Application of Microwave-Assisted Technologies

for the

Analysis of Chlorinated Solvents in Rock Samples

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

It has been a direction for research of late to examine the extraction process of volatile organic compounds (VOCs) from solid matrices. Removal of VOCs from a solid matrix can be challenging due to the nature of the analyte and that of the containing media. There are established techniques that have been employed in the past; however when dealing with matrices of low permeability, the established methods are not up to task. They fail due to one or more of the following reasons: prohibitive time requirements, which can be as high as eight weeks; cost due to solvent purchasing and disposal, labor, etc.; or negative bias resulting from analyte loss, a regularly experienced issue when measuring compounds of high volatility.

The need for an efficient process, both in time and cost, that can avoid the all too common analyte loss or equally as serious issue of cross contamination is great. The wide spread appearance of these compounds coupled with their harmful effects makes the need to quantify them (and remediate if necessary) a high priority.

The objective of this research project was to use microwave assisted technologies in the analysis of chlorinated solvents present in rock samples. The rock samples used in this research were collected from a sampling site in Guelph, Ontario, Canada. The rock cores were from a dolostone aquifer, and as such possessed low permeability for analyte extraction while containing significant moisture internally in micropores.

Through the use of microwave heating, purge-and-trap concentration, as well as cryotrap focusing, the technique allows obtaining results comparable to the established MAE-GC-μECD method without the additional cost of extraction solvent, as well as without the risk of analyte loss or sample cross-contamination from aliquot removal. Additionally, the method is more

selective, as it allows the operator to monitor relevant ion fragments owing to the use of a mass selective detector. This selectivity is invaluable when performing extractions of environmental samples that often can be contaminated with numerous pollutants.

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Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

Extraction of volatile organic compound (VOC) contamination from solid matrices for the purpose of quantification can be extremely challenging at times. Contrary to the assumption based solely on their classification, VOC contamination is not limited to the atmosphere. While the compounds are volatile, they can often be found in groundwater, as well as rocks and soils, as a result of accidental spills, improper disposal techniques, or leaks from storage facilities (see Chapter 1.2). According to Environment Canada, more than 30% of the Canadian public access their drinking water from groundwater sources (Table 1).

Table 1: Percentage of population reliant on groundwater (municipal, domestic, and rural only) [1]

	YT	NT and NU	BC	AB	SK	MB	ON	QB	NB	NS	NL	PE	CAN
% GW Used	47.9	28.1	28.5	23.1	42.8	30.2	28.5	27.7	66.5	45.8	33.9	100	30.3

The quality of that groundwater can be affected for long periods of time if the surrounding rock or soil becomes contaminated. The rock formations are inhomogeneous, and possess extensive fracture networks. VOCs can migrate through these fracture networks, ultimately diffusing into the matrix itself. Were this to occur, the rock itself then may become a source of long-term low level contamination.

Quantification of these VOCs is extremely important. Exposure to these pollutants can be toxic, carcinogenic, or even mutagenic creating a need to accurately and quickly measure their

presence in the environment in case the levels are such that immediate remediation is required. Having an efficient method of extraction that is accurate with regard to identification as well as quantification is therefore of great interest. Methods that allow for the extraction to proceed quickly, such as pressurized solvent extraction or supercritical fluid extraction, often suffer from the loss of the more volatile compounds. With methods that reduce the risk of volatile loss, the procedures can run from hours to even weeks, such as with the shake flask extraction method. This prevents field use and increases laboratory costs.

The response to this need was the application of microwave assisted extraction. This method allows for the efficient heating of sample and solvent inside of a close extraction vessel. The closed nature of the vessel permits the extractions to take place at elevated temperatures and pressure, without risking the loss of volatiles. Joining this method of extraction with a sensitive detection and separation instrument combination is required to attain accurate and precise values for the ever decreasing maximum concentration levels. With microwave closed vessel extraction, aliquots of the methanolic extract are removed and introduced to the analytical column via cool on-column injection. This method attains low reporting limits (~1 ppb) due to elimination of the solvent exchange step and the use of a μ-ECD as the detector. For the subgroup of VOCs known as chlorinated solvents, the μ-ECD is a particularly adept detector due to the electronophilic nature of chlorine atoms. The ability of chlorine to readily capture electrons makes its detection particularly sensitive with this detector. However, complications arise when the analyte of interest coelutes with other matrix components. In such cases greater selectivity is required in addition to good sensitivity.

The goal of this research was to develop a system for the determination of chlorinated solvents in rock samples characterized by good sensitivity and selectivity required when

processing environmental samples. In order to accomplish this task, microwave assisted extraction was once again utilized; however this time an extraction solvent was not employed. In addition, a cryofocusing module, a modified purge-and-trap system, as well as a GC-MS system operating with splitless injection in selected ion monitoring mode were combined to create a method capable of the required selectivity and still able to accurately detect analyte at the levels of interest.

1.1 Description of Compounds

Over the years, many anthropogenic compounds found their way intentionally or not into the environment, and in doing so created a health risk for those exposed. The behaviour of the compounds once they enter the environment determines the ease with which they can be removed, as well as the type of exposure risk they present. A group of compounds that are particularly difficult in this regard due to their behaviour in the environment are DNAPL compounds. DNAPL is an acronym for dense non-aqueous phase liquid. These compounds are characterized by density greater than water (1.01 g/mL), with a solubility in water of less than 2% (or 20000 mg/L), and a vapour pressure of less than 300 torr.[2]

Among the DNAPL group of compounds chlorinated solvents are a class of chemicals that many deem to be of the utmost importance. Chlorinated solvents are deserving of attention due to their high densities relative to water, with viscosities being similar. Introducing compounds with these properties into the environment, either individually or in mixes, creates a problem as they are difficult to remediate, to track movement of, can persist in the environment for long periods of time, and pose significant risks to nearby populations. They are a common contaminant of groundwater and have been found at many sites. In a study of 1070 wells in New

Jersey, USA, chlorinated solvents trichloroethylene, carbon tetrachloride, and perchloroethylene were found in 58%, 65%, and 43% of them, respectively.[3]

Many chlorinated solvents also have the designation of being volatile organic compounds. A volatile organic compound is one of a large group of substances that typically have low molecular weight, small specific gravity, low water solubility, and low boiling point. While these compounds readily volatilize, when spilt in significant quantities they permeate the soil and pass through the water table without dissolving significantly. The results are "puddles" of liquids or liquid mixtures that form under the water table, creating sources of long-term contamination of groundwater.

1.2 Sources

In the past, use of chlorinated organic solvents was widespread and had already begun early in the last century. Production of carbon tetrachloride began in the United States as early as 1906. It was used as a solvent in oils, fats, lacquers, varnishes, waxes and resins, as well as in dry cleaning and seed fumigation. From this point on the use of chlorinated solvents grew quickly. In the United States, trichloroethylene (TCE) and perchloroethylene (PCE) became the most widely used solvents in the country. Applications of these solvents included adhesives, dry cleaning, metal cleaning and degreasing, as well as paint removal.[4,5]

As widespread as the applications are now the locations of sites where they persist as contamination in the environment whether in soil, groundwater or sediment. In the United States, a test of 1428 landfill sites from the Environmental Protection Agency's National Priority List

found trichloroethylene at 861.[4] The following are probable source types for the contamination of groundwater by chlorinated solvents:[2]

- Leaking storage tanks (above or underground)
- Leaking drum storage areas
- Leaking buried chemical distribution pipelines
- Spillage at chemical loading and off-loading facilities
- Spillage during highway accidents and train derailments
- Assorted intentional spillage scenarios

1.3 Detection and Movement

The detection of DNAPL compounds has become important over the years but has remained a complicated process. It is often difficult to determine the presence of contamination based solely on visual evidence.[2] In addition, even when DNAPL compounds do exist on site, because of their position in the subsurface their detection is not a guarantee. Some of the chlorinated solvents, such as TCE and PCE, fluoresce on exposure to ultraviolet-visible light.[2] Detection based on fluorescence is done with the sample being placed first in a plastic bag to minimize the loss of volatiles.

The following properties of chlorinated solvents provide them with increased underground mobility:[2]

- Low liquid viscosity
- Low interfacial tension with water

- Relatively high volatilities, which allow compounds to travel in the gas phase into unsaturated zones
- Low solubility in water
- Low ability to partition into soil, which prevents a retarded progress due to materials in the aquifer
- Low degradation rate in this environment

These properties result in the frequency of detection of this group of VOCs at spill sites second only in occurrence to trihalomethanes.[6] They also make modeling of their transport difficult, making estimation or prediction of contamination levels away from the spill site difficult. The degree of movement for DNAPL plumes is surprisingly large relative to the volume of the spill. In the past, plume length have been calculated to be several kilometers long with spills of between 0.5 to 70 drums of liquid solvent.[7] When plumes travel to a point where they reach surface water (rivers, lakes) the level of risk associated with contamination drops, due partially to volatilization and dilution.

1.4 Compound Health Risks and Environmental Effects

Since the 1970s the pervasiveness of chlorinated solvents in the environment, especially in groundwater, has become a recognized issue.[2] Aqueous solubility of these compounds, while low, is sufficient to pose health risks due to the fact that the maximum concentration limits (MCLs) are so low.

1.4.1 Trichloroethylene (TCE)

The compound has been widely used since after the Second World War. It is a volatile clear liquid. Main past uses have been as a solvent and degreaser, but there were many other uses as well.[8] When exposure occurs it is mainly through inhalation or the skin, often with a noticeable slightly sweet smell.[9] Trichloroethylene attacks the central nervous system upon exposure and can lead to drowsiness, headaches, and vertigo.[10] As a volatile organic compound with a relatively high vapour pressure, the majority escapes to the atmosphere where it possesses a relatively short half-life (7 hours). Long-term contamination from the compound results from the portion that enters the subsurface. In this location TCE slowly biodegrades as a result of reductive dechlorination, with the half-life in aquifer studies ranging from 35 days to 6 years.[11]

1.4.2 Tetrachloroethylene (PCE)

PCE is a non-flammable compound with high thermal stability, which led to its use as a heat transfer liquid in transformers. It is also colourless in its natural form, making detection by visual inspection difficult. The compound has seen the widest use in the dry-cleaning sector, as well as being used as a degreaser and a chemical intermediate in the production of fluorocarbons. The most common exposure route is via inhalation where it affects the central nervous system in ways similar to TCE but more intensely. In high enough concentrations it can lead to unconsciousness, and in animal tests it has been proven to cause cancer as well as affect their reproduction. This information has resulted in it being labeled as a probable carcinogen. With such widespread applications the contaminant has a wealth of anthropogenic sources but no natural sources. In the case of spills, the high vapour pressure leads to significant losses to the vapour phase where the half-life in the atmosphere is 96 days. The portion that makes its way

below the surface has moderate mobility. It is often detected in groundwater and slowly biodegrades in both anaerobic and aerobic environments.[11]

1.4.3 cis-1, 2-Dichloroethene (c-DCE)

This chlorinated solvent is a colourless flammable liquid that possesses a harsh odour at high enough concentrations (0.08 ppm).[12] It has many uses in industry, from a wax and resin solvent to the use in the manufacturing of pharmaceuticals and extraction of oils and fats from fish and meat. According to the US EPA Phase II Rule (1992), the recommended maximum contaminant level in drinking water is 70 ppb.[12] Long term exposure at these levels will likely result in liver damage. There are no natural sources for this compound. Anthropogenic sources of release include industrial chemical factories, disposal sites and breakdown product from other chlorinated solvents. When released into the environment the compound will both evaporate into the atmosphere where it will degrade slowly, or leech into the groundwater system. Once in the subsurface, the solvent biodegrades at a very slow rate.[11]

1.4.4 trans-1, 2-Dichloroethene (t-DCE)

This chlorinated solvent has similar properties and applications to its cis-isomer. The trans- isomer has a maximum contamination level that is higher than the cis-isomer of 100 ppb in groundwater. Sources of t-DCE in the environment could be from the environmental breakdown of chlorinated products like TCE and PCE. It is also released into the environment with the burning of vinyl. Research up until this point seems to suggest that it does not accumulate in tissue; however, at high concentrations (3000 µg/mL) it has been shown to have acute effects in rats that include liver damage and reduced blood cell count.[13] It also degrades slowly in the atmosphere which suggests that it possesses considerable dispersal distance. Trans-DCE is considered a priority pollutant while the cis- isomer is not; however the current EPA method

does not allow for differentiation between the isomers leading to false detects of the trans-isomer.[13]

1.5 Purge and Trap

The use of a purge-and-trap instrument can benefit a user interested in concentrating a volatile compound or a selection of volatiles from a range of different matrices. The instrumentation differs depending on the sample matrix, but one constant is the use of purge gas. The purge gas selected is a high purity and highly inert gas (He and N_2 are common selections). The purge gas is passed through the matrix, with the analyte contained partitioning into the gas phase. The inert gas passes through a solid sorbent, where the analyte is concentrated while the carrier gas passes out to vent. Conventionally, the analyte is then desorbed from the trap onto the analytical capillary, once flow has been split at the injector port.

1.5.1 Applications

As maximum allowable concentration limits are decreased in response to the results from new studies and legislation, the requirement for instrumentation providing low detection limits is ever more important. Occasionally traditional instrumentation fails to provide sufficiently low limits, especially in the case of environmental samples where analyte levels can often fall into the sub-part per billion range. Traditional isolation and preconcentration methods, such as solvent extraction and concentration, are carried out before analysis in these cases. However, when the analyte possesses significant volatility, the traditional methods may result in significant analyte losses during the solvent concentration step. In such situations the application of a purge-

and-trap instrument will allow for the concentration of analyte without the same risk of loss as with traditional methods.

Purge-and-trap devices are currently being used on a variety of matrices in order to concentrate moderate and highly volatile compounds. The first application of the instrument was in the 1960s in the analysis of body fluids.[14] It was in the 1970s that the application expanded to include volatile halogenated compounds in drinking water in the part-par-quintillion range.[15] Current application is for concentration of volatile organic compounds in a range of sample types including environmental as well as liquid and solid foodstuffs.[16] The USEPA still recommends its use for extractions from contaminated soils, but this was proved inadequate in past studies.[17]

1.5.2 Operation

The purge-and-trap instrument concentration cycle has 3 main phases:

- Purge phase
- Desorb phase
- Bake phase

The purge mode is the first mode to commence (Figure 1). The sample to undergo extraction is placed in the purge vessel. Vessel type may differ depending on the state of the matrix and the volatility of the analyte. In the majority of cases the extraction vessel is made out of glassware with or without an attached heater. The purge gas is high purity helium or nitrogen. The gas enters the vessel through a needle sparger if it is a solid matrix and a frit sparger if a liquid. As the gas passes through the vessel, the analytes partition into the gas

phase and are carried out. With the selection of a proper trap, the analytes will be carried along and deposited on the trap sorbent while the purge gas passes out to vent.

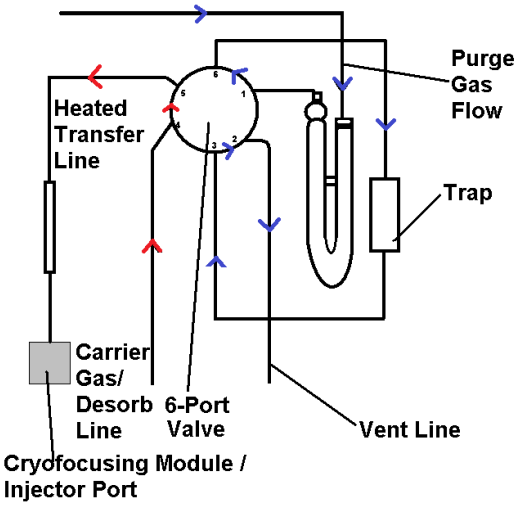

Figure 1: Gas flows during the purge phase

The volume of gas used during this mode is referred to as the purge volume. The amount of analyte collected varies relative to the purge volume. There is a decrease in efficiency with purge flow rates set too high or too low. It is widely held that the purge flow rate is optimally set at 40 mL/min.[18] Efficiency of the extraction is dependent on analyte vapour pressure and its solubility in the matrix. Passing extraction gas through the purge vessel at a sufficient rate replaces the gas with which the analyte has equilibrated with "clean" gas, thus increasing the efficiency of extraction.

During the purge phase of operation a sufficient amount of water may amass on the trap as to interfere with subsequent separation and detection. The most straightforward solution to remove moisture that has accumulated on the trap is a dry purge step. During the dry purge step, inert gas is passed through the trap in the same direction as during the previous purge

mode. This gas bypasses the extraction vessel, so as not to accumulate any further moisture. Passing through the trap the gas carries the moisture out to vent. Operators who choose this method of drying the sorbent in the trap should be aware that the volume of gas used counts towards the maximum breakthrough volume. As such, this method would not be recommended when concentrating analytes of higher volatility that in turn would possess low breakthrough volumes. A second option for drying is the inclusion of a moisture control module. The module uses a fan and a heat sink to dry the gas through the condensation of hot water vapour as the contents of the trap pass from the solid sorbent to the heated transfer line that delivers them to the cryofocusing module. The condensed water is then removed from the moisture control module as it is then resistively heated to expel the water inside. This instrument attachment has several shortcomings. The trap must be cooled to a low temperature in order to condense the water effectively (default value is 0^0C).[19] This temperature takes a considerable time to reach, which can lead to unwanted analyte drift on the trap, negatively affecting future chromatography. An additional issue faced when using the moisture control module occurs when concentrating less volatile compounds. These compounds of higher boiling points may condense at the temperatures at which the water is being removed. In addition to loss of sensitivity if these compounds are not removed when the module is later heated to expel the condensed water, it may create a source of contamination for future runs. The final option for moisture removal is the inclusion of a Nafion® dryer (Figure 2).

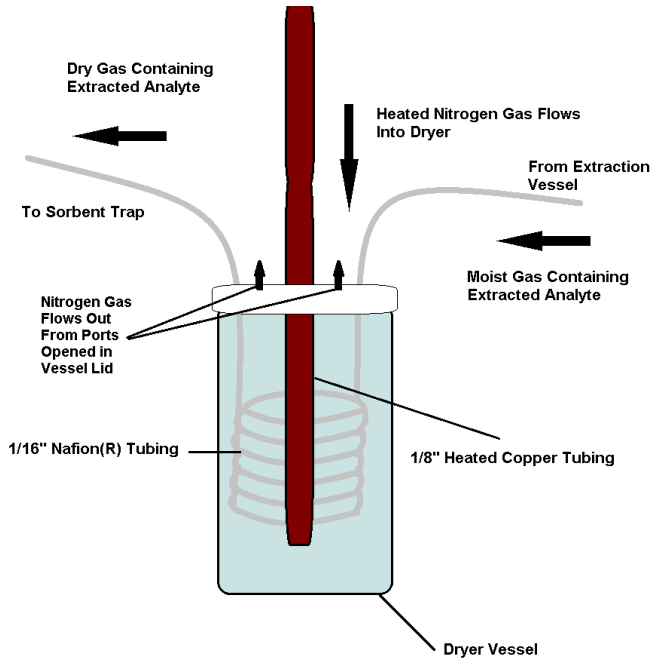

Figure 2: Self-assembled Nafion(R) dryer with heated nitrogen line

A Nafion® dryer provides an effective means of removing sample moisture before it reaches the trap. Placed in series between the sample vessel and the six port valve, the dryer in principle consists of a segment of Nafion® tubing (length selected based on sample moisture content). Nafion® is a copolymer of perfluoro-3, 6-dioxa-4-methyl-7octene-sulfonic acid and Teflon®. The sulfonic acid groups in this copolymer act to remove water from vapour or liquid phases that are passed through the tubing. The sulfonic acid groups form ionic channels through the bulk hydrophobic polymer through which water is freely passed.[20] To increase effectiveness at which this occurs, heated nitrogen gas can be passed over the surface of the tubing. The heated tubing also allows for the ready removal of methanol while remaining impermeable to compounds such as halogenated organic analytes. Due to its Teflon® backbone, the co-polymer is capable of functioning at elevated

temperatures – as high as 190^0C. Similarly to the moisture control module, this drying option may become a source of memory effects in later runs if the temperature of the vessel is not sufficiently elevated as to prevent condensation.

If the sample is known to be sufficiently dry, the second step is analyte desorption (Figure 3). During this phase of the extraction cycle the trap upon which the analyte has been deposited is heated quickly and the flow of gas passing through it is reversed. The reversal of gas flow is a requirement in order to obtain narrow injection bands. The time and temperature of the desorption step both affect the chromatography to occur later. While the effects of both are lessened through the use of a cryofocusing module, it is still important for proper chromatography to have the desorption step occur at as high a temperature and as short a period of time as possible. Temperature is limited by two factors: the upper limit of the trap, as well as the thermal stability of the analyte. Time must be kept as short as possible while still allowing for quantitative transfer from the trap. Average desorption time for a VOCARB^{TM} 3000 trap can be as low as 4 minutes (at 1 mL/min flow rate), although most of the sample is transferred in the first minute.

Increasing desorption efficiency is another way to reduce injection volume and thus the sensitivity. To this end a pre-heating step is often employed. During this step the trap is heated to nearly the desorption temperature, while no gas passes through it. This leads to partial desorption of the sample from the trap without analyte migration. When the temperature is then increased and gas flow begins, the analyte leaves the trap in a more concentrated gas cloud.

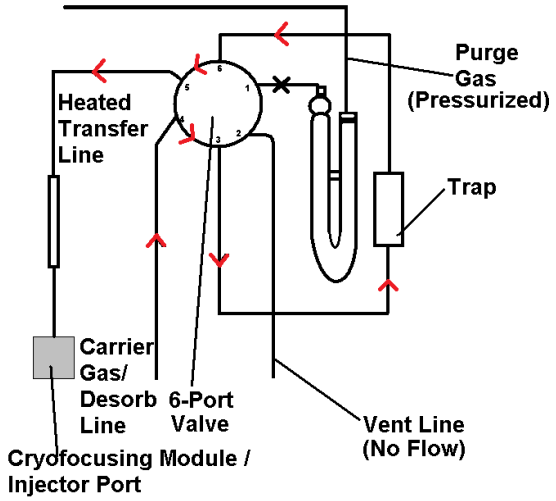

Figure 3: Gas flows during analyte desorption

The final step involved in the extraction process is the trap bake out. This step conditions the trap sorbent in preparation for the next analysis. During the extraction, compounds of lower volatility, as well as possibly water, may become deposited on the trap. Removal of these compounds with the bake out step prevents interaction with analytes in future samples. In this step, the temperature of the trap is raised to 10-20 $^{\circ}C$ above that the desorption temperature. As gas passes through the trap, unwanted compounds are directed out to vent. Completing this procedure with clean dry gas is important, and therefore with certain matrix types it is recommended to direct the gas flow around the purge vessel rather than through it as is the default. For instance if the sample to be concentrated is liquid, it is possible to automatically drain the extraction vessel before passing the bake gas through it; however, if the sample matrix is a solid with high moisture content, a bake gas bypass would be recommended.

1.6 Purge and Trap Instrumentation

1.6.1 Traps

The trap and the proper selection of trap type are arguably the most important factors in successfully operating a purge-and-trap instrument. Trap material determines the effectiveness with which the analyte is concentrated following removal from the sample matrix. A trap can be as specific as a one agent to retard the passage of a single compound class or a combination of trapping agents to capture several compound classes. Proper trap selection requires fulfilling four main conditions:

1) The trap must retain compounds of interest while disregarding other gases present (O_2, H_2O, He, N2).
2) When heating during desorption mode, the trap releases compounds quickly.
3) Repeated heating/cooling does not result in generation of volatile compounds.
4) Under high temperatures the trap must not catalyze reactions with trapped analytes.

Trap temperatures and trap materials are the two main factors in determining retention volumes. Temperature of the trap is set to the lowest practical value prior to the beginning of the purge cycle (25-35^{O}C). Retention volumes vary inversely with temperature, which allows for long purge cycles (and large purge volumes) at low temperatures, and quick, efficient desorptions at high temperature. Trap materials are chosen for their high affinity for the analytes and possibly low affinity to interferences. Retention ability cannot be too high, as this would prevent efficient desorption. In cases where two or more trap agents are used in the same trap, the stronger sorbent is placed last, so as not to come into contact with the less volatile analytes. Analytes of low volatility interacting with strong sorbents may result in their inefficient

desorption from the trap, which results in poor chromatography or even non-quantitative transfer to the injector port.

When dealing with samples containing significant moisture levels it is possible for H_2O to be introduced from the trap to the GC column. The result of this is interference, especially with early eluting compounds. There are two traps in particular that have low affinity for water: the Tenax® TA trap, and the VOCARB^{TM} 3000 trap. Tenax® TA is a polymer of 2, 6-diphenyl-p-phenylene oxide and is particularly good at trapping non-polar compounds, while generating little bleed during desorption. The hydrophobic nature makes it a natural choice when working with wet matrices. However, it is limited to lower desorption temperatures, which range from 180 to 250 °C.[21] In cases where higher desorption temperatures are required due to lower volatility of analyte, the VOCARB^{TM} 3000 trap is a better choice. Made of three graphitized carbon adsorbents (10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001), the trap can efficiently desorb at temperatures as high as 270^{O}C if installed with a graphite ferrule.[22]

1.6.2 Cryofocusing Module

The cryofocusing module, also known as a cryotrap, can be installed in series between the transfer line and the GC injection port. Installation of a cryotrap allows for the injection of entire samples following desorption from the purge-and-trap sorbents. Without the module, the injection volume and band width would be too large for the capillary column without splitting a portion of the carrier gas. Installation of the cryotrap helps eliminate the need for split injection, avoiding what is in effect a loss of analytes, and consequently lowering detection limit.

While different purge-and-trap cryofocusing modules exist, the basic design of an external cryotrap remains the same. In this design (Figure 4), liquid nitrogen is used to cool down a segment of the column.

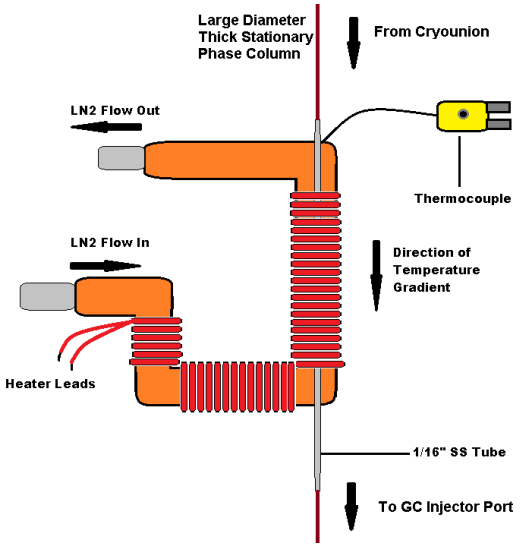

Figure 4: Cryofocusing trap

The segment of column to be cooled is passed through a 1/16” stainless steel tube. The tube is welded to a cold finger and a thermocouple. Also present in this design are heating coils. Heating coils are responsible for heating the column segment faster on the inlet side (side closest to the heated purge-and-trap transfer line at the top of the trap) than the exit (GC injector port side). The purpose for differently heating the column is to create a temperature gradient. Due to the creation of the gradient, the different compounds are forced into a narrow band in the column. If the column segment chosen is one of a larger film thickness and internal diameter, it allows the operator to choose higher focusing temperatures without reducing the focusing effectiveness (while reducing liquid nitrogen use/cost). It is of value to note that some extracted samples may introduce water to the trap. This moisture will form ice blockages at the

temperatures the cryofocusing module operates at. To prevent the formation of ice, it is recommended to include a dry purge step (which increases the possibility of analyte trap breakthrough) or use a drying apparatus (a moisture control module or a Nafion® dryer).

1.7 Microwave Assisted Extraction

The use of microwaves as a tool for sample heating began as an unplanned offshoot from radar development during the Second World War. The use of microwave radiation in both commercial and industrial applications was recognized and today has applications that range from the removal of organic sulphur in coal to the drying of pasta products.[23] The first extraction application was made in 1986. Ganzler et al. used microwave radiation to aid in the extraction of crude fat and anti-nutrients from food, as well as pesticides from soil.[24] Its main advantage over traditional conductive heating (hotplates, flame, etc.) is in the efficiency. Heating through microwave radiation allows for direct absorption of energy. In addition to the benefits of direct heating, microwave extraction processes may be automated to increase sample throughput, and require smaller amounts of organic solvents versus other established methods. However, the method is not completely without shortcomings. When using microwave radiation as a heat source in an analytical chemistry lab, it is possible to face issues such as smaller samples being insufficiently heated after being placed in cool spots inside the microwave cavity, and volatile sample loss due to inappropriate heating container selection.

1.7.1 Microwave Heating Theory

The microwaves that heat compounds in both industrial and commercial microwave ovens are electromagnetic radiation that is generated by a magnetron. The radiation is non-

ionizing. When microwave radiation is incident upon a sample, it may cause molecular heating by means of migration of ions and rotation of molecular dipoles. The frequency range for radiation in the microwave region of the spectrum is between 300 and 300000 MHz. In the United States, the Federal Communications Commission has set aside four frequencies in that range for use in industrial, scientific, and medical purposes: 915, 2450, 5800 and 22125 MHz. The most common of the four in use today is the 2450 MHz frequency, used in the majority of ovens.

The energy outputs of microwave ovens differ depending on their use; however, most are in the range of 600-700 W, resulting in ~43 kcal of energy supplied to the cavity in a five minute period.[25] While the amount of energy supplied to the cavity is consistent, the heating of samples differs, being partially dependent on the dissipation factor (also known as loss tangent) of the compound (tan δ).

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad \textbf{Equation 1}$$

Where, ε'' is the dielectric loss constant, and ε' is the dielectric constant. The dielectric loss constant is a value that describes how well the energy absorbed is dissipated as heat. The dielectric constant describes how well a sample hinders the passage of microwave energy. An example of a microwave transparent material is Teflon; an example of a microwave reflective material is sheet metal.

Table 2: Dissipation factors and physical constants from references 26 and 27

Compound	Dielectric Constant	Dipole Moment (D)	Dissipation Factor (tan δ x 10^4)	Boiling Point ($^{\circ}C$)	Closed-Vessel Temperature
Methanol	23.9	2.87	6400	65	151
Water	76.7	1.86	1570	100	-
Ethanol	24.3	1.96	2500	78	164
PCE	2.5	~0	-	-	-
TCE	3.4	0.8	-	-	-

Looking at the above table (Table 2), it is of interest to compare two solvents: methanol and water. Water has a dielectric constant over twice that of methanol. The result of this is that water is capable of absorbing microwave radiation much better than methanol can. However, looking at the values for tan δ, it is clear that methanol is the solvent more capable of dissipating that energy as heat.

As stated before, microwave energy is typically absorbed through two mechanisms: ionic conduction and dipole rotation. The applied electromagnetic field results in a migration of ions in the sample; this in turn leads to heating due to resistance to that migration. The flow of the migrating ions is determined by their concentration as well as their mobility in the sample (mobility is determined by conductivity, size and charge). Tan δ will increase when there is an increase in ion concentration and mobility. Effectively this means that with an increase in temperature, there will be an increase in the dissipation factor for samples containing ions (ion mobility increases with temperature).

The second mechanism is dipole rotation. The dipole of a molecule can either be permanent or induced. In either case the dipole will rotate to align with the electric field it is exposed to. When the field strength increases, it imposes more organization on the molecules, and when the field intensity decreases, the molecules return to their normal order. The rate at which the natural order returns is dependent on the dielectric relaxation time of the sample, which in turn is reliant on the temperature and viscosity of the sample.

The selection of microwave frequency also has an effect on the way the sample being heated is warmed. The maximum value of dielectric loss (as a result of dipole rotation) occurs when the value of angular frequency of the microwave energy is equal to the inverse of the dielectric relaxation time: $\omega = 1/\tau$. Since angular frequency (ω) is equal to 2πf, this means that the input frequency that results in the maximum dissipation factor is:

$$\boldsymbol{f = \frac{1}{\tau \times 2\pi}} \qquad \textbf{Equation 2}$$

The practical application of this theory is to be able to heat a sample selectively. For smaller samples requiring low penetration and high rate of heating, the frequency of the microwave radiation should be increased. For larger samples requiring higher penetration, the rate of heating could be sacrificed by reducing the input frequency. This increases the difference between angular frequency and 1/τ, reducing absorbance of energy.

The viscosity of the sample has an influence on how effectively it is heated. When a sample is viscous, the ability for the molecules to rotate to align with the field is retarded. This results in a decrease in the dielectric dissipation factor. An example of this is in the case of water (Table 3):

Table 3: Dissipation factor compared to temperature for H_2O at 3000 MHz[28]

Temperature (°C)	Dielectric Dissipation Factor
1.5	$3100x10^{-4}$
25	$1570x10^{-4}$
95	$470x10^{-4}$

This trend does not progress indefinitely with rising temperature. As water becomes less viscous at higher temperatures, the effect of rotation becomes less important and the effect of dielectric relaxation time becomes more important in determining the dissipation factor.

Microwave heating is an example of direct rather than indirect heating, as is the case with conventional methods. However, that is not to say that no indirect heating occurs. An example of this would be a sample larger than the depth of penetration of the incident microwave energy. Molecules closer to the surface of the vessel would become heated and distribute their absorbed energy through thermal conduction. If complete heating of the sample via microwave radiation is the goal, the sample size must be monitored. Too large a sample would result in incomplete direct heating; too small would result in too much energy reflecting back to the magnetron, potentially damaging it.

1.7.2 Instrumentation

There are two general types of MAE instrumentation that are currently in use today. The selection of instrument type depends on the nature of sample being heated. The first is known as an atmospheric, focused, or "open" system (Figure 5). In this system the sample is placed inside a heating vessel that resembles a test tube that often contains an extraction solvent. The solvent

selection is made based on affinity towards the analyte, degree of interaction with microwave radiation, as well as the boiling point. Temperature measurement can be carried out using an IR sensor. The top of the extraction vessel has an air/water condenser attached to minimize loss of volatiles. This instrument is not applicable in situations that require high temperature/high pressure extractions. Typical operating conditions of such an instrument are: [29]

Temperature: Boiling point of the extraction solvent

Extraction time: 5-20 minutes

Power settings: 300 W

This instrument is often used in digestions with high boiling point acids, such as sulphuric acid. Occasionally additional reagents are added, such as hydrogen peroxide, increasing the oxidative potential, as well as acting as a way to convert more of the microwave energy into heat due to its relatively high dielectric constant value.

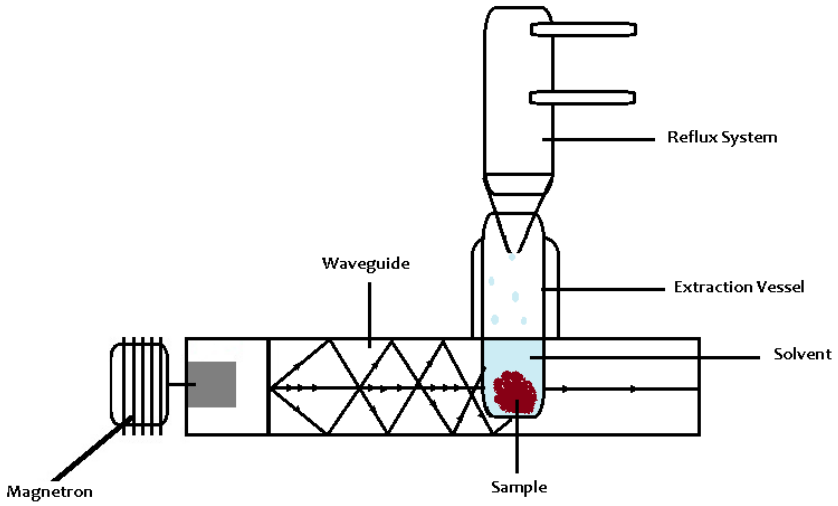

Figure 5: Open vessel microwave extraction

The second type of instrumentation is the pressurized or "closed vessel" device.[29] A sample heated using this method is exposed to increased temperature and pressure compared to

the open vessel method. In addition, this instrument permits multiple samples to be processed at the same time, each sealed in a heating vessel made of microwave-transparent material. Sample vessels are placed in a carousel. They are rotated 180 degrees in one direction, then 180 degrees in the reverse direction. Movement of the samples inside the instrument cavity prevents incomplete extractions due to cold spot position, in effect averaging the incident microwave radiation.

Extractions often require the addition of a solvent to aid in the partitioning of the analyte from the sample. Incident microwave radiation may cause this solvent to expand inside the vessel. If the pressure inside increases higher than the limits of the heating vessel, potentially flammable and toxic organic solvent may be released from the vessel. It is for this reason that industrial ovens are typically built with solvent alarms to alert the operator while shutting off the magnetron.[30] With the magnetron shut off, the exhaust fan continues to run to evacuate the cavity of the released solvent. It is relevant to note that this continuously running exhaust fan results in vessel heat lost, that would otherwise remain inside the cavity. It is for that reason that pressure inside the closed reaction vessel is lower than would be predicted at certain set temperatures.[31]

To prevent the release of solvent from occurring, most closed vessel ovens are built with probes to measure both the temperature and pressure. A commonly employed pressure sensor is a H_2O manometer; it is capable of measuring pressure inside a vessel up to 200 psi. The temperature is monitored using a temperature probe. A typical probe employed for this purpose is a fibre optic phosphor sensor that has a range of 20 to 200 °C.[32]

The extraction vessel is formed of two materials suited to extractions at high temperature and pressure: an outside layer of polyetherimide, with an inner layer of Teflon perfluoroalkoxy

(Teflon PFA) .The Teflon lining provides low chemical reactivity between analyte and lining while maintaining transparency to microwave radiation. In one design a rupture membrane is located at the top of the vessel, it is designed to fail if the pressure inside increases past 200 psi. When an extraction is completed using the MAE pressurized method, a cooling period of 20-30 minutes is recommended post-extraction before opening the extraction vessel. Not waiting for the sample to cool can result in likely loss of volatiles as well as potential injury to the operator.

The major components of both domestic and industrial microwave heating instruments are similar:[33]

1) Magnetron: It is responsible for the generation of microwave radiation. It is a cylindrical diode with both an anode and a cathode. Superimposed on the diode is a magnetic field that is aligned with the cathode. In the anode there is a ring of communally coupled resonant cavities. When a high voltage is applied across the diode, electrons are generated. A magnetic field radiates from the antenna enclosed in the vacuum envelope of the tube, which causes the generated electrons to oscillate.
2) Waveguide: Made out of microwave reflective materials like sheet metal. The wave guide directs microwaves from the magnetron to the cavity.
3) Cavity: Void volume created from a microwave reflective material. The sample to be heated is placed inside the cavity. Microwaves reflect off the surfaces until they are absorbed by the sample. The cavity is usually coated with chemically resistive, but microwave-transparent material.
4) Mode stirrer: Incident microwaves exiting the waveguide are distributed by a mode stirrer. The stirrer consists of several blades made of microwave reflective material. It rotates in order to direct microwaves in multiple directions inside the cavity. The addition

of a mode stirrer serves to homogenize the microwave radiation inside the cavity, which reduces the effect of sample placement on heating.

5) Terminal circulator: When microwave radiation is reflected back into the magnetron, it is possible to damage the microwave generator. The circulator uses ferrites and static microwave fields to divert reflected waves to a dummy load.
6) Dummy load: An addition included in the microwave oven to prevent damage to the magnetron. Reflected microwaves directed to the load will cause it to become hot, but the waves will not damage the magnetron.

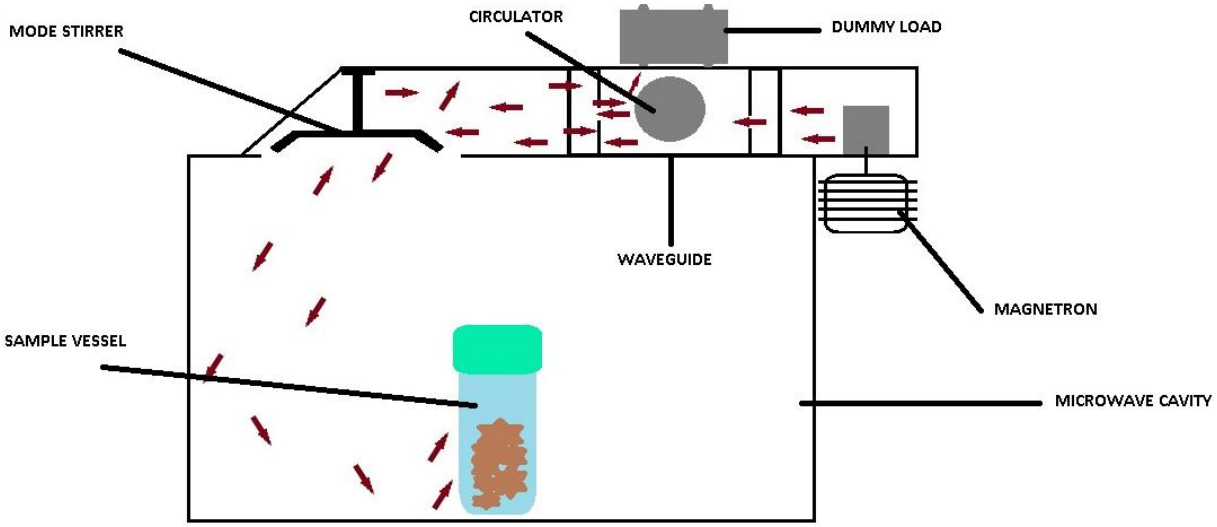

Figure 6: Closed vessel microwave instrument

1.7.3 Past Applications of Microwave Heating

The range of applications for microwave heating is diverse. Previously completed work suggests that the effect of microwave radiation on compounds, in regards to their molecular stability is low. Work completed on phenols suggested that compounds with fewer substituents on the aromatic ring did have higher stability than compounds with more substituents.[29]

When comparing microwave assisted extraction (MAE) versus other extraction methods, MAE performed comparably or better than the other methods. Extractions completed by Soxhlet, sonication, MAE, and SFE of 94 compounds from the USEPA method 8250 in freshly spiked soil were compared in a 1996 publication.[34] The results are summarized in Table 4:

Table 4: Comparison of percent recoveries via different extraction methods

Percent Recovery	>80%	50-79%	20-49%	<19%
MAE	51	33	8	2
Soxhlet	50	32	8	4
Sonication	63	25	4	2
SFE	37	37	12	8

Additionally, comparison for precision of the results determined that MAE provided the best level of precision with RSDs ≤ 10% for 90 of the 94 compounds. The traditional Soxhlet method provided the worst precision with RSDs ≤ 10% for 52 of the 94 compounds.

Extractions of volatile and semi volatile compounds do not only have to occur in a pressurized microwave extraction vessel. In a 2004 publication, researchers removed essential oils generally present at low concentrations from three spices.[35] The spice plant material was heated in the microwave in a solventless extraction. The water within the plant material was heated by the microwave radiation making the glands and oleiferous receptacles burst. The essential oils were then carried with the water vapour up a reflux condenser where the distillate was collected and the water refluxed back down into the extraction vessel. The extraction results were comparable to the accepted method of hydrodistillation, and surpassed it in regards to

rapidity, efficiency, as well as not requiring a solvent. This work puts forth that extractions on samples with water already present may be possible and even produce comparable results with less requirements of time and money. Additionally, work was completed where the use of microwave heating was applied for headspace analysis of VOCs. When compared to the conventional 30-minute static headspace sampling apparatus, it resulted in higher detector responses with better precision and less time.[36]

Microwave heating is not limited to extraction in an analytical laboratory. Since its inception it has been adopted for use in many fields. In soil remediation, microwaves are especially effectual at removal of volatile and semi-volatile contaminants.[37] In waste treatment, microwave heating is used to recover valuable metals from used circuit boards, while reducing the overall waste volume.[38] Even in the mining sector, microwave radiation is used to selectively heat ore reducing the cost of grinding it to recover the metal inside.[39]

1.8 Established Methods for VOC Extraction from Low Permeability Media

1.8.1 Combined Sonication and Agitation Extraction on Clayey Soils[40]

The benefit of agitation on the equilibrium time during extractions with solvents had already been noted for some time before the development of this method. The conventional method of using solid liquid extraction required a significant time commitment (5 days) for clay sample processing that prevented its deployment in the field.[41] The goal was to use the addition of sonication to reduce that processing time, while still allowing for some level of mobility. When this method was being developed, the researcher considered the factors that are important

when discussing the extraction of organic solvents from environmental samples such as soils: mineralogical composition, particle size, sample density, and porosity.

The process was established using clay samples collected from a site of long term TCE contamination. Portions of the matrix were removed from the sampling sites below the surface. The adsorption capacity of the sample was noted to be influenced by moisture content, thus it was relevantly noted that they were taken from below the water table and thus were water-saturated. Moisture content reappears as an extremely relevant factor in future extraction research.

The novel supplement was to augment the traditional solvent extraction process with the addition of sonication. This increased the rate of extraction into the methanol solvent as it assisted in the breakdown of the solid aggregates, increasing the surface area of the matrix. With an increase in the surface area solvent penetration into the matrix was improved. Combination with the orbital shaker prevented the clay particles from settling into a layer that would impede mass transfer to the solvent. The device design (Figure 7) proved capable of comparable results to the traditional solvent extraction method, in far less time (2 hours). The extracted analyte was transferred into hexane via a solvent exchange procedure before 1µL liquid injections were analyzed on a HP6890 GC equipped with a µ-ECD detector. The use of the device to a matrix type such as rock would be far less efficient, as the ability of the sonicator to further reduce crushed rock matrix into smaller particles would be negligible.

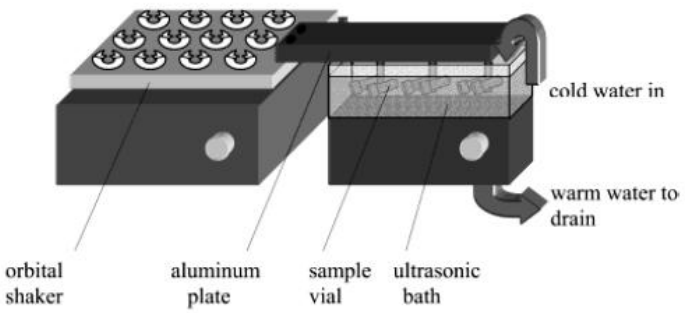

Figure 7: Schematic diagram of the sonication/agitation device (from reference 40)

1.8.2 Microwave Assisted Extraction of Clay[42]

Extractions can be completed from sample matrices faster when there is greater contact between the solvent and the analyte. If the extraction is carried out inside a closed vessel, increased pressure within the vessel allows more efficient penetration of the extraction solvent into the matrix. In addition, when the analytes in question are volatile, the addition of heat during the extraction process can often lead to significant losses. Completing the extractions in a closed vessel can prevent these losses while benefitting from the increase in diffusivity of the analyte and the solvent, as well as the rate and extent of desorption. The vessel in this study required the construction of a custom PFTE container that could withstand the increased internal pressure resulting from the heating of the extraction solvent and sample. The container was designed with a lid thinner than the walls. This was done to allow for the release of pressure if it were ever to build up to dangerous levels inside the extraction vessel (Figure 8).

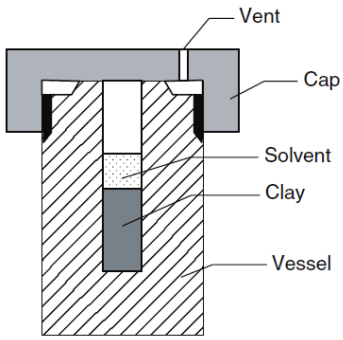

Figure 8: PTFE vessel constructed for MAE of clay samples (from reference 42)

The added benefit of increased temperature and pressure allowed for an improvement in extraction efficiency over the sonication and agitation design. It has been suggested that microwave heating of the clay, oxides, and water in the matrix could lead to the formation of gas bubbles, with subsequent local pressure build-ups. This should result in destruction of the macrostructure of the matrix, thereby increasing the surface available for the extraction solvent.[43] As well, by careful selection of the extraction solvent, a mixture of solvents was found to reduce the extraction time to a maximum of 10 minutes, while allowing for direct injection of the non-polar-polar extraction solvent mixture (acetone-hexane) resulting in an approximate 76 time increase in sensitivity. Lowering the extraction time to 10 minutes from the previous 2 hours marked a significant improvement in efficiency for clay matrix samples.

1.8.3 Microwave Extraction of Rock Samples[44]

The removal of analyte from a rock matrix is a difficult process as the rate of molecular diffusion through the rock is controlled by the concentration gradient of the compound inside the matrix and the pore size, and in most cases proceeds slowly. This is illustrated with the traditional process of solid-liquid extraction, a procedure that requires up to eight weeks to reach a steady state. In order to expedite the process, the sample and extraction solvent were placed

inside a closed extraction vessel heated by microwave radiation. The closed vessel once again allows for the heating of both the solvent and the sample without the risk of volatile loss. The vessels used in this method were manufactured from TFM Teflon® which possesses a very dense structure with smooth surfaces and low permeability/reactivity to gases and vapours. The microwave systems (Figure 9) used in such extraction methods are likely to be more advanced than typical home ovens, as they are equipped with monitoring systems for vessel temperature and accidental solvent release. The extraction solvent was methanol, which would lead to complications if injected splitless into a non-polar GC column used for separation of volatile organic compounds. Solvent exchange can be performed, but it results in loss of sensitivity. It is for this reason that the extraction solvent aliquots were injected via a cool on-column injection method that refocused the analytes on the head of the column using the retention gap effect. The method as described retains sensitivity comparable with the traditional solid-liquid extraction method, but reduces extraction time requirements from the eight weeks to approximately 2 hours.

Figure 9: Milestone Ethos microwave solvent extraction labstation (from reference 44)

1.9 Objectives

The objective of this study was to develop methods for the extraction of chlorinated solvents from low permeability rock matrices that would complement the existing methods in terms of selectivity and sensitivity. The currently used method, microwave assisted extraction of the rock samples using methanol as the solvent combined with cool on-column injection to a gas chromatograph equipped with an ECD detector, provides good sensitivity; however, selectivity of the method might be insufficient when dealing with complex environmental samples. To overcome this problem, it is necessary to use a mass spectrometer (MS) for the detection. Since mass spectrometers are usually less sensitive to chlorinated compounds than electron capture detectors, it is necessary to increase the amount of analytes introduced to the system to maintain (or improve) the sensitivity of the method. One way to accomplish this goal is to use a purge-and-trap (PT) system for the analysis of the methanolic extracts obtained by MAE. Under typical conditions, the volume of the extract that can be introduced to the GC via PT can be increased by a factor of ~100 compared to on-column injection. This should allow the new method to be at least as sensitive as cool on-column injection with ECD while providing the selectivity typical of mass spectrometers.

The sensitivity of the method for the analysis of volatile compounds in rock samples can be improved further by introducing the total amount of the analyte contained in a given mass of the sample to the chromatographic system. It is proposed to accomplish this goal by developing a solventless microwave-assisted purge-and-trap extraction method. The new method would be applicable to samples in which analytes cannot be detected using the standard methods.

Chapter 2: Experimental

2.1 GC Method (Liquid Injections, MAE Solventless Sand and Rock Extractions)

The GC instrument used in these parts of the study was an HP 5890 (Hewlett-Packard, Palo Alto, CA, USA). The detector used for this study was an HP 5970 Mass Selective Detector. The analytical column installed in the GC was a 30 m x 320 µm x 1 µm HP-1 capillary fused silica column (Agilent Technologies Inc.). The injection volume for splitless manual injections was 1µL, completed manually using a 10µL Hamilton syringe via the hot needle injection technique. This technique was chosen as it was found to be superior to/equal to other manual injection techniques.[45] Discrimination between analytes is possible when using this technique if analysis includes high boiling point compounds. However, as the compounds in this study have a maximum boiling point of 121 °C, they all readily volatilize with an injector temperature of 250 °C. For the hot needle injection technique, the sample is withdrawn into the barrel of a standard syringe, pulling back until the liquid sample is 1-2 cm away from the entrance of the needle. The needle is inserted into the heated injector port, allowed to heat for 3-5 seconds, then the plunger is quickly depressed. If completed properly, the vaporization will occur almost entirely in the syringe needle (except for higher boiling compounds). During injection the split vent on the gas chromatograph is closed. Preventing flow of the vapour mixture in the injector port out of the split vent is important when trying to attain high levels of sensitivity. The issue that can arise with splitless injections is high volume of solvent vapour upon volatilization. This limits the volume of liquid sample injection to no more than 2.5µL.[46] The splitless period selected must be sufficient to allow complete transfer onto the column while producing as narrow a solvent peak as possible.[47] For this reason a split vent time of 0.75 mins was selected at a vent flow of 15

mL/min. The carrier gas was ultra-high purity helium (Praxair, Kitchener, Ontario, Canada) set to a column flow rate of 1 mL/min. The injections were methanolic dilutions of a custom VOC standard of several compounds (S-8241A-R2-5ML AccuStandard, Inc., New Haven, CT, USA). The initial oven temperature was 35 °C, held for 2 min, then ramped to 140 °C at 10 °C/min, held for 0 minutes, then ramped to 250 °C at 70 °C/min. The MSD interface temperature was set at 280 °C. The instrument control software was HP ChemStation.

2.2 MAE with Solvent - GC Method (Rock Extractions with Methanol)

In order to validate the solventless extraction method being developed in this study it was necessary to have rock samples split and run concurrently in order to evaluate the results via comparison. The established method is microwave assisted extraction as mentioned in section 1.8.3 and completing analysis using cool on-column injection onto a GC column with μECD detection. The standard operating procedure followed in the analysis was prepared by and last updated in August 2008 by Maria Górecka, University of Guelph, School of Engineering. It is based on the paper by Górecka et al. (2001), as well as the Master's thesis of Yongdong Liu (2005).[44]

The microwave extraction instrumentation was an Ethos SEL Labstation (Milestone Srl., Italy). The microwave extractor was equipped with a 12 vessel MPR-600/12S medium pressure segmented rotor that allows for up to 12 vessels to undergo extraction simultaneously. The vessels are made of chemically inert and microwave transparent TFM Teflon. Rock samples and methanol are transferred from the post-crushing sample vessels, using an additional 5 mL of clean solvent to assure complete sample transfer. Sample vessels are closed and weight recorded before heating the vessels at high temperature (120 °C) for 40 minutes. After extraction, the vessels and contents are cooled in an ice bath prior to opening. An extract aliquot (4 mL) is

removed for analysis, while the remainder is transferred into the initial sample vessel (40 mL VOA vial).

The GC used for this part of the study was an Agilent 6890 GC with computer control, equipped with a cool on-column injector, auto-injector, µECD, polar deactivated pre-column (2 m x 0.32 mm, Supelco, Bellefonte, PA), and an analytical capillary column HP-1, 30 m x 0.32 mm x 5 µm (Agilent Technologies Inc., Palo Alto, CA, USA). The injection volume was 1 µL. The temperature program of the injector was an initial temperature of 55 °C, ramped to 250 °C at 150 °C/min and held for 25 min. The GC oven temperature program had an initial temperature of 55 °C held for 2.5 min, then ramped to 150 °C at 10 °C /min, then a secondary temperature ramp to 220 °C at 35 °C /min and held for 10 min. The carrier gas was UHP helium at a flow rate of 3 mL/min. The µECD detector temperature was 300 °C with nitrogen used as the make-up gas at a flow rate of 60 mL/min.

2.3 Preparation of spiked samples (Sand Extractions)

The preparation of spiked samples for solventless VOC extraction from sand matrix was a three step process. First, 300 g of silica sand, measured dry bulk density of ~1.69 g/mL (Barnes Environmental International, Waterdown, ON), was dried overnight in an oven at 170 °C. Samples were weighed (~25 g) directly into 40 mL EPA vials. In each sample set one weighed vial was set aside to confirm that volatile compounds that may have been present were in fact baked out. The custom standard VOC mix S-8241A-R2-5ML (AccuStandard, Inc., New Haven, CT, USA) was diluted using purge-and-trap grade methanol (Sigma-Aldrich Corp., St. Louis, MO) to the required concentration for a given set of extractions.

2.4 Core Retrieval for Real Rock Samples

The rock core retrieval, sampling, and storage methods as only outlined here are described in full in a standard operating procedure for the Centre for Groundwater Research, University of Guelph.[48] Rock core samples used in this study were collected from a site in Guelph, Ontario, Canada. The technique used in the removal process is known as wireline core drilling.

A five foot long section of rock is cut and the core is removed using a wireline system. The cores are then placed in foil lined PVC tubes and removed from sunlight and wind to prevent loss of volatile organic compounds. Sample cores are removed for the purpose of analyte analysis and determination of physical properties. Samples for analytical analysis are crushed and placed in sample vials onsite; those for physical properties are wrapped in foil, saran wrap, Parafilm, and bagged.[49] They are stored at 4^0C in a cold room.

2.5 Rock Sample Processing and Selection

The range of concentrations from one section of rock core to another can be very large, it is therefore important to complete multiple extractions from a single core in order to form a reasonable conclusion as to the contaminant level in the subsurface. In general, sample selection is completed in relation to the observed rock fractures. This means that sample "pucks" are removed from the core adjacent to fractures, as well as measured distances away to gain insight into the diffusion of the analyte into the rock matrix.

Extractions are carried out by first selecting a section of the rock core 2-6 cm long. The sections were removed from the rock cores that were collected and stored for analysis of physical

properties. Using a mallet and chisel, a puck-shaped piece of the core is removed from the original sub-section, and its rind is removed. This is necessary, as during the drilling process the edge of the rock core may have inadvertently come into contact with the drilling fluid, which then may act as contamination during analysis. Secondly, while care has been taken to prevent VOC loss, it is inescapable that some may have occurred from the surface of the sample. Selecting the center section prevents the results from being influenced by the negative bias and possible contamination.

Trimmed samples are quickly placed into a crushing cell. Extractions on rock matrices require them to be crushed in order to accelerate the extraction process. Extraction occurs more quickly for crushed rocks due to increased surface area of the matrix, decreased distance between the solvent (where applicable) and contamination, as well as allowing for rapid solvent penetration of the matrix. A hydraulic crushing system is used for this purpose (Figure 10). The hydraulic press crushes the samples in seconds under 4000-7000 psi of pressure. Once crushed, the cell is inverted, and the matrix is funneled into the awaiting weighed extraction vessel. Proper cleaning of the crushing apparatus between sample processing runs is important, as it prevents cross-contamination. The procedure for cleaning the apparatus consists of five steps: wash with phosphate free detergent, rinse with tap water, methanol rinse, organic-free water rinse and drying with a paper towel.

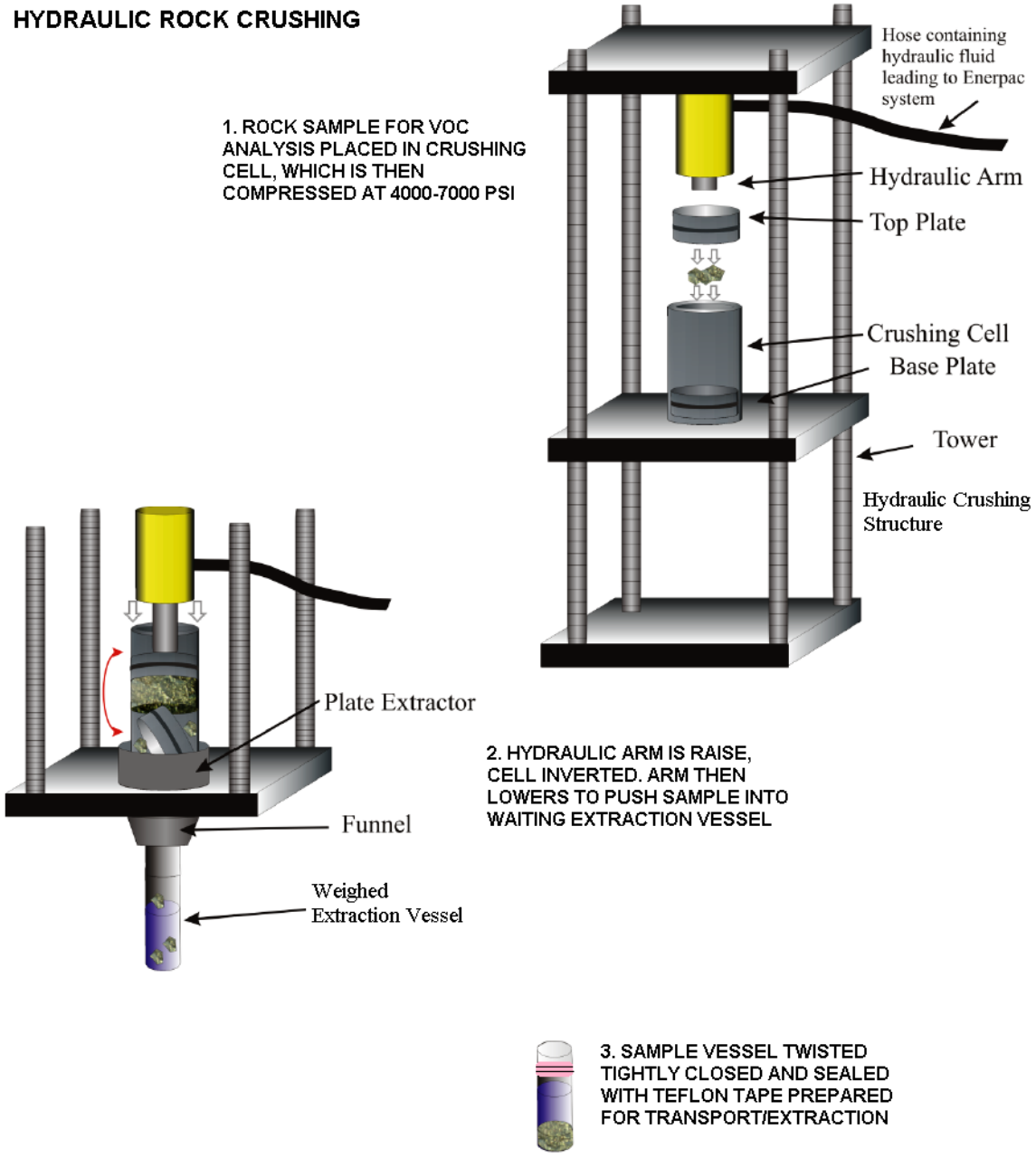

Figure 10: Hydraulic rock crushing sequence (modified from figure in reference 44)

2.6 Conditioning and Spiking of Rock Matrices

Creating standard samples using real rocks and analyte standards of known concentration is a difficult process when compared to the spiking of soils. When dealing with soils (such as sand), the small movable particles allow for high availability of surface area upon which the standard can absorb, and relatively simply mix in with the mass of the matrix. Mass concentration in a rock matrix is not limited to the surface of the sample. Therefore, spiking of a rock matrix likewise cannot be limited to the surface.

2.6.1 Rock Sample Matrix Conditioning

Prior to using a rock as a matrix for standard extractions it was necessary to prepare the rock. Dolostone rock samples that had previously been extracted of analyte were placed in a thin layer on an aluminum tray in an oven overnight (>10 hours) at a temperature of 170 °C. The purpose of this process was to remove any analyte mass that may have still been present in the rock matrix after the previous extraction. The least volatile compound of this study was PCE, with a boiling point of 121 °C. Thus in the range of volatility of concern for this study there was complete removal of residual analyte. The rock matrix was then allowed to cool in a desiccator filled with treated silica gel that had been washed in cobalt chloride. The blue colour of the desiccant was noted to confirm effectiveness at keeping the matrix dry while cooling. Once cooled, the rock was weighed on an analytical balance. With the mass recorded, the rock matrix was placed inside a Scienceware® vacuum desiccator (Bel-Art Products, Pequannock, NJ) and rough pump attached to create vacuum. The purpose of creating vacuum was to remove the air from inside the micropores of the rock matrix that were vacated of liquid during the bakeout step.

2.6.2 Rock Spiking Procedure

With the vacuum created, an aqueous solution of 500 mL of MilliQ water and spiking analyte standard was introduced into the vacuum desiccator through the stopcock nozzle. The volume of the aqueous spiking solution was chosen as to be sufficient to submerge the rock matrix completely (Figure 11).

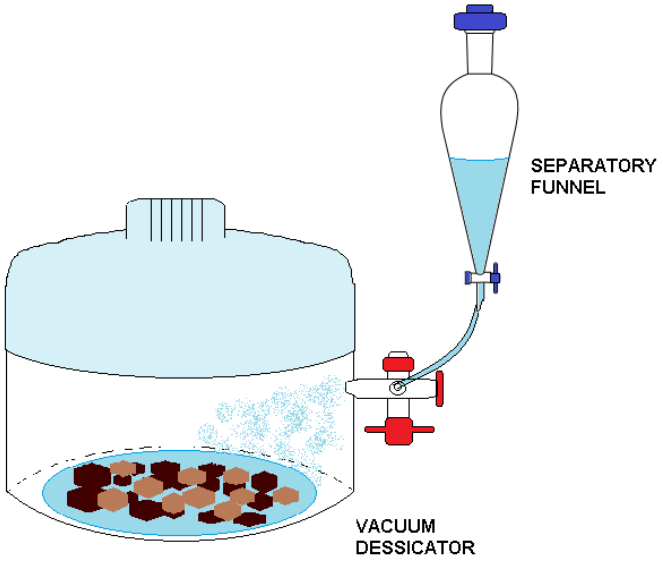

Figure 11: Rock Matrix Spiking Procedure

After the aqueous solution was introduced into the vacuum desiccators, it was allowed to sit at room temperature for 30 minutes with the cover of the desiccator on and the stop cock closed. Using the known volume of the desiccator, the known volume of the aqueous solution, the average volume of the micropores gathered from porosity measurements (Section 3.4.1), and the known concentration of the aqueous solution, it was possible to use the dimensionless Henry's law constant at 25 °C to calculate maximum possible concentration of the analyte in the rock matrix. Using the values in Table 5:

Table 5: Henry's law constants for analytes at 25 °C (from reference 2)

Air-Water Partitioning Coefficients for Chlorinated Ethenes	
Analyte	**Henry's Law Constant**
1,1-DCE	1.04
c-DCE	0.15
t-DCE	0.37
TCE	0.38
PCE	0.71

An example calculation of this for TCE would be:

$$K'_H = \frac{C_{gas}}{C_{water}}$$ **Equation 3**

In a closed vessel

$$Fraction\ in\ gas\ phase = \frac{V_{gas}}{V_{gas} + \frac{1}{0.38} \times V_{water}} = 0.957$$ **Equation 4**

With K_H' = 0.38, V_{gas} = 11.8 L, V_{water} = 0.2 L

For a matrix mass of 100g, and a percent connected pore volume by weight of 2.9%, the total connected pore volume in the rock matrix was 2.9 mL and therefore the fraction of aqueous phase in rock matrix at most was:

$$\frac{2.9\ mL}{200\ mL} = 0.0145$$

To complete this example for TCE: if the spiking amount was: 2.4µL × 180 mg/mL = 0.432 mg then the amount mass per gram of sample would be:

$$0.432mg \times (1 - 0.957) \times \frac{0.0145}{100g} = \frac{2.69ng}{g} of\ rock\ matrix$$

2.7 Purge-and-trap and Cryofocusing Method (Sand Extractions, Rock Extractions)

The purge-and-trap instrument used in this study was a Liquid Sample Concentrator 2000 (Tekmar Company, Cincinnati, OH, USA). The sorbent trap employed during these sections of the study was Tenax TA® trap model number 21060-U (Sigma-Aldrich Corp., St. Louis, MO, USA). Purge gas was ultra-high purity helium (Praxair, Kitchener, ON, Canada); set to a flow rate of 40 mL/min. Purge pressure was set at 20 psi. Purge time was 14 minutes at a trap temperature of 30 °C. The desorb gas was also ultra-high purity helium (Praxair, Kitchener, ON, Canada). Desorb time was 4 minutes at a temperature 180 °C, at a flow rate of 1 mL/min. Bake-gas-bypass mode was set to ON, with delay set for 120 seconds. The temperature of the six port valve was set to 140 °C to prevent condensation. Heated transfer line temperature was set to 150°C. Cryofocusing union was set for 160 °C. Cold trap temperature was set to -60 °C. Injection temperature was set to 200 °C over 45 seconds. The cryofocusing capillary was a 17 cm segment of a 0.53mm x 5µm MXT-1 column (Restek, Bellefonte, PA). Bake temperature was set to 260 °C for 8 minutes.

2.7.1 Purge-and-trap & Cryofocusing Method (Methanolic Extract Purge from Purified Water)

Settings for this section of the study were similar to those mentioned in Section 2.7 Purge-and-trap and Cryofocusing Method (Sand Extractions, Rock Extractions), with a few notable changes. The purge time was shorter at 11 minutes while maintaining the flow rate of 40 mL/min. The trap used in the concentration step was a Tenax® TA trap and with a desorb temperature of 180 °C. Prior to the modifications made later in the study, the extraction of the methanol diluted standard from water was carried out in a 5mL sparging vessel (the actual volume of the vessel is greater than 5 mL). The introduction of liquid sample was done using a Hamilton 5 mL gas tight syringe with a metal Luer lock. The syringe was rinsed with methanol, and then Milli-Q water. The syringe was filled with 5 mL of water, and then another needle containing the spiking standard was inserted to deliver 100 µL of the methanol spiking standard. The Luer lock on the syringe was then connected to the female connector in the sampler assembly, the three port valve was manually opened, and the liquid sample was injected into the pre-rinsed glass sparging vessel. After injection, the valve was closed, the syringe removed and rinsed. A 5 mL metal sparger was used at this stage of the study.

2.8 MAE Instrumentation (Sand Extraction, Rock Extraction)

The microwave oven used in this study was a modified conventional oven (MQ6614XW, Matsushita Electric Works, Ltd). The oven was modified to include a temperature control system. The system consisted of a shielded thermocouple and a temperature control module. The thermocouple was a J type ungrounded thermocouple model JMTSS-020U-6 (Omega Engineering, Inc., Stamford, CT, USA). Ungrounded thermocouples are isolated from the

protective sheath, which is then electrically grounded to the microwave cavity to prevent arcing. The temperature controller was an R/S model number 689-0010 (Barrington, IL, USA). The temperature controller would supply power to the magnetron during the temperature program of 14 minutes concurrent with the extraction. To prevent excessive reflection of microwave radiation that could damage the magnetron, a glass vessel with water was placed in the cavity along with the sample to absorb excess radiation. The microwave cavity was altered in two ways (Figure 12) by Science Technical Services, University of Waterloo. The first was to install a jack for the thermocouple with two purposes. The jack allows for the thermocouple to connect to the temperature controller without risking possible damage from arcing. As well, it provides a point of contact for the thermocouple to ground itself to the cavity wall. The second way in which this cavity was modified, was to create an opening in the cavity through which the Teflon tubing could be passed. This channel created in the microwave cavity had to be precisely measured to prevent microwave leakage. A significant leak would result in both a danger to the operator as well as a loss in heating efficiency.

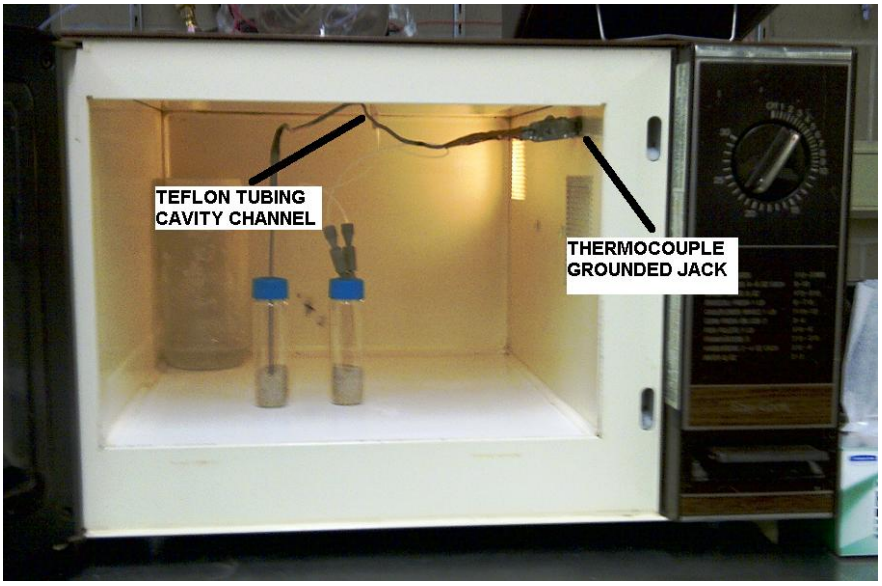

Figure 12: The microwave cavity with two modifications highlighted

The extraction/temperature vessels used for the extraction of sand matrix as well as real rock samples were 40 mL EPA clear vials with polypropylene open top aqua caps & Teflon/silicone septa (5/120) product number C85276740 (Chromatographic Specialties Inc., Brockville, ON, Canada). The temperature control vessels were used during the entirety of the sand extraction work, but their use was discontinued when the switch was made to rock, due to early shortages of rock matrix as well as the less effective heating of the rock matrix samples. The temperature controller would supply power to the magnetron while the temperature reported by the thermocouple in the temperature control vessel was less than the set temperature of 110^0C. The sand would readily attain that temperature at which point the power to the magnetron would cycle on and off so as to maintain it. The rock temperature would reach a maximum reported temperature of 105^0C during the purge cycle. The result was the magnetron was never cycled off. For this reason, the rock matrix extractions were carried out with no temperature control. The septa piercing capillaries were megabore deactivated tubing cut to lengths of 11 cm (purge gas flow in) and 4 cm (purge gas flow out) from a larger column, 2m x 0.53 mm product number

J1602535S2 (Chromatographic Specialties Inc., Brockville, ON, Canada). The Teflon transfer line for purge gas flow into and out from the extraction vessel was TFE Teflon tubing 1.58 mm O.D. (Sigma-Aldrich, Oakville, ON, Canada). The connector between the Teflon tubing and the septa piercing capillary was a 1/16" to 1/32" reducing union made of high pressure PEEK, product number ZRU1.5TFPK (VICI Valco Canada, Brockville, ON, Canada). For the extraction of spiked rock matrices the sample vial sizes were reduced along with the sample mass. The vials employed were 20 mL EPA clear vials with polypropylene open top aqua caps & Teflon/silicone septa (5/120) product number C85276720 (Chromatographic Specialties Inc., Brockville, ON, Canada).

The Teflon transfer line carrying the analyte/He gas mixture out from the microwave oven was kept heated with a strip of resistively heated tape attached to the tubing with nylon high temperature tape. The temperature of the heating tape against the tubing was 120 °C to prevent condensation.

The drying apparatus (Figure 2) was made of a 1 L glass vessel with the lid punctured to allow for tubing to pass through. Nafion® tubing 5m x 1/16" O.D. TT-060 (Perma Pure LLC, Toms River, NJ, USA) dried the gas of moisture and methanol before entering the purge-and-trap instrument. To aid in the drying process, heated nitrogen gas was blown through the container, with the temperature inside the drying vessel reaching 110 °C. The following diagram (Figure 13) illustrates the arrangement of the instrumentation as it would appear during solventless extraction from a solid environmental matrix.

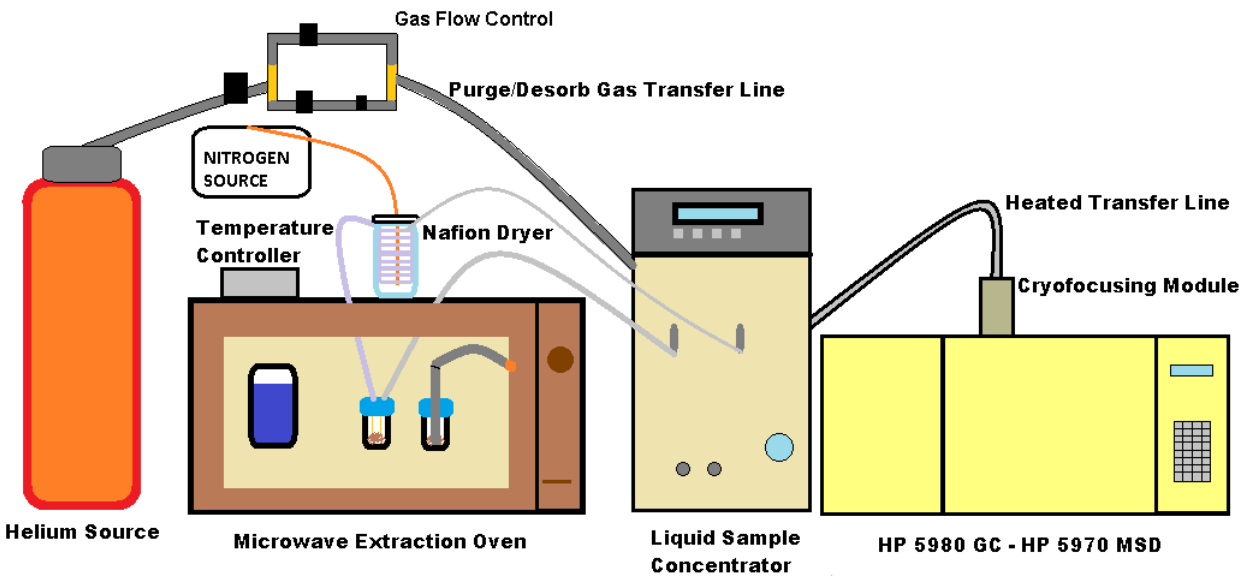

Figure 13: Diagram of the instrument arrangement as designed for solid matrix extractions

Chapter 3: Results and Discussion

In refining the efficiency of the newly developed extraction-concentration method, it was necessary to begin by starting at simpler principles. The primary step was to gauge the effectiveness of the concentrator. This was carried out by completing a series of extraction-concentrations of methanolic standards from Milli-Q water. The methanol diluted standards were used as a surrogate for methanolic extracts that are produced from methods that are already established (shake-flask, closed vessel MAE). The secondary step was to use refined procedures from the water purging series to complete dynamic headspace analysis of volatile organic compounds from a solid matrix that is more permeable than rock. This was carried out using sand matrices spiked with methanol diluted standards. Once again the process was refined in order to adapt to the new matrix type. The third step was to complete the extraction from the dolostone rock matrix of low permeability. This portion of the study had two stages. The primary stage was to create rock matrix standards. The standards would then be used to refine the process for the real matrix. The secondary stage was to use real rock samples to carry out comparison extractions with the standard method: microwave assisted extraction of rock matrices with cool on-column injection method and μ-ECD detection. In this study, the extractions of the established method were carried out by personnel of the Centre for Applied Groundwater Research at the University of Guelph according to the established standard operating procedure.[50]

3.1 Purging of Methanolic Extracts from Milli-Q Water

According to the US-EPA Method 5030C that deals with the purging of methanolic extracts of volatile organic compounds from aqueous matrices, the volume of extract for a 5 mL

aqueous sample should be 100 µL (in the 500-10000 µg/kg analyte range). The method also suggests that the dilutions of the standards in the aqueous matrix be carried out in volumetric flasks, then those flasks be poured into the 5 mL injection syringes. It was found to be a simpler procedure with no decrease in analyte response to carry out the spike of the Milli-Q water inside the 5 mL glass injection syringe, and introduce the aqueous sample together through the sample inlet. The method also recommends using an uncoated fused silica precolumn as the cryo-capillary cooled to -150 °C, heated in a flow of carrier gas to 250 °C. The column selection has a direct impact on the cooling temperature. The higher the capacity of the column, the higher the temperature can be set. Therefore using a large diameter column, with a large film thickness allowed for much higher trapping temperatures.[52] The column that best fit these requirements was found to be an MXT-1 0.53 mm x 5 µm column (Restek, Bellefonte, PA), which allowed for a cryofocusing temperature of -60 °C. Injection temperature correlates with injection time. A high injection temperature allows for volatile compounds to be rapidly driven from the trap, but also requires a longer injection time. The injection time is the amount of time required for the trap to rise from the trapping temperature to the injection temperature plus an additional 15 seconds, therefore increasing the injection time increases the time the GC must operate in splitless mode. The result of all this is that to allow a trapping temperature and high injection temperature as the EPA method outlines, the coolant costs would be excessive, the injection efficiencies would be reduced, as well as produce split peaks could be produced in the case of the more volatile compounds.

3.1.1 Precision Measurements of the Purging of Methanolic Extracts from Water

The extractions of methanolic extracts for the purpose of determining precision of the method were made at three spiking concentrations: 0.01, 0.001, 0.0001 µg/100 µL. Diluting with

5 mL of Milli-Q water, the concentration of the analyte in the aqueous solution would be: 0.002 µg/mL, 0.0002 µg/mL, and 0.00002 µg/mL. The settings for the instrument were mentioned in the experimental chapter. The results were:

Table 6: Precision at 100 µg/L level for methanolic extracts (n=6 determinations)

Concentration: 100 µg/L	
COMPOUND	%RSD
cis-1,2-Dichloroethene	1.3
trans-1,2-Dichloroethene	3.3
1,1,1-Trichloroethane	2.9
Carbon tetrachloride	2.4
Trichloroethylene	1.3
Perchloroethylene	2.6

Table 7: Precision at 10 µg/L level for methanolic extracts (n=6 determinations)

Concentration: 10 µg/L	
COMPOUND	%RSD
cis-1,2-Dichloroethene	2.7
trans-1,2-Dichloroethene	2.4
1,1,1-Trichloroethane	1.7
Carbon tetrachloride	2.4
Trichloroethylene	2.4
Perchloroethylene	6.3

Table 8: Precision at 1 µg/L level for methanolic extracts (n=6 determinations)

Concentration: 1 µg/L	
COMPOUND	**%RSD**
cis-1,2-Dichloroethene	11.9
trans-1,2-Dichloroethene	10.4
1,1,1-Trichloroethane	2.8
Carbon tetrachloride	5.8
Trichloroethylene	1.7
Perchloroethylene	8.1

The limit of detection was estimated as 3 times the standard deviation of the noise level of a blank. The result of this work is the following:

Table 9: Estimated limit of detection for the methanolic extracts (n=6 determinations)

COMPOUND	Limit of Detection (µg/L of H_2O)
cis-1,2-Dichloroethene	0.182
trans-1,2-Dichloroethene	0.130
1,1,1-Trichloroethane	0.087
Carbon tetrachloride	0.114
Trichloroethene	0.046
Perchloroethene	0.168

Comparing the above list of compounds with previously established limits of detection for the cool on-column method of injection:[53]

Table 10: Comparison of limits of detection for cool on-column and PNT

Compound	On-Column	PNT
	Detection limit [µg/L]	Detection limit [µg/L]
cis-1,2-Dichloroethene	3.5	0.182
trans-1,2-Dichloroethene	5.3	0.130
Trichloroethene	0.07	0.046
Tetrachloroethene	0.07	0.168

The table shows that the limits of detection for the method proposed were comparable or lower for all the compounds, with the improvement being the most significant for the more volatile compounds. This follows what would be expected when comparing the two methods. For the established method, the detector being used (µECD) has higher sensitivity for compounds with higher degree of chlorination because of larger electron capture cross-section of such compounds. Also relevant to note is that the mass selective detection used with the PNT method is capable of selectivity not achievable using a µ-ECD. While not relevant when measuring detection limits with known standard mixtures it becomes increasingly so with environmental samples potentially containing unknown complex mixtures.

3.2 Purge-and-trap Extractor Pneumatic Manipulation for Increasing Desorption Efficiency and Method Sensitivity

The ability of the trap to retain the analyte can be manipulated through the adjustment of two factors: trap temperature and the flow of inert gas through the trap. Efficient removal of analyte from the trap is important for several reasons:

- Faster desorption results in lower desorption gas volume, improving chromatographic peak shape.
- Poor efficiency may lead to incomplete desorption, resulting in loss of analyte during bake cycle and elevated detection limits.
- Long desorption cycles result in extended periods of time when the solid sorbent is exposed to elevated temperatures, shortening trap lifespan.
- Shortening desorption time results in a lower overall time for the extraction procedure, increasing throughput and decreasing costs.

Trap temperature is the simplest means by which trap desorption efficiency is increased. That is the reason why a pre-heating step is used prior to the desorption step. The trap temperature is raised to: [desorption temperature] - 5^0C, before the trap is back flushed with the inert gas. The maximum desorption temperature is limited by the trap material, as well as the thermal degradation limits of the analytes. This leaves the researcher with the option of increasing the flow rate. To this end, work was completed in order to increase the rate at which the analyte would be removed from the trap, by increasing the flow rate of the desorption gas.

Typically the flow of desorption gas is limited by the method of separation/detection being employed. When using a GC/MS system, the flow rate of the carrier gas must be limited to ~1 mL/min. This in turn would limit the flow rate of the desorption gas to the same rate unless the desorption of the gas was split off at the injector port. Splitting at the injector port to allow for fast desorption would lead to such significant analyte loss that the increase in sensitivity resulting from the better desorption efficiency would be far less than what was lost.

To prevent loss of analyte while maintaining the benefits of efficient extraction a new system needed to be developed. Such a system was developed where the flow of helium gas into the separation capillary did not follow the traditional route and the benefits of cold trapping were employed. Control over the flow rate of helium gas was the first issue that was addressed. The flow of helium gas could not be controlled by the purge-and-trap system. The flows of gas into the instruments desorb gas line port equals the flow exiting the heated transfer line. This meant that the flow needed to be monitored, controlled, and able to be quickly switched depending on the extraction stage. This was completed using three mass flow controllers. The flow controllers (50, 20, 20 SCCM, He gas, MKS Instruments, Boulder, CO) were used to control the flow of the gas before it entered the purge-and-trap instrument via the desorb gas inlet. The controllers were adjusted and monitored by a four channel readout digital controller (MKS Type 24D Four Channel Readout, MKS Instruments, Boulder, CO).

The first controller adjusted the total flow rate to 16 mL/min. At this point the flow was split using a three port Swagelok union. Two 1/8" copper lines were connected to this union, as well as two other flow controllers. The two flow controllers (2 and 3) were adjusted to allow flow rates of 15 and 1 mL/min respectively. The flow from controller 3 was always allowed to flow unimpeded into the purge-and-trap instrument. However, for controller 2 the flow was only allowed to flow into the instrument during desorption and post injection to purge the injector port. When allowed to flow into the PNT instrument, the flow rate was equal to 16 mL/min, considerably more than 1 mL/min, and thus capable of similarly more efficient removal of analyte mass from the sorbent trap. When not required, such as during the splitless injection, the flow was vented through the inclusion of a three port solenoid valve. When switched on, the

valve vented the additional flow of helium, quickly switching the total flow to a controlled 1 mL/min.

Using this arrangement it was possible to increase the flow during desorption. The analytes were quickly removed from the trap, where they travelled down the transfer line and were retained in the cryo capillary at the low temperature attained using liquid nitrogen. The additional volume of helium would pass through the capillary and vent out the split vent of the injector port. When desorption was completed, the solenoid valve was switched to allow 1 mL/min flow, and the split vent was closed, allowing for fast desorption while maintaining splitless sensitivity. The layout of this novel arrangement is illustrated in Figure 14:

The arrangement as displayed allowed for desorption times of ~1 min to occur in split mode. Its use was discontinued as it was determined that the faster desorption flow rate through the trap led to an increase in ice plug formation from the water that accumulated on the trap. The manipulation of flow using the mass flow controllers was still used in order to purge the injector port post-injection. However, the arrangement could still be reemployed in situations where the sample matrix contained less moisture or if the purge gas was dried prior to passing through the trap through the use of a Nafion® dryer.

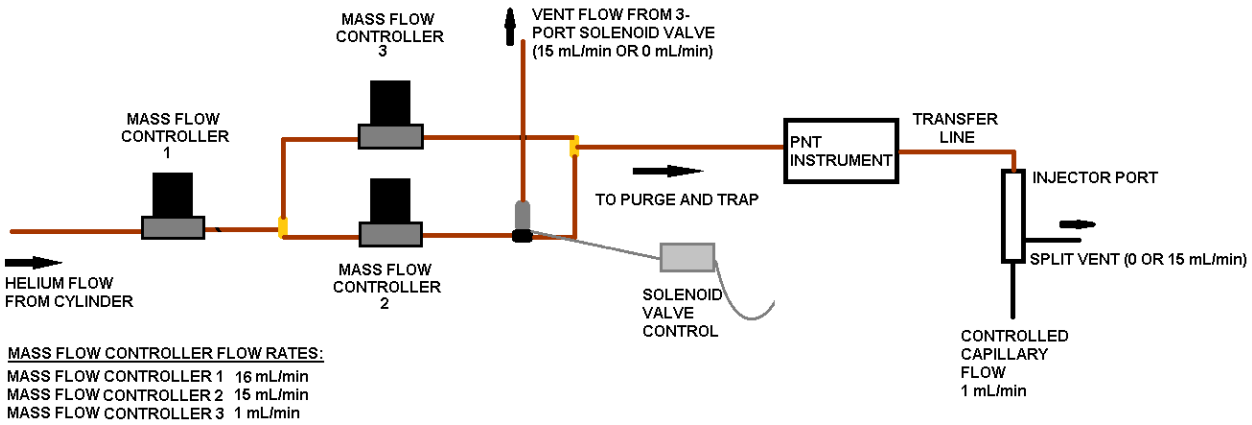

Figure 14: Diagram of the pneumatic arrangement controlling helium desorb/carrier gas flow rate

3.3 Extractions of Volatile Organic Compounds from Sand Matrices

The widely accepted method of extracting VOCs from soil type matrices is that of US-EPA method 5035A. For analyte concentrations in the low range (0.5-200 µg/kg) the method suggests a relatively small sample size of 5 grams.[54] The sampling occurs onsite, directly into pre-weighed VOA vials. Also, when the VOC analysis is for chlorinated aliphatic hydrocarbons such as was the case with this work, there is no need to include a preserving solution. The method suggests the addition of water either prior to adding the sample to the vial, or just before the extraction via vapour partitioning in a closed-system purge-and-trap. The aqueous solution is introduced into the extraction vial to suspend the solid matrix through which purge gas is passed. The method utilizes a system whereby the seal on the sample vessel is never broken between the time of sampling and the time of analysis. The remaining settings recommended by the method are the same as those outlined for the purging of methanolic extracts from water in the previous section. As done before with the methanolic extractions, the procedure followed differed

significantly from the proposed method. The main divergence between the EPA recommended method and the method used in this project is that there is no addition of any purging water solution. Because the standard matrix was baked prior to analyte spiking a small volume of water is injected along with the standard spike to interact with the microwave radiation heating the analytes and aiding in their volatilization.

3.3.1 Determining Maximum Purge Time

Purge time selection is an important aspect when discussing the development of this method and because of the strong differences between this method and the proposed EPA method purge times needed to be determined independently. The purging of methanolic extracts from water is not the same task as purging analyte spiked into a sand matrix. Efficiency of the extraction is directly affected by the availability of matrix surface area to the purge gas. In purging of the methanolic extracts in the previous section, the purge gas was passed through the sample matrix in the form of fine streams of bubbles. This allows for the maximum contact between the analyte in the water and the purge gas. When purging from a sand matrix, the same contact is not possible. This resulted in a need to increase the purge time from the 11 minutes used for the extractions from water. The first step was to estimate the maximum allowable purge volume. The purge volume limit is set relative to the most volatile compound. In this section of the study that compound would be one of the isomers of 1,2-dichloroethylene. The trap being employed when doing purge time evaluation was a Tenax® TA trap. The trap being used was 1/8” in diameter and 24 cm in length, resulting in an estimated trap volume of 0.605 mL. According to the manufacturer (Supelco), the packing density of the solid sorbent is 0.28 g/mL. Overall mass of sorbent in the trapping column was therefore estimated at 0.1694 g. According

to a Tenax® distributor, the breakthrough volumes for this trap during this part of the study were as follows (Table 11):

Table 11: Calculated breakthrough volumes of compounds in spiking standard for the sorbent trap as a function of temperature

TEMPERATURE (°C)	Breakthrough Volume (L)				
	1,2-DCE	1,1,1-TCA	CT	TCE	PCE
20	1.49	1.86	3.56	7.45	35.57
40	0.37	0.46	0.81	1.52	6.78
60	0.11	0.15	0.22	0.39	1.52
80	0.04	0.05	0.07	0.13	0.37

A plotting of the points from the above Table resulted in the following (Figure 15):

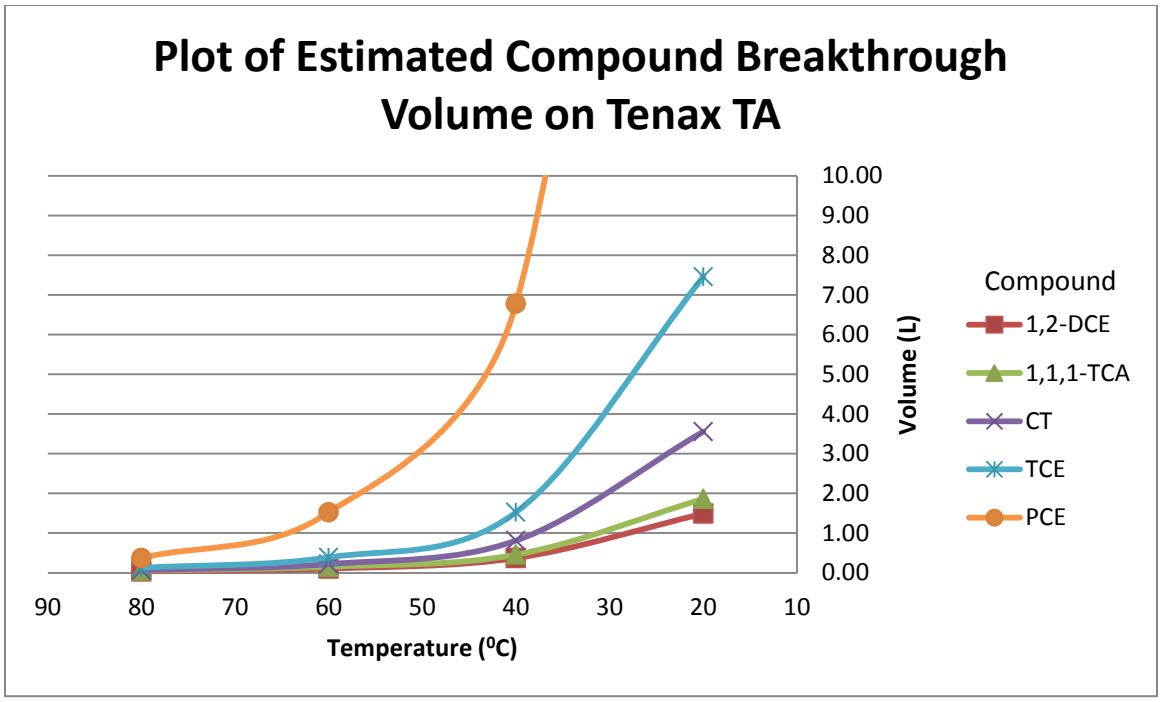

Figure 15: Plot of calculated breakthrough volumes versus temperature

By plotting a trend line along the points it was determined that the breakthrough volume on the trap varied exponentially with temperature. Using the equations of the trend lines it was possible to estimate the maximum purge volume allowable at the starting trap temperature of 30^0C (Table 12):

Table 12: Estimates of breakthrough volumes of the trap at study temperature

TEMPERATURE (°C)	Breakthrough Volume (L)				
	1,2-DCE	1,1,1-TCA	CT	TCE	PCE
30	0.76	0.92	1.70	3.36	15.52

As these compounds are all of the same class (chlorinated aliphatic hydrocarbons), they share similar affinity for the trap sorbent, making their breakthrough volumes a function of their volatility. At a purge rate of 40 mL/min it would be possible to extract for 65 more minutes if the

quantitation analyte was trichloroethylene rather than a 1,2-dichloroethylene isomer. Dynamic headspace analysis extractions on solid matrix samples must be carried out exhaustively so adjusting purge time based on target compound volatility is required.

Using the maximum purge volume of 760 mL as a guideline, a series of extractions were carried out to determine the actual maximum purge volume. Sand matrices were spiked as outlined in the experimental section to a concentration of 0.05 µg/25 g sample. The extractions were carried out in increasing one minute increments to determine the maximum purge time allowable. Microwave heating was applied so as to run concurrent with the purge cycle. The results of this work are presented in the following plot (Figure 16).

The purge times as calculated in the plot were determined early on during the sand matrix extraction phase of the research. At that point in the work there was still a need to include a dry-purge step in the extraction cycle. During a dry-purge step, the flow of purge gas was diverted from flowing through the extraction vessel and instead it passed through the solid sorbent trap in a bid to dry out the trap prior to desorption. The volume of purge gas that flows during the dry-purge step must be included when calculating total purge volume. Therefore, at a purge gas flow rate of 40 mL/min, the total volume must be increased by a minimum of 80 mL to overcome the negative effect (cryo-capillary blockage) from 200 µL of Milli-Q water introduced to the matrix. During the previous methanolic extract purging phase a dry-purge step was not required. It is likely that the microwave heating promoted the transfer of water from the extraction vessel to the trap to a greater degree than occurred when purging a larger volume of water at room temperature.

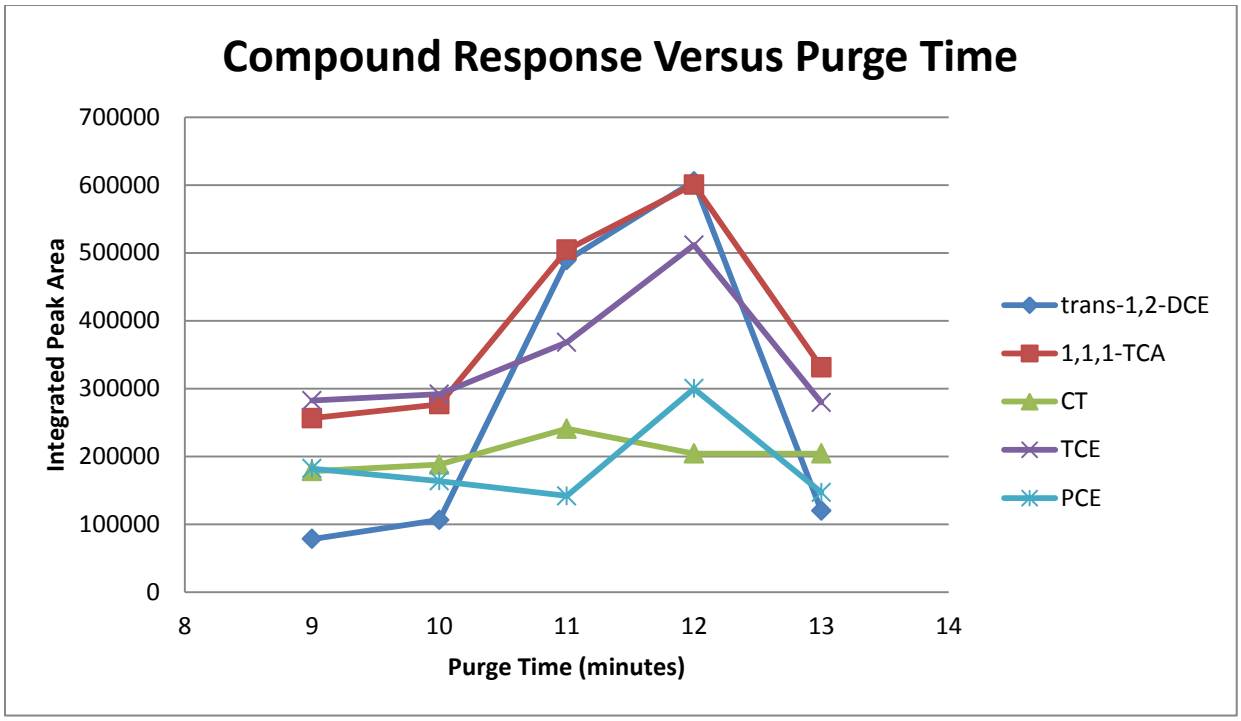

Figure 16: Plot of integrated peak response versus purge time

On inspection of the data from this series it was determined that the appropriate maximum purge time was 12 minutes, instead of the estimated 17 minutes. The reduction of purge time from the estimated value can be explained via one or both of the following two scenarios: the packing density of the solid sorbent was less than the manufacturer reported, or allowing the water to make its way to the trap led to competitive adsorption. The relative ratio of water molecules to TCE molecules in the extraction vessel was roughly 30000000:1, creating the potential for competitive adsorption, even on a hydrophobic sorbent.

3.3.2 Determining the Effect of Microwave Pre-heating

As stated in the previous section, the purge time for a given extraction is limited by the breakthrough volume of the trap sorbent for the most volatile compound of interest. To that end, it is of interest to a researcher to increase the efficiency of the extraction method. An avenue explored to accomplish this task was to pre-heat the extraction vessels with microwave radiation prior to the extraction process. Observation of the temperature controller display showed that the extraction vessel reached its maximum temperature of 100 °C after 1-2 minutes of heating. It was considered that perhaps pre-heating the extraction vessel for approximately two minutes prior to extraction with the purge gas would increase the extraction efficiency. The sample vessels for the extraction were made as in the previous section, and allowed to "pre-heat" in one minute increments from 0 to 3 minutes. The purge times were kept constant at the determined purge time of 12 minutes. The results from the experiments on pre-heating the sample vessel are displayed in the following plot (Figure 17):

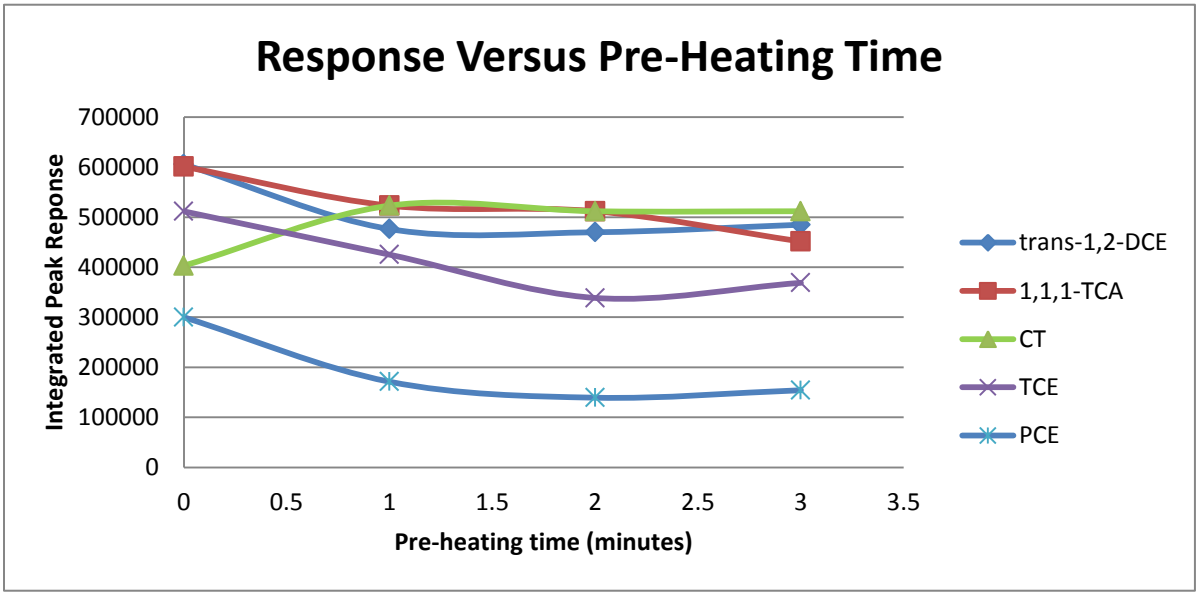

Figure 17: Plot of detector response versus pre-heating time

Upon inspection of the plot data it was determined that pre-heating the sample did not benefit the efficiency of the extraction process. For all compounds, except for carbon tetrachloride, there seemed to be a general decline in recorded analyte response as the length of the pre-heating increased. The results displayed here are not counter-intuitive as they give more credence to the previous assertion of competitive adsorption resulting in reduced response. Heating the extraction vessel prior to beginning the purge cycle would increase the amount of water in the headspace versus the volatile analyte concentration at the beginning of the extraction process. It would likely increase the total amount of water that left the extraction vessel and therefore the amount on the trap.

Additionally further analyte loss may occur through the punctures in the extraction vial seal. In some experimental runs helium was detected to be leaking from around the capillary puncture locations. This suggests losses are possible at this location, even though at volumes insufficient as to result in detection with a leak detector.

3.3.3 Effect of Nafion® Drying Apparatus

The reduction of moisture content in the extraction purge gas is of the utmost importance to the successful method execution. With the moisture content as low as ~0.8% w/w there was already evidence of negative effects on the trap as shown in the previous section. From this need came the implementation of a Nafion® dryer. The dryer is capable of removing water as gas is purged through it. According to the manufacturer of the Nafion® tubing the maximum operating temperature is 190^0C. The process by which water is removed from the gas follows first order reaction kinetics, where an increase in temperature would lead to an increase in the rate at which water passes through the ionic channels that extend from the inside to the outside of the tubing. The manufacturer (PermaPure LLC.) states that for every 10 °C increase in operating

temperature there is a doubling in the rate of water absorption. There have been some examples of organic compounds that undergo unwanted chemical reactions at higher operating temperatures due to acid catalysis. The temperature was therefore adjusted to 120 °C, with the heat introduced into the drying vessel using a steady flow of heated nitrogen gas. The heat and the flow of nitrogen increase the efficiency of water removal by the tubing, allowing for a shorter segment of tubing to be used. The heat of the nitrogen gas also prevented the condensation of any of the less volatile compounds in the transfer line.

The placement of the Nafion® dryer in the extraction process not only allowed the purged extraction gas to be dried prior to making contact with the solid sorbent trap, but in doing so also prevented the risk of ice blockages in the cryo-focusing capillary from the desorbed water. As an added benefit, the tubing also allows for >90% loss of methanol, removing the small amount of the solvent introduced via spiking. The following two chromatograms illustrate the benefit to using the Nafion® dryer. The first was obtained with the Nafion® dryer installed, the second without.

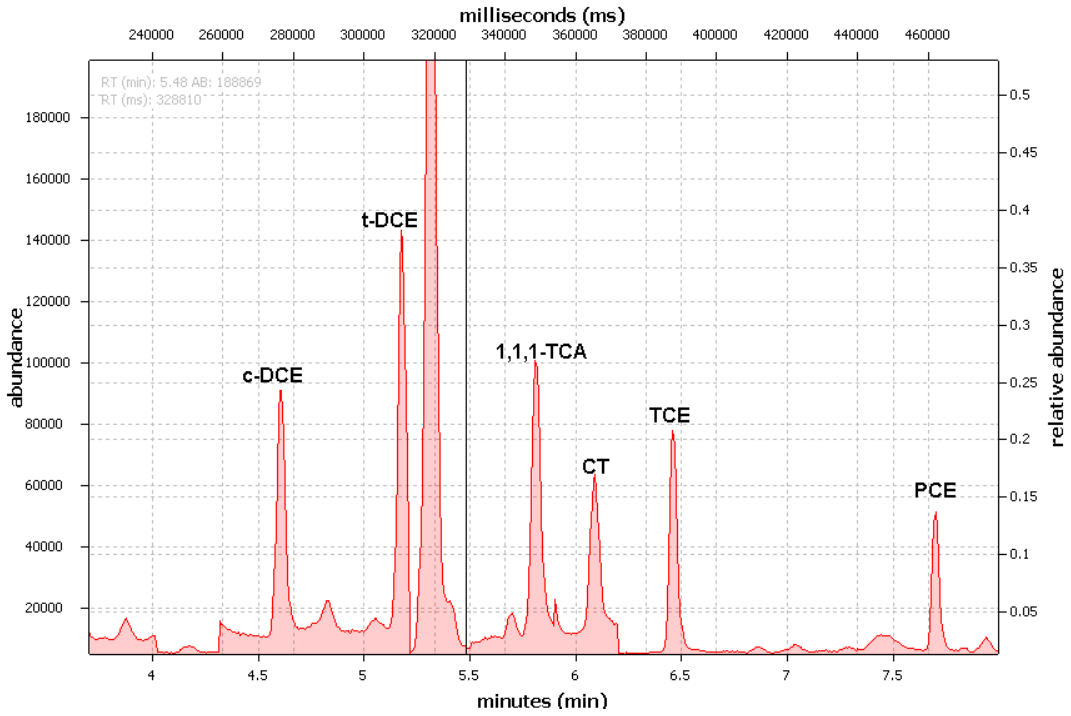

Figure 18: Chromatogram of sand extraction (0.01µg/25 g of sand) completed with Nafion ® dryer

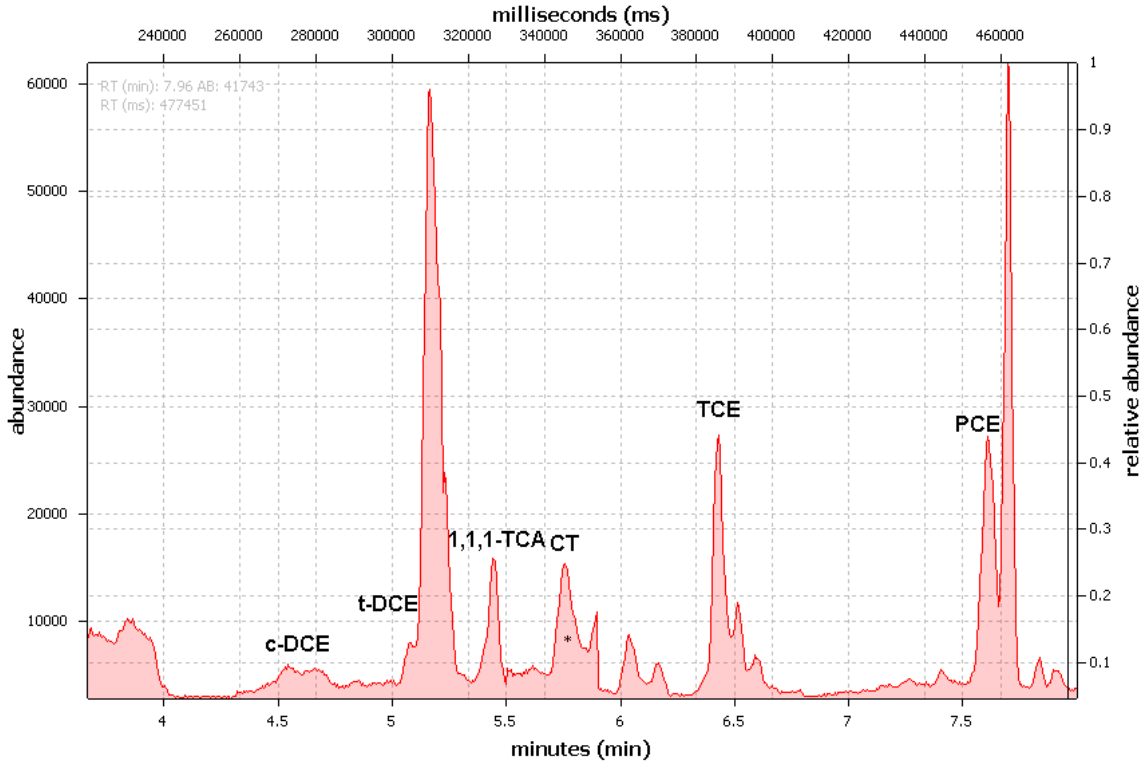

Figure 19: Chromatogram of sand extraction (0.01µg/25g of sand) completed without Nafion ® dryer

The non-use of the Nafion® dryer results in lowered response, poor peak shapes, co-elutions, and the introduction of a relatively large amount of solvent/water onto the analytical column and detector.

The addition of the Nafion® dryer also allowed the maximum purge time to be increased from the previously determined 12 minutes, to 14 minutes. This was a direct result of no longer requiring a dry purge step in the extraction cycle.

3.3.4 Precision Measurements of Microwave Assisted Extractions from Sandy Soil Matrix

The extractions of methanolic extracts for the purpose of determining precision of the method were made at three spiking concentrations: 0.1, 0.01 and 0.0005 µg/µL. 1 µL injections of the spiking standard were mixed with 100 µL of water. The aqueous mixture would be introduced directly onto the sample matrix in the extraction vessel. The sample would then be thoroughly mixed for 20 seconds with the aid of a Vortex Genie, directly followed by analysis. The settings for the instrument during analysis are mentioned in the Experimental section. The results are summarized in the following tables:

Table 13: Precision at 4 µg/kg sample level for sand extracts (n=5 determinations)

Concentration: 4 µg/kg	
COMPOUND	%RSD
cis-1,2-Dichloroethene	7.2
trans-1,2-Dichloroethene	7.1
1,1,1-Trichloroethane	9.6
Carbon tetrachloride	9.0
Trichloroethylene	11.7
Perchloroethylene	12.5

Table 14: Precision at 0.4µg/kg sample level for sand extracts (n=5 determinations)

Concentration: 0.4 µg/kg	
COMPOUND	**%RSD**
cis-1,2-Dichloroethene	10.8
trans-1,2-Dichloroethene	8.6
1,1,1-Trichloroethane	11.9
Carbon tetrachloride	10
Trichloroethylene	13.4
Perchloroethylene	13.2

Table 15: Precision at 0.2 µg/kg sample level for sand extracts (n=5 determinations)

Concentration: 0.2 µg/kg	
COMPOUND	**%RSD**
cis-1,2-Dichloroethene	11.8
trans-1,2-Dichloroethene	10.8
1,1,1-Trichloroethane	12.6
Carbon tetrachloride	14.4
Trichloroethylene	15.3
Perchloroethylene	16.4

The limit of detection was estimated as 3 times the standard deviation of the noise level of a blank. The result of this work is summarized in following table:

Table 16: Estimated limit of detection for sand extractions (n=5 determinations)

Compound Name	Limit of Detection (ng/kg of Sand)
cis-1,2-DCE	4.104
trans-1,2-DCE	5.372
1,1,1-TCA	1.796
CT	0.544
TCE	0.574
PCE	0.456

The precision (%RSD) was worse for this method than for the purging of methanolic extracts. The introduction of the standard was similar to the method used for the purging of methanolic extracts from water (mixing standard spike with water inside syringe). Therefore if the variability stemmed from the spiking method, similar variability would be present. There are two uncontrollable variables, one of which is the amount of incident microwave radiation. The conventional microwave oven used in this study was an older model without a rotating table. The rotation of the table averages the effects of hot and cold spots formed in the cavity. The second is the nature of the matrix. While the fine sand can give the impression that it is homogenous, the makeup of one gram of sand differs significantly from another. Also, while the distribution of standard and the placement of the purge gas capillaries were completed as identically as possible between experimental runs, the matrix structure would not be identical. Water and the analytes would deposit themselves differently, and the pathways through the matrix that the purge gas would follow would be different for each extraction.

Comparing the completed runs with methanol liquid injections made at the same analyte levels, it was determined that the extractions were carried out exhaustively as was the intention during method development.

3.4 Extractions of Volatile Organic Compounds from Rock Matrices

The method for the extraction of VOCs from rock matrix still requires further development but the preliminary results have been promising. The initial stage of the study required the manufacturing of standards that had an analyte mass distribution similar to real rock samples. Spiking methods used with the sandy soil matrix could not be reapplied in this development section. Spiking directly onto the matrix would only represent the proportion of analyte to be found on a rock surface. Of the total analyte mass in a rock sample, the volatile analyte found on the surface would be the most likely to have escaped during the sampling procedure. It is the analyte inside the matrix that comprises the bulk of what is detected during extraction procedures. That is why the use of past EPA methods for solid matrices would not be effective at the extraction of analyte from within the micropores of a low permeability matrix.[55] This would be analyte located in fractures, micropores, and inside the bulk mass.

3.4.1 Determination of Connected Porosity for Spiking Mass Calculation

In order to create rock standards with distribution of analyte similar to real samples it was first necessary to measure the volume of connected porosity. A real rock sample that had been pre-screened and deemed too highly concentrated to be run using this method was used to determine porosity. The rock sample was divided into five sub-samples of approximately 3.5 grams. These samples were weighed as wet as they were, then baked out in an oven overnight at

170 °C. The samples were allowed to cool in a desiccator to room temperature, and reweighed. From the weight difference and the density of water taken as 1.01 g/mL, the volume of connected porosity was estimated. The results from this work are summarized in the following table (Table 17):

Table 17: Results from connected porosity measurements

GUELPH SAMPLE:GWD-BH301-PP-0017					
Vial Label	**Sample weight (g)**	**Vial Pre-heating (g)**	**Vial Post-heating (g)**	**Difference in weight (g)**	**% Moisture by weight**
1	4.1545	18.6987	18.5904	0.1083	2.61
2	3.5619	18.2344	18.1466	0.0878	2.46
3	3.6244	18.2104	18.1248	0.0856	2.36
4	3.7113	18.2134	18.1339	0.0795	2.14
5	3.4345	17.9817	17.8903	0.0914	2.66
					Average
					2.45

The calculation of spiked concentrations was determined using this volume. Example: for 100 grams of rock, there would be internal volume of ~2.45 mL to be filled with the aqueous solution.

3.4.2 Microwave Assisted Extractions from Spiked Rock Matrices

The value of spiking a matrix with standard prior to extraction is that a known amount of standard will be introduced. Extraction efficiency can be determined by comparing the results for a given analyte to the introduced amount. The rock matrix does not allow for simple spiking procedures. As outlined in Section 2.6, a procedure of rock matrix conditioning and spiking was required in order to manufacture material possessing similar analyte mass distribution to real rock samples. Spiking in the past has been carried out through introduction onto the surface of the matrix. This procedure would result in lower variability between standard extractions;

however, it would not in any meaningful way represent the actual location of analyte within a real rock sample. For this reason, the results in this section describe those collected via the method outlined in the experimental section of this thesis.

Sample extractions were initially carried out on samples of approximately 20 g. The number of extraction cycles required to exhaustively remove the analyte from the matrix was deemed too high at this mass (up to 8). The benefit of a large sample size is the averaging effect it has. Results from rock core samples can differ dramatically due to the nature of the matrix: sampling a larger size can provide a better picture as to the total analyte amount present. However, reducing the sample size from 20 g to 5 g does not reduce the averaging effect enough to exchange it for the reduced number of extraction cycles to completely extract contained analyte (2-3). Consequently, the standard sample size was reduced to 5 (±0.25) g. The extractions were carried out exhaustively, with the response taken as the total sum of responses for the runs. The maximum possible concentrations were calculated using the dimensionless Henry's constant, with the known volume of aqueous phase of 500 mL, and the volume of the container of 12 L. The concentrations of analytes in the aqueous phase upon introduction were all the same. However, at equilibrium the concentration in the aqueous phase was different for each analyte based on the partitioning constant. The volumes of 180 µg/mL standard introduced per 500 mL of water were: 1, 2.4 and 10 µL. The estimated concentration in the rock was then based on the Henry's Law calculations and the average connected porosity that was measured. The result of the work is shown in the following Tables:

Table 18: Precision at third concentration level (10 µL/500 mL aqueous phase; n=5 determinations)

COMPOUND	Concentration (ng/g)	%RSD
cis-1,2-Dichloroethene	18.85	20.1
trans-1,2-Dichloroethene	9.06	17.8
Trichloroethylene	8.71	19.3
Perchloroethylene	4.95	18.1

Table 19: Precision at second concentration level (2.4 µL/500 mL aqueous phase; n=5 determinations)

COMPOUND	Concentration (ng/g)	%RSD
cis-1,2-Dichloroethene	4.52	21.2
trans-1,2-Dichloroethene	2.17	22.5
Trichloroethylene	2.09	22.9
Perchloroethylene	1.19	19.5

Table 20: Precision at first concentration level (1 µL/500 mL aqueous phase; n=5 determinations)

COMPOUND	Concentration (ng/g)	%RSD
cis-1,2-Dichloroethene	1.88	22.5
trans-1,2-Dichloroethene	0.91	24.1
Trichloroethylene	0.87	25.6
Perchloroethylene	0.49	25.5

The limit of detection was estimated as 3 times the standard deviation of the noise level of a blank. The result of this work is summarized in following table:

Table 21: Estimated limit of detection for rock extractions (n=5 determinations)

Compound Name	Limit of Detection (ng/g of Rock)
cis-1,2-DCE	0.1256
trans-1,2-DCE	0.0684
TCE	0.0684
PCE	0.0161

The amount of analyte recovered at the three concentration levels from spiked rock standards was well within the same order of magnitude as the maximum concentration calculated. The relative standard deviation of these results was higher than the values attained in past work, as was to be expected.[43] The method used to spike the analyte into the rock matrix as opposed to onto it would result in such values. Rock porosity measurements made to calculate concentration were averaged values not true values. In addition, the dimensionless Henry's law constant values used were taken at 25 °C, and would different significantly with changes in temperature.[56]

3.4.3 Microwave Assisted Extraction on Real Rock Standards: Comparison with the Established Method

The extraction of real rock samples was necessary to compare the effectiveness of this method versus the method currently being employed. In the current method, the extraction is carried out at elevated temperature and pressure inside of a closed vessel. Both are known to improve the rate at which an extraction occurs. The extractions are carried out in a closed vessel

to prevent volatile loss. The aliquots of methanolic extracts do not require to undergo solvent exchange as they are introduced using a cool on-column injection method. The detector used in this study was a μ-ECD. Typically a micro electron capture detector is considerably more sensitive in the detection of chlorinated compounds than the HP5970 mass selective detector used in this study. The purpose of employing the concentration and introduction methods mentioned in past sections was to increase the sensitivity to comparable if not higher levels, with the added benefit of greater selectivity provided by the mass-selective detector.

The number of samples that were compared in this section of the study was limited by the time remaining during this work as well as the small number of samples collected. Three samples had to be rejected from processing due to the high levels of the analyte that were potentially contained within. The Teflon® lines used in this study experienced memory effects at high concentrations, but no such issues developed at lower concentrations or higher concentrations on previous matrices. One possible explanation could be that the memory effects were due to a non-analyte compound present in the rock matrix sample collected. As is illustrated in the Figure below, there were more than just the analytes present as contamination in the real rock sample matrix (Figure 20).

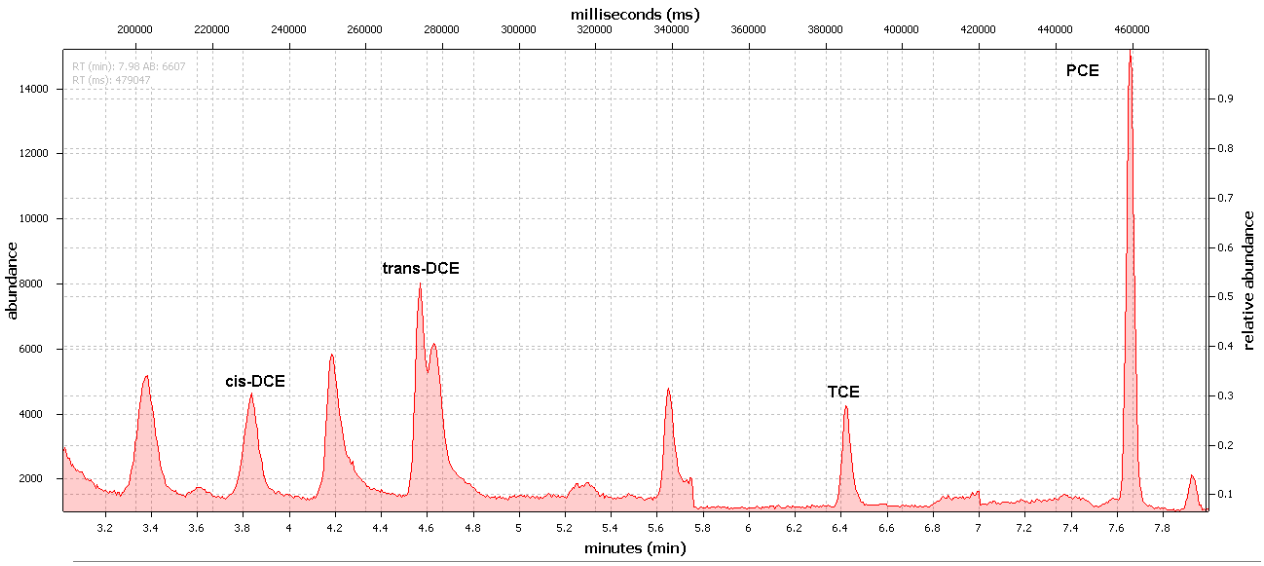

Figure 20: Chromatogram generated from the run completed on real rock sample in SIM mode

A less volatile compound could be purged from the vessel to coat the Teflon® line, acting as a type of stationary phase for the analytes, causing non-permanent memory effects.

The following table (Table 22) summarizes the results of the comparison study between MAE-PNT-GC-MS, and MAE-Cool On-Column-µECD. The results indicate what was expected in this study. The concentrations of the analyte differed significantly between samples, even when selected from the same "puck". A future study with more points of comparison would allow for a statistical comparison of the two methods.

Table 22: Summary of comparison work between the established and the new method (PCE)

File Name	Sample Name	Sample Weight (g)	Extraction Number	Concentration PCE (µg/g)	Concentration PCE (µECD) µg/g Established Method	% Difference
R160.D	GWD-7A	15.31	1	4.67E-05		
R161.D	GWD-7A	15.31	2	6.06E-06		
R162.D	GWD-7A	15.31	3	1.75E-06		
R163.D	GWD-7A	15.31	4	6.03E-07		
Total Conc				**0.0001583**	**0.000242017**	41.8%
R165.D	GWD-8A	20.889	1	0.000102231		
R166.D	GWD-8A	20.889	2	1.09589E-05		
R167.D	GWD-8A	20.889	3	1.17436E-05		
Total Conc				**0.000358434**	**0.000560798**	44.0%
R169.D	GWD-9A	15.455	1	3.4829E-05		
R170.D	GWD-9A	15.455	2	7.37042E-06		
R171.D	GWD-9A	15.455	3	6.702E-06		
R172.D	GWD-9A	15.455	4	6.11379E-06		
R173.D	GWD-9A	15.455	5	7.05849E-06		
R174.D	GWD-9A	15.455	6	6.08705E-06		
R175.D	GWD-9A	15.455	7	3.36882E-06		
Total Conc				**0.000205219**	**0.0000790253**	-88.8%
R199.D	GWD-10A	14.095	1	0.000101435		
R200.D	GWD-10A	14.095	2	4.30268E-05		
R201.D	GWD-10A	14.095	3	5.69521E-05		
R202.D	GWD-10A	14.095	4	4.2802E-06		
Total Conc				**0.000590137**	**0.000334148**	-55.4%

The above Table contains only the results for PCE and not for TCE. For the latter compound the established method resulted in non-detectable levels of the analyte in these four

samples. The following table (Table 23) summarizes the concentrations calculated for TCE in those rock samples:

Table 23: Summary of comparison work for the new method (TCE)

File Name	Sample Name	Sample Weight	Extraction Number	Concentration TCE (µg/g)
R160.D	GWD-7A	15.31	1	1.75E-05
R161.D	GWD-7A	15.31	2	7.72E-06
R162.D	GWD-7A	15.31	3	2.73E-06
R163.D	GWD-7A	15.31	4	1.70E-06
Total Conc				**2.97E-05**
R165.D	GWD-8A	20.889	1	1.16E-04
R166.D	GWD-8A	20.889	2	4.60E-06
R167.D	GWD-8A	20.889	3	1.04E-05
Total Conc				**1.31E-04**
R169.D	GWD-9A	15.455	1	4.56E-05
R170.D	GWD-9A	15.455	2	2.15E-05
R171.D	GWD-9A	15.455	3	7.33E-06
R172.D	GWD-9A	15.455	4	3.52E-05
R173.D	GWD-9A	15.455	5	9.84E-06
R174.D	GWD-9A	15.455	6	4.05E-06
R175.D	GWD-9A	15.455	7	6.16E-06
Total Conc				**1.30E-04**
R199.D	GWD-10A	14.095	1	9.81E-05
R200.D	GWD-10A	14.095	2	3.56E-05
R201.D	GWD-10A	14.095	3	2.96E-05
R202.D	GWD-10A	14.095	4	7.52E-07

Total Conc				**1.64E-04**

The above results suggest that at the very least the new method is capable of detection of analyte at levels comparable to the established method.

Chapter 4: Conclusions

A purge-and-trap method for the analysis of methanolic extracts obtained by the standard MAE method was successfully developed. The new method significantly improved the selectivity of the analysis while providing comparable or better sensitivity and very good precision. It can be used as a direct replacement for the currently used method based on cool on-column injection and ECD detection.

The purge-and-trap system was also combined with a novel solventless microwave extraction apparatus. This combination of instrumentation significantly improved the limits of detection of chlorinated solvents in rock matrices when compared to the established methods. The new method allows for exhaustive extraction and quantitation to be completed in relatively short time, from 26 minutes for larger but more permeable samples of soils to 78 minutes for smaller, much less permeable samples of rock that could take up to 8 weeks to reach a steady state concentration using a standard shake flask method. Excellent reproducibility of the method was also demonstrated. Considering the experimental nature of the new method and its limited throughput, though, its intended role is to compliment the established methods when their sensitivity is insufficient. The solventless nature of the new method allows the costs and dangers related to solvent purchase and disposal to be completely eliminated, and qualifies the method as a “green” one.

The sampling and sample handling procedure proposed helps preserve the integrity of the samples. Once the weighed vessel is filled with the sample in the field, it is sealed and never opened, only being pierced for the insertion of the capillaries when the extraction begins.

Further comparison work is warranted between the established and the new method to allow for statistical comparison between the two. With the introduction of the Nafion® dryer, the risk of moisture interfering with the analysis should be minimized, which should allow the application of the fast desorption pneumatics system in the extraction of rocks.

Results generated in this study were obtained using a set of instruments where the most current one was over twenty years of age. Using more contemporary instrumentation would most likely allow the method limits of detection to be significantly lowered. Also, the processing time could possibly be significantly reduced through more intense heating possible with focused microwave heating systems.

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