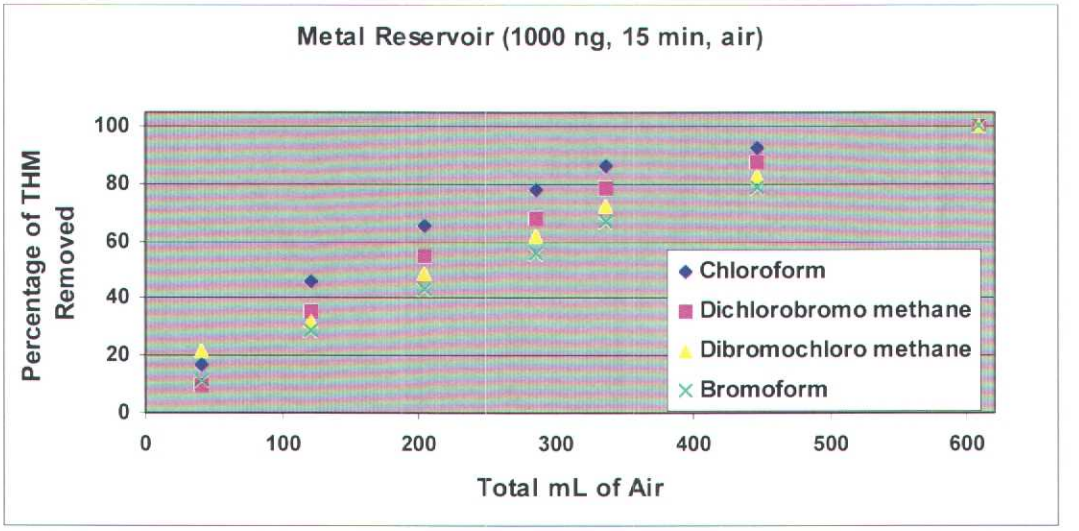


Figure 25: Purging efficiency of 4 THMs during 15 min. purge, 1000 ng initial spike level.

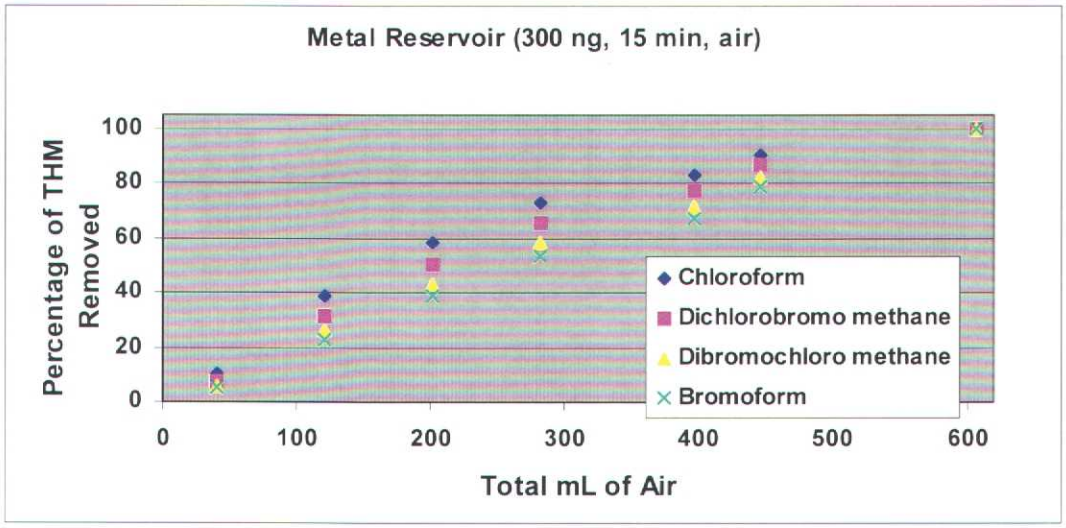


Figure 26: Purging efficiency of 4 THMs during 15 min. purge, 300 ng initial spike level.

4.2 Preconcentration

Over the course of the project several types of preconcentrator devices were tested for capacity, robustness, rejection of water, and release kinetics (fast desorption). These are briefly presented. Photos of each type are shown in the Experimental Details section of this document. Microfabricated preconcentrators used in other applications have low collection efficiency which was not acceptable for this application.

Glass-packed bead PCs (OBPC)

These are also referred to as Ohmic Bead PCs (OBPC), because the concept uses the inherent resistance of carbon-based bead adsorbent materials for resistive heating. Results are shown in Figure 27 for a THM mixture collected on an OBPC, desorbed into different separation columns, and detected by a SAW detector. Even the best separation (3m COTS SPB-624 column) demonstrates that the release kinetics of this PC are slow and generate broad peaks. Sharper peaks are desired for more analytical resolution and better detection limits. This design was rejected due the broadening factor and corrosion of the leads required for electrical contact.

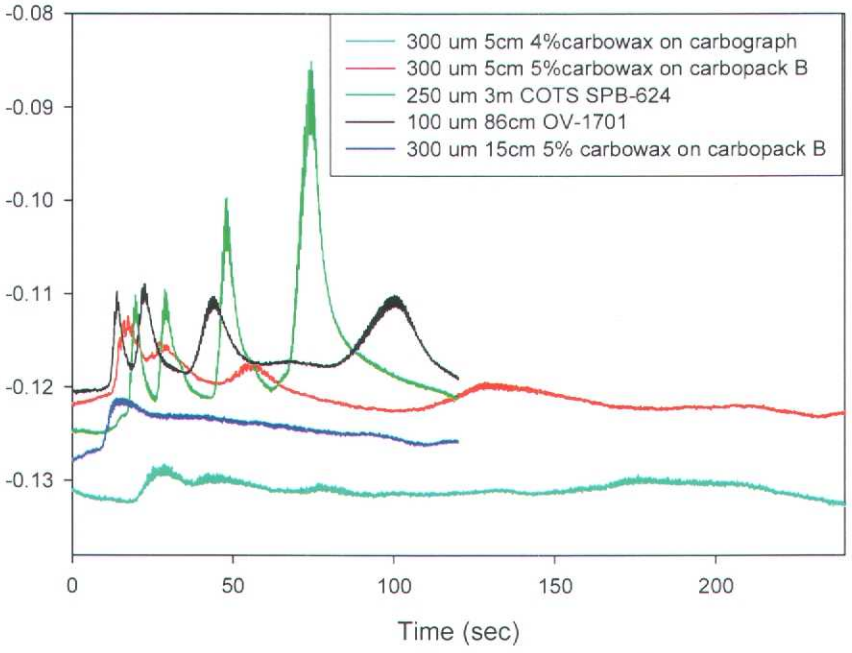


Figure 27: Chromatograms of THM mixture separation after collection and desorption from an ohmic bead PC (using SAW detection).

"Cannonball" packed PCs

A smaller (shorter) version of the OBPCs was investigated, using pogo pins for electrical contact. These gave better desorption kinetics but the resistance was found to change with use, causing uncertainty and drift in the desorption temperature.

Nichrome-wrapped PCs

These preconcentrators (photo in Experimental Details section) are essentially smaller versions of commercial desorption tubes used in a variety of laboratory methods. While they are not "micro", they were found to have acceptable release kinetics and good flow and efficiency characteristics. This design also allowed the use of commercial adsorbents (packings) such as Hayesep D, Tenax, Carboxen 1000, and Carboxen 569. These were tested for their efficiency, "bleed" (loss of collected analyte), and release efficiency. The data indicated that Hayesep D was the best material in these categories overall. It fully releases bromoform (the lease volatile), holds chloroform (the most volatile), rejects water vapor, and has good efficiency.

These preconentrators are heated resistively via the nichrome wire wrapped around the tube, with a thermocouple embedded for temperature measurement. An example mounted in the field system is shown in Figure 28.

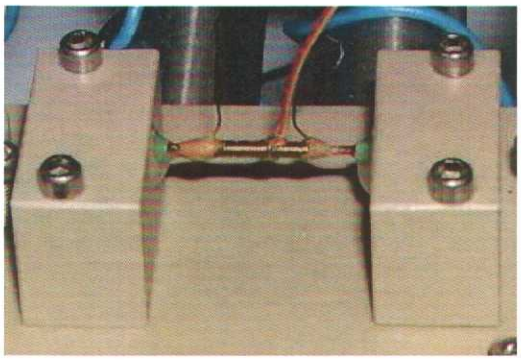


Figure 28: Photo of nichrome-wire wrapped preconcentrator mounted in field system.

Desorption kinetics of these type of PCs was investigated with respect to the voltage profile used. Plots of the temperature profiles generated are shown in the next figures. "Spike and hold" consisted of 8.4V for 1.2 seconds followed by 1.95V for 1 minute, a "slow ramp" consisted of 1.95V for 4 min; and a "spike, no hold" consisted of 7.4V for 1.8 seconds. While the "spike and hold" provided the best desorption and temperature profiles and least power consumption, the "spike, no hold" was simpler to implement with the infrastructure in place for the field system. It is presented here as a possible improvement in future versions if sharper desorption profiles or lower power consumption is desired.

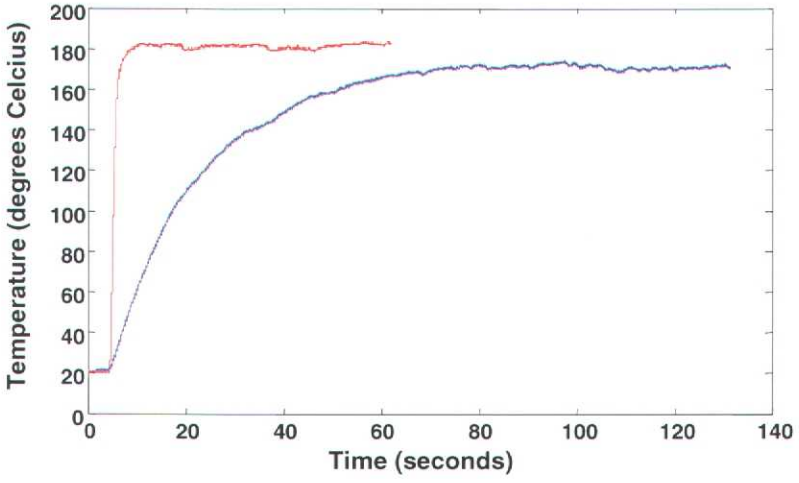


Figure 29: Temperature profile with low voltage (blue) or spike and hold voltage (red).

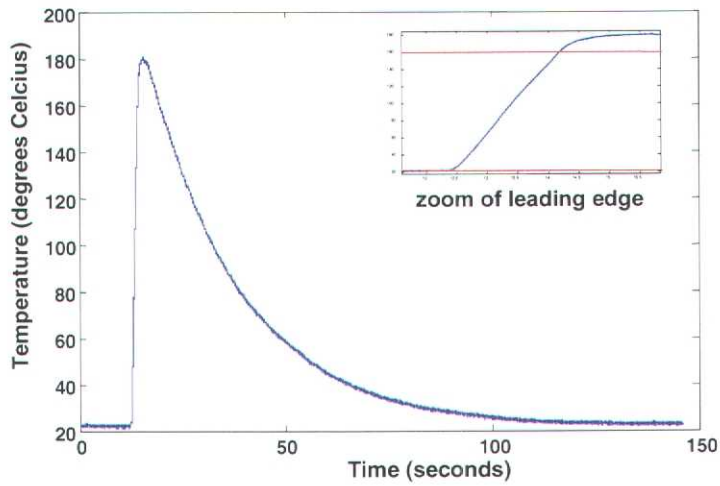


Figure 30: Temperature profile with low voltage (spike, no hold).

4.3 Gas chromatography

As with any chromatographic application, a wide variety of separation conditions are available. Several columns were tested for compatibility (pressure requirements, resolution, and analysis time) for a field system. Both commercial fused silica columns and microfabricated columns were tested.

Commercial Columns

Several column phases mentioned in EPA methods for volatiles were tested; some example separations are shown in Figure 31. Pressures, column lengths, and temperature ramps were tested that would be amenable to the field system.

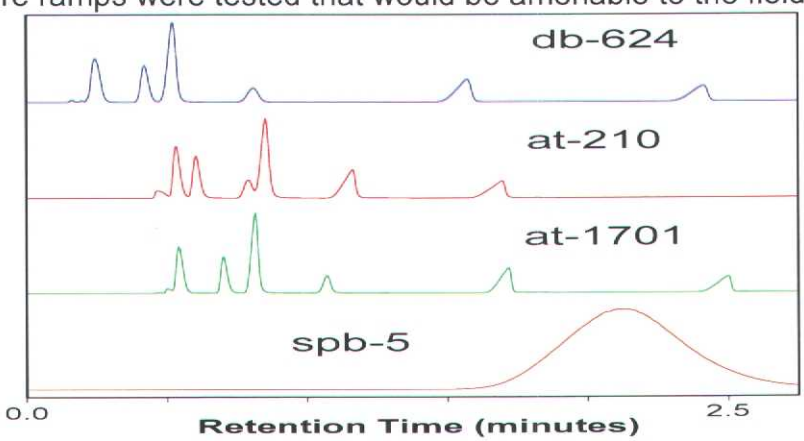


Figure 31: THM separation using different commercial column stationary phases.

Based on this data the choice was made to include a three meter db-624 column for the field system. Initial design parameters targeted a temperature ramped separation, however the cool down time between each analysis, even for a moderate ramp, became the limiting factor for the overall system cycle time. For this reason a study was undertaken to determine if a set of conditions existed that would provide a reasonably fast (less than 5 minutes) separation under isothermal

conditions and field-capable flows. These experiments suggested a temperature of 40°C would be suitable with a 3 meter column. The field system column (nichrome-wrapped) was tested under these conditions. The separation performance was compared between heating the column with a laboratory oven and heating the column with its own nichrome resistive heater (see Figure 32). This shows that any irregularities in heating with the nichrome are minor for this separation.

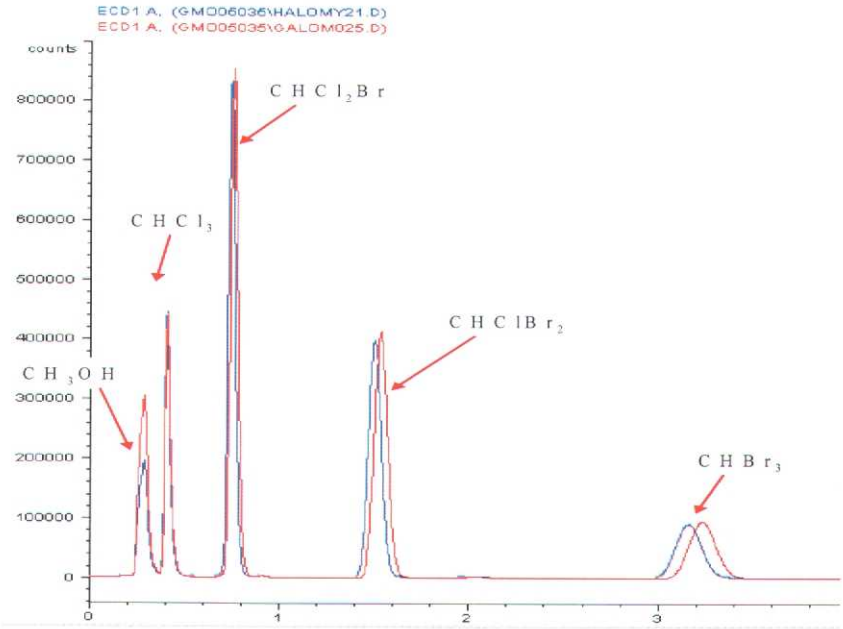


Figure 32: Chromatography comparison between oven heating and nichrome wire-wrapped heating.

Open microfabricated columns

Preliminary studies on the speciation of THMs with open "tubular" microfabricated columns showed that the short lengths available (1 meter) and relatively thin coatings were not sufficient to resolve THMs. Thicker phases or longer lengths could allow this type of column to be used in this application in the future.

Packed microfabricated columns

Microfabricated columns of appropriate dimensions can be packed with commercial separation media. While this might seem a "retro" approach, the volatility of THMs allow for rapid separations nonetheless. A preliminary test with a 36 cm packed column (see Figure 33) packed with a 10% SP-1000 material demonstrates reasonable separation. Separations of THMs on a shorter (15 cm) microfabricated packed column are shown in Figure 34. Even at 40°C full separation is possible in less than 1.5 minutes. Faster separations are possible with temperature ramping. A microGC column doesn't require much power to perform these ramps, and the smaller mass should allow more rapid cool-down times compared to a commercial GC column.

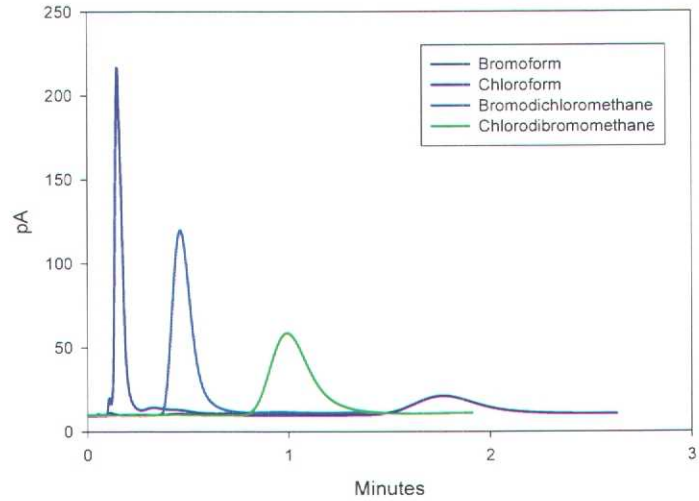


Figure 33: THM separation on a packed 36cm microGC column.

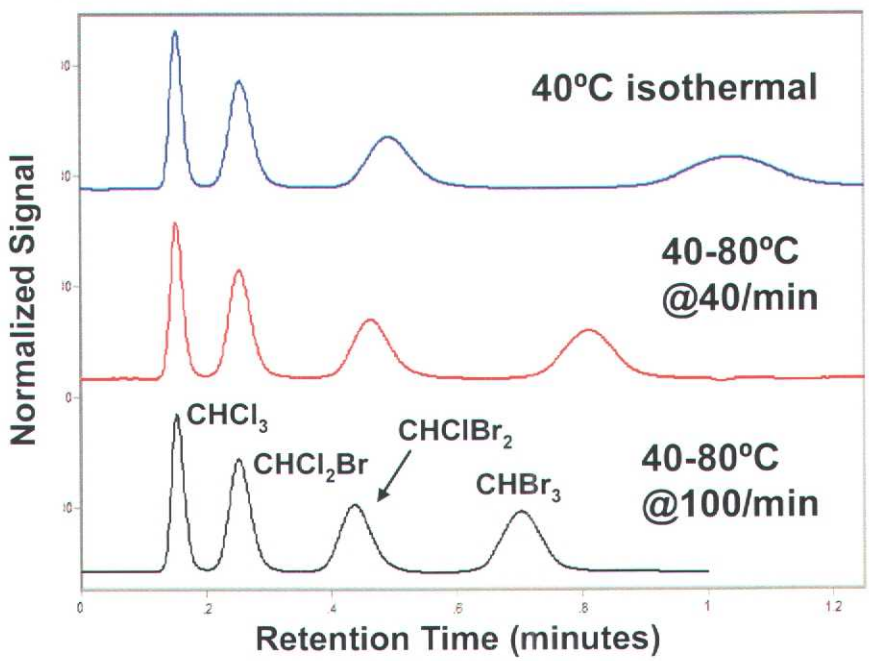


Figure 34: Separation of THMs on packed microGC, 15cm, 1701 phase, FID detection, temperature ramps indicated.

4.4 Surface Acoustic Wave (SAW) Detection

Coated SAW detection relies on the partitioning of the analyte into a polymer coating on the surface of the SAW. Many different polymers were tested for THM sensitivity. Quantitative comparison is difficult due to the variation in coatings (mass, coverage, thickness), and each polymer must be optimized individually. Of the coatings tested, the modified polio designated as "DKAP" performed well and had rapid and reversible response. Achieving the sensitivity needed for this application was possible; however improved methods of optimization would reduce

the labor involved. THM detection on a three channel SAW array is shown in Figure 35. Channel 1 (Chan. 1) is DKAP-coated. The polymer coating designated "PPP" (phenylated polyphenylate) had a larger response, however at room temperature the peaks are also broader, suggesting slower release kinetics with respect to the other coatings. A solution to this might be to heat the SAW, although there is a potential for decrease sensitivity due to changes in the partitioning at elevated temperatures.

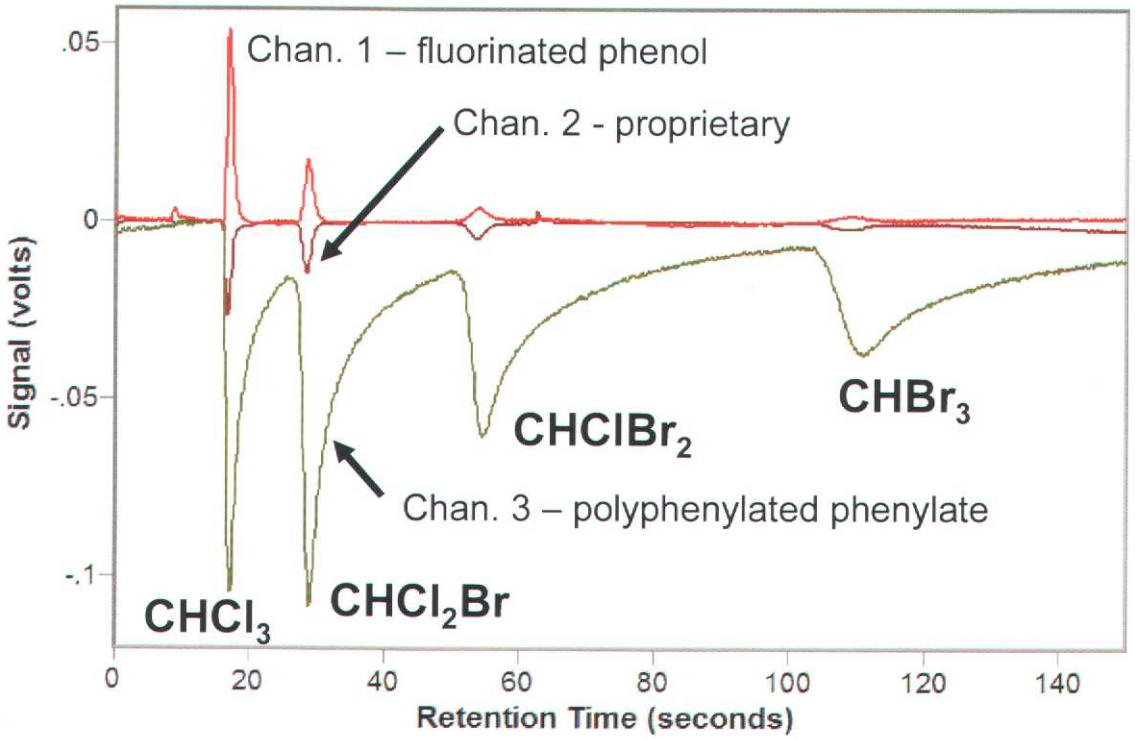


Figure 35: Field box GC column, headspace THM mixture, SAW rh45e5.

The data plotted in Figure 35 used the field system db-624 nichrome wrapped GC column described previously.

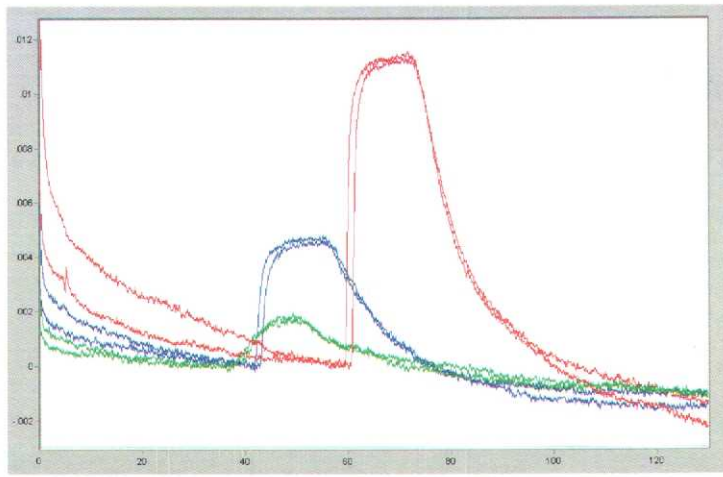


Figure 36: Signal (volts) versus time for chloroform detection to determine SAW channel sensitivity, sample loadings of 13.8 (green), 23.8 (blue), and 47.6 (red) micrograms.

4.7 Benchtop Prototype System

In order to perform component testing on PCs, GCs, and SAW array detectors, a benchtop prototype system was developed early in the course of the LDRD. It uses commercial power supplies, switching electronics, and a Visual Basic™ computer program to control timing, voltages, and data collection. This system serves as a general laboratory asset that can be quickly used to evaluate components for new applications. It is flexible with several control circuits for triggering multiple devices such as PCs or heating devices. A screenshot of the software is shown in the next figure. It stores the data from each SAW channel, a temperature profile, and a comment file.

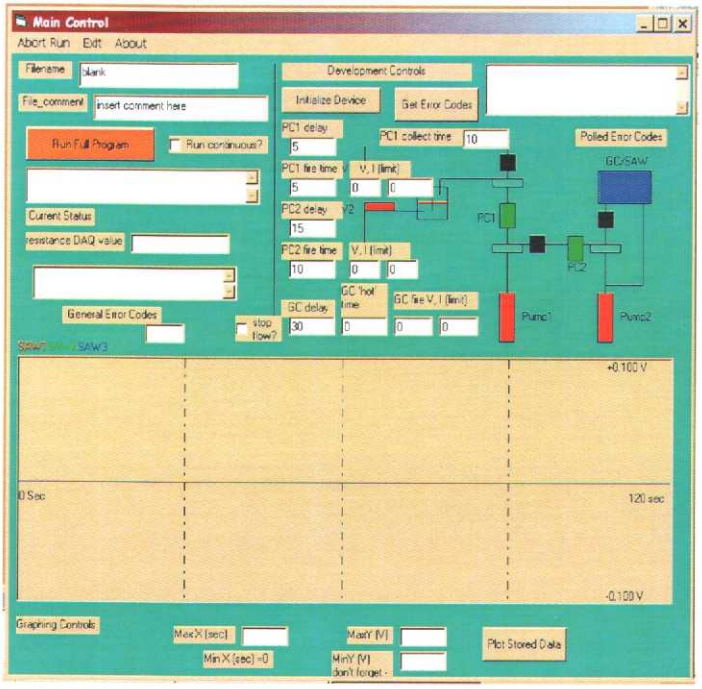


Figure 37: Screenshot of benchtop software interface.

The full benchtop protoype system is shown in a composite photograph below. The relay switch was added in order to control the application of an unswitched higher amperage power supply to either a PC or GC. Each component can be swapped out.

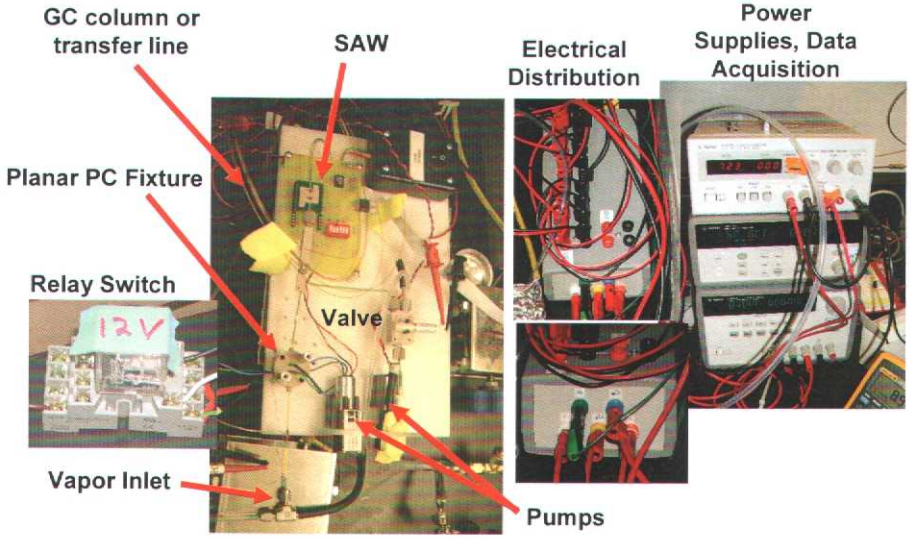


Figure 38: Composite photograph of benchtop prototype system.

4.8 Field THM Detection System

The goal of the LDRD was to create a field portable THM detection system based upon purge and trap and µChemLab™-based components. The final system is shown in Figure 39. The box itself is 22 by 13 by 7 inches, and the computer

shown can be stowed inside. The heaviest and largest part of the system is the batteries. While the system has not been field tested, it has been operated and been through several rounds of operational debugging. Figure 40 shows a closer view of the analytical components, control electronics, and water vessel.

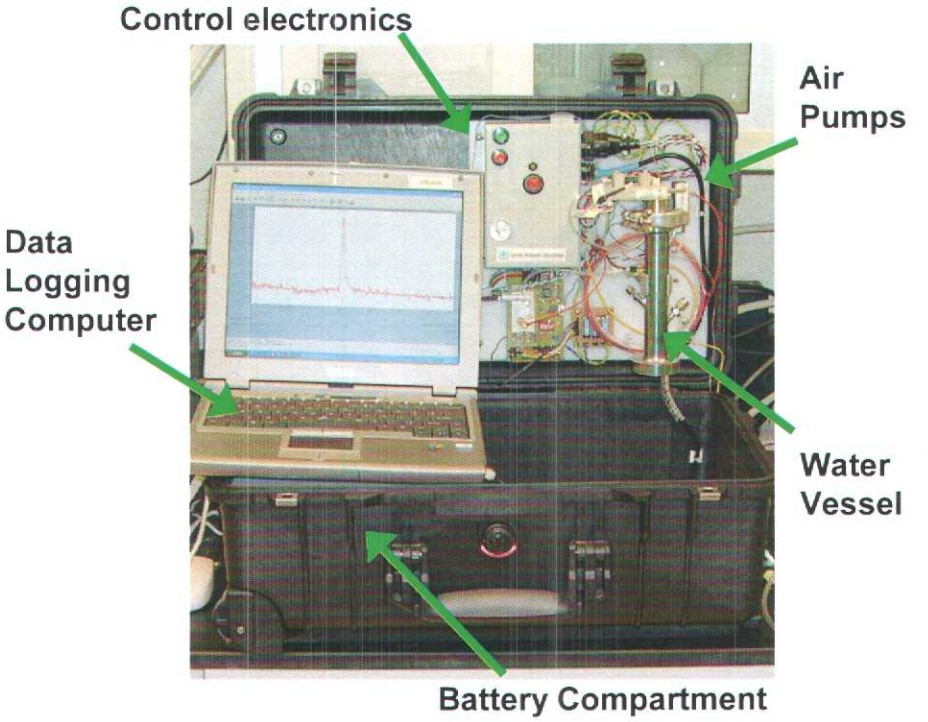


Figure 39: Photo of final field THM detection system.

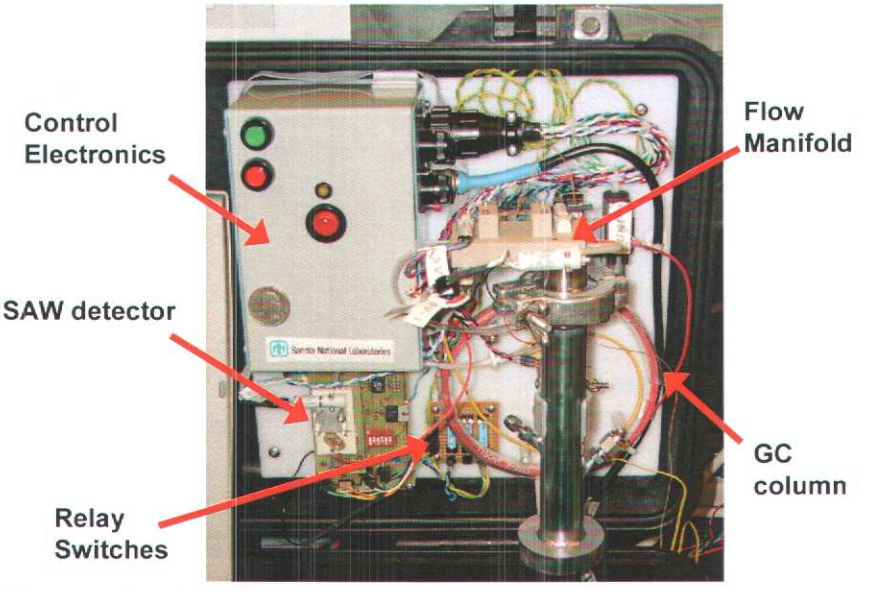


Figure 40: Close-up photo of fluidics, electronics, and water vessel.

An expanded view of the electronics components shows the location of the programmable integrated circuit (PIC) controller, and the SAW printed circuit

board. The PIC is removable from a zero insertion force socket so that the system program can be changed or alternate programs can be inserted.

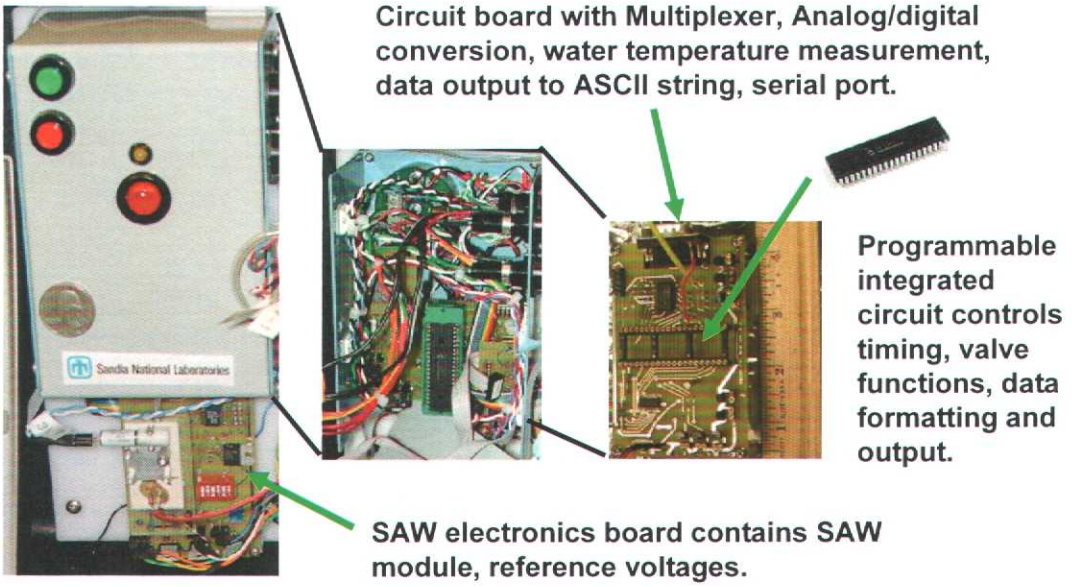


Figure 41: Expansion view of system electronics.

The power consumption of the system was measured using a precision resistor to determine current, the results showing the average power during sample analysis (separation and detection) is about 9 W and a maximum power of 16 W during desorption. The design criteria was to have the field system operate on batteries for 2 hours (or as long as the laptop computer batteries), and during tests the batteries held up over 4 hours.

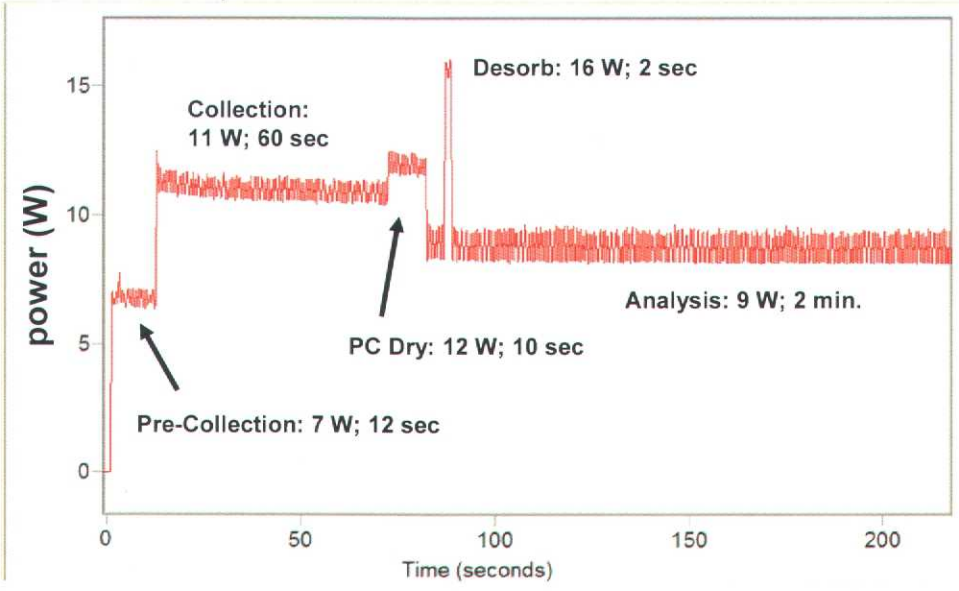


Figure 42: System power (Watts) versus time during a 1 minute collection and 2 minute analysis cycle.

System testing indicated that the noise level was higher than the benchtop system, yet very similar electronics boards are used. An example is shown below. Similar magnitude signals were observed for similar chloroform exposures. Mitigation of this noise and tests to determine the source are underway.

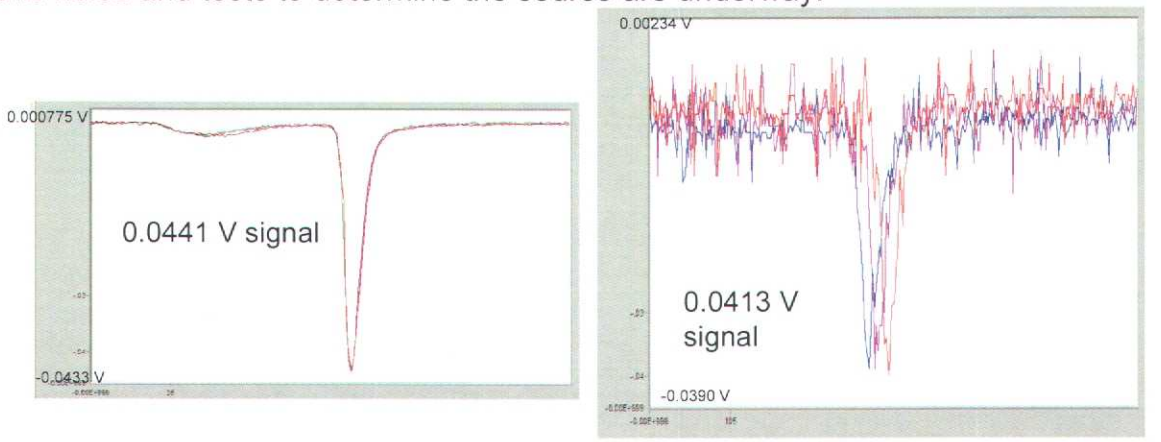


Figure 43: SAW signal comparison, benchtop system electronics versus field system, ~3000 ng desorbed by PC to SAW.

The noise has an element of SAW device dependence, as the following data was collected with a different SAW and has less noise. The signal broadening in this data is because this test used the PPP polymer on the SAW, which has slower than desired kinetics at room temperature.

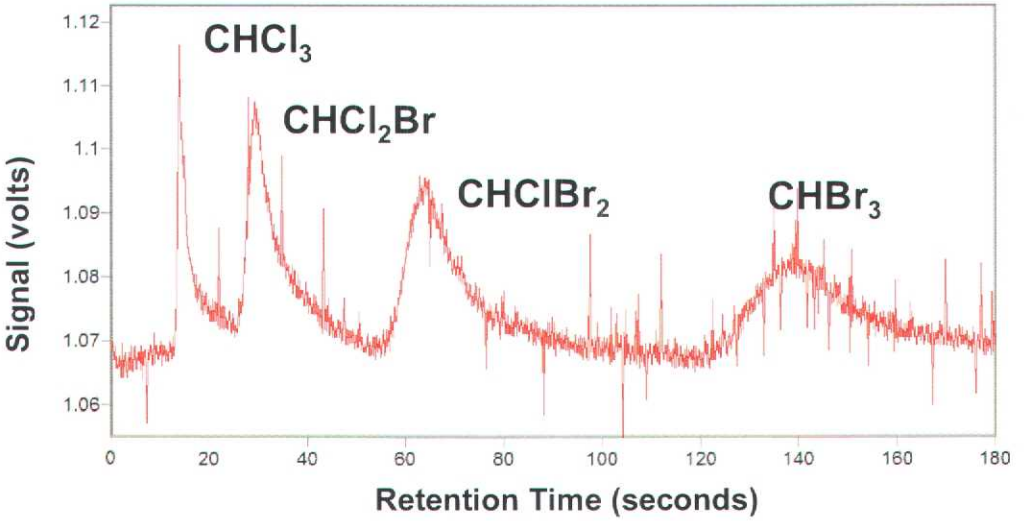


Figure 44: headspace vapor, field PC, GC (43C), 2cc/min. flow, and SAW rh31h5.

5.0 Conclusions

As a result of this three year LDRD project, the application of microfabricated components toward the detection of water-borne contaminants has been demonstrated. More specifically, a new method for the extraction of semi-volatile compounds such as chemical weapons agents was demonstrated as well as a

technique for extracting and derivatizing acidic water contaminants such as haloacetic acids which are of regulatory and health concern. A field THM detection system has been designed, assembled, and tested in the laboratory. While the goal of a field test was not accomplished, the system requires optimization of a SAW coating and replacement of a couple components to be ready for qualification of detection limits and field testing.

The portable system for the detection of the trihalomethane group (THMs) of disinfection byproducts provides a small footprint, low cost, sensitive, and quickly deployable water sensor. The self contained system weighs less than 32 pounds, occupies a carry-on luggage sized case, and performs THM analysis in less than four minutes. The technique of purge and trap (P&T) is performed on a water sample followed by isothermal gas chromatography. A three sensor surface acoustic wave (SAW) detector array, which provides a set of three responses for additional confidence, detects the THMs. An inexpensive programmable integrated circuit (PIC) processor handles heating, timing, valve control and data collection functions for the system. Plotting and analysis are performed with a portable computer.

This work has been presented at several conferences and resulted in new intellectual property, and it is anticipated to attract additional customers and funding.

References

1. K. Kruawal, F. Sacher, A. Werner, J. MāƒÂ¼Ller, T.P. Knepper, Chemical Water Quality in Thailand and Its Impacts on the Drinking Water Production in Thailand, in *Science of the Total Environment, The*, vol. 340, pp. 57-70, 2005.
2. C.J. Lu, E.T. Zellers, A Dual-Adsorbent Preconcentrator for a Portable Indoor-Voc Microsensor System, in *Anal. Chem.*, vol. 73, pp. 3449-57, 2001.
3. W.C. Tian, S.W. Pang, C.J. Lu, E.T. Zellers, Microfabricated Preconcentrator-Focuser for a Microscale Gas Chromatograph, in *J. Microelectromech. Syst.*, vol. 12, pp. 264-72, 2003.
4. WWW resource: *Scientific Instrument Services, Inc. Homepage Www.Sisweb.Com*, 2005.

Appendix A: THM and HAA Chemical Reference Information.

Table 7: Physical properties of THMs.

	MW	Bp	OHE		ChemFinder		
Compound			VP (torr)	Temp	VP (torr)	Temp	Solubility g/100mL
CHCl3	119.38	61	245	30	159	25	0.795
CHBr3	252.73	149	100.8	30	5	25	0.301
CCl4			145	30	91	25	
$CHBrCl_2$	163.83	88.5	?				0.6735
$CHBr_2Cl$	208.28	122	?				0.4

Table 8: CAS# and Antoine coefficients for THMs.

		Antoine's Coefficient				
Name	CAS #	A	B	C	pressure	Temp.
Chloroform	67-66-3	6.4934	929.44	196.03	194.25	25
Bromodichloro -methane	75-27-4				1	25
Dibromochloro -methane	124-48-1				1	25
Bromoform	75-25-2	6.8218	1376.7	201	5.37288	25

Table 9: Henry's Law constants for THMs (higher value is easier to strip from water).

		Henry's Law Constants in atm @20-25C			(Pressure/mole fraction)	
	CHCl3	170	161.2	189	295	
	CHCl2Br	11.8				
	CHClBr2					
	CHBr3	35				
	TCE	550	850.7	160	1032	
	1,1DCE	834	10564	834		
	CCl4	1290				
	Cl2	578				
	CH2Cl2	111				
	1,1,2-TCE	41.2				
ethane	1,1,2,2-TCD	21.1				

Table 10: Physical properties of haloacetic acids.

Name	CAS #	MW	bp	mp	density	pKa	Ka	calc Ka
Chloroacetic acid	79-11-18	94.5	189	62	1.58	2.86	1.40E-03	0.00138
Dichloroacetic acid	79-43-6	128.94	193.5	9.7	1.563	1.29		0.051286
Trichloroacetic acid	76-03-9	163.39	196.5	57.5	1.629	0.64		0.229087
Bromoacetic acid	79-08-3	138.95	208	50	1.93	2.86		0.00138
Dibromoacetic acid								
Tribromoacetic acid	75-96-7	296.74	245	129				
Bromochloroacetic acid								
Dibromochloroacetic acid								
Bromodichloroacetic acid								
Acetic Acid	64-19-7	60.05	118	16.7	1.053	4.78	1.80E-05	1.66E-05
Formic Acid						3.75	1.80E-04	0.000178

Appendix B: Reference THM retention data.

Phase name and chemical structure:
1701 packing 14% cyanopropylphenyl/86% dimethyl polysiloxane (Restek)
624 6% cyanopropylphenyl/94% dimethyl polysiloxane (Restek)
502.2 = diphenyl / dimethyl polysiloxane phase (proprietary)

Rretention times DB-624 J&W 3micron film 30 m
(40°C for 5 min, 40-260°C at 10°/min, 260°C for 3 min)
10.64 bromodichloromethane
15.61 bromoform
5.30 methyl tert-butyl ether (MTBE)
7.75 chloroform
13.25 chlorodibromomethane

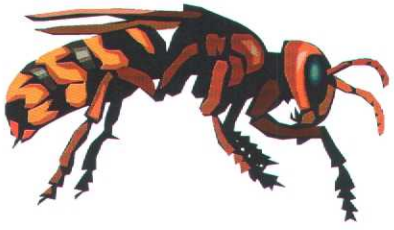
Retention times (MINUTES) Restek (restek, adsorbent stripping.pdf)

Component Name	Rtx-502.2	Rtx-1	Rtx-624	**rtx-1701**
chloroform	18.104	14.659	18.625	11.79
dibromochloromethane	30.685	26.024	26.639	18.28
bromodichloromethane	24.743	20.545	23.045	15.48
bromoform	36.123	30.983	29.746	20.64
1,4-dichlorobutane	36.471	31.864	30.377	21.14
MTBE	6.67	6.28	8.21	6.34

Appendix C: Field Operations Notebook.

μ-W.A.S.P

Water **A**nalysis **S**urety **P**rototype



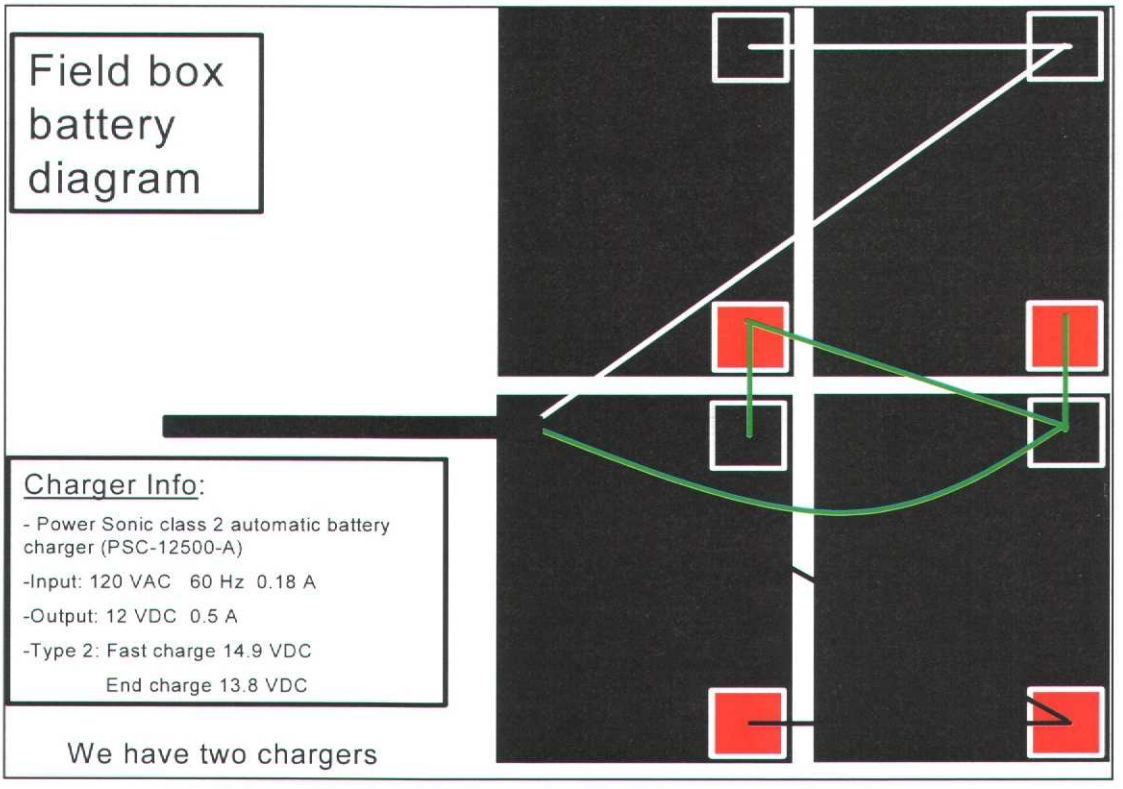
Field Operations Notebook

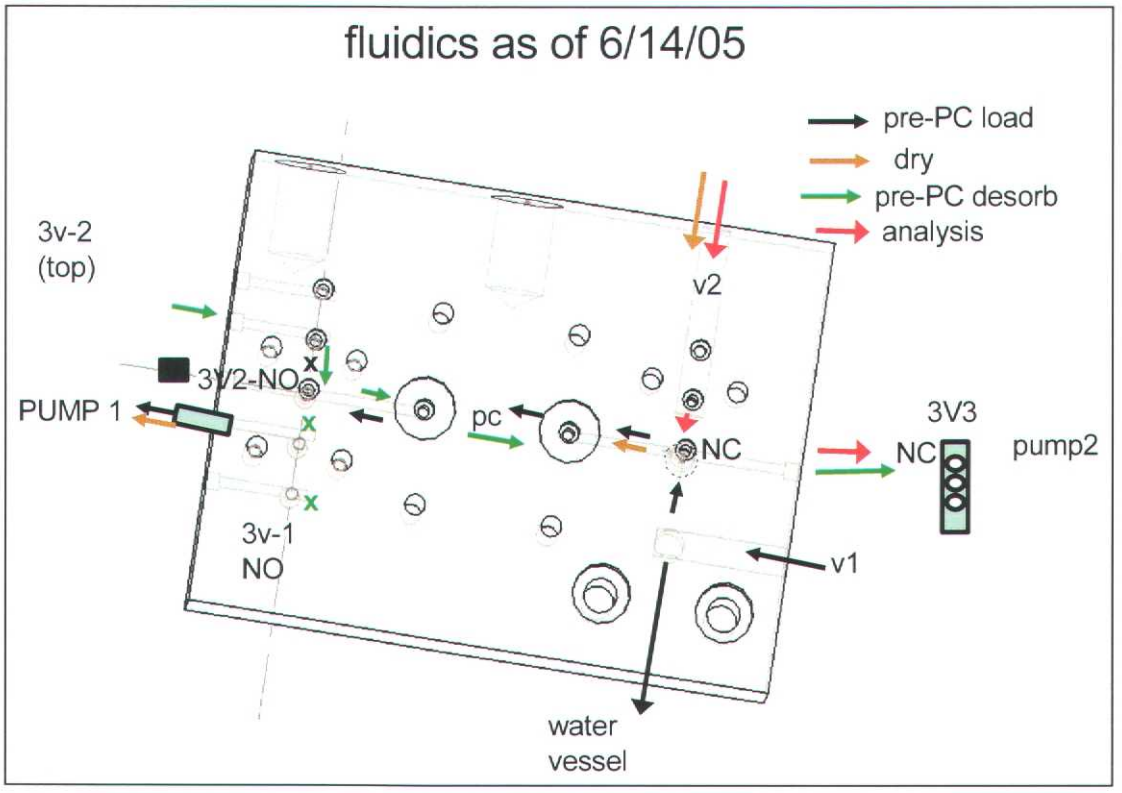
Sandia National Laboratories

LOCKHEED MARTIN

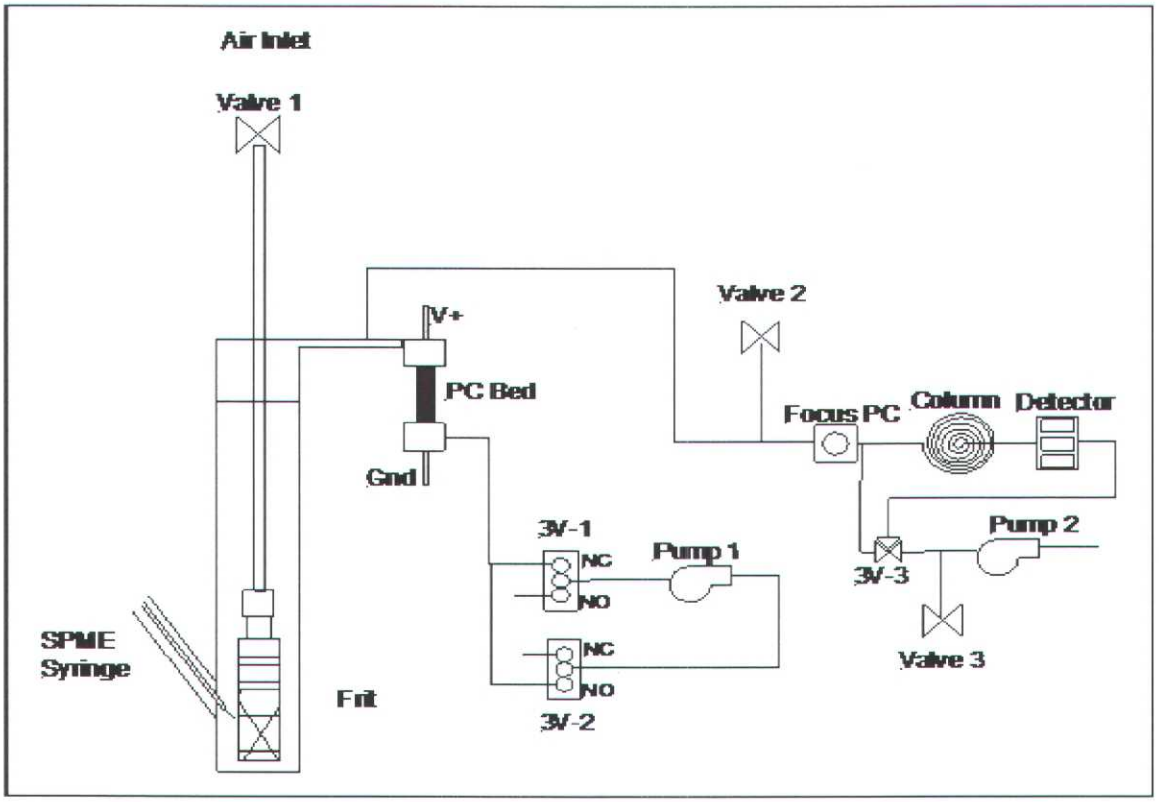
Field Equipment Checklist

- ☐ Water Box
  - ○ PC
  - ○ GC
  - ○ SAW
  - ○ Batteries
  - ○ bong
    - ▪ bong clamp
    - ▪ O-ring
- ☐ Laptop
  - ○ Mouse
  - ○ spare battery
  - ○ power supply
- ☐ Serial Cable from Box to Laptop
- ☐ Extra Parts
  - ○ PC
  - ○ GC
  - ○ SAW
  - ○ Bong
  - ○ Frit
- ☐ Extra batteries
  - ○ charger
  - ○ power strip
- ☐ PIC Programmer Boards
  - ○ power supply
  - ○ extra PICs
  - ○ serial cable
- ☐ Omega Temperature Readout
- ☐ Flowmeter
  - ○ tubing remnants
- ☐ Multimeter
  - ○ Test Leads
- ☐ Glass Unions
- ☐ Tools
  - ○ 5/64" allen (valves)
  - ○ 3/32" allen (reservoir)
  - ○ wire clippers
  - ○ pliers
  - ○ needlenose pliers
  - ○ small phillips
  - ○ large phillips
  - ○ jewelry screwdriver set
  - ○ dental tools
  - ○ epoxy chipper
  - ○ capillary cutter
- ☐ 5-minute epoxy
  - ○ aluminum tins
  - ○ stirrer
  - ○ capillary applicator
- ☐ PEEK
  - ○ 1/16" green
  - ○ 1/8" brown
- ☐ Parker #2-006 O-Rings
- ☐ Extra Pumps and Valves
- ☐ Grounding Strap & Cable
- ☐ 1/8" Plastic Ferrules
- ☐ 9 V batteries
- ☐ Lab Tape
- ☐ Camera
- ☐ Field Equipment Notebook
- ☐ Fuses

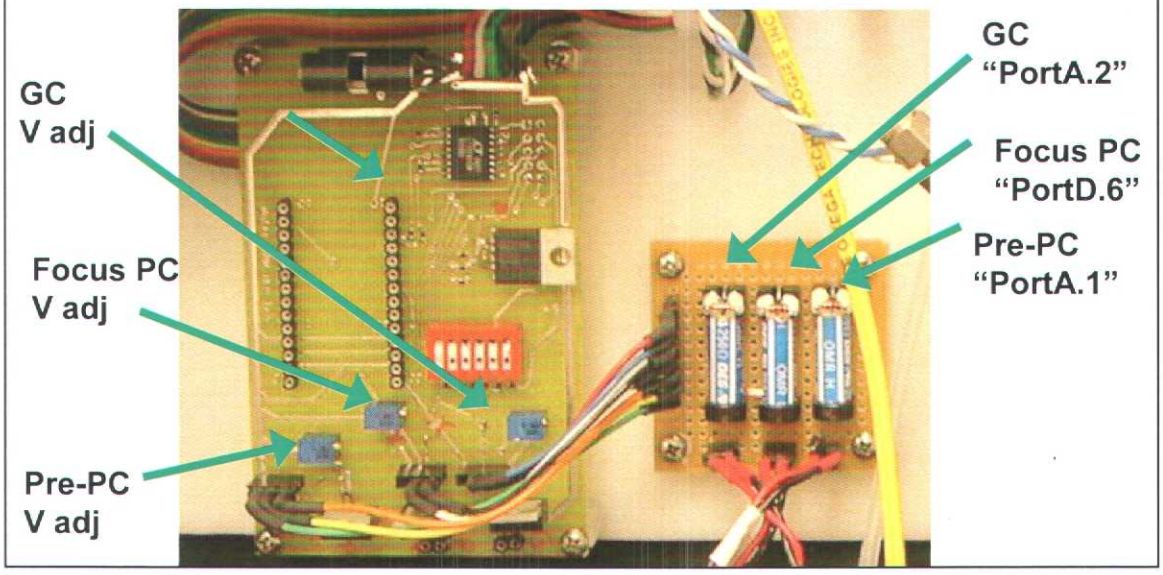

Field box battery diagram
Charger Info:
- Power Sonic class 2 automatic battery charger (PSC-12500-A)
-Input: 120 VAC 60 Hz 0.18 A
-Output: 12 VDC 0.5 A
-Type 2: Fast charge 14.9 VDC
End charge 13.8 VDC
We have two chargers


fluidics as of 6/14/05
pre-PC load
dry
pre-PC desorb
analysis
3v-2
(top)
v2
3V2-NO
PUMP 1
pc
NC
3V3
NC
pump2
3v-1
NO
v1
water
vessel

Fluidic Schematic



Voltage Outputs Verified 6/14/05



PIC Re-Programming Instructions

Insert the PIC Chip into the LAB-X1 card so that the divot on the corner of the chip is near the metal lever. Fasten the chip by pushing the lever down.

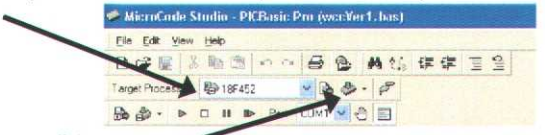
Start > All Programs > MicroCode Studio >MicroCode Studio.exe

File > Open > (the most current *.bas file)

Right-click on any other open tabs and click "Close Page."

Make the programming changes.

Verify that the correct processor (located on the top of the PIC) is selected.



Click on the "Compile and Program" button.

The program will assemble:  Click "OK" on the "Info" menu after assembly.

meProg.exe will open automatically with the compiled *.hex file. (See next slide)

PIC Re-Programming Instructions (contd.)

In meProg, verify that the correct chip is selected.

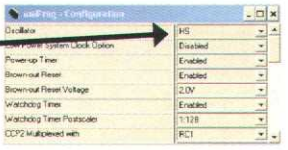
Program > Blank Check

If the device is blank, click "OK" on the "Information" menu.

If the device is NOT blank: Program > Erase.

On the meProg screen, click on the "C."

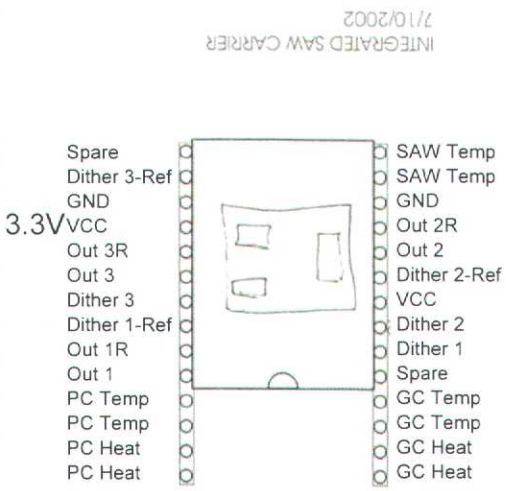
Change the Oscillator to "HS."

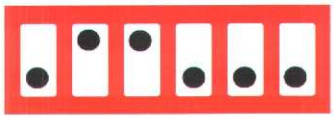


On the meProg screen: Program > Program.

The PIC will be re-programmed.

SAW Dither Settings





Dither	Voltage*
Dither 1	-3.28 V
Dither 2	0 V
Dither 3	-3.28 V

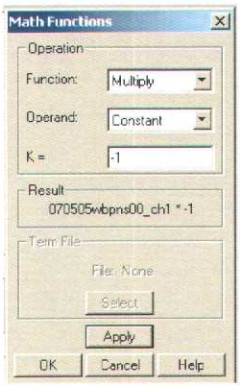
* - common on dither, positive on ref

How to make use new calibration curve w/ GRAMS:

Data Prep:

- Convert all *.prn files to *.cgm files.
  Start > Programs > Galactic > GRAMS AI.
  Once GRAMS opens, click on File > Import/Export.
  Choose: ASCIIXYS: ASCII X,Y Data Pair Format (Non-Even X Spacing) and click on Import.
  Navigate explorer to the *.prn data files, and select them all. (They will probably be in C:/Data.)
  Click "Open."
  In the File Import window, under "Output Rename" click Automatic.
  Under "Output File Type" select "Chromatograms (*.cgm)"
  Click "OK."

- Flip any negative analyte peaks.
  Open any *.cgm files that have negative analyte peaks. These files will be located in the same folder as the *.prn files that were chosen for conversion.
  Highlight the file name in the "Interactive Data Viewer."
  Applications > Spectral Math.
  Click "No" on the option to convert to Y-only.
  In the "Math Functions" menu:
  For "Function," select "Multiply."
  For "Operand," select "Constant."
  K = -1.
  Click "Apply" then "OK."
  Choose to "Replace" the file, on the pop-up menu.



Continued

How to use a calibration curve w/ GRAMS (contd.):

Data Prep:

- See "Data Prep" section of "How to Make a Calibration Curve w/ GRAMS"

Using the Chromatography Application to ID Unknown Samples:

In GRAMS: Applications > Chromatography.

Click "Load Existing Method."
Choose the calibration curve *.mtd file.
On the "Chromatography Navigator," click on "Predict Unknown Chromatograms."
Verify that the correct *.mtd file is shown as the "Method File."
Enter a report title.
Choose "Complete" for the "Report Format."
Choose "Report File (.TXT)" for "Send Output to:"
Click "Browse" near the "Report File" option, and choose a location to save the report.
Click on "Edit List"
On the "Sample List Editor" menu, click "Add" and choose the files to compare to the standards.
By clicking on the "Memo" cell, one can add a comment that will show up in the final report.
After you have added all files (there is no maximum to the amount of files) click "Exit."
Choose "Yes" to save the "Sequence List File." This file will only be used for one comparison, but is required each time.
Back on the "Batch Prediction of Chromatograms" menu, click "Calculate."
The report will be created.

How to make a new calibration curve w/ GRAMS (contd.):

Using the Chromatography Application:

- If needed, creating a new method.

In GRAMS: Applications > Chromatography.
Click "Create a New Method."
Enter a filename, and save the *.mtd file in a known place. (This is the calibration curve file.)
On the "Chromatography Navigator," click on "Set Peak Picking and Calibration Parameters."
On the "Peak and Calibration Options" menu, click "Add" and choose the converted *.cgm file with the lowest concentration of analyte.
Make sure the "Threshold Y Level" is less than the smallest analyte peak height. Then click "OK"
Add files of increasing concentration. Peaks should be automatically identified.
After adding all files, click on the "Peaks" tab on the "Peak and Calibration Options" menu.
Starting from left and moving right, right click on the highest point of each peak.
For each peak, move the tan "Begin Peak Zone" square to the baseline in front of the peak. Then, in the "Peak and Calibration Options" menu, name each peak based on the analyte that it represents.
Click "Calculate." The application will select the same bounds for the remaining data files.
Click on the "Calibration" tab of the "Peak and Calibration Options" menu, and enter the concentrations for each peak, of each data file.
Choose "Linear" for the "Curve Type" and click "Calculate." The data will be fitted to a linear curve.
Click "Exit."
On the "Chromatography Navigator" click "Save Method."
A calibration curve has now been created.

Distribution

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5	MS 1425	Alex Robinson
12	MS 0892	Curtis Mowry, 1722
1	MS 0892	Richard Cernosek
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2	MS 9018	Central Technical Files, 8945-1
2	MS 0899	Technical Library, 4536
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