INSTRUMENTATION AND METHODS FOR THE EXAMINATION OF VOLATILE ORGANIC HALOCARBONS IN AQUEOUS ENVIRONMENTAL SAMPLES

A Thesis

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By

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ABSTRACT

An experimental apparatus was assembled for the purpose of analyzing environmental liquid samples for volatile organic halocarbons. The apparatus consists of a novel sample introduction system for purging volatile analytes from liquid media into a commercial preconcentration system connected to a gas chromatograph. The gas chromatograph is fitted with both flame ionization and electron capture detectors, which permit the detection of light halocarbon species. The preconcentration system enhances detection sensitivity, allowing the detection of analyte concentrations far below what is normally possible with the detection system alone.

The apparatus was used to examine environmental liquid samples for a small number of commonly found analytes. Methods were developed for the detection of these analytes in ice core samples as well as natural liquid samples. While the method shows promise for both types of samples, the analysis of the ice core samples uncovered problems in sample handling and storage that confounded the analytical results. The natural liquid samples were not affected by these difficulties, and produced meaningful analytical results. A proof of concept experiment found carbon tetrachloride to be present in two different drinking water sources at 238 ± 9 ppt and 214 ± 3 ppt, and chloroform present at 124 ± 17 ppb and 100 ± 9 ppb, respectively.

Dedicated to my family

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LIST OF ABBREVIATIONS

BPRC	Byrd Polar Research Center
CCRC	Climate Change Research Center
°C	degrees Celsius
ECD	electron capture detector
EPA	(United States) Environmental Protection Agency
FID	flame ionization detector
g	gram(s)
GC	gas chromatograph
h	hour(s)
HPDI	high purity deionized (water)
IR	infrared spectroscopy
k	kilo
L	liter(s)

LC	liquid chromatography
M	Mega; moles per liter
μ	micro
m	milli; meter(s)
min	minute(s)
mol	mole(s)
MS	mass spectrometry
n	nano
Ω	ohm(s)
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
rt	room temperature
W	watt(s)

CHAPTER 1

INTRODUCTION

The study of environmental samples provides valuable insight into the past and present condition of our planet. Through the ice core record the history of our climate can be elucidated, while the study of natural liquid samples provides insight into the current state of our environment. While many of the compounds of interest in these matrices are concentrated at levels below the typical lower detection limit for gas chromatographic detection, apparatus and methodology exist that permit the quantification of these compounds. This document details one such apparatus as well as the methods involved in identification and quantification of a sampling of commonly occurring environmental contaminants.

The climatic history of the planet is regularly examined through the study of both firn (unconsolidated snow) air and the ice core record. A recently published study details the examination of methyl bromide in Antarctic ice cores. In this study, the authors mechanically shredded ice core samples in a stainless steel vacuum chamber in order to extract and examine the gases trapped in the core (Saltzman, Aydin et al. 2004). The analytical method was gas chromatography coupled with a mass spectrometer detector

(GC-MS). Using this method and apparatus, the authors were able to conclude that the global atmospheric burden of methyl bromide appears to have increased by approximately 50% over the last century when compared to the preindustrial level (Saltzman, Aydin et al. 2004). It is noteworthy to mention that the authors also detected an unknown modern source of methyl bromide that is not completely anthropogenic in origin. This was done by calculating the known atmospheric sources of methyl bromide with respect to its known sinks, assuming the unknown source to be completely anthropogenic, and then comparing the calculated preindustrial value to the concentration of methyl bromide found in the ice cores (Saltzman, Aydin et al. 2004).

A similar methodology was employed for the study of atmospheric carbon disulfide in Antarctic ice cores. Again, the experimenters mechanically shredded the core samples under vacuum and analyzed the liberated gases using GC-MS (Aydin, Bruyn et al. 2002). It is important to realize that these studies focused on the gases mechanically trapped within the ice cores rather than the compounds dissolved within the frozen water itself. The authors of the study determined that the preindustrial levels of carbon disulfide were approximately 25% lower than current levels, and that the methods and apparatus can be used to establish a long-term atmospheric record for the gas (Aydin, Bruyn et al. 2002).

Firn air samples can also provide valuable insight into the atmospheric history and the effect of mankind on the environment. Several recent studies detailed the atmospheric record of halocarbons during the twentieth century through the examination of firn air. In 1999, a report by Butler et al. found that with the exception of methyl chloride and methyl bromide, virtually all of the studied chlorofluorocarbons,

hydrofluorocarbons and hydrochlorofluorocarbons were derived entirely from emissions during the twentieth century (Butler, Battle et al. 1999). The authors collected firn air gas that had been pumped directly from the snow into collection canisters and analyzed this gas by GC-ECD and GC-MS. Similarly, Schwander et al analyzed firn air by GC-MS in order to develop a model for air occlusion in ice cores (Schwander, Barnola et al. 1993). It is relevant to note that in both cases, problems relating to contamination of samples with chlorofluorocarbon and hydrochlorofluorocarbon species were encountered (Schwander, Barnola et al. 1993; Butler, Battle et al. 1999).

Study of natural liquid environmental samples can yield information that affects our everyday life. A study published in 2000 detailed the byproducts formed in drinking water when agents such as ozone, chlorine dioxide, chloramine, and chlorine are used to disinfect that water (Richardson, A.D. Thruston et al. 2000). The authors of this study used a host of analytical techniques, including GC-MS, LC-MS, and GC-IR over a period of eight years to identify more than 200 disinfection byproducts formed during water treatment. Data from studies such as this can directly impact the way we currently treat drinking water. For example, the study found that when comparing disinfection agents, chlorine treatment produced more halogenated byproducts than did ozone, chlorine dioxide, or chloramine (Richardson, A.D. Thruston et al. 2000).

The purge and trap chromatography method (coupled with a variety of detectors) is often used for the study of groundwater samples, and is directly relevant to the contents of this document. In 1996 Amaral et al. examined tap and riverine waters near a chlorinated organic solvent factory (Amaral, Otero et al. 1996). The analytical method utilized for quantification of volatile organic compounds was purge and trap gas

chromatography with both flame ionization detection and electron capture detection, while semi-volatiles were identified and quantified by GC-MS. Results of this study could potentially affect the population in the vicinity of the solvent factory. Instead, the authors found that the tap water contained no evidence of contamination by the factory, but uncovered chlorinated byproducts from the chlorine disinfection being performed at the local water treatment plant (Amaral, Otero et al. 1996).

Purge and trap GC-MS was used to study a number of drinking water samples in Mexico in 2000. The authors of the study used this technique to determine that byproducts from the chlorine disinfection of water were ubiquitous in the sample area, at many times higher than the internationally accepted drinking water standards (Gelover, Bandala et al. 2000). Such findings can influence societal activity by changing the processes that generate these contaminants. For example, the presence of the volatile organic compounds in the Mexican study was attributed to poor management of wastewater, leaking sewage systems, use of wastewater for irrigation, and intense chlorination (Gelover, Bandala et al. 2000).

The common theme of the studies detailed in this chapter is the use of analytical instrumentation and methodology to yield information about our past and present environment. To further this body of information, technology and techniques were developed for the examination of ice cores and natural liquid environmental samples.

CHAPTER 2

EXPERIMENTAL SETUP FOR THE STUDY OF ICE CORE SAMPLES

The motivation for the analysis of ice core samples was generated by promising results obtained in a preliminary experiment in which ice cores were studied by Raman spectroscopy. In this experiment, ice core samples were obtained from the Byrd Polar Research Center that had originated from both Tibet and Greenland. Each sample was mounted between two glass slides, which had been previously cleaned by thoroughly washing with nanopure deionized (18.3 MΩ·cm) water and allowed to air dry. The mounted samples were stored refrigerated at about –12 °C. For analysis, each sample was subjected to the Raman source laser operating at a wavelength of 532 nm with an output power of approximately 45 mW for five seconds. The resulting Raman spectra suggested the presence of hydrocarbons in the ice cores by the appearance of several small peaks in the range of 2700-3000 wavenumbers. Peaks in this region are well known to be indicative of carbon-hydrogen bond stretching. An example of a Raman spectra obtained from an ice core appears in Figure 2.1. Based upon these results, it was decided that a more rigorous study of the contaminants in ice core samples was merited.

The technique chosen for ice core study was purge and trap gas chromatography. A block diagram of the experimental setup appears in Figure 2.2. In this setup, the helium supply gas sweeps any analyte contained in the melted ice core into a collection

canister. The canister is then connected to the preconcentrator system where it is concentrated, then automatically injected into the gas chromatograph system, which is equipped with both a flame ionization detector and electron capture detector. The voltage output signals from these detectors are sent to a data collection computer, where they are interpreted so as to identify and quantify each analyte of interest.

The novelty of this setup lies in the purge gas inlet system leading to the collection canister. Individual ice core samples are stored in gas tight glass septa bottles. As opposed to commonly used purge and trap inlet systems, this arrangement permits rapid sample interchange without exposure to the laboratory environment. Development of the apparatus involved in the purge gas inlet for the preconcentration system is detailed in Chapter 3.

Because the apparatus is experimental, the proposed analytical strategy included verification of the method using established techniques. For this reason, ice core samples were transported to the Climate Change Research Center located at the University of New Hampshire for the purpose of purging samples into canisters and utilizing the instrumentation in that laboratory to examine the gas contained within the canisters. The purge gas was then to be analyzed using the experimental apparatus described above and the results compared to those obtained using the established method. It is important to mention that due to the results obtained by the established technique (i.e. evidence of sample contamination), the study of the ice core samples was terminated before they could be examined using the experimental apparatus. Full details of this experiment and its results are given in Chapter 4. However, much of the technology was adapted for the

later study of natural liquid environmental samples. Therefore, further description of the development of the apparatus is justified.

The collection canister was used rather than a direct connection from the sample vial to the preconcentrator for several reasons. Because the preconcentrator has a limited water management capacity, the volume of humidified purge gas that can be sent to the preconcentrator is limited to 400-600 cubic centimeters. Use of the collection canister permits larger volumes (more than 3000 cubic centimeters) of purge gas to be sent through the sample, which is more effective at stripping the analytes. Also, a single purge of the melted ice core into the can provides sufficient volume for multiple analyses of the same sample, which permits validation by established techniques. Finally, use of the collection canister eases the storage and transportation restrictions inherent with the fragile glass sample vials containing the frozen ice cores.

The canisters are silica lined in order to minimize chemical adsorption of the analyte molecules to the stainless steel canister surface. Canisters are precleaned by evacuation followed by flushing with ultra high purity helium. The helium gas is supplied as ultra high purity grade and is further purified by passing through molesieve traps immersed in liquid nitrogen. This evacuation and flushing procedure is repeated three to five times, and then the canister is evacuated to approximately 10 mtorr (Sive 2004).

A more detailed schematic of the sample collection system appears in Figure 2.3. Analytes contained within the melted ice cores are purged into the collection canister by way of a helium gas stream. The helium gas is ultra high purity (UHP) grade, supplied by a commercial manufacturer. The gas is regulated using a specialized high purity gas

regulator designed to minimize contamination. The helium travels through 1/8" stainless steel tubing into a helium purification pack. Upon exiting this pack, the helium is at least 99.99999% pure, meaning trace contaminants that may exist in the supplied gas are removed such that their concentration is less than 100 ppb. The purge gas is then sent through a stainless steel 18 gauge needle via a stainless steel Luer fitting. This needle is passed through the septa of the vial containing the ice core sample.

The sample vial itself is designed for environmental samples, in order to keep contamination to a minimum. Each case of vials comes with a certificate of analysis, which details maximum contaminant concentration. Before the sample itself is purged, the vial headspace must be cleared of air trapped at the time of sampling. While the ice core is maintained in a frozen state, a known amount of UHP helium is flushed through the vial and vented to the atmosphere, creating a headspace of pure helium. The volume of gas required to completely flush the headspace was determined experimentally (detailed below). The ice core sample is then allowed to melt and UHP helium is bubbled through the melted sample creating a positive pressure inside the vial. It is this pressurized headspace gas that contains analytes of interest, and it is this same gas that is sent to the collection canister.

The headspace gas is transferred to the collection canister by way of a modified collection needle arrangement. In this setup, a 1" 16-gauge stainless steel needle is fitted directly with 1/16" compression fittings. The short length of the needle insures that the needle will not become submerged in the liquid sample, while the large bore size reduces any gas flow restrictions. The needle is connected to 1/8" stainless steel tubing via a 1/8" to 1/16" reducing coupling and this tubing is connected to the inlet of a mass flow

controller (MFC). The MFC permits monitoring and control of gas flow rate in the sample collection system, which is useful for both sample collection and leak detection. The outlet of the MFC is connected by 1/4" stainless steel tubing to a stainless steel T-valve. This valve permits flushing of the system dead space before collection in the canister. The volume of the connection between the T-valve and the collection canister is minimized by keeping the length of the 1/4" connection tubing as short as possible. This small volume is also flushed with UHP helium before sample collection. Once the desired volume of headspace gas has been transferred to the collection canister, the canister may be stored or the contents may be analyzed immediately.

Because the preconcentrator system concentrates both analytes and potential contaminants by an enormous factor (150,000-400,000), the cleanliness of all components involved in the sample collection arrangement is of paramount importance. Each part is handled with nitrile gloves during assembly and disassembly. All components are constructed of 316-grade stainless steel (with the exception of the sample vial itself). The internal flow path of the mass flow controller is constructed of stainless steel and Teflon. Initially, components were cleaned by sonicating in acetone for five minutes, then sonicating in nanopure deionized water for five minutes. The sonication in water was repeated before placing in an oven at approximately 140 °C. However, this sonication cleaning method was determined to be too aggressive for the compression fittings, rendering them difficult to assemble in a gas-tight manner. Instead, components of the collection system are cleaned in between individual samples by first heating as above, and then allowing them to cool in a glass vacuum chamber. The mass flow controller cannot be placed in the oven because it contains electronic components, but is

cleaned by placing in the glass vacuum chamber. Cleanliness of the sample collection components is further insured by thoroughly flushing with UHP helium prior to sample collection. The volume of gas used to flush the sample collection components was determined experimentally as part of the vial headspace purge test. In this test, incremental amounts of the purge gas were passed through the system and analyzed. Total purge volume was recorded upon the disappearance of peaks common to the laboratory environment. This total purge volume was approximately thirty times the volume of the sample headspace.

Sample analysis is performed by first connecting the collection canister directly to the preconcentrator inlet by a 1/4" to 1/16" reduction coupling. A measured portion of the gas contained within the collection canister is then sent to the preconcentrator. Within the preconcentrator, the moisture component of the gas is removed along with bulk gases such as air, nitrogen and argon. The remaining portion (the analytes of interest) are concentrated and injected onto the chromatography column. The preconcentrator function is detailed below.

The 1/16" sample inlet line of the preconcentrator is heated to 80 degrees C to minimize condensation. The sample gas travels this line, passing through an internal mass flow controller. The flow rate of the gas measured by the mass flow controller is integrated by the instrument to deliver the desired sample volume. This volume is set by the operator, and in this case was chosen to be 400 cubic centimeters in order to minimize the amount of moisture delivered to the instrument.

Once inside the preconcentrator, the gas is transferred among three "modules" before injection on the GC column. The first module consists of cryogenically cooled

glass beads. These beads are cooled to –150 degrees C with liquid nitrogen. The sample is concentrated to approximately a 0.5 cubic centimeter volume on these beads. This module is then flushed with 75 cubic centimeters of helium in order to eliminate any remaining air from the module. The glass beads are then heated to 10 degrees C while a stream of helium sweeps the analytes to the second module. A total transfer volume of 40 cubic centimeters at a flow rate of 10 cubic centimeters per minute is ideal for transferring gas components to the second module while leaving most of the water behind on the first module (Entech Instruments). The second module consists of a Tenax trap maintained at a temperature of –60 degrees C with liquid nitrogen. Tenax is a high surface area porous material consisting of polymerized 2,6-diphenyl-1,4-phenylene oxide. This material selectively interacts with hydrocarbons while allowing carbon dioxide and any remaining water to pass through the trap unimpeded. The analytes are then thermally desorbed at 180 degrees C while being transferred to the third module by the GC carrier gas. The third module consists of an open-tubular trap maintained at -170 degrees C, which focuses the analytes for rapid injection onto the GC column. This final module, called the "cryofocuser," is heated very rapidly (about 170 degrees C/second) and the concentrated analytes are injected directly onto the column. Between individual sample concentrations, the preconcentrator heats all of its trapping components to desorb any remaining sample or contaminants, effectively cleaning the modules in preparation for the next run.

The analytes are transferred directly onto the chromatography column, rather than passing through the injector. The transfer line from the preconcentrator to the GC is constructed of silco (deactivated fused silica-lined stainless) steel maintained at a

minimum temperature of 100 degrees C, and is connected directly to the column with a 1/16" coupling union utilizing graphite ferrules. The OV-624 chromatography column stationary phase is 6% Cyanopropylphenyl / 94% Dimethyl Polysiloxane, which is designed to separate commonly found environmental pollutants utilizing EPA method 502.2 for volatile organics. The column length is 60 m, with an inner diameter of 0.25 mm and a film (stationary phase) thickness of 1.4 μm. The column was chosen specifically for the separation of light halocarbons.

The GC method is a modified version of the EPA 502.2 method for volatile organics. The oven (column) temperature is held for six minutes at 35°C and then ramped to 220°C at 25°C/min where it is held for 10 minutes. The column flow is 1.0 mL/min with a linear velocity of 20 cm/min. Though the injector is not connected directly to the column, its temperature is maintained at 270°C and both detectors are maintained at 280°C. Though the EPA method calls for additional temperature programming, the abbreviated method described above adequately separated the analytes of interest.

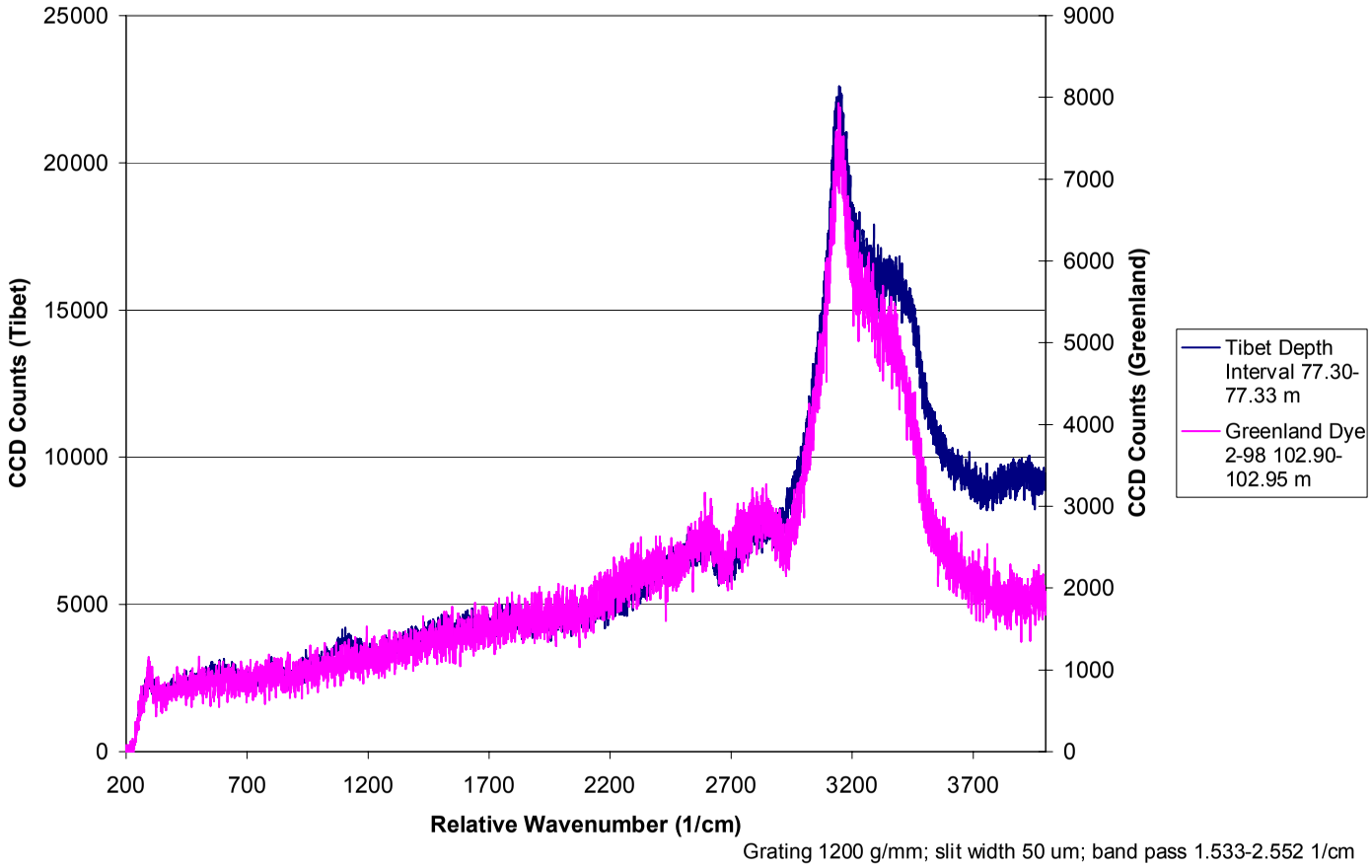

Figure 2.1: Example of Raman spectra obtained from ice cores in preliminary experiments. Source 532 nm operating at ~45 mW, acquisition time = 5000 msec, temperature = -11.9°C

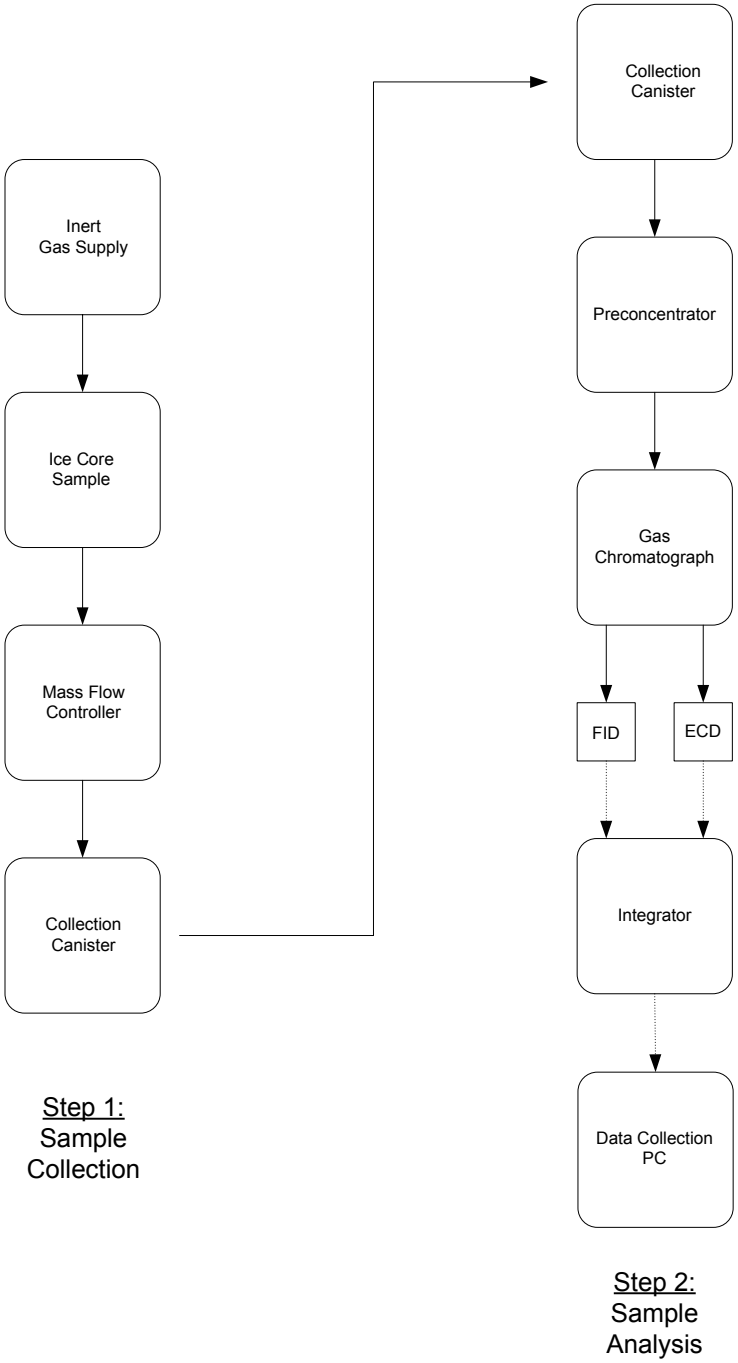

Figure 2.2: Block diagram illustration of ice core analysis experimental setup

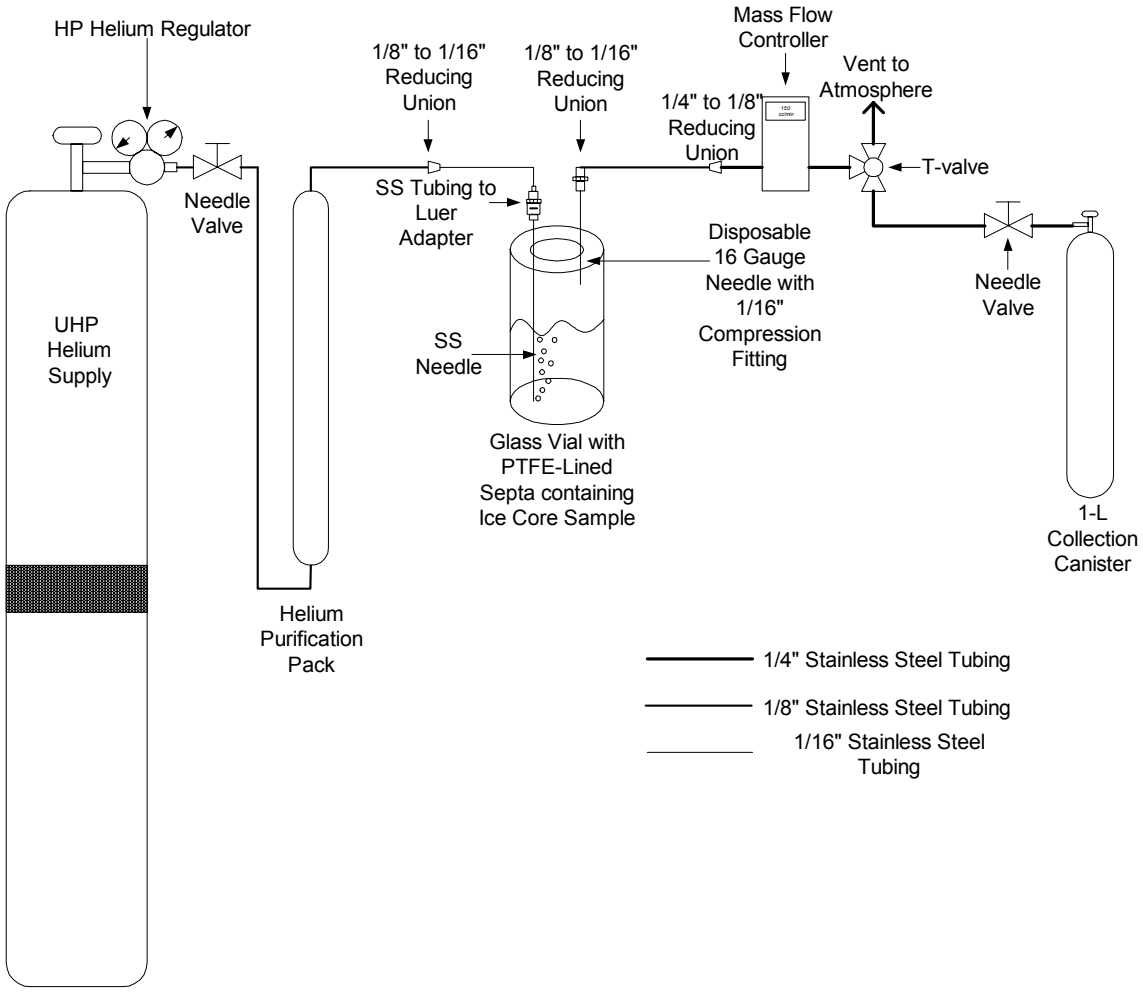

Figure 2.3: Detailed schematic of purge inlet system for ice core analysis. Components not to scale.

CHAPTER 3

DETAILED DEVELOPMENT OF THE INLET PURGE APPARATUS

Transferring the gas from the pressurized vial to the collection canister is not a trivial matter. The first choice for sample collection would be a modified cap for the vial that incorporates a fitting such that the canister inlet line can be connected directly to the vial cap. The time and cost for modifying each sample vial cap would be excessive and thus prohibitive. A better choice might be a collection needle that is also passed through the septum into the headspace above the melted sample, being careful that the needle itself does not actually become submerged into the sample. If the collection needle becomes submerged, the liquid sample itself will be transferred to the collection canister, rather than the gaseous analytes of interest. In addition, excessive liquid in the collection canister could later be transferred to the preconcentrator. This would far exceed the water management capability of the preconcentrator device, and possibly lead to the injection of neat water onto the chromatography column, which can shorten the lifetime of the stationary phase.

The first attempt at a collection needle system proved to be a failure because the Luer fitting used to couple 1/16" stainless steel tubing to the disposable 16-gauge needle tip could not be made to be gas tight. In addition, the plastic Luer fitting sleeve on the disposable needle tip proved to be a source of contamination. Switching to an all

stainless steel needle solved the contamination problem, but the fitting still could not be made gas tight. Although this is the same configuration used for the inlet needle system, the possibility of a leak at that fitting is of less concern. This is because the inlet fitting is under direct positive pressure from the supply gas, so that if any leaks are present in the fitting, the helium pushes ambient air away from the leak, and keeps it from entering the system. This is not necessarily the case for the collection fitting, because that side of the system experiences a vacuum from the collection canister. In this configuration, the collection canister may pull in some amount of ambient air along with the vial headspace gas.

The next attempt at sample collection was made using a regular piece of 1/16" stainless steel tubing connected to the canister inlet. One end of this tubing was left bare while the other was fitted with a 1/16" compression fitting. The end of the tubing with the compression fitting was connected to the canister inlet via a 1/4" to 1/16" stainless steel reduction coupling. The bare end of the collection tube was pushed through the vial septa into the headspace above the melted sample. The length and internal diameter of this tubing were chosen in order to minimize the dead space inside the tube. The length was approximately four inches while the internal diameter was 0.01". The outside diameter of the tubing was kept at 1/16" to prevent making a large hole in the vial septa.

The above collection tube configuration proved to be problematic for a number of reasons. First of all, pushing the bare tubing through the vial septa is an inefficient way of puncturing the septa. Because the tubing has a square ending rather than a sharpened tip, the hole created when puncturing the septa may compromise the ability of the vial to remain gas tight. The tubing end may also become clogged with septa material as it

pushes its way through the septa. On several occasions, small pieces of the Teflon that coat the internal side of the septa were observed clinging to the tube end after the tubing had punctured the septa. In this situation, transfer of sample to the canister is blocked. In an attempt to mitigate this problem associated with the collection tube, the vial septa was first punctured using a large bore (16 gauge) disposable needle tip, and then an attempt was made to pass the bare end of the collection tube through the hole made by the needle. While this operation appeared to solve the problem of septa material becoming clogged in the collection tube, it was not only time intensive, but also produced a hole in the septa large enough to compromise the ability of the vial to remain gas tight. Attempts to "sharpen" the end of the collection tube in order to mimic the end of a needle proved futile, as the sharpening operation usually sealed the hole in the tubing.

Another problem associated with the collection tube configuration became apparent when a mass flow controller was placed in between the collection tube and the collection canister. In this configuration, the goal was to pressurize the canister with the vial headspace gas to approximately 30 psig. This target pressure was chosen because it not only proved more than sufficient pressure for the preconcentrator system, but also allows the canister to hold sufficient sample to be examined in duplicate by the verification lab at the CCRC. Using the Boyle equation, it was calculated that in order to imbue the evacuated canister with 30 psig of pressure, a volume of about 3 liters of headspace gas needed to be forced into the canister. The helium purge gas regulator was set at 30 psig and the canister needle valve was opened. In theory, when the mass flow controller reads a flow rate of zero, the system (supply gas, vial, and canister) is equilibrated at 30 psig. However, the mass flow controller never read a zero-flow

condition, and even when this flow was minimal, the volume of sample transferred to the canister was calculated to be far less than the target volume.

The volume of headspace gas transferred to the canister was calculated by recording the flow rate displayed by the mass flow controller at various time intervals throughout the canister filling operation. The points of time and flow rate were plotted and a curve was fit to the plot. The equation describing the curve (having a fit value of >0.99 R2) was integrated over the approximate filling time. The resulting value should be the volume transferred into the canister, and this value was approximately 825 mL. Therefore, the canister was not even filled to contain a volume of gas that produced a pressure equal to atmospheric pressure. While this volume is still technically enough to supply the preconcentrator with sufficient sample, in practice it is too difficult for the preconcentrator to pull the sample from the sub-atmospheric pressure canister. In this situation, the preconcentrator samples less than the optimal amount of gas, and the resulting analyte amount injected onto the GC column is too small to be detected reliably.

The issue described above can be directly attributed to the collection tube setup. Essentially, the tubing internal diameter is so small that the collection tube acts as a flow restrictor in the system. This explains the non-zero flow rate measured by the mass flow controller (although flow is greatly restricted, it cannot reach zero until the system is at equilibrium). This is a fundamental flaw in the collection tube system. Because pressure is dependant upon area, the area of the collection tube hole is so small that even excessive pressurization of the sample vial cannot overcome the pressure drop that exists due to the flow restricting collection tube. While a solution might be to increase the pressure of the

UHP helium purge gas, this resulting high-pressure environment inside the glass sample vial could cause a dangerous situation if the sample vial explodes under the pressure.

The solution to the sample collection problem became evident upon the realization that the disposable 16 gauge needle tips have the same outside diameter as 1/16" tubing. Thus, a compression fitting meant for 1/16" stainless tubing could be fit directly on the needle. The disposable needle comes equipped from the manufacturer with a plastic Luer sleeve that is attached to the stainless needle with an adhesive compound. This plastic sleeve was removed by carefully crushing the sleeve with pliers until it could be removed from the needle, without deforming the steel needle itself. The remaining adhesive was scraped from the needle. In order to insure that the needle was free of adhesive, the needle was sonicated in acetone for five minutes, and then sonicated in nanopure deionized water for five minutes. The sonication in nanopure deionized water was repeated once more with a fresh portion of water, and then the needle was dried overnight in an oven at 140 degrees Celsius. A nut and 1/16" ferrules were then fitted to the clean needle and this modified needle configuration was used as the gas collection system.

The modified needle collection configuration solves the problems associated with the previous collection arrangements. The compression fittings form a gas tight seal, preventing the leaks that were present in the initial needle collection system. Also, the plastic sleeve that was the source of contamination in the initial needle collection system is no longer part of the arrangement. In fact, because all of the parts in the modified collection needle configuration are stainless steel, it can be cleaned by sonication in solvent and dried in an oven without the worry of chemical attack or thermal breakdown.

The flow restriction imposed by the collection tube arrangement is removed because the 16 gauge needle has a much larger internal diameter than the 0.01" stainless steel tube. In addition, the modified needle pierces the sample vial septum cleanly, allowing the vial to remain gas-tight. Because the needle is designed to pierce septa, the problems associated with the collection tube becoming clogged with septa material are also mitigated. For these reasons, the modified collection needle configuration was chosen as the best arrangement for transferring gas from the sample vial to the collection canister.

CHAPTER 4

ANALYSIS AND RESULTS OF ICE CORE EXPERIMENTS

A set of forty-nine ice cores was collected from The Byrd Polar Research Center (BPRC) on December 9, 2003. Along with the ice cores, three method blanks and four deionized water blanks were acquired. The purpose of these blanks was to insure the integrity of the data collected for the real samples by allowing corrections to be made for sampling technique and sample storage. The sample collection method is detailed below. All of these samples were stored in a freezer maintained at -18°C until they were shipped overnight in refrigerated boxes to the Climate Change Research Center (CCRC) at the University of New Hampshire on 4/15/2004.

The purpose of the visit to CCRC was to collect data for the ice cores using established instrumentation and methods, and then compare this data with information to be collected later with the experimental apparatus, i.e. method validation. The facility at CCRC contains similar equipment to the experimental apparatus described in chapter two, except the CCRC instrumentation is set up to regularly analyze gaseous samples for compounds normally found in air samples. In addition, the gas chromatographic instrumentation at CCRC possesses a mass spectrometer (MS) detector system, which permits more rapid identification of unknown compounds.

Ice cores collected were part of the Bona-Churchill Core 1, which was acquired in May 2002 in the col between Mt. Bona and Mt. Churchill in the Wrangell-St. Elias National Park, Alaska at an elevation of approximately 4420 meters above sea level. Based upon preliminary dating information furnished by BPRC, the samples obtained for this experiment cover the period from about 1899-1901 AD. BPRC regularly analyzes ice cores for oxygen isotopes, dust, and major anions and cations (Mashiotta 2004).

Samples were collected by sectioning the core with a modified band saw in a refrigerated room. The size of each section was about 6.5 cm by 4 cm by 2 cm (volume of approximately 50 cubic centimeters). The individual samples were placed in collection cups and transferred to a class 100 cleanroom. In the cleanroom, each sample was thoroughly rinsed with high purity deionized water and then sealed inside individual gas-tight septa bottles and labeled.

Method blanks were created by freezing high purity (at least 18.2 MΩ·cm) deionized (HPDI) water inside the freezer facility at BPRC on 11/26/03. During a meeting on 11/18/03, it was decided to create this blank by freezing the water in a non-airtight Teflon beaker with a Teflon lid. On the sample collection date, this method blank was warmed slightly to free the ice from the beaker, and then sectioned to create three samples of a size similar to the ice cores samples. The blanks were transferred to vials in exactly the same manner as the ice cores samples described above.

Deionized water blanks were created by filling four separate gas-tight septa bottles with the water used to rinse the ice core samples and the method blanks. It is important to mention that these samples were collected as liquid water, and were never frozen until they reached the freezer at the Allen lab.

Ice core samples, method blanks and deionized water blanks were stored in a dedicated freezer at approximately –18 °C (-0.4 °F). The temperature of the freezer was checked periodically throughout storage. On 4/15/04, samples were packed in coolers filled with dry ice and shipped overnight to the CCRC. Upon receipt, the samples were noted to be in good condition and still frozen.

At the CCRC, the analytical technique involved first concentrating compounds which may be trapped within the ice cores, then injecting this concentrate directly onto the GC column. Any compounds present are separated by the column before passing through a variety of detectors. Note that this method is very similar to the experimental method described in chapter 2.

Each of the vials containing ice cores includes a headspace above the sample; air trapped at the time the sample was sealed inside the vial. This headspace was purged with ultra-high purity (UHP) helium while the core was still frozen. The core was then melted by gently warming to room temperature with a water bath. The UHP helium was then bubbled directly through the liquid sample, purging compounds that may be contained in the sample. This gas is condensed (trapped) on glass beads cooled with liquid nitrogen. The beads are then warmed to about 90 °C, volatilizing the compounds of interest while leaving the water behind. GC carrier gas is passed through the beads, sweeping the compounds onto the GC column. Compounds are separated by the column and passed through detectors, where they are identified and may be quantified.

The analysis of the ice cores at the CCRC produced several key results. First, analysis of an empty vial produced a chromatogram with very few peaks. The magnitude of these peaks were low, relative to those found in the ice core, suggesting that the gas

purging hardware and vial were contaminant free. In addition, analysis of the BPRC deionized water blank 1 (of 4) showed very few peaks with low relative magnitude, suggesting that storage of samples and subsequent sample shipment had contributed no contamination to the samples. Analysis of core sample 2-6 (BPRC ID: Tube 157, Sample 6, Depth 162.09 m) produced a chromatogram with numerous peaks, suggesting multiple compounds trapped within the core.

Problems with sample storage were uncovered during subsequent sample analysis. Method Blank 2 produced a chromatogram with multiple peaks of high relative magnitude. The retention times for these peaks correspond directly with the peaks found in ice core sample 2-6. Partial identification of these peaks indicated the presence of refrigerants in the sample. This in itself would suggest that a possible source of contamination for the compounds of interest is in the storage freezer at BPRC. Subsequent analysis of BPRC deionized water blank 2 (of 4) showed multiple peaks of high relative magnitude. The retention times for these peaks correspond directly with the peaks found in ice core sample 2-6 and Method Blank 2. This data does not agree with that obtained from BPRC DI water blank 1, suggesting variability in sample storage conditions (i.e. septa bottles). Testing of a number of empty vials for leak rates using UHP helium produced varying results, suggesting a high level of variability among the septa bottles. Analysis of an ice core obtained at the CCRC (source: Antarctica, age: approximately 5000 years) produced a chromatogram that lacked many of the peaks observed in sample 2-6, Method Blank 2, and BPRC DI water blank 2. This further suggests compromised sample storage prior to analysis, though not a conclusion as we might expect these very different ice cores to produce different chromatograms.

Although precautions were taken to ensure sample integrity (e.g. collection of method blanks, cleanroom handling, temperature controls, etc.) it appears that at least some of the samples were compromised due to variability in the sample storage containers. This variability is plainly illustrated by the difference in chromatographic results obtained from BPRC DI water blanks 1 and 2 (Figure 4.1). It is important to mention that one of the septa bottles was previously checked for leaks, and found to be leak-free. Because of limited supply, and under the assumption that these bottles are identical, it was concluded that all the bottles were leak-free. This assumption was faulty.

Since the septa bottles may not be gas-tight, some of the samples were exposed to the environment during storage and shipping, explaining the presence of refrigerants in the samples. This is illustrated in Figure 4.2, a comparison of the chromatograms obtained from Method Blank 2 and BPRC DI Blank 2. Because the DI water blank was never in the freezer at BPRC, the source of the compounds present in the sample must be either the storage conditions between collection and analysis (including the septa bottle itself), or the sample shipment.

It is of interest that the magnitudes of the peaks obtained from Method Blank 2 are generally greater than those obtained from Core 2-6 (Figure 4.3). This might be attributed to the fact that the method blank was frozen within the BPRC freezer, and the liquid water absorbed components of the environment to a greater degree than the ice cores themselves (frozen ~100 years ago in Alaska, then stored in the freezer). However, due to the results obtained from the deionized water blank, no meaningful conclusions can be drawn.

It is also of interest to compare the chromatograms obtained from Alaskan core sample 2-6 and the Antarctic core sample (Figure 4.4). Although the chromatograms do differ, they share some of the same peaks. This might suggest that storing cores in a non-air tight environment (the only condition that these two cores have in common) could confound this type of analysis in the future. Again, because of the variability in the control samples, no meaningful conclusions can be drawn.

Given the analytical results obtained thus far, the analysis of the remaining ice core samples was discontinued. First, the analysis requires melting the sample, which may render the samples useless for other types of analysis not affected by the leaking vials. For example, useful information might still be obtained from these samples using a similar concentration and separation routine, but employing mass spectrometric detection in single-ion mode. This method might allow identification and quantification of analytes present in the ice cores that are not the result of contamination. Furthermore, though the sample containers may not be gas-tight, they still provide a physical barrier for macroscopic contaminants. Because the act of analysis breaks this seal (by puncturing the septa), attempts to continue analysis might further jeopardize these valuable samples.

For similar work that may be performed in the future, data obtained from this experiment warrant several important suggestions. Clearly, use of a leak-free sample storage container is of paramount importance. Also, because the sample container headspace might contain contaminants, purging the headspace with inert gas at the point of sample collection (e.g. at the BPRC cleanroom) might be justified. Finally, due to the difficulty involved in acquiring the samples, it might be recommended that samples

destined for this type of analysis be stored in gas-tight containers from the point of sample acquisition in the environment, prior to being refrigerated.

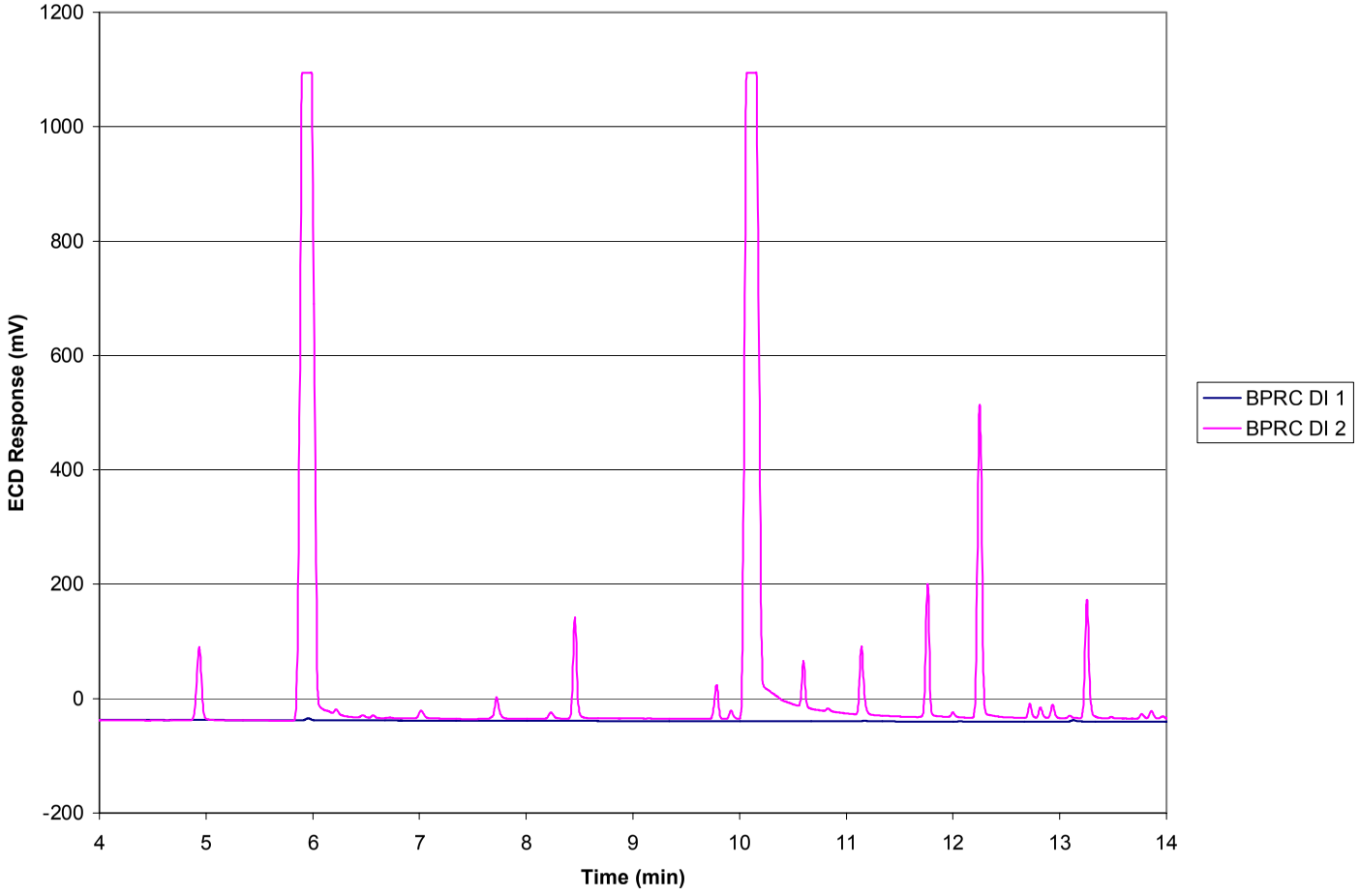

Figure 4.1: Chromatographic comparison of deionized water blanks

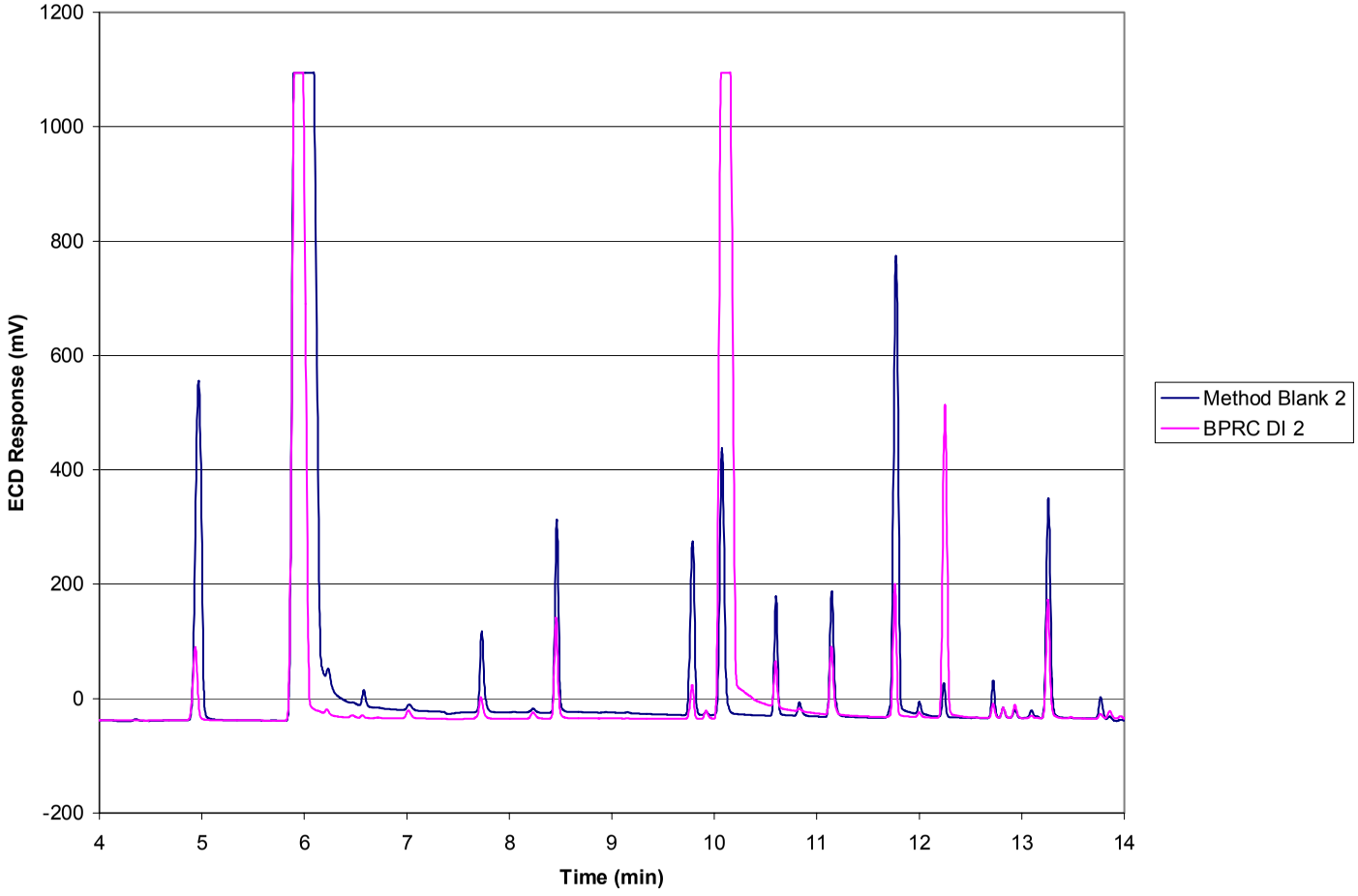

Figure 4.2: Chromatographic comparison of method blank 2 and deionized water blank 2

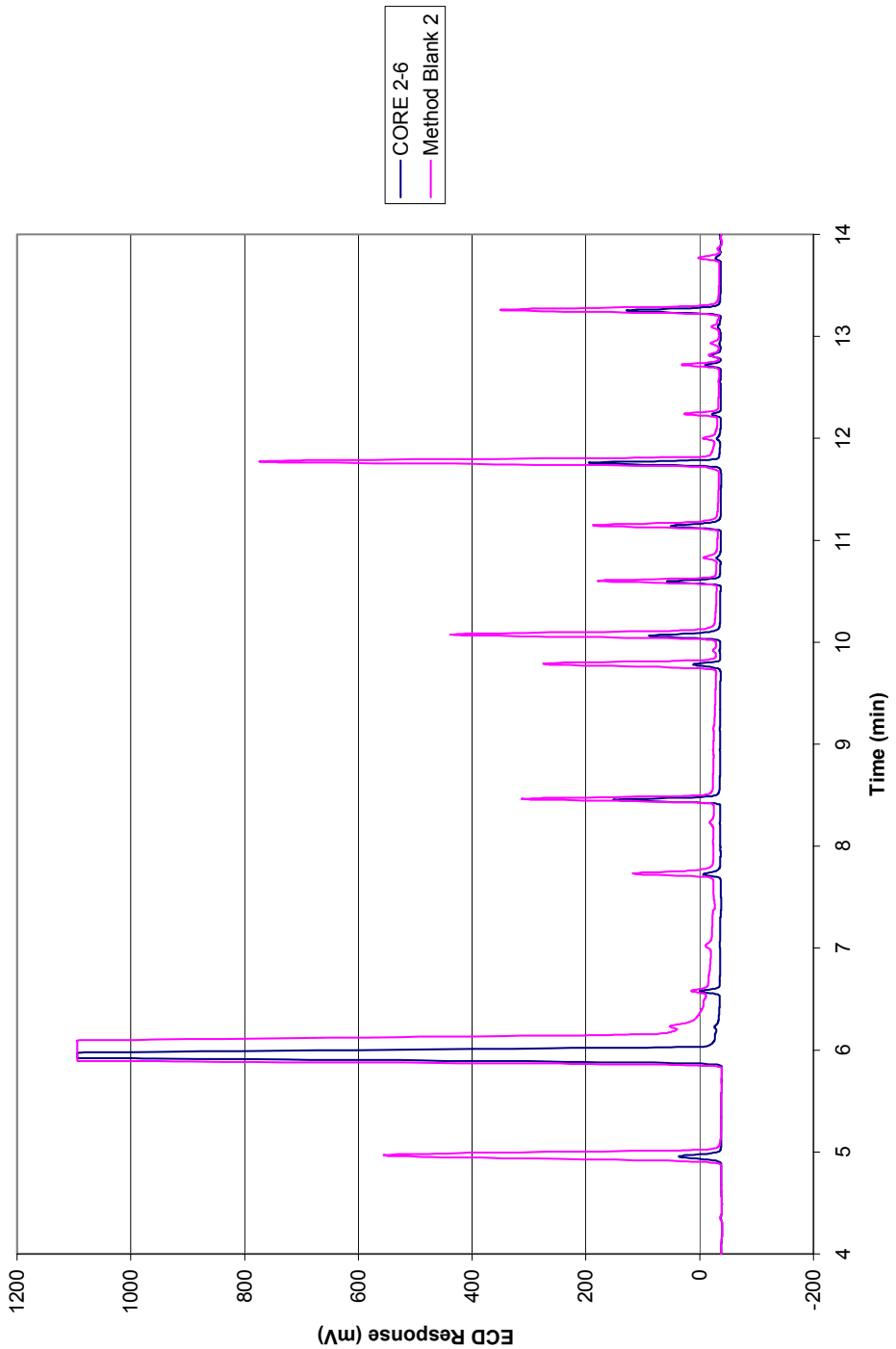

Figure 4.3: Chromatographic comparison of method blank vs. ice core sample

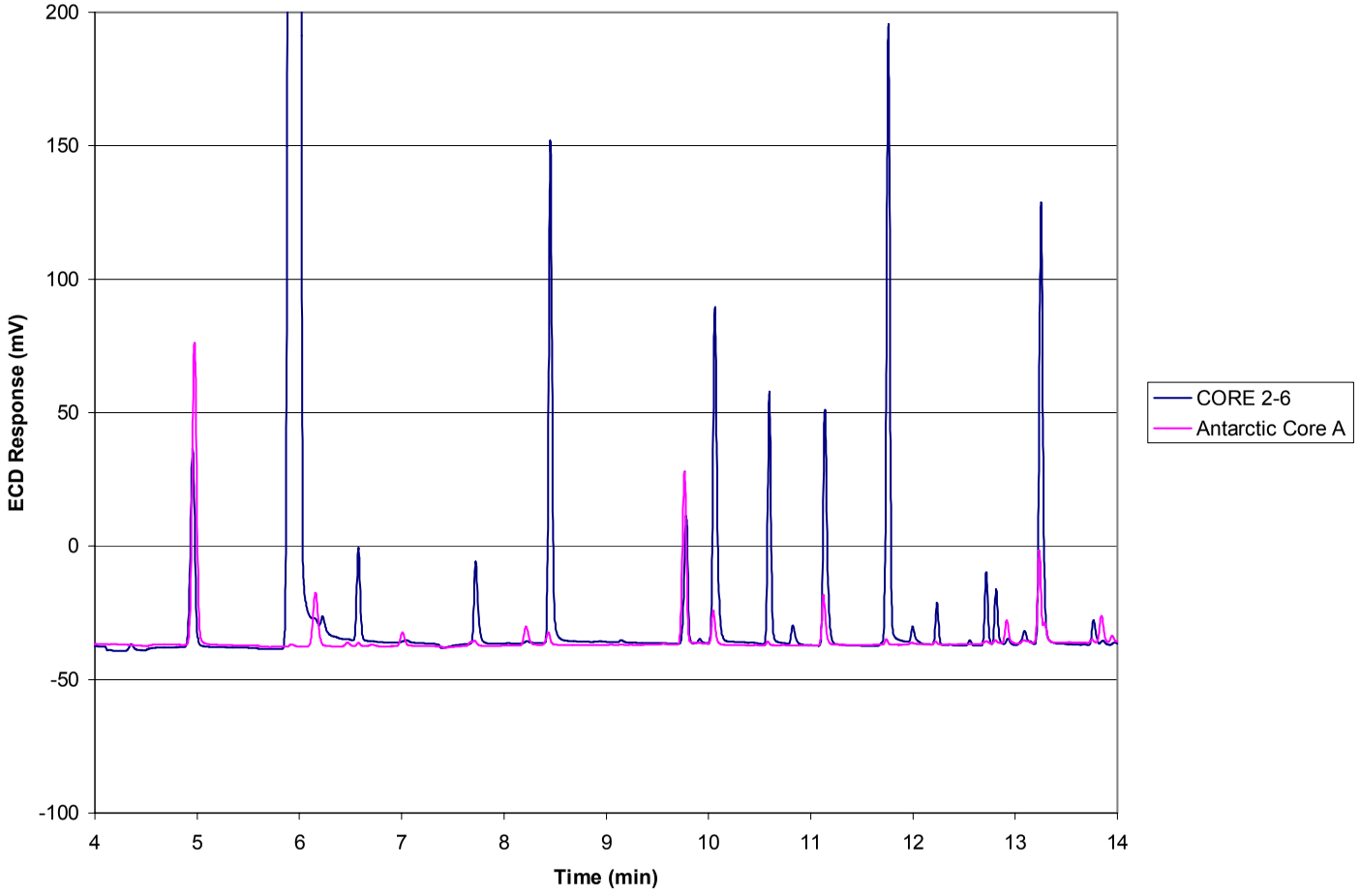

Figure 4.4: Chromatographic comparison of Alaskan and Antarctic ice core samples

CHAPTER 5

APPARATUS FOR THE STUDY OF NATURAL LIQUID SAMPLES

Though the study of ice core samples was discontinued due to the contamination described in Chapter 4, much of the experimental apparatus that had been assembled for their study was later used to successfully examine natural liquid environmental samples. In addition, many of the techniques developed for the proposed ice core study were further refined after the data acquisition visit to the CCRC.

Following the ice core study, the inlet purge system was reconfigured in order to minimize sample contamination, leaks, and sample carryover. These changes were a direct result of the lessons learned in the ice core study. A schematic of the updated inlet purge system appears in Figure 5.1. In this configuration, the mass flow controller has been moved to upstream of the sample vial, the tubing to Luer adapter at the inlet needle was replaced by a compression fitting, a needle valve is added downstream of the sample, silco steel tubing was exclusively used downstream of the sample, and a heater box has been added between the sample and the preconcentrator inlet. Finally, new sample vials were obtained from a different commercial vendor to minimize the possibility of leaks. This configuration proved successful in providing meaningful data.

Because the mass flow controller is easily contaminated and difficult to clean, movement of the unit to a position upstream of the sample yielded several advantages. First, the opportunity for the mass flow controller to become contaminated was negated (except in the case of sample backflush), which eliminated the need for vacuum chamber cleaning of the unit. Secondly, the position of the controller allowed for direct leak checking of each sample vial prior to analysis. In fact, each component of the inlet purge system can be systematically checked for leaks with minimal labor. Finally, the mass flow controller is essentially an extra valve between the purge gas supply and the sample, giving the operator greater control over the system as a whole.

Replacement of the tubing to Luer adapter at the inlet needle by a compression fitting attached directly to the bore of the needle closed a significant source of system leaks. Addition of the needle valve immediately downstream of the modified collection needle permits leak checking for the entire sampling system (inlet needle, vial, and collection needle). Finally, the addition of the heater box between the sample and the preconcentrator inlet minimizes the possibility that sample will condense on the either the needle or T valve before reaching the heated preconcentrator inlet. The heater box consists of a Lucite box, thermocouple, temperature controller and heat gun.

Aside from the changes to the inlet purge system described above, the remainder of the mechanical system (preconcentrator and gas chromatograph) was left unchanged. There were additional improvements to sampling technique, which will be described in chapter 6.

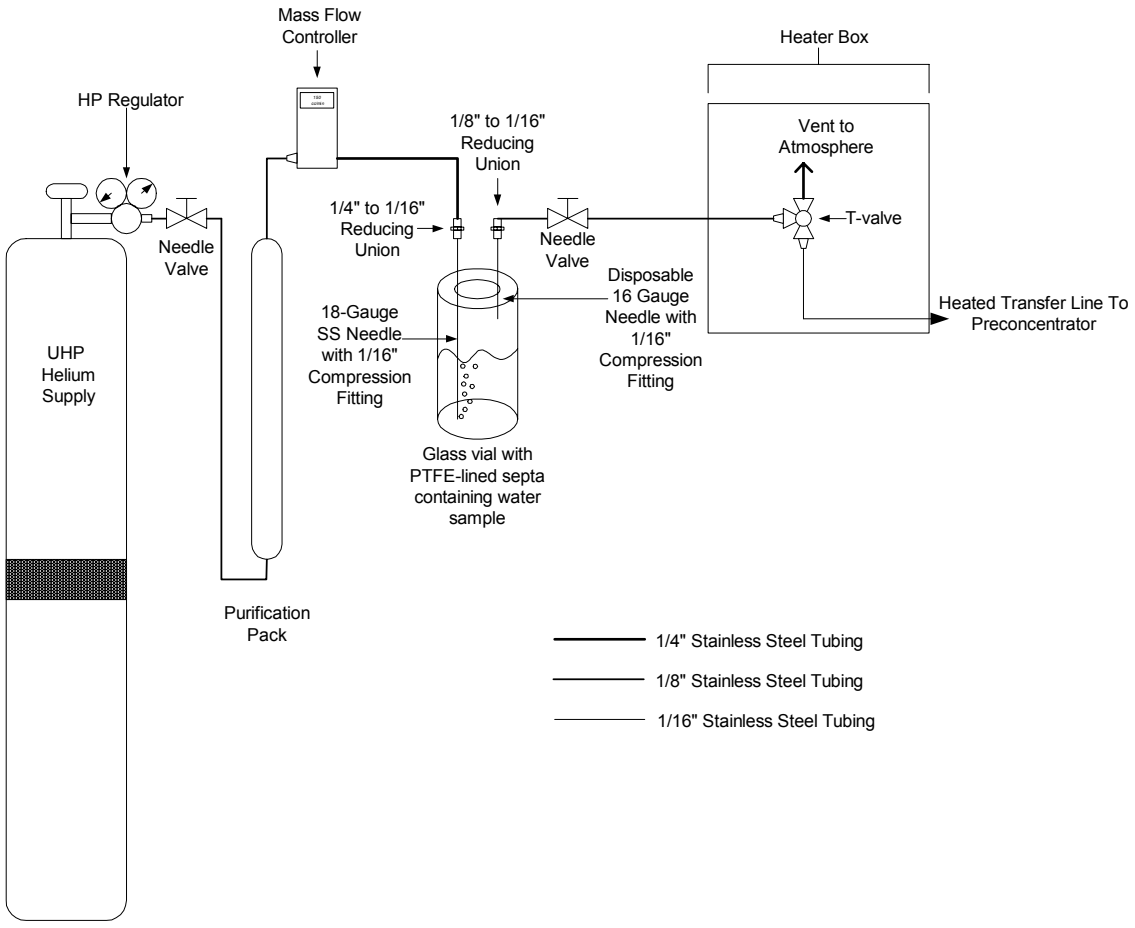

Figure 5.1: Detailed schematic of purge inlet system for water analysis. Components not to scale.

CHAPTER 6

ANALYSIS OF NATURAL LIQUID ENVIRONMENTAL SAMPLES

As a test of the apparatus and methods developed for the study of liquid environmental samples, a proof of concept experiment was designed and executed. This experiment consisted of obtaining drinking water from two sources and quantifying a small number of analytes in these water samples for comparison. These analytes included chloroform, benzene, toluene, trichloroethylene, tetrachloroethylene and bromoform. From a U.S Geological Survey report issued in 2003, these analytes were expected to be found in concentrations ranging up to several hundred ppb (Delzer and Ivahnenko 2003).

Dilute aqueous standards for each of the analytes listed above were prepared in order to identify and quantify each of the compounds in drinking water. Neat solutions of each compound were obtained from Sigma-Aldrich Corporation (St. Loius, MO). Dilution water had a minimum resistivity of 18.2 MΩ·cm and was further exposed to an ultraviolet lamp operating at a wavelength of 254 nm overnight in order to photo-oxidize organic contaminants (Otson, Polley et al. 1986). Pyrex volumetric glassware was prepared by rinsing eight times with high purity deionized water, then drying overnight at 155°C. Glass septa vials meant to hold both calibration solutions as well as samples were prepared by rinsing eight times with high purity deionized water and drying overnight at

225°C. The caps for these vials were rinsed in a similar fashion, and dried under ultra high purity nitrogen overnight.

Qualitative identification of each compound was achieved using "retention time standards" consisting of a single analyte at approximately 500 ppt. Each of these standards was individually analyzed and the retention time of the resulting peak was recorded. A chart that illustrates the relationship between column retention time and analyte boiling point can be found in Figure 6.1. The relationship exhibits excellent linearity, which was expected.

A single sample of drinking water was analyzed in order to semi-quantify the analytes of interest and provide information to be used to generate calibration solutions. The standard purge volume of 400 cubic centimeters produced a chromatogram in which the ECD was repeatedly saturated, Figure 6.2. Based upon this information, the purge volume was reduced to 150 cubic centimeters. From this point forward, all calibration standards, blanks, and samples were purged with the same 150 cubic centimeter volume in order to retain experimental consistency.

Quantification of analytes was achieved by generating mixtures of each analyte at known concentrations. Specifically, mixtures containing analytes of interest concentrated at 62.5, 125, 250, and 1000 ppt were analyzed. The peak area for each analyte was calculated and plotted against analyte concentration. Because the electron capture detector is more sensitive than the flame ionization detector, these calibration standards produced quantifiable peaks using the ECD, while no peaks were visible on the FID. The linearity of the calibration curves generated using data obtained by the ECD is greater than 98% for chloroform, Figure 6.3.

Problems were encountered while trying to construct calibration curves for the remaining compounds (benzene, toluene, trichloroethylene, tetrachloroethylene and bromoform). First, benzene and toluene are essentially invisible to the ECD as they lack strongly electronegative functional groups. In addition, the calibration curves for trichloroethylene, tetrachloroethylene and bromoform were extremely nonlinear. Most importantly, these halogenated compounds began to appear in subsequent "blank" runs, indicating possible system contamination. Attempts to clean both the inlet purge system (by storing components overnight in a vacuum chamber) and the GC (by baking the column overnight) did not affect the appearance of trichloroethylene, tetrachloroethylene and bromoform peaks in the blanks. This suggested that the source of contamination was inside the preconcentrator itself, even though the unit automatically bakes between analyses. Further study of the preconcentrator system logs indicated that while the cryofocuser is programmed to heat to 150°C during injection, it typically did not heat past approximately 77°C. A telephone conversation with the preconcentrator manufacturer confirmed that the cryofocuser rarely heats past about 80°C (Bosquez 2004).

The failure of the cryofocuser to independently heat past approximately 80°C during GC injection means that compounds with boiling points higher than this temperature might be problematic to quantify, as they cannot be completely volatilized for transfer and subsequent injection to the GC. This design feature explains both the nonlinearity of the calibration curves for trichloroethylene, tetrachloroethylene and bromoform as well as the lingering presence of the compounds in the device.

For the reasons described above, carbon tetrachloride was added as an analyte because it has a boiling point below 80°C (boiling point = 76.7°C) and commonly appears in environmental water samples (Delzer and Ivahnenko 2003). The column retention time for carbon tetrachloride was determined to be 12.9 min, which agrees with the established relationship between retention time and analyte boiling point (Figure 6.4). Aqueous calibration standards containing carbon tetrachloride at 62.5, 125, 250 and 1000 ppt were generated as above and analyzed. The resulting calibration curve displayed excellent linearity (Figure 6.5).

Semi-quantitative analysis of the drinking water sample also necessitated that additional calibration curves be generated for the quantification of chloroform. This is because while carbon tetrachloride appears at about several hundred ppt, chloroform appeared at several hundred ppb. Therefore, additional aqueous standards of both chloroform and carbon tetrachloride were prepared at 100, 200 and 400 ppb. The resulting FID calibration curves for chloroform (Figure 6.6) and carbon tetrachloride (Figure 6.7) were also highly linear ($R^2 > 98\%$).

With qualitative and quantitative information for both chloroform and carbon tetrachloride in place, the analysis of actual drinking water samples was performed. 250-mL amber glass collection bottles were rinsed eight times with high purity deionized water, and then muffled overnight at 225°C. Teflon-lined caps for these bottles were similarly rinsed and then dried overnight under a stream of ultra high purity nitrogen gas. Two sources of water were chosen, a drinking fountain in the basement of the Newman & Wolfrom Chemistry laboratory on the campus of Ohio State University ("NW Water") and a drinking fountain located on the fourth floor of the Science and Engineering library

on campus ("SEL Water"). Drinking water fountains were run for approximately one minute to achieve thermal equilibrium before filling collection bottles, which were sealed and shaken to rinse the bottles. The contents were then emptied and the bottles refilled with source water to contain little or no headspace. The NW water sample was collected at 9:15 PM EST on 5/14/2004 and analyzed immediately. The SEL water sample was collected at 11:30 PM EST on 5/14/04 and analyzed within twelve hours. In the interim, the water was stored in a dark cabinet at room temperature. At the time of analysis, three 5-mL samples of each water source were transferred to precleaned 20-mL septa vials, in order to obtain a triplicate set of results.

The step-by-step procedure for purging and analyzing each sample is located in Appendix ##. Before each sample analysis, the system was checked for leaks (Appendix ##), and system blanks were run at the start of each day and in between source samples.

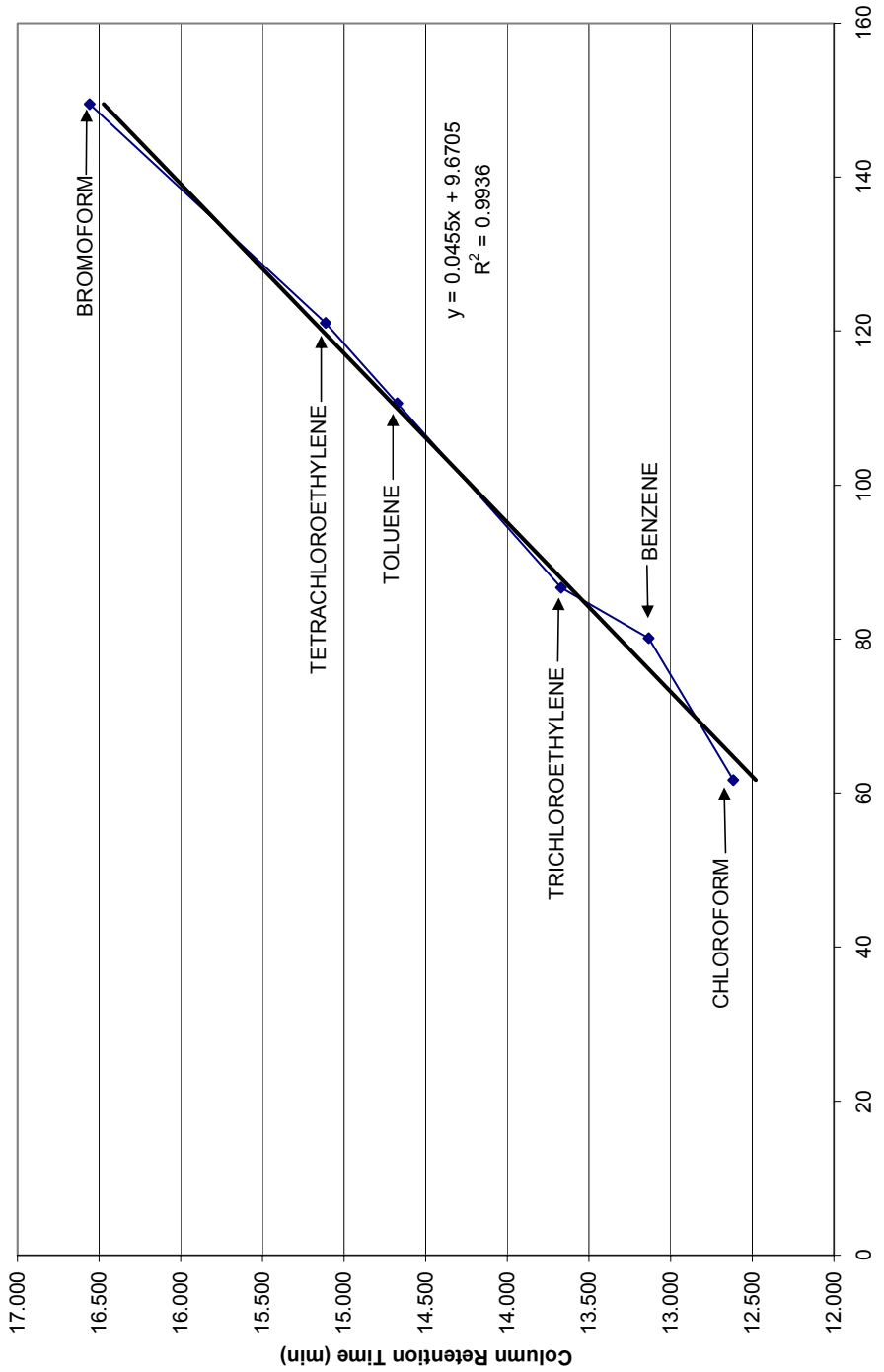

Figure 6.1: Column retention time vs. analyte boiling point for six analyte set

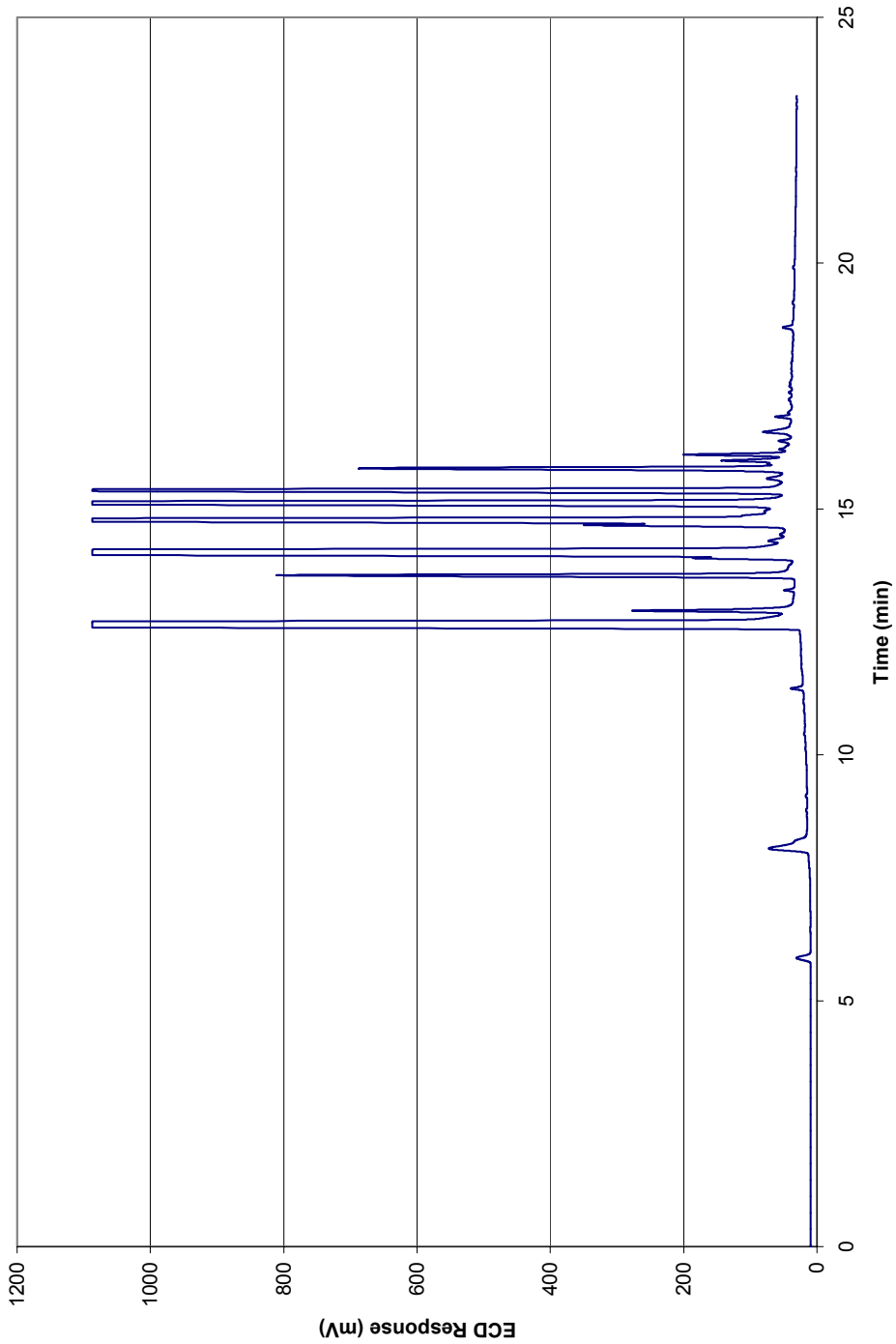

Figure 6.2: Sample ECD chromatogram using 400 cc purge volume

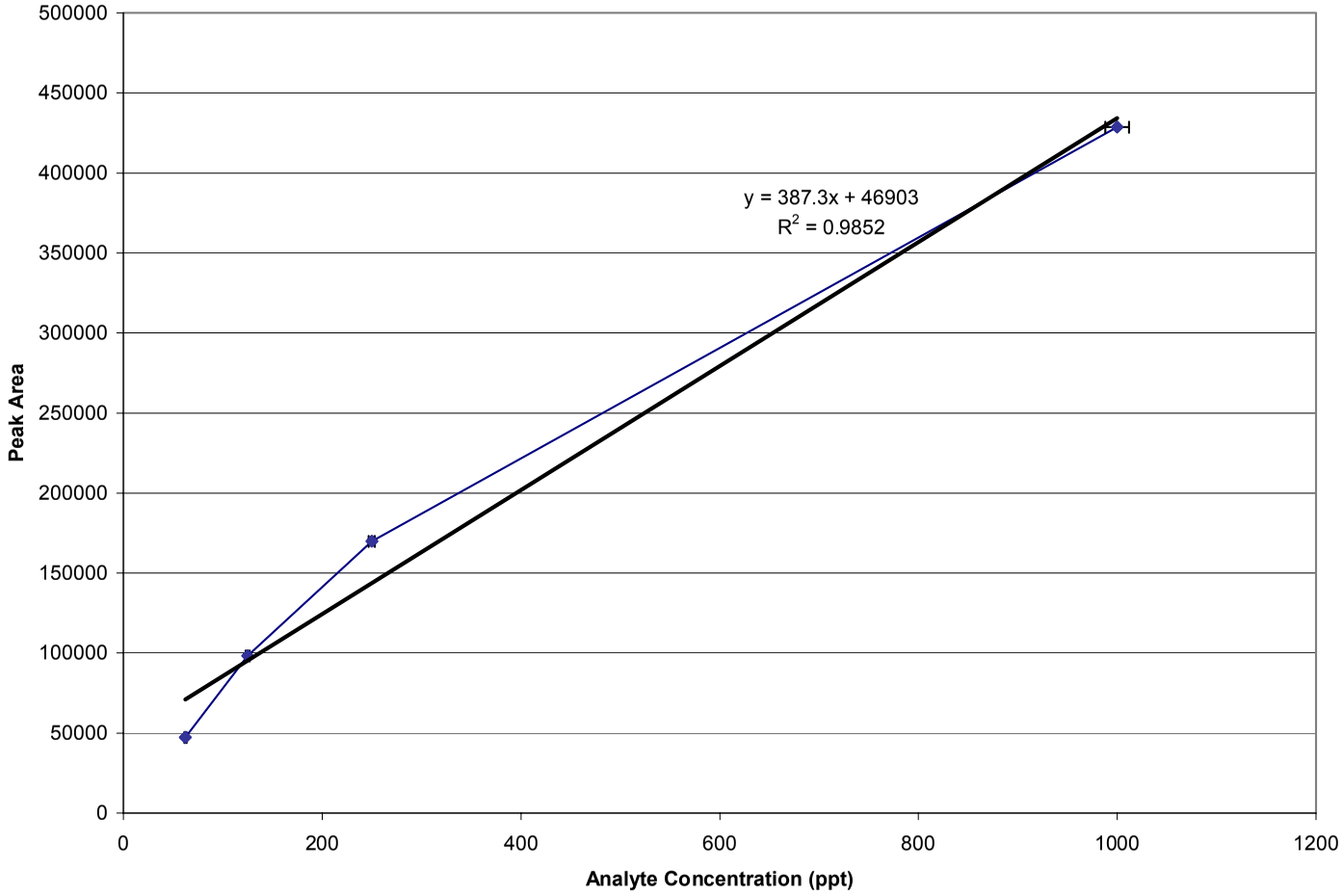

Figure 6.3: ECD calibration curve for chloroform

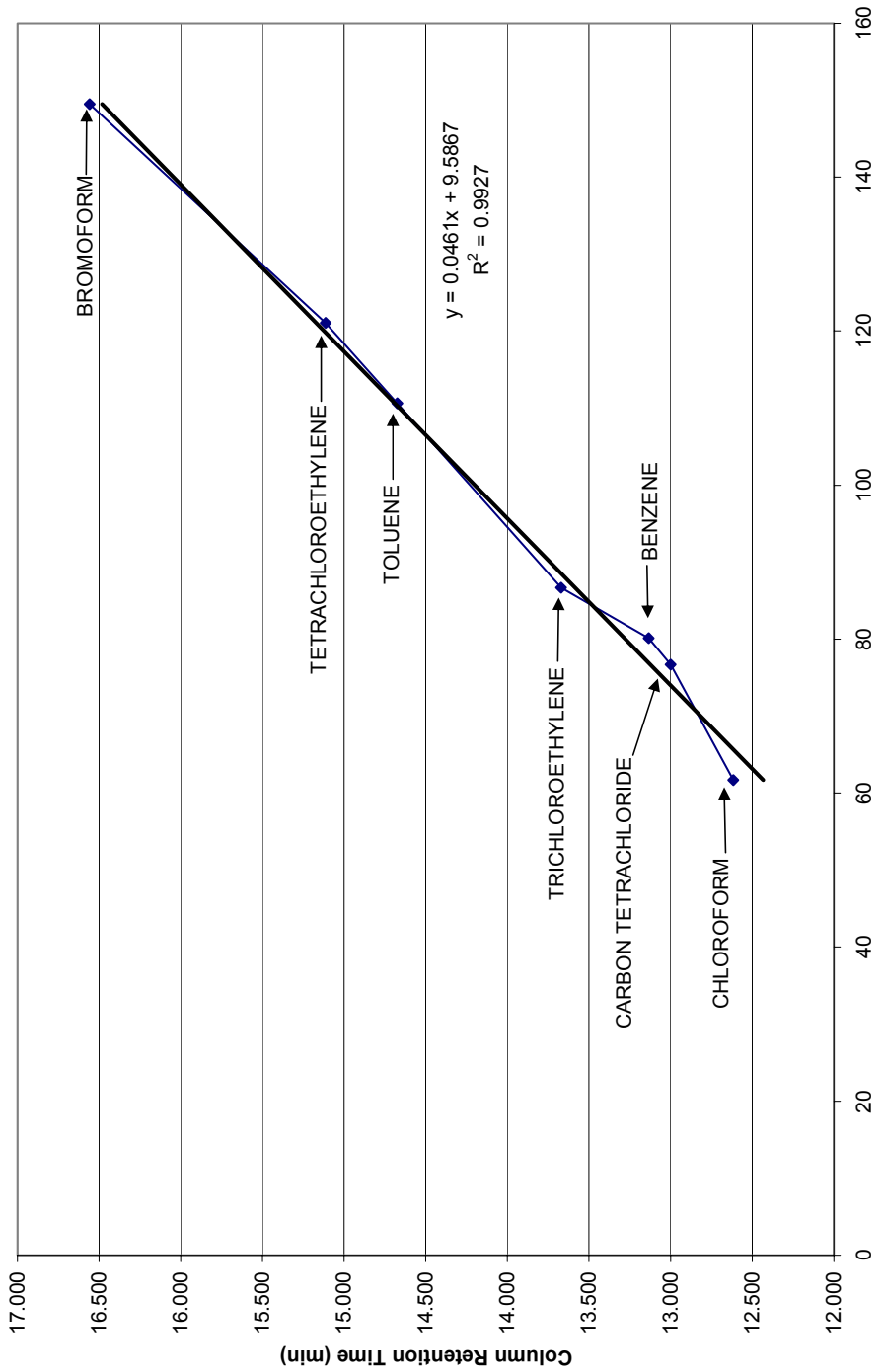

Figure 6.4: Column retention time vs. analyte boiling point for seven analyte set

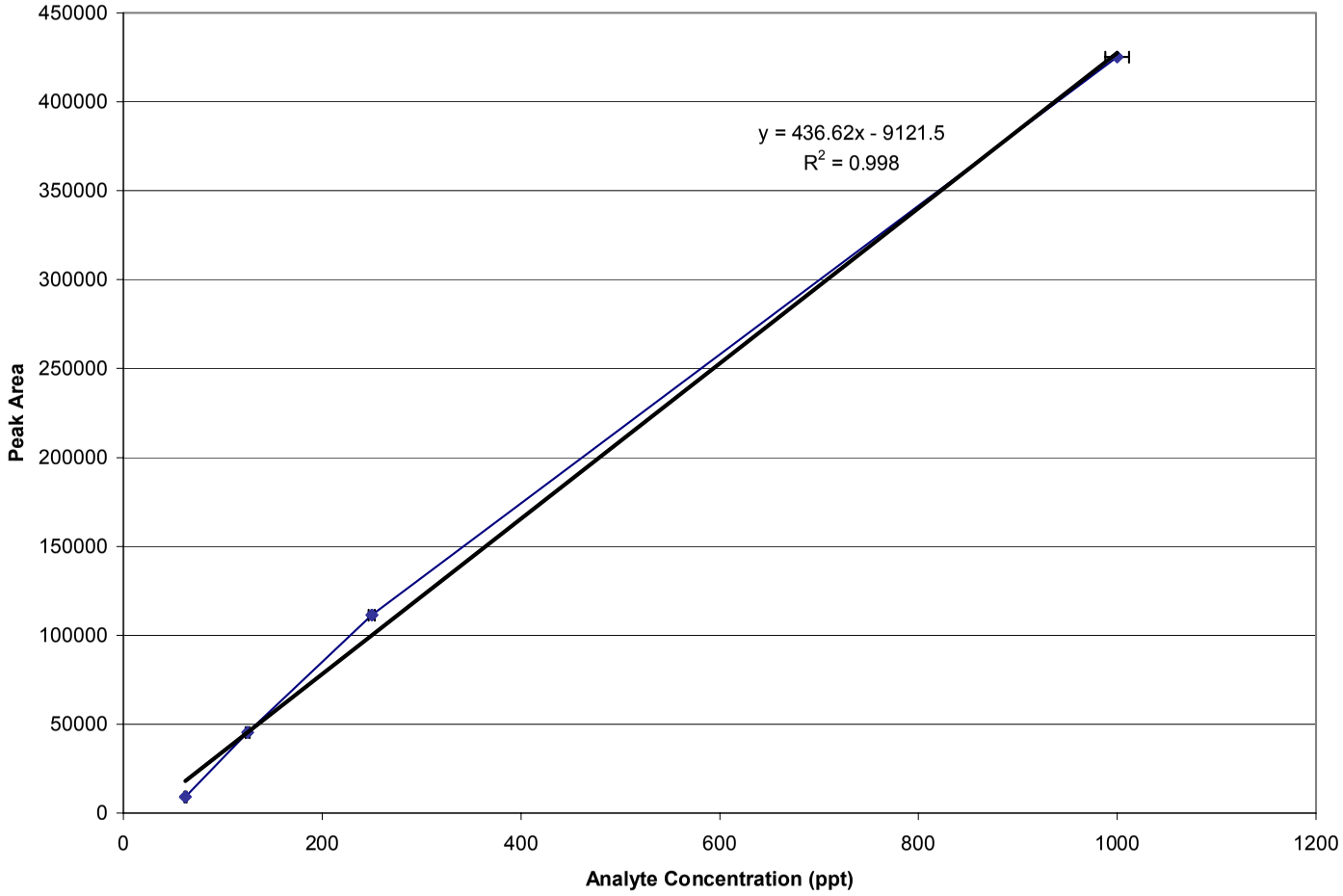

Figure 6.5: Carbon tetrachloride calibration curve by ECD

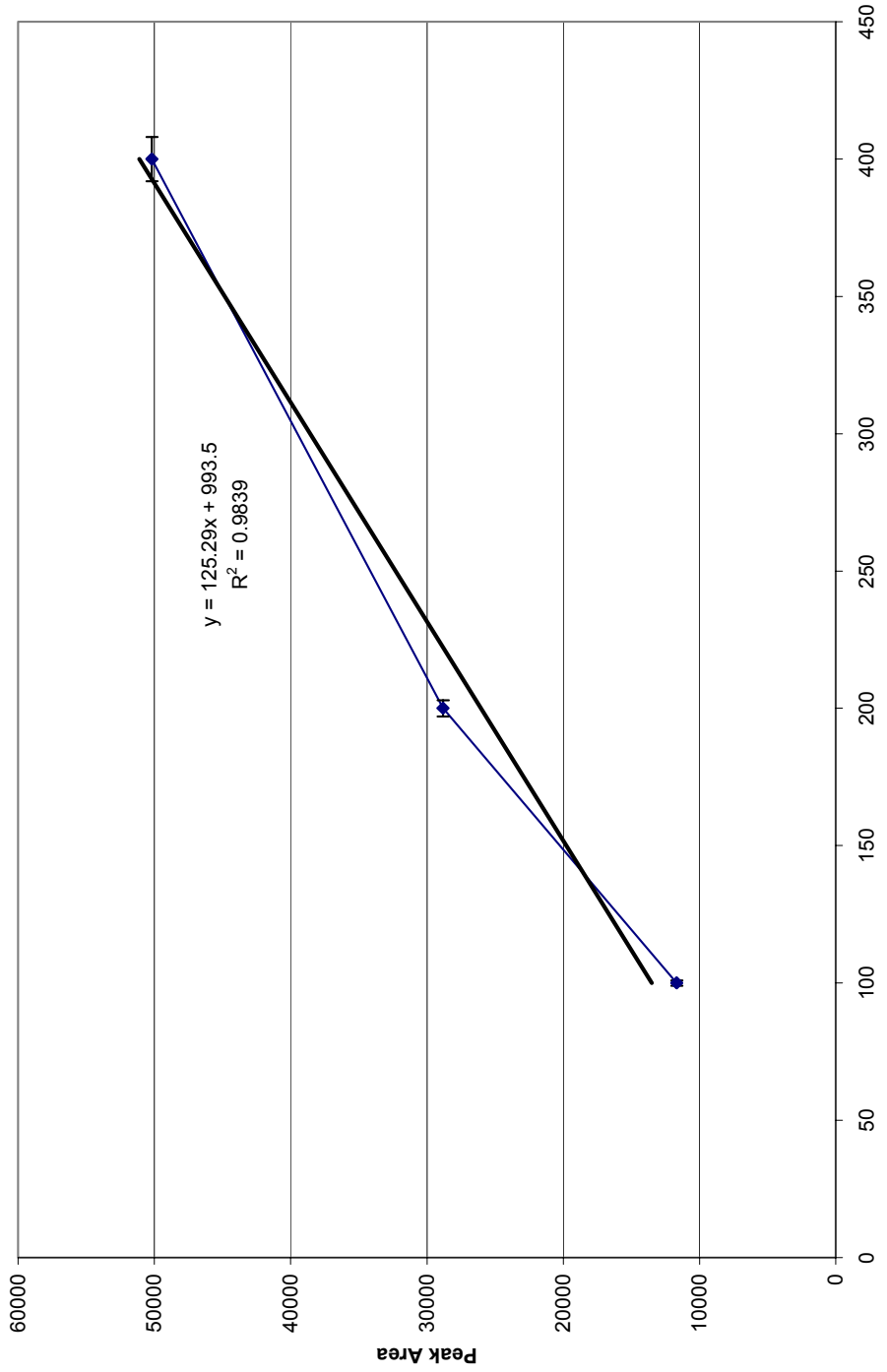

Figure 6.6: Chloroform calibration curve by FID

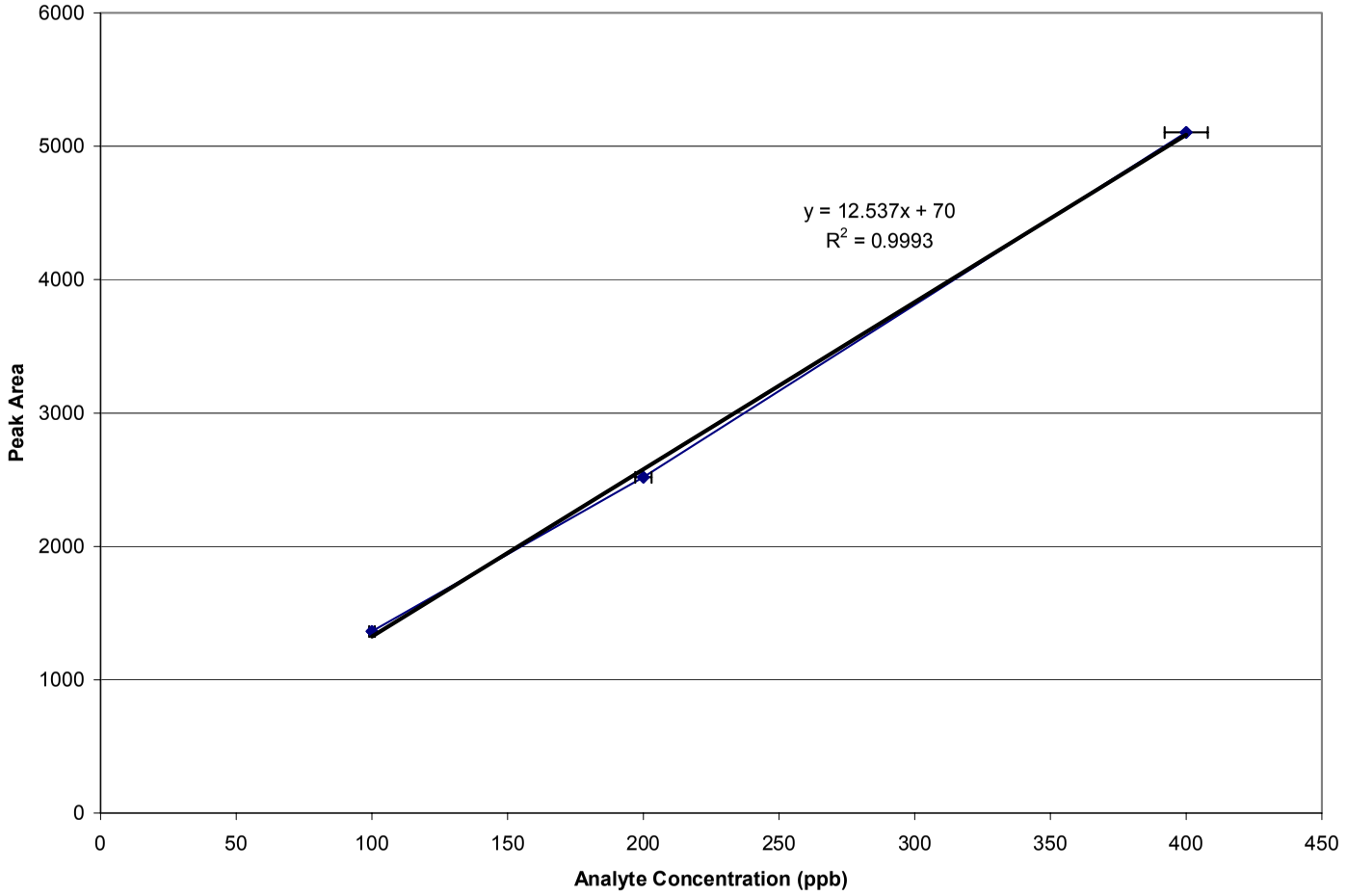

Figure 6.7: Carbon tetrachloride calibration curve by FID

CHAPTER 7

ANALYTICAL RESULTS FOR NATURAL LIQUID SAMPLES

Analytical results for the proof of concept experiment are reported in table 7.1 (chloroform) and table 7.2 (carbon tetrachloride). Graphical summaries of the data can be found in Figures 7.1 (chloroform) and 7.2 (carbon tetrachloride).

The results of the proof of concept experiment are within expectations. In general, more precise measurements were obtained for carbon tetrachloride than chloroform. Also, the SEL water measurements had better precision than the NW water measurements. This difference in results by source may be a direct reflection on operator consistency when following the procedures detailed in Appendix ##.

The calculated concentration of carbon tetrachloride in the drinking water is reasonable. The United States Environmental Protection Agency classifies carbon tetrachloride as a "probable human carcinogen" and sets a maximum contamination level (MCL) at 5 ppb (U.S. EPA 2004). The NW and SEL drinking water was found to contain 238 ± 9 ppt and 214 ± 3 ppt carbon tetrachloride, respectively (Table 7.2). In addition, the study completed by the United States Geological Survey found that the median concentration for carbon tetrachloride in all community water systems (n = 134) was 0.75 ppb (Delzer and Ivahnenko 2003). The concentration of the analyte found in this experiment is below this median value.

The calculated concentration of chloroform in the drinking water in comparison to permissible limits is somewhat more perplexing. The U.S. EPA has set the proposed limit for total trihalomethanes at 80 ppb (under review) and classified chloroform as "likely to be carcinogenic to humans" under high dose conditions that lead to cytotoxicity and cell regeneration (U.S. EPA 2004). At the same time, the U.S. EPA has classified chloroform as "not likely to be carcinogenic to humans" at a dose level that does not cause cytotoxicity or cell regeneration (U.S. EPA 2004). The NW and SEL drinking fountain water was found to contain 124 ± 17 ppb and 100 ± 9 ppb of chloroform, which is slightly above the maximum contamination level for total trihalomethanes. The calculated concentration of chloroform is less precise than the carbon tetrachloride measurements (note the larger error bars in Figure 7.1 compared to Figure 7.2). Because both analytes were in the mixture, this difference cannot be ascribed to the system operator. The difference may be attributed to the greater polarity of the chloroform molecules (with respect to carbon tetrachloride), which may cause them to selectively adsorb to the surfaces within the system to a greater degree than the carbon tetrachloride.

Sample Description	Chloroform Peak Area by FID	Calculated Chloroform Concentration (ppb)
NW Water Replicate 1	14002	104
NW Water Replicate 2	17270	130
NW Water Replicate 3	18369	139
Average NW Values	16547	124
Standard Deviation (1σ)	2272	17
Relative Deviation (1σ)	13.73%	13.73%
SEL Water Replicate 1	14669	109
SEL Water Replicate 2	13626	101
SEL Water Replicate 3	12326	90
Average SEL Values	13540	100
Standard Deviation (1σ)	1174	9
Relative Deviation (1σ)	9%	9%

Table 7.1: Numerical summary of chloroform concentration in drinking water samples

Sample Description	Carbon Tetrachloride Peak Area by ECD	Calculated Carbon Tetrachloride Concentration (ppt)
NW Water Replicate 1	98264	246
NW Water Replicate 2	95194	239
NW Water Replicate 3	91376	230
Average NW Values	94945	238
Standard Deviation (1σ)	3451	9
Relative Deviation (1σ)	3.63%	3.63%
SEL Water Replicate 1	84652	215
SEL Water Replicate 2	85128	216
SEL Water Replicate 3	82642	210
Average SEL Values	84141	214
Standard Deviation (1σ)	1320	3
Relative Deviation (1σ)	2%	2%

Table 7.2: Numerical summary of carbon tetrachloride concentration in drinking water samples

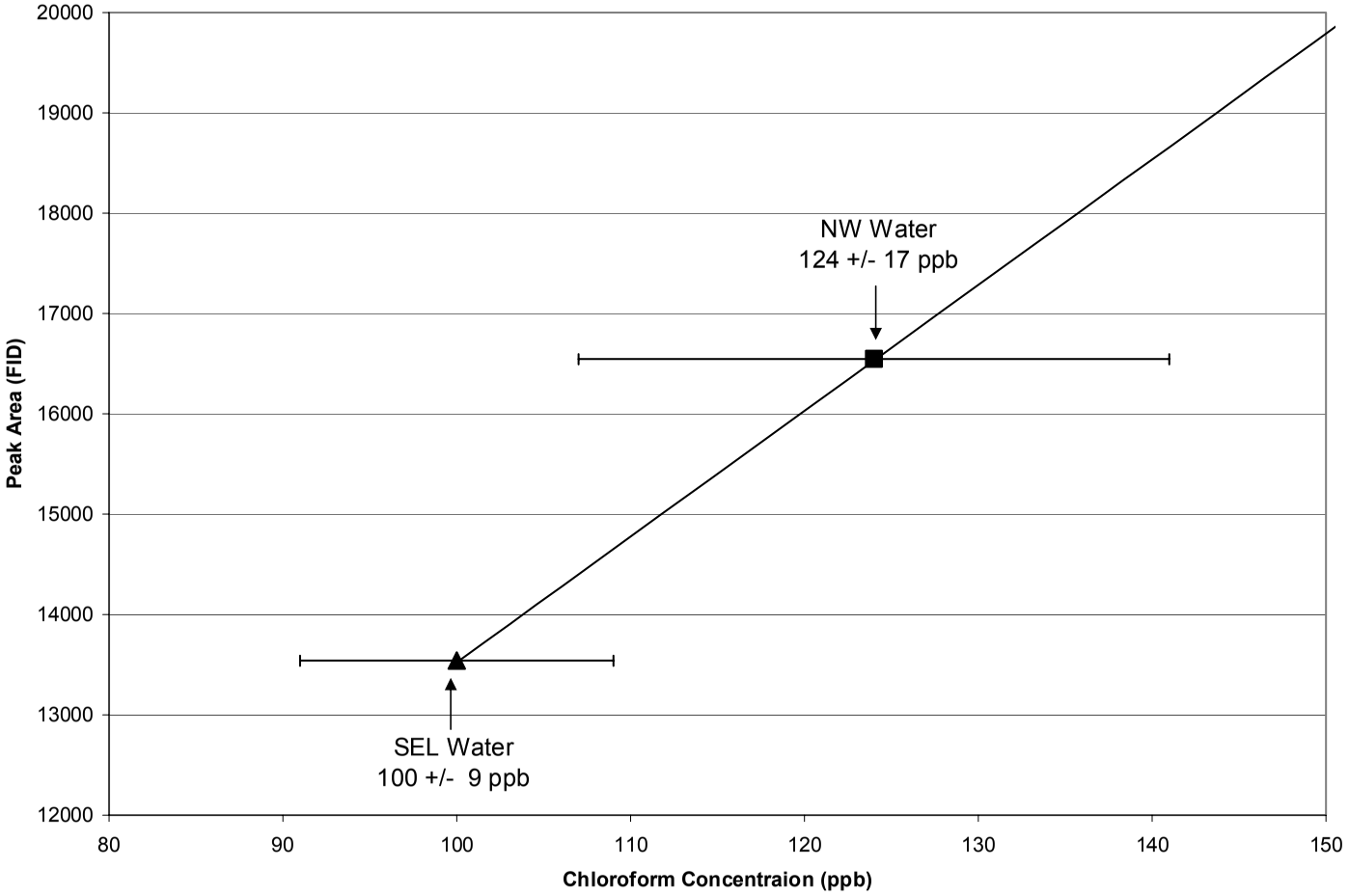

Figure 7.1: Graphical summary of chloroform concentration in drinking water samples

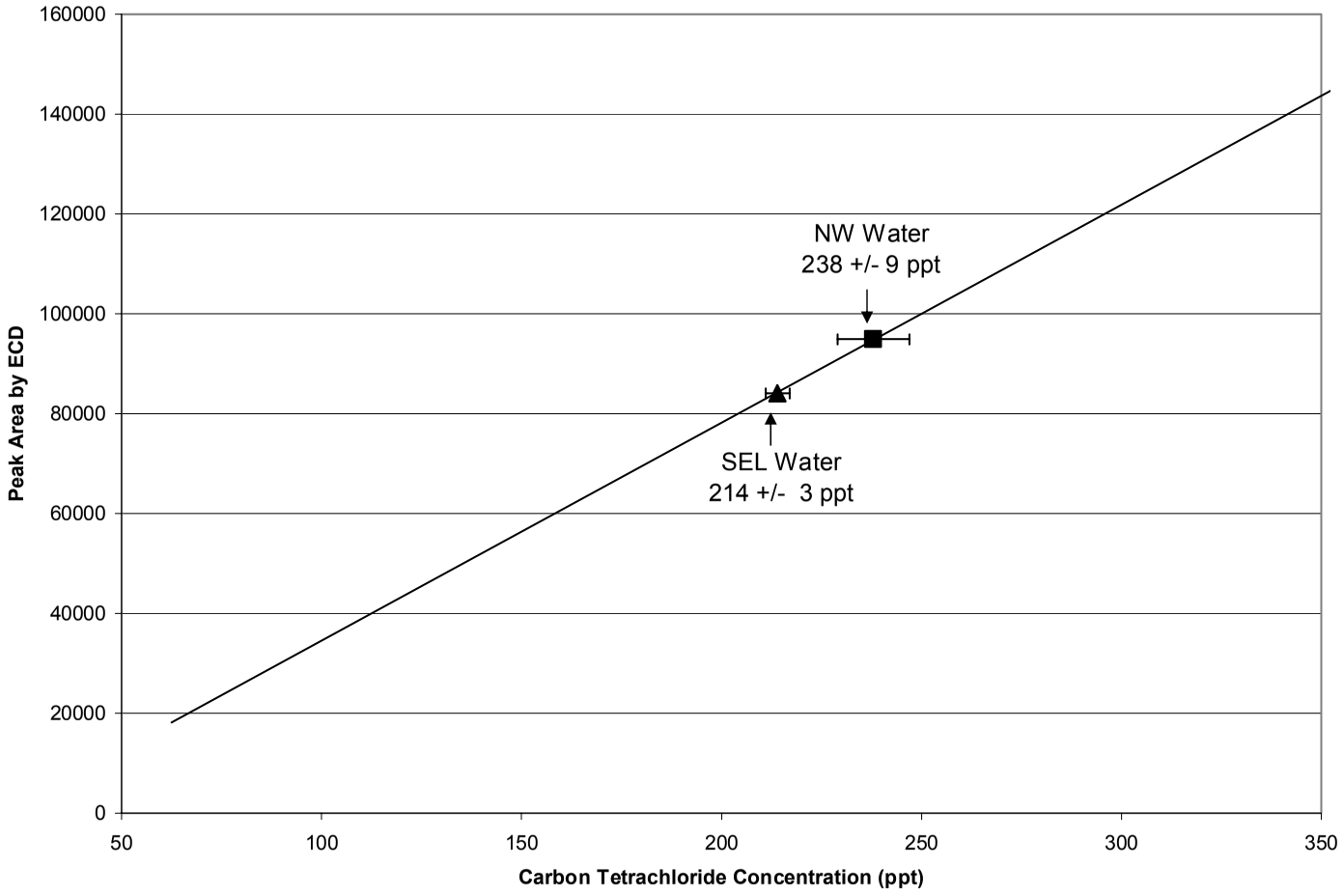

Figure 7.2: Graphical summary of carbon tetrachloride concentration in drinking water samples

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Instrumentation and methods were successfully developed which allow identification and quantification of volatile light halocarbons in aqueous environmental samples. While the apparatus was not used to successfully examine ice core samples for these compounds, the technology was adapted to provide meaningful and reasonable data for natural liquid environmental samples. In the proof of concept experiment, chloroform and carbon tetrachloride were identified as components of drinking water and their concentrations were calculated to be at or near expected values. In addition, the ability of the experimenter to rapidly interchange samples without exposing them to the laboratory environment is a novel attribute of the inlet purge system.

Because this document details instrumentation and method development, several recommendations for future experiments are warranted. Future study of ice core samples may be possible provided care is taken with the samples from the point of acquisition. As mentioned in Chapter 4, choice of a leak-free sample storage container is of paramount importance. In terms of mechanical improvement of the system, inclusion of the needle valve immediately downstream of the modified collection needle into the heater box apparatus will further minimize the possibility of analyte condensation prior to entry into the preconcentrator. Also, cryocooling of the GC column will permit the study of analytes with boiling points lower than room temperature. Finally, though

chromatographic resolution was sufficient for the proof of concept experiment, separation of target analytes may be improved by returning to the U.S. EPA method 502.2 parameters.

The most important recommendation for future experiments deals with the design feature of the preconcentrator described in Chapter 6 wherein the cryofocuser typically reaches a temperature of approximately 80°C during GC injection. If the experimenter wishes to study analytes with higher boiling points, a modification of the preconcentrator (i.e. addition of a cryofocuser heater) is highly recommended.

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APPENDIX A

SYSTEM STARTUP , SHUTDOWN, AND LEAK CHECKING

Preconcentrator & Gas Chromatograph Nightly shutdown procedure:

1. Extinguish GC-FID (IGNIT → 1 → OFF → ENTER)
2. Turn off hydrogen gas supply at regulator
3. Turn off compressed air gas supply at regulator
4. Close liquid nitrogen supply valves (liquid and vent)
5. Turn off preconcentrator vacuum
6. Shut down preconcentrator control software
7. Shut down GC control software
8. Lock GC keypad (LOCK → ENTER)

Preconcentrator & Gas Chromatograph Daily startup procedure:

1. Unlock GC keypad (LOCK → ENTER)
2. Open hydrogen gas supply at regulator
3. Open compressed air gas supply at regulator
4. Ignite GC-FID (IGNIT → 1 → ON → ENTER) and wait for asterisk to appear beside the number 1 on the keypad display
5. Open liquid nitrogen supply valves (liquid and vent)
6. Turn on preconcentrator vacuum
7. Startup preconcentrator software
8. Bakout preconcentrator by pressing “BAKE” button on control software
9. Startup GC control software
10. Unlock GC keypad (LOCK → ENTER)

Leak Checking the Preconcentrator System Prior to Sample Analysis:

1. Connect sample canister to preconcentrator inlet line, making sure canister needle valve is closed
2. Within SmartLab software, depress “Manual” button
3. Select the appropriate valve position for the inlet line connected to the sample canister (e.g. Valve position 5 for Inlet Line 1, and Valve Position 6 for Inlet Line 2) by pressing the up or down arrows next to the “Valve Position” window

4. Select “Update” and verify that the desired valve position appears in the “Actual” window
5. Select “Pressurize” and wait for the timer window to reach 30 seconds
6. Select “Isolate” and wait for the timer window to reach 50 seconds
7. Select “Vacuum” and wait for the timer window to reach 30 seconds
8. Select “Isolate” and wait for the timer window to reach 50 seconds
9. Repeat steps 5 and 6
10. Repeat step 7. After 30 seconds under vacuum, the system should obtain a pressure of approximately 0.8-1.0 psia.
11. Repeat step 8. After 20 seconds, the system should equilibrate at a pressure of 1.4-1.8 psia. Record the pressure at the 20 second mark. When the timer reaches 50 seconds, the record the pressure. If the two pressure readings differ by more than 0.2 psia:
    a. Repeat steps 9-11 several times; this will often produce the desired pressure differential (air and moisture are purged from the lines with each repetition)
    b. Tighten connection to the sample canister and verify that the canister needle valve is closed. Repeat steps 9-11. If satisfactory results are not obtained, consult the instrument manual or contact the manufacturer support personnel
12. When the leak rate is determined to be less than or equal to 0.2 psia in the isolation period between 20 and 50 seconds, depress the “Exit” button within the Manual window and commence sample preconcentration

APPENDIX B

SYSTEM TROUBLESHOOTING

Symptom	Possible Cause	Solution
Preconcentrator traps are not cooling	1. Insufficient liquid nitrogen supply 2. Liquid nitrogen valves are closed 3. Liquid nitrogen valves are blocked	1. Obtain more liquid nitrogen 2. Verify liquid nitrogen tank valves are completely open (fully counterclockwise) 3. Gently tap valves with solid object to loosen possible ice blockage or gently heat valves with hot air gun
Preconcentrator is not collecting sample at desired rate	1. Vacuum pump is off, broken, or leaking 2. Flow restriction in sampling system	1. Verify vacuum pump operation and vacuum tube connection 2. Check that sampling system tubes are free of obstructions and of sufficient width for free gas flow
Preconcentrator software lists a “heater error” at startup	1. Software malfunction 2. Hardware malfunction	1. Try restarting control software and or preconcentrator 2. Contact manufacturer
GC cannot consistently maintain temperature	GC oven door open	Verify GC oven door is latched
No FID response	1. FID has not been ignited 2. FID feed gas empty	1. Ignite FID 2. Verify sufficient hydrogen and air

Symptom	Possible Cause	Solution
	3. FID feed gas not properly pressurized 4. Integrator box error	supply 3. Verify proper hydrogen and air pressures (FILL IN PROPER PSI HERE) 4. Restart integrator box by unplugging and replugging, then restarting GC control software
Noisy GC Baseline	1. Leaks in system 2. System components dirty 3. Preconcentrator sweep gas supply at insufficient pressure 4. UHP Helium supply is of insufficient purity 5. Helium gas purifier is exhausted	1. Perform preconcentrator leaks checks (both pressure and vacuum) per manual instructions 2. Heat inlet components in oven, cool in vacuum chamber. Perform preconcentrator bakeout cycle. Perform GC bakeout cycle. 3. Verify that sweep gas is at 10-15 psi (control knob on back of preconcentrator) 4. Verify UHP helium is in use, at least 99.999% pure (see parts list) 5. Replace helium gas purifier (see parts list)
Preconcentrator delays at start of cycle	Preconcentrator did not finish "Post injection delay" or was not in "Standby" mode before the next run was initiated	1. Allow preconcentrator to finish "post injection delay" (verify Standby mode on "View" screen) before starting next

Symptom	Possible Cause	Solution
		run 2. Reset "post injection delay" in method to reflect desired delay time 3. Depress "Skip" button during post injection delay and verify that the preconcentrator is in standby mode before starting next run
Large dip in ECD response at start of run followed by poor quality chromatogram	1. Preconcentrator water-management limit exceeded 2. Preconcentrator water-management failed	1. Reduce effective sample humidity by reducing purge temperature or purge volume 2. Verify trap cooling operations
No ECD response or ECD only responds at high temperature	1. ECD emitter foil is fouled	1. Increase ECD supply current in GC software. If current is already at maximum, ECD source may require replacement (contact manufacturer).
Chromatographic peaks appear during blank run immediately after sample run	Carryover from last run; system contaminated	1. Clean components of purge system 2. Bakeout preconcentrator 3. Bakeout GC

APPENDIX C

SYSTEM COMPONENT LIST

Description	Part Number	Vendor	Price (USD)
Helium UHP 99.999% 218cuft size K	98425	OSU Stores Gas Cylinder Warehouse	$69.83
Nitrogen UHP 99.999% 228cuft size K	98287	OSU Stores Gas Cylinder Warehouse	$41.28
Hydrogen, UHP 99.999% 197cuft size K	98272	OSU Stores Gas Cylinder Warehouse	$51.95
Air-Zero grade (FID) 232cuft size K	98768	OSU Stores Gas Cylinder Warehouse	$49.43
Cylinder bracket-bench w/strap	98991	OSU Stores Gas Cylinder Warehouse	$30.12
High Purity CGA-580 Gas Regulator	E11244D580	Fisher Scientific	$204.62
Hydrogen Regulator CGA-350	98912	OSU Stores Gas Cylinder Warehouse	$153.13
Air (FID) Regulator CGA-590	22-162412	Fisher Scientific	$274.74
Air (Standard) Regulator CGA-346	98952	OSU Stores Gas Cylinder Warehouse	$166.40
Stainless Steel Nut, 1/8” OD	SS-202-1	Scioto Valve & Fitting Co.	$1.53
Stainless Steel Ferrule Set, 1/8” OD	SS-200-SET	Scioto Valve & Fitting Co.	$1.68

Description	Part Number	Vendor	Price (USD)
Premium Grade Stainless Steel Tubing tubing length× O.D.× I.D. 50 ft× 1/8 in. (3.18 mm)× 0.085 in. (2.1 mm)	20526U	Supelco (A Sigma-Aldrich Company)	$109.00
Tube Dressing Kit for use with 1/16 in. tubing	58691U	Supelco (A Sigma-Aldrich Company)	$126.00
Helium Gas Purifier (Scrubber)	05-730-1	Fisher Scientific	$175.96
Stainless Reducing Union, 1/8 in. OD - 1/16 in. OD	SS-200-6-1	Scioto Valve & Fitting Co.	$11.00
Premium Grade Stainless Steel Tubing tubing length× O.D.× I.D. 100 ft× 1/16 in. (1.59 mm)× 0.010 in. (0.254 mm)	20552	Supelco (A Sigma-Aldrich Company)	$172.00
Stainless Female Connector, 1/16 in. OD - 1/16 in. Female NPT	SS-100-7-1	Scioto Valve & Fitting Co.	$11.90
Male LUER-Lock to Male Pipe Thread, 1/16 in. Stainless Steel Adapter	316-MLL/MP062-6H3	Microgroup, Inc.	$20.29
Deflected Noncoring Septum Penetration Needles, 18 Gauge, 6 " (12/PACK)	14-825-15AJ	Fisher Scientific	$96.71
8 oz. Tall, 250-mL, clear glass vial with septa, PC CLASS (12/CASE)	0250-0610	Environmental Sampling Supply	$24.24/CASE

Description	Part Number	Vendor	Price (USD)
20-mL clear glass vials with septa, series 200 (72/CASE)	05-719-116	Fisher Scientific	$75.56/CASE
Fisherbrand PTFE Beaker, 600-mL (2/CASE)	02-593-5D	Fisher Scientific	$101.60/CASE
BD PrecisionGlide Disposable Needles, Stubs Gauge: 16	14-826-18A	Fisher Scientific	$18.33/Pack 100
Stainless Union, 1/16 in. OD	SS-100-6	Scioto Valve & Fitting Co.	$11.50
Stainless Union Tee, 1/16 in. OD	SS-100-3	Scioto Valve & Fitting Co.	$28.70
Stainless Low Dead Volume Tee, 1/16 in. OD	SS-1F0-3GC	Scioto Valve & Fitting Co.	$73.20
Stainless Reducing Union, 1/4 in. OD - 1/16 in. OD	SS-400-6-1	Scioto Valve & Fitting Co.	$9.30
Premium Grade Stainless Steel Tubing tubing length× O.D.× I.D. 50 ft× 1/4 in. (6.35 mm)× 0.209 in. (5.3 mm)	20527	Supelco (A Sigma-Aldrich Company)	$175.00
Tubing Bender (Three-Size)	20857	Supelco (A Sigma-Aldrich Company)	$43.10
Tubing Cutter (1/8 in. to 5/8 in. OD)	22410U	Supelco (A Sigma-Aldrich Company)	$23.30
Tubing Reamer	20389	Supelco (A Sigma-Aldrich Company)	$34.90
Teflon Tape 1/2" Wide x 288" in length	20808U	Supelco (A Sigma-Aldrich Company)	$10.70
Open end wrench set	22442	Supelco (A Sigma-Aldrich Company)	$31.80
Adjustable wrench	22439U	Supelco (A Sigma-Aldrich Company)	$24.90