PERMEATION SAMPLING OF BTEX AND GASOLINE

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Cody A. Anderson

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Cody A. Anderson

Thesis

Approved:	Accepted:
_____	_____
Advisor James K. Hardy	Dean of the College Chand K. Midha
_____	_____
Faculty Reader Helen W. Richter	Dean of the Graduate School George R. Newkome
_____	_____
Department Chair Kim C. Calvo	Date

ABSTRACT

A method for solventless extraction and determination of gasoline components in water has been developed. This method uses silicone polycarbonate permeation membranes to extract the components, and collect them on a Tenax TA adsorbent. Samples were thermally desorbed into a gas chromatograph with flame ionization detection for separation and determination of the components. Time-weighted average (TWA) concentrations were determined by plotting the amount of analyte collected versus the product of concentration and time (ppb•hr). A linear response was seen in the TWA curves for benzene, toluene, ethylbenzene and the three isomers of xylene (BTEX). These components had detection limits from 1.4 ppb for m- and p-xylene to 2.7 ppb for toluene. The effects of temperature and common environmental contaminants were examined. The advantages of this method include being environmentally friendly due to the lack of solvent and having less steps for analysis than many standard methods.

DEDICATION

To Ris, your support and love has been so important to me while I work. You have given me everything you can to help.

ACKNOWLEDGEMENTS

Dr. James K. Hardy has given me his continued support throughout my endeavors. He has help developed both my knowledge and skills as a researcher. I would like to thank Heather Steele for teaching me and passing on what she learned. Also, thanks to Tammy Schumacher for all the help she provided.

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CHAPTER I

INTRODUCTION

Contamination of water by petroleum products is currently a top concern in the United States. As of June 4, 2010, the *Deepwater Horizon* oil spill has contaminated the shorelines in four US states and covered an area of nearly 10,000 square miles (1,2). The environmental impact of this disaster will be seen for years to come as cleanup efforts have work nonstop to save both wildlife and sensitive environmental areas. Heavy petroleum components of crude oil are the most visible contaminants and are easy to detect, whether it is in layers on the surface of the water or tar soaking into shorelines and covering wildlife. Other lighter and more water soluble components are much more difficult to detect. The compounds can linger in water supplies and not be treated by standard cleanup efforts.

Detection of volatile organic contamination in water typically involves grab sampling of a water sample for analysis. A purge-and-trap method is then often used to extract and analyze the contaminants. It is also common to use solid-phase microextraction in the analysis. In this method polymer coated fibers collect the contaminants from the sample and then the fibers are desorbed inside a gas chromatograph. One problem with these methods is the need to keep samples refrigerated during transport to the laboratory to prevent volatilization. Another issue is

grab samples only represent a single point in time. Fluctuation in concentration may occur at a particular location and could not be accounted for by grab sampling.

Permeation sampling can eliminate some of the problems with traditional methods. In this research a semipermeable membrane is placed between the water sample and a collecting adsorbent. The membrane allows only organic components to pass through and be collected. After the exposure time, the adsorbent in removed and thermally desorbed into a gas chromatograph. Time-weighted average concentrations are then recorded. This method can account for fluctuations in concentration by determining the average concentration over the exposure time. Also, field permeation samplers could be built for this method. This would require only the adsorbent to be transported back to the laboratory for analysis, and make transportation and storage easier.

CHAPTER II

HISTORICAL

Before the formation of the EPA in 1970, the United States government took several steps to regulate the spread of pollution in the environment. The River and Harbor Act of 1899 banned the dumping of any type of refuse into navigable waterways or their tributaries without a permit. The main goal of this act was not to deal with health concerns but the economic impact of blocked waterways. There were also provisions to limit people's ability to excavate, fill, or alter the course, condition, or capacity of any water source under the act's control. Some of the controls are still active today although most have been superseded by newer legislation (3).

In 1948 the Federal Water Pollution Control Act (FWPCA) was the first legislation to both control and work to eliminate pollution in water supplies. It provided money for water pollution research as well as loans for the construction of sewage treatment works. The Department of Justice was put in charge of pollution violation on interstate waterways (4). States were encouraged to develop measures to reduce pollution and set methods of enforcement within their boundaries.

This Act was amended in 1956 to give the federal government more power in enforcement (5). The government was allowed to directly pursue violators of the legislation and withhold federal funding from states that produced insufficient protection

plans. In 1961 it was updated to allow enforcement on all navigable waterways, not just those traveling interstate (6). The Water Quality Act of 1965 required states to set water quality standards and enforcement programs (7). The Clean Water Restoration Act of 1966 then gave financial support to state programs that complied with the new regulations (8).

The Air Pollution Control Act of 1955 was the first federal legislation involving air pollution (9). This act set up a program for the federal government to research and give out information to state and local governments on air pollution prevention and abatement. Amendments to this act in 1963 and 1967 expanded the scope of the government research to include air pollution monitoring and control as well as establishing active monitoring sites (10,11). The Clean Air Act Extension of 1970 developed comprehensive federal and state regulations to limit emissions (12). Funding was given to states that submitted acceptable enforcement plans. One of the major provisions of the Clean Air Act was to reduce automobile emissions. This Act set limits on hydrocarbon, carbon dioxide and nitrogen dioxide emissions produced by automobiles.

EPA History

Alongside the Clean Air Act, the federal government wanted to create a dedicated government agency for the protection of the environment. President Nixon wanted this agency to work on all aspects of the environment including air, water, solid waste and

radiation (13). A plan was eventually approved and the Environmental Protection Agency began operations on December 2, 1970.

The Federal Water Pollution Control Act of 1972 was written to give a similar structure to water pollution regulations as that of air in the Clean Air Act (14). The EPA would establish water quality and effluent standards for specific toxic pollutants. Efforts would be made to protect marine life and limit dumpage into waterways. Also, sewage treatment facilities would be constructed for both land based sources and marine vessels. An amendment to this Act known as the Clean Water Act of 1977 added regulations on the release of toxic substances into sewers and surface waters (15). It also mandated the EPA to create standards to account for all of the 65 substances placed on the Toxic Pollutant List. This list was later turned into the 129 compounds on the original Priority Pollutants List.

The Clean Air Act was also amended in 1977 adding provisions to prevent deterioration of air quality in areas already meeting the national air quality standards (16). This amendment dealt with geographical areas deemed “non-attainable” with current technologies such as adding stricter regulations on new construction in areas with below standard air quality. The Clean Air Act was again amended in 1990. A major part of the new law was in the area of smog prevention (17). Programs were initiated to reduce the production of ozone from stationary sources as well as reformulating gasoline. A list was also created of 189 toxic air pollutants, and regulations were set to monitor and reduce any major source of these pollutants.

In 1974, the Safe Drinking Water Act was passed. This Act ensured water quality in all public drinking water systems (18). Contamination concentrations are set for both hazardous substances and those causing aesthetic effects such as color and turbidity. Contaminants were divided into several classes including inorganic, organic, bacteriological and radiological. Two levels of regulations are set. The mandatory requirements are the Maximum Contaminant Levels (MCLs) and the nonenforceable health goals are the Maximum Contaminant Level Goals (MCLGs). Differences between the two levels were often based on technological restrictions for the determination of the contaminants. The Safe Drinking Water Act Amendments of 1986 expanded the list of contaminates to be monitored as well as mandating requirements for filtration and disinfection of eligible drinking water supplies (19). In the Safe Drinking Water Act Amendments of 1996 a "right-to-know" program was created requiring all community water systems to provide annual reports on detected contaminants, possible health effects and the source of the water distributed (20). This amendment also strengthened programs to improve infrastructure and management practices.

BTEX and Gasoline

Benzene, toluene, ethylbenzene and xylene (BTEX) are the simplest alkylbenzenes. They are all liquids at room temperature and are characterized by high vapor pressures and moderate solubility in water. Some physical properties of BTEX are shown in Table 1. Each component of BTEX is a commonly used solvent in industries

ranging from paints and plastics to food and pharmaceuticals. In 2008, benzene and ethylbenzene were the 11th and 20th most produced chemicals, respectively, in the United States (21).

The components of BTEX are known to cause serious health effects in humans. Benzene exposure can cause damage to bone marrow, decrease in red blood cells, excessive bleeding, and damage the immune system (22). Benzene is also a known carcinogen that can lead to leukemia (23). Toluene is known to cause liver and kidney damage as well as disrupting the function of the nervous system (24). Ethylbenzene exposure has been found to cause damage to the inner ear and hearing (25). The IARC also list it as being a possible human carcinogen (26). Xylene can have affects on the nervous system, and is believed to cause damage to the kidneys (27).

Table 1. Physical properties of BTEX components.

Component	Molecular Weight	Density (g/cm^3) (25°C)	Boiling Point (°C)	Log Octanol/Water Coefficient	Solubility in Water (g/L) (25°C)
benzene	78.11	0.873	80	2.13	1.80
ethylbenzene	106.17	0.867	136	3.15	0.16
m-xylene	106.16	0.860	139	3.20	0.16
o-xylene	106.16	0.876	138	3.13	0.17
p-xylene	106.16	0.857	144	3.15	0.16
toluene	92.44	0.867	111	2.73	0.52

The EPA regulates the release of BTEX components into the environment, and they appear on the Clean Air Act's list of hazardous air pollutants, the Safe Drinking Water Act's List of Contaminants and (except for xylene) the Clean Water Act's List of Priority Pollutants (17,28,29). The most specific regulations are found in drinking water standards. These regulations apply to public drinking water sources and government facilities. The Maximum Contaminant Levels (MCLs) for BTEX can be found in Table 2. Other than benzene, these standards allow higher concentration of the contaminants than other organic compounds on the list, but detection of other BTEX components can indicate the presence benzene (30). It is also important to note that benzene breaks down slower in water and soil than in air (22). Therefore benzene can stay longer in underground contamination and be transmitted through the groundwater.

Table 2. Maximum Contaminant Levels (MCLs) for BTEX components in drinking water.

Component	MCL (mg/L)
benzene	0.005
ethylbenzene	0.7
m-xylene	10*
o-xylene	10*
p-xylene	10*
toluene	1

*Xylenes are monitored as total xylene content.

Gasoline is a complex hydrocarbon mixture formed by the distillation of petroleum. The composition of gasoline has changed significantly since it was first produced. Pure distilled gasoline was used in the early part of the last century to run internal combustion engines and for cooking fires. This form is still available and is know as camp fuel or Coleman$^{(R)}$ Fuel (32). Additives are added to gasoline to enhance different properties in its storage and use. Tetraethyl lead was a common additive for several decades as an anti-knocking agent. The Clean Air Act phased out lead additives beginning in the 1970s due to their toxicity and interference with the catalytic converters of newer automobiles (12).

Methyl *tert*-butyl ether (MTBE) is also an anti-knocking agent that is being phased out by the EPA. MTBE was originally added to gasoline to replace the lead components. It has a higher water solubility than other components of gasoline and can easily contaminate a water supply if there is a gasoline spill. The main concern with MTBE is a strong odor and taste that makes water undrinkable. Replacements for MTBE have included compounds such as ethanol which is of no environmental concern (35). BTEX components are currently the most common additives to gasoline in the United States. They are added as an inexpensive way to increase the octane ratings (34). The average blend of gasoline contains between 12 and 18% BTEX by volume (31). This value is higher in the winter time because higher concentrations of volatile components are added to improve engine performance in cold weather. The EPA has set the limit of benzene concentration in gasoline to be <0.62% (v/v) by 2011 (35).

Underground Storage Tanks

The most common storage mechanism for gasoline and other fuel oils is in underground storage tanks (USTs). The EPA regulates the construction, operation and decommissioning of these tanks. An UST is defined as:

> "...any tank used to store petroleum or hazardous substances... the volume of which is 10% or more beneath the surface of the ground. This does not include, among other things, any farm or residential tank of 1,100 gallons or less capacity used for storing motor fuel for noncommercial purposes, tanks used for storing heating oil for consumptive use on the premises, or septic tanks (36)."

All operating USTs must have features including corrosion resistant shielding, automatic and manual monitoring systems for both soil and groundwater contamination, catch basins around tanks and piping to prevent spills and procedures for inventory control recording.

Even with current regulations there are thousands of UST leaks every year, most of which occur from gasoline tanks (37). The U.S. government has put a program in place to oversee the cleanup of hazardous waste sites, including gasoline leaks. This program is known as Superfund and was initiated in the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 and gained most of its financial support after the Superfund Amendments and Reauthorization Act of 1986 (38,39). The Superfund is responsible for treatment of hazardous waste sites ranging from emergency situations where there is an immediate threat to health or the environment, to remediation of less critical sites that have been placed on the EPA National Priorities List. Another product of the Superfund is the creation of the Agency for Toxic Substances and Disease

Registry (ATSDR). The ATSDR is responsible for implementing health related laws regarding hazardous waste in the environment. They work with the EPA who oversees the environmental aspects of Superfund cleanup and determines responsibility for the waste.

Methods of BTEX Determination

The EPA has developed standard methods for the determination of pollutants in water. These methods have been rigorously tested to provided the most accurate and precise ways to detect components with the technology currently available. By studying the results of many laboratories performing analyses on a particular contaminant, Practical Quantitation Limits (PQLs) have been set for the detection of all pollutants in their respective mediums. A PQL is defined as "*the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions* (40)." These are the goals set for all laboratories performing EPA analyses.

Most official EPA methods for extraction and analysis of BTEX from water use purge-and-trap along with GC-MS (41-43). In purge-and-trap, volatile organics are stripped from the sample by bubbling through an inert gas such as He or N_2. The analytes are then collected on an adsorbent placed in the gas flow. This adsorbent is thermally desorbed by rapid heating in a flow of inert gas directed into the gas chromatograph for analysis. While mass spectrometry is the most common detection used, the EPA has

maintained purge-and-trap methods using photoionization detection, electrolytic conductivity detection and even a combination of both detection methods in series (41,42,44).

Other extraction methods for BTEX have been developed and are in wide use. For these procedures not defined by official methods, the EPA has method approval and validation processes for laboratories wishing to use them. One popular method is headspace solid-phase microextraction (HS-SPME). This method has been used with success since the early 1990's (45-49). The procedure relies on an equilibrium between an aqueous sample and the vapor phase above it. The concentration of components in the vapor phase is proportional to that in the liquid phase. A coated silica fiber is exposed in the headspace region and collects the analytes. The fiber is then heated and thermally desorbed into a GC. A similar method of direct SPME is also used (48). In this procedure the fiber is exposed in the aqueous sample itself. This method is not preferred since equilibrium with the fiber take longer to occur, and the water samples need to be relatively clean (49).

Another method of analysis uses direct aqueous injection (DAI). In DAI, a water sample is injected directly into a GC. The large volume of water, as compared with the analytes, can be dealt with in one of two ways. First, the water is trapped in highly polar column while the nonpolar analytes continue through for detection (50-52). The water is then baked out of the column after analysis. The other procedure used to deal with the water is to trap it in an adsorbent in the injection port (53). The injection port is heated after analysis to desorb the water and vent it out of the injection port. DAI provides a

faster and simpler analysis than many other methods. Disadvantages of the method include the need for specialized equipment either in the injection port or the detector to handle the water and the water samples need to be clean.

With a combination and modification of two standard methods, GC-FID has also been used for detection of BTEX (54). One of which was designed for volatile aromatics, and the other was for nonhalogenated volatiles. Some methods have been adapted for use with LC. The most common detector in a LC system is UV, but FID and MS have also been used (49).

Permeation Sampling

Permeation sampling relies on the transport of an analyte through a semi-permeable membrane where there is a concentration gradient between either side of the membrane. As the membrane is exposed to the analyte solution, analytes begin to dissolve into the membrane. The analytes are transported through to the low concentration side at an increasing rate until the rate of diffusion reaches a steady state. The analytes are then collected and analyzed (55). A variety of polymer membranes have been developed for use with different types of analytes. Many factors contribute to an analyte's ability to permeate through a membrane including: size, shape, chemical properties of the analyte and membrane and interactions between the membrane and the analyte. The rate of diffusion is often controlled by maintaining a zero concentration zone, or “zero-sink”, at the collecting side of the membrane.

The performance of a polymer membrane can be described by the equation:

$$P = DS \quad (1)$$

where P is the permeation coefficient, D is the diffusion coefficient and S is the solubility coefficient. The diffusion coefficient is a characteristic of the polymer membrane relating the thickness of the membrane to the time it takes for an analyte to reach steady state through the membrane, also know as the lag time. The solubility coefficient is a factor related to the solubility of the analytes in the polymer membrane. From this equation it is shown that permeability is related to both thermodynamics in the solubility term and kinetics in the diffusion term (56). Since solubility is an equilibrium term, it can be calculated easily for conventional thermodynamics. On the other hand, determining diffusion in polymers is much more difficult. Some molecular dynamics calculations have been performed on small gas molecules, but the results have been limited (55).

There are two models used here to describe permeation, resistance-in-series and solution-diffusion. The resistance-in-series model is composed of a series of five steps which describe the movement of analytes through the membrane (57).

1. Diffusion through the boundary layer.
2. Sorption into the membrane.
3. Diffusion through the membrane.
4. Desorption out of the membrane.
5. Diffusion through the boundary layer.

At each of these steps, the analytes encounter a certain amount of resistance to the permeation process. This cumulative effect of this resistance defines the molar flux of

the membrane. Molar flux is the rate at which molecules can move through a membrane per unit area given in mol/($cm^2 \cdot s$). Under steady state conditions the molar flux is constant and has the same value at any point on the membrane (58).

The boundary layer can be described as a thin layer of immobile fluid that covers the surface of the membrane. This layer is different from the rest of the solution in both composition and behavior. As permeants are depleted from this layer and move into the membrane, the concentration in the boundary layer becomes lower. The nonpermeating molecules will tend to move out of the boundary layer as permeants are drawn in by the concentration gradient and move toward the surface of the membrane (59).

The solution-diffusion model permeation can be described by two processes, dissolution into and out of the membrane and diffusion through the membrane. Diffusion occurs from random motions of molecules moving through a concentration gradient. In the present research it is assumed the diffusional flux is effectively constant due to short lag times and the change in concentration of the analyte solution is zero. With these assumptions, diffusion can be describe by Fick's first law of diffusion:

$$J = -D\frac{dC}{dx} \tag{2}$$

where J is the diffusional flux with units of mass per unit time (M/t), D is the diffusion coefficient, and dC/dx is the change in concentration inside the length of the membrane (60). Flow occurs in one direction and moves from high to low concentration as is indicated by the negative sign.

Integrating Fick's first law over the length of the membrane the diffusional flux can be described as:

$$J = DA\,\frac{(C_1 - C_2)}{L} \tag{3}$$

where A is the area of the membrane, L is the length of the membrane, and C_1 and C_2 are the concentrations of analyte just inside the membrane immediately after sorption and just prior to desorption, respectively. By Henry's law, both C_1 and C_2 are proportional to the concentration of analytes on either side of the membrane. Therefore, C_1 is the concentration of analyte solution, C, multiplied by the solubility coefficient of the membrane, and C_2 is zero. This gives:

$$J = \frac{DACS}{L} \tag{4}$$

For this research, the values of D, A, S, and L are all constants and can be combined into one permeation constant:

$$K = \frac{DAS}{L} \tag{5}$$

giving:

$$J = KC \tag{6}$$

By multiplying both sides of this equation by time, t, a working form is given as:

$$M = KCt \tag{7}$$

where M is mass in μg, K has units of μg/(ppb•hr), C is in ppb and t is in hours.

Advantages in the use of permeation sampling arise from it traditionally being a passive sampling technique, though there has been some work combining permeation membranes with active sampling techniques (61). Passive sampling is any technique in which analytes move from a sampling medium to a collecting medium due only to a difference in chemical potential. The sampling devices require no pumping or other

electronic equipment. The lack of pumping action can prevent agitation of still-water sources such as groundwater wells (62).

There are two types of passive sampling techniques, equilibrium and kinetic. Equilibrium sampling works on a time scale where there is a thermodynamic equilibrium between the analyte solution and the collecting medium. These types of samplers are often used when exposure time is not taken into account during analysis. This allows for simpler determination of analyte concentrations. Disadvantages of equilibrium samplers include equilibrium times changing for different analyes and results being affected by variations in analyte concentrations (63). Kinetic samplers function based on a linear rate of flow of analytes from the analyte solution to the collecting medium. This one-way flow provides time-weighted average concentration information. This can account for any fluctuations in concentration during the exposure time. Other advantages of kinetic passive samplers include the ability to detect ultra-trace level contaminants at long exposure times (64).

In this project, kinetic passive sampling was used to created a method for determination of gasoline in water. Sampling devices with a semi-permeable membrane were used to selectively extract gasoline components. The sampling devices contained an absorbant to collect the permeates and maintain a "zero-sink". Analytes were then desorbed from the adsorbent using thermal desorption into a gas chromatograph to separate and quantify the components. Time-weighted average concentrations were then determined from the total mass of analyte collected.

CHAPTER III

EXPERIMENTAL

Permeation Sampling Devices

The construction of sampling devices used a 5.5 cm glass tube on which a 0.001 mm silicone polycarbonate membrane (MEM-213 copolymer, Silicone Specialty Products, Ballston Spa, NY) was affixed using a low VOC silicone sealant (DAP Aquarium Sealant, Baltimore, MD). To reduce volatilation from the sample solution, 2 L Erlenmeyer flasks were cut at the top so that the sampling devices would fit inside. Foam tape (1/2" X 1/16", 3M, St. Paul, MN) was placed around the sampling devices to hold the membranes at a consistent depth in the flasks during exposure. The sampling devices were also capped with a size 12 stopper and a 1 mL pipette to allow minimal venting while maintaining ambient pressure. Figure 1 shows a diagram of the completed sampling device.

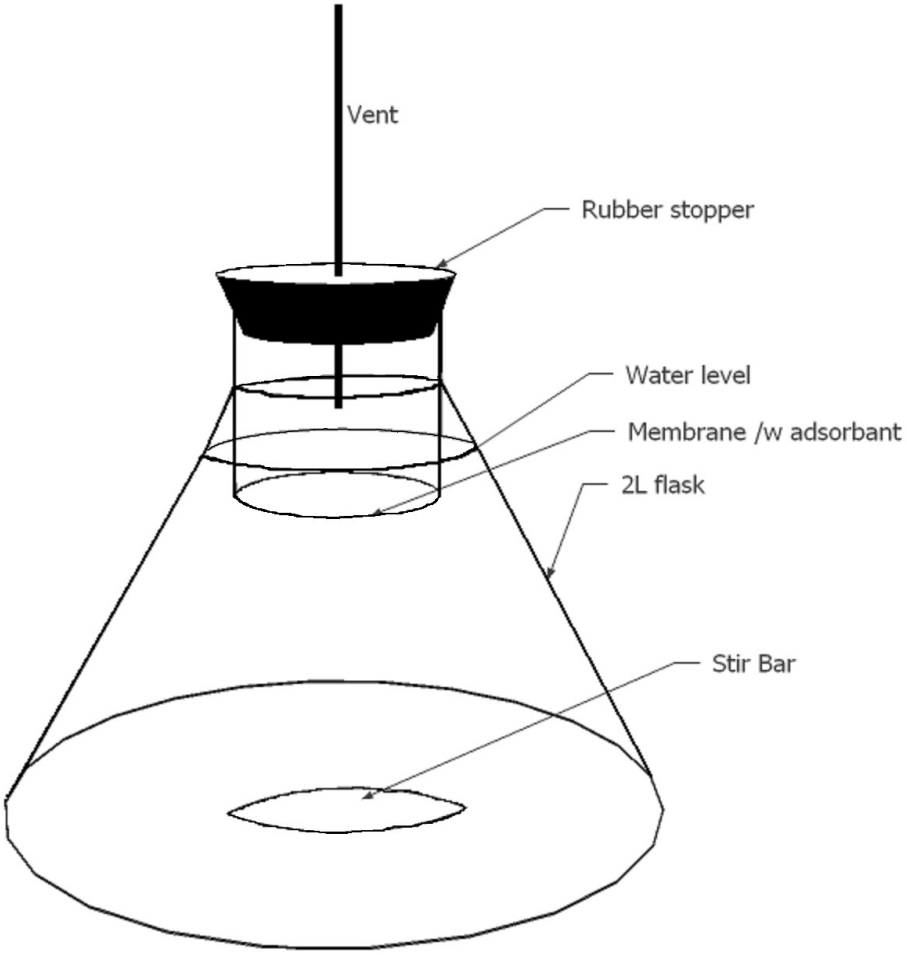


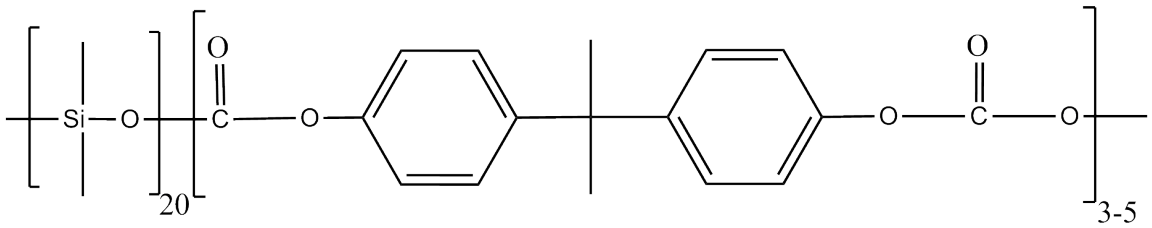
Figure 1. Permeation sampling device.

Thermal Desorption

A mass of 100 ±1 mg Tenax TA (mesh 35/60, Scientific Instrument Services, Ringoes, NJ) was placed in the sampling devices and exposed to solutions of BTEX or gasoline. Tenax TA was chosen as the adsorbent due to its high thermal stability up to 350 ºC. Chemical structures for Tenax TA and the copolymer membrane are shown in Figure 2. The exposure temperatures were controlled for all samples with a VWR Refrigerated Circulator Model 1160S (VWR, Chester PA). The solutions were mixed during the exposure using a stir bar. At the end of the exposure time the Tenax TA was poured into a thermal desorption tube for immediate analysis. The thermal desorption tubes were plugged at one end with glass wool (Supelco, Bellefonte, PA) to retain the Tenax TA but allow the volatilized components to pass through the tube.

The analysis was performed with an Envirochem Thermal Desorption Unit Model 850 (Supelco, Bellefonte, PA) connected to a Hewlett-Packard 5890 Gas Chromatograph (Agilent, Santa Clara, CA) with a flame ionization detector. A Petrocol DH 50.2 (Supelco, Bellefonte, PA) 50 m column with an internal diameter of 0.2 mm and a film thickness of 5 µm was used. The valve compartment of the thermal desorption unit was maintained at a temperature of 250 °C with a transfer line to the GC at 200 °C. The samples were desorbed at a temperature of 250 °C. The detector was set at 310 °C. The initial temperature was held for 5 minutes at 35 °C, then raised at a rate of 3 °C/min to 70 °C and held at that temperature for 5 minutes. The final step raised the temperature 10 °C/min to 250 °C and held for 5 minutes.

(a)



(b)

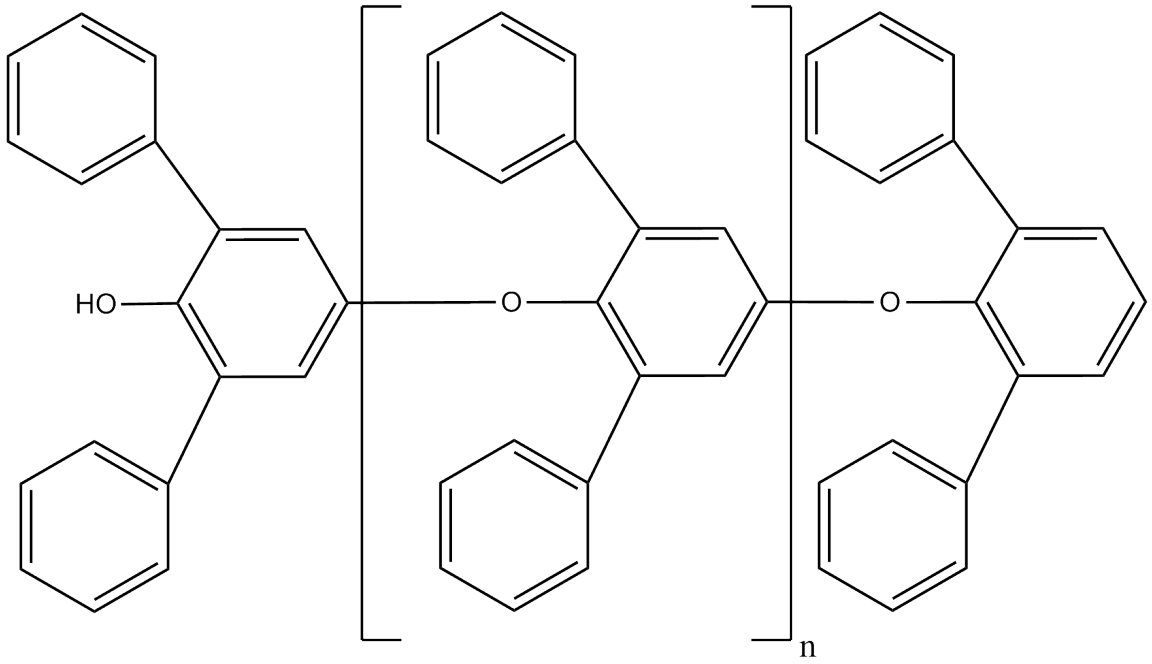


Figure 2. Structure of (a) MEM-213 copolymer membrane and (b) Tenax TA adsobent.

The Tenax TA was cleaned and recycled after desorption. It was first washed and filtered with methanol. Then, it was placed in an oven at 100 °C for one hour to remove a majority of the methanol. Finally, the Tenax TA was heated under a flow of nitrogen to a temperature of 300 °C for at least 2 hours to remove any remaining contaminants.

Calibration of Sampling Devices

Calibration curves were created by exposing Tenax TA to aqueous solutions of BTEX. Standard BTEX solutions were made by diluting in methanol (ACS Certified, Fisher, Fairlawn, NJ) the six BTEX components: benzene (ACS Certified, EM Science, Gibbstown, NJ), toluene (GC Grade, Burdick & Jackson, Muskegon, MI), ethylbenzene (ACS Certified, Aldrich Chemical Co., Milwaukee, WI), m-xylene (Puriss., Fluka Analytical, Buchs, Switzerland), o-xylene (Reagent Grade, Aldrich Chemical Co., Milwauke, WI) and p-xylene (Pure, Acros Organics, Fairlawn NJ). Aliquots of the BTEX standards were added to water to achieve the desired concentrations. The temperature of the solutions was controlled using a VWR Refrigerated Circulator Model 1160S (VWR, Chester, PA). At set periods of time the samplers were removed and the Tenax TA was analyzed using thermal desorption. By varying both the concentration and exposure time, time-weighted average plots were created from peak areas of the chromatograms. A linear relationship of these plots provided the means to calculate the concentrations of each of the components in a solution containing gasoline. Aqueous solutions of gasoline were analyzed using the same method as BTEX. Time-weighted average (TWA) plots of gasoline solutions were used to determine the amounts of gasoline contamination that is present in a water sample.

Lag Time

The lag time of each BTEX component was determined in the sampling devices. The lag time is the time it takes for the components to reach steady-state diffusion through the membrane. The lag time is used to determine the minimum exposure time to produce a linear response in the TWA plots. Determination of lag time was accomplished by performing exposures at constant BTEX concentration and temperature. These samples covered a range of short exposure times less than those used in calibration. BTEX concentrations were kept at 100 ppb and the temperature was 20 ºC. The exposure times ranged from 2 to 30 minutes, and exposure time versus amount of analyte collected was plotted to determine the actual lag times of each component.

Temperature Effects

Changes in temperature can have an effect on the permeation of components through the membrane. This information can be used the adjust the calibrations of the method for different exposure temperatures. The effect of these changes was studied by performing BTEX exposures at constant concentration and exposure time while varying the temperature. The solutions were kept at a concentration of 50 ppb and exposed for 2 hours. The temperature was varied in a range from 6 to 25 ºC and held constant during the exposure time. Plots were made to examine the effects of temperature on each of the BTEX components.

Interferents

In real world water samples there may be compounds in the water that interfere with the analyses being performed. These contaminants can come from many different sources and appear in a water supply. Some common environmental contaminants were studied that could affect on the permeation rates of BTEX. The interferents studied were sodium chloride (Fisher Scientific, Fairlawn, NJ), sodium nitrate (EM Science, Gibbstown, NJ), and sodium sulfate (Fisher Scientific, Fairlawn, NJ). Sodium chloride was used to see the effects of a compound with high ionic strength on permeation. Nitrate and sulfate are common because one of their sources is acid rain which forms from pollution in the atmosphere (65). Sodium sulfate is also a weak base and can cause small changes in the pH. Related work has shown pH not to affect permeation in monocyclic aromatics (66).

The amount of each contaminant was varied in accordance with normal environmental levels. Sodium sulfate and sodium chloride were examined in a range of 2.5 to 10.0 mM. Sodium nitrate was studied in a range of 1.0 to 4.0 mM. Each of the interferents were tested in a solution with a concentration of 1 ppm gasoline and a temperature of 20 ºC for 1 hour.

Stability

Due to the high volatility of the components being studied, their stability in solution had to be monitored to ensure accurate results. The samples were immediately analyzed after exposure to minimize volatilization of the components from the adsorbent at room temperature. Stock solutions were kept in a refrigerator at 8 ºC and only removed to prepare aqueous solutions. Sample responses were monitored over time to watch for any change in average response. The component expected to be most affected was benzene due to it having the highest volatility. At any significant reduction in response, a fresh standard was prepared.

The stability of BTEX solutions in the sampling apparatus were also analyzed. Samples of constant concentration and temperature were analyzed at various exposure times. A plot of response versus exposure time was made for each component. The plots were examined to determine at what point the response began to drop off and was no longer linear. This information was used when developing calibrations so that they can be performed under linear conditions. Stability of this type is not an issue in real world samples because the source water will be continuously refreshed during the sampling period.

CHAPTER IV

RESULTS

Method Development

The initial step in developing a procedure for the analysis of gasoline in water was to adapt a gas chromatography method. This method had to satisfy two main conditions. First, the BTEX components had to be adequately resolved. Second, the method had to elute all high molecular weight gasoline components during analysis to prevent carryover of the peaks. A Petrocol DH 50.2 column which was specially designed to work with petrochemicals such as gasoline was chosen for the analysis. It has been reported that for complete separation of all BTEX components (particularly the m,p-xylenes), a column length of 100 meters is needed (67).

Initial solutions of gasoline diluted in methanol were injected into the gas chromatograph for analysis. It was confirmed in this initial evaluation the column had insignificant length for complete separation. The decision was made to treat the m,p-xylene peak as a single peak for evaluation. This approach has been used in previous work (51,53,54). The results for this peak were recorded as the average concentration of the two components. It was assumed that these components have a similar permeation rate.

The temperature program of the gas chromatograph was set up having an initial slow temperature ramp that would separate and elute the BTEX components. Then, a faster temperature ramp was used to elute all of the rest of the possible components in gasoline. After switching from liquid injection to thermal desorption, a peak broadening issue developed. A temperature hold period was added to the middle of the temperature program to promote separation of the closest eluting BTEX peaks, ethylbenzene and m,p-xylene.

BTEX Calibration

Previous work has shown that benzene, ethylbenzene, and toluene have a linear response with respect to concentration and exposure time though the membrane used (68). Time-weighted average (TWA) plots were created by performing exposures while varying the concentration and exposure time of the samples. Standard solutions of BTEX diluted in methanol were mixed with ultrapure water to achieve the desired concentrations. A chromatogram of the BTEX is shown in Figure 3. The concentration of the solutions ranged from 1 to 100 ppb, and the exposure times were in the range of 1 to 4 hours. Plots of exposure level (in ppb•hours) versus amount of analyte collected were created for each of the components. It was found that all of the BTEX components had a linear response with the thermal desorption setup. These plots are shown along with their linear regressions in Figure 4.

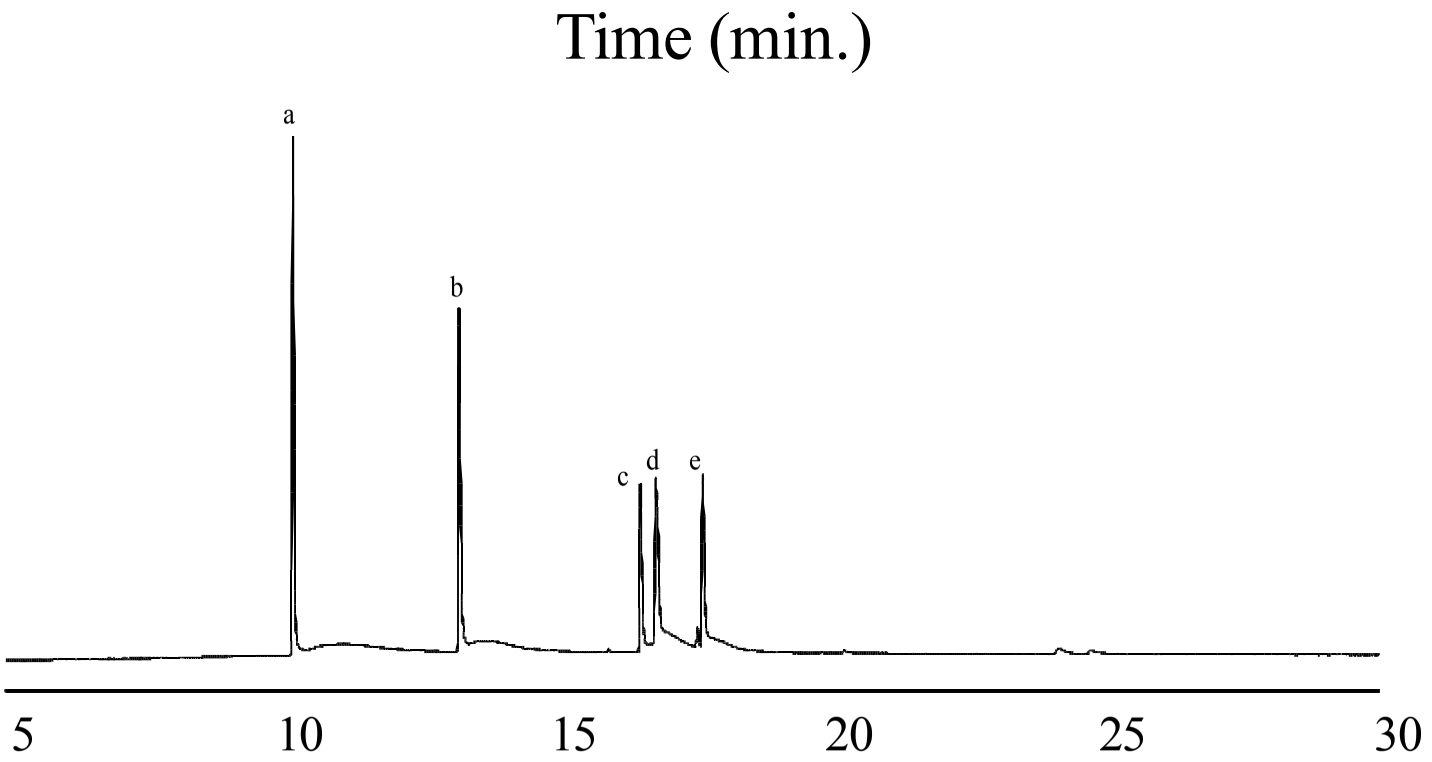


Figure 3. BTEX chromatogram. (a) benzene, (b) toluene, (c) ethylbenzene, (d) m,p-xylene, (e) o-xylene.

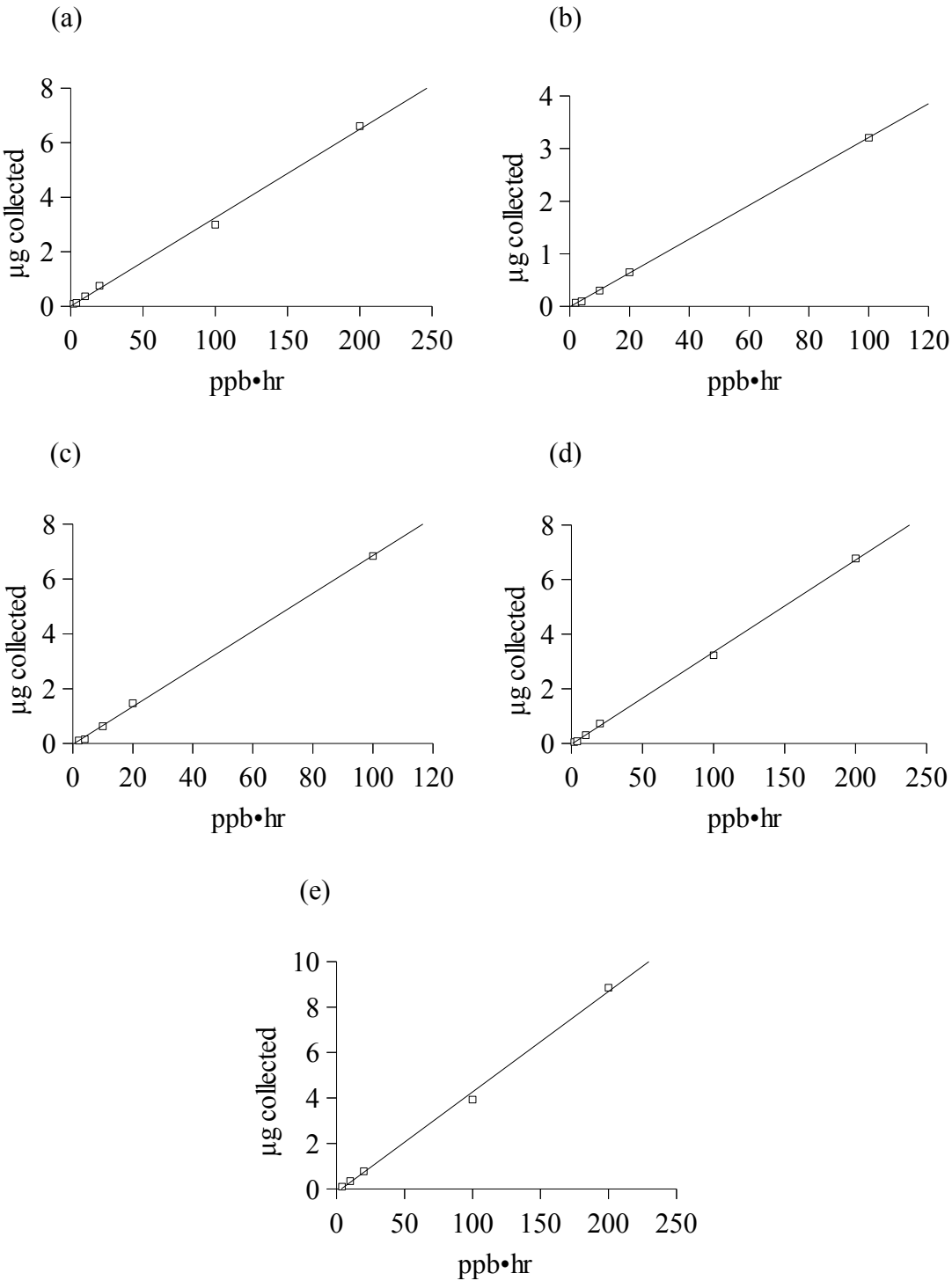


Figure 4. Time-weighted average plots for: (a) benzene, (b) ethylbenzene, (c) m,p-xylene, (d) o-xylene, and (e) toluene.

Table 3 shows the results from the calibration curves. Permeation constants, K, were calculated for each of the components using the slopes of the calibration curves. Since m-xylene and p-xylene coeluted, K is reported as the average permeation rate. The permeation constants were determined to be in the range from 0.0322 μg/(ppb•hr) for ethylbenzene to 0.0442 μg/(ppb•hr) for toluene. The R^2 values for the plots ranged from 0.9973 to 0.9998. The precision of the method calculated from 12 solutions at 30 ppb•hours and the %RSD was less than 18% for all components.

Gasoline Calibration

The results from the BTEX calibrations were used to create calibration curves of gasoline in water. The gasoline used for calibration was purchased from BP on 9/21/2008 and had an octane rating of 87. Due to the time of year, this gasoline was a summer blend. Summer blends of gasoline have lower concentration of volatile components, and would therefore be more difficult for this method to determine BTEX concentrations. This gasoline was mixed and placed in sealed sample containers for the creation of standard solutions later. When standards were created, a sample container was opened and the required amount of gasoline was remove and diluted with methanol. The rest of the sample container was discarded. These one-time-use samples help to reduce the loss of volatile components.

Table 3. Calibration results for BTEX.

Component	Concentration Range (ppb)	Exposure Range (ppb•hr)	K (µg/ppb•hr)	R^2	%RSD
benzene	1 – 100	2 – 200	0.0324	0.9975	14.3
ethylbenzene	1 – 100	2 – 100	0.0322	0.9998	16.4
m,p-xylene	1 – 100	2 – 100	0.0345	0.9993	15.5
o-xylene	1 – 100	2 – 200	0.0337	0.9994	17.6
toluene	1 – 100	4 – 200	0.0442	0.9973	12.1

Aliquots of the gasoline standards were added to water and analyzed using the same method as BTEX. A chromatogram of the gasoline samples is shown in Figure 5. The concentration of gasoline ranged from 100 ppb to 2.5 ppm, and the exposure times were between 1 and 4 hours. TWA plots were created by relating the exposure level of gasoline (in ppm•hours) to the apparent exposure level of each of the BTEX components (in ppb•hours). A linear relationship between BTEX and gasoline is shown in Figure 6 for all of the BTEX components. The results from the calibration of gasoline are shown in Table 4. It is expected that the complex mixture of gasoline may have an effect on the precision of the results. It can be seen from the graphs that this may be somewhat true, but the components still had good precision with R^2 values ranging from 0.9352 for benzene to 0.9609 for o-xylene.

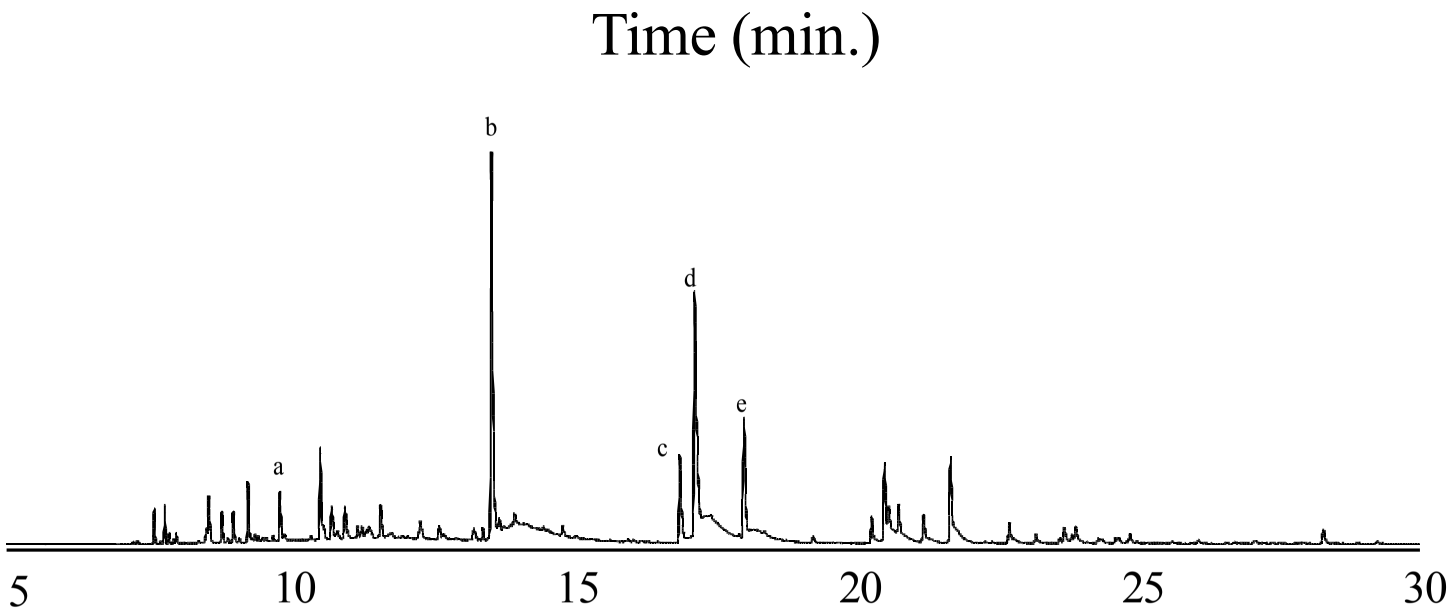


Figure 5. Gasoline chromatogram. (a) benzene, (b) toluene, (c) ethylbenzene, (d) m,p-xylene, (e) o-xylene.

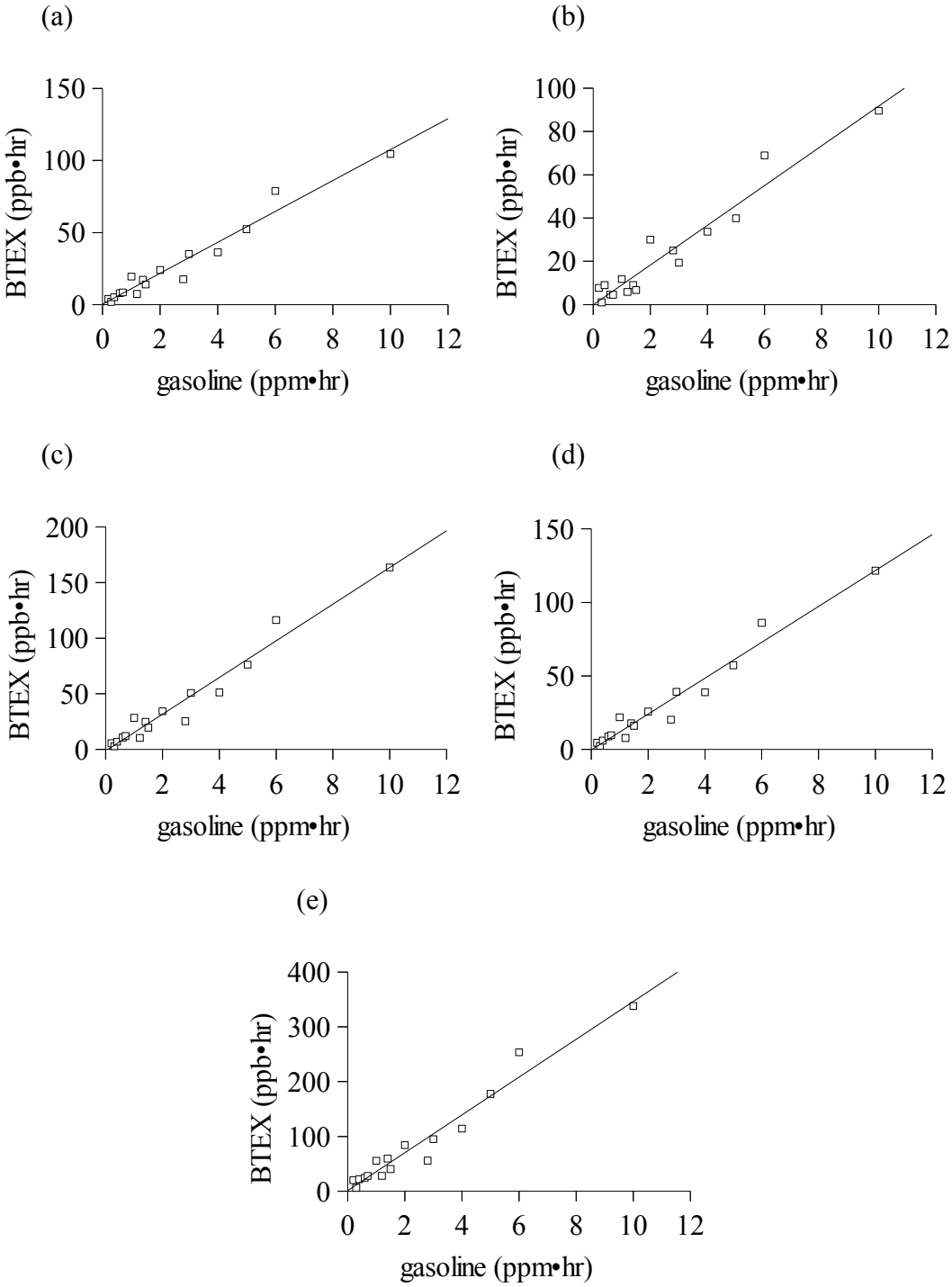


Figure 6. Time-weighted concentrations of components in gasoline for: (a) benzene, (b) ethylbenzene, (c) m,p-xylene, (d) o-xylene, and (e) toluene.

Table 4. Calibration results for gasoline sample.

Component	Concentration Range (ppm)	Exposure Range (ppm•hr)	R^2	% of gasoline
benzene	0.1 – 2.5	0.2 – 10	0.9352	0.92
ethylbenzene	0.1 – 2.5	0.2 – 10	0.9561	1.07
m,p-xylene	0.1 – 2.5	0.2 – 10	0.9586	2.80
o-xylene	0.1 – 2.5	0.2 – 10	0.9609	1.22
toluene	0.1 – 2.5	0.2 – 10	0.9548	3.45

The concentration of each of the components in the water sample is calculated by dividing the exposure level by the number of hours of exposure. This information was used to calculate the composition of the gasoline used. The composition of BTEX in the gasoline was determined from a 5 ppm•hr sample. The component concentrations ranged from 0.92% for benzene to 3.45% for toluene. These values fall within the normal composition range of gasoline (69).

Detection Limits

The limits of quantification (LOQ) were calculated for both BTEX and the gasoline used for evaluation. Determination of the detection limits was achieved by performing blank exposures. These exposures involved filling the sampling devices with ultrapure water and no other components. The exposure were performed at a temperature of 20 °C for 1 hour. The LOQs were calculated at ten standard deviations of the blank using the regression equations for the BTEX components. Table 5 shows the detection limits determined which range from 1.395 ppb for m,p-xylenes to 2.747 ppb for toluene.

Table 5. Detection limits of BTEX and the required concentration of gasoline to achieve those limits.

Component	BTEX LOQ (ppb)	BTEX LOQ (µg/L)	MCL (µg/L)	Gasoline LOQ (ppm)
benzene	1.408	1.230	5	0.146
ethylbenzene	1.845	1.599	700	0.196
m,p-xylene	1.395	1.198	10,000*	0.170
o-xylene	1.790	1.568	10,000*	0.173
toluene	2.747	2.382	1000	0.115

The BTEX LOQs were used to determine the detection limits of the gasoline sample in water. For each of the components, the minimum amount of gasoline needed to be in solution to reach LOQ was calculated. These results are also in Table 5. Ethylbenzene (which was the second lowest concentration component) required the highest concentration of gasoline to be present for detection. Therefore, for the gasoline sample studied, 0.196 ppm of gasoline needed to be present to detect all of the BTEX components.

The EPA has set Maximum Contaminant Levels (MCLs) for all of the BTEX components. The MCLs have been set in µg/L so the values used in this study in ppb need to be converted for comparison. From Table 5 it can be seen that this method detects concentrations below the MCLs for all of the components. The EPA has also set detection limits (DLs) on all methods used for determination of pollutants. The DLs for all of the BTEX components in water are set at 0.5 µg/L (70). The method here has not met the requirements for an EPA approved method of analysis for any of the components. The LOQs may have been reduced by a more thorough cleaning of equipment from run to run including the sampling devices and the Tenax TA.

Lag Time Determination

Lag time is the time it takes for chemicals to reach steady-state permeation through the membrane. This is the minimum time of exposure for which the method will give linear results. All exposure times used in calibration have to be significantly longer than the lag time to minimize the effects from the pre-equilibrium state of the samplers.

The lag time was determined by using short exposure times (in the minute range) and evaluating the lower limit of linear response. Exposures were preformed at a concentration of 100 ppb BTEX. The exposure times used ranged from 2 to 30 minutes. Plots were made of exposure time versus amount of analyte collected for each of the BTEX components. An example lag time plot is shown in Figure 7 for benzene. The lag time of each of the components is calculated as the x-intercept from a linear regression. Table 6 shows the calculated lag times for each of the components. It can be seen that the minimum exposure time used in calibration (1 hour) was sufficiently longer that any of the lag times.

Table 6. Lag time of permeation for each component.

Component	Lagtime (min.)
Benzene	0.73
Ethylbenzene	1.48
M,p-xylene	1.72
O-xylene	1.46
Toluene	0.82

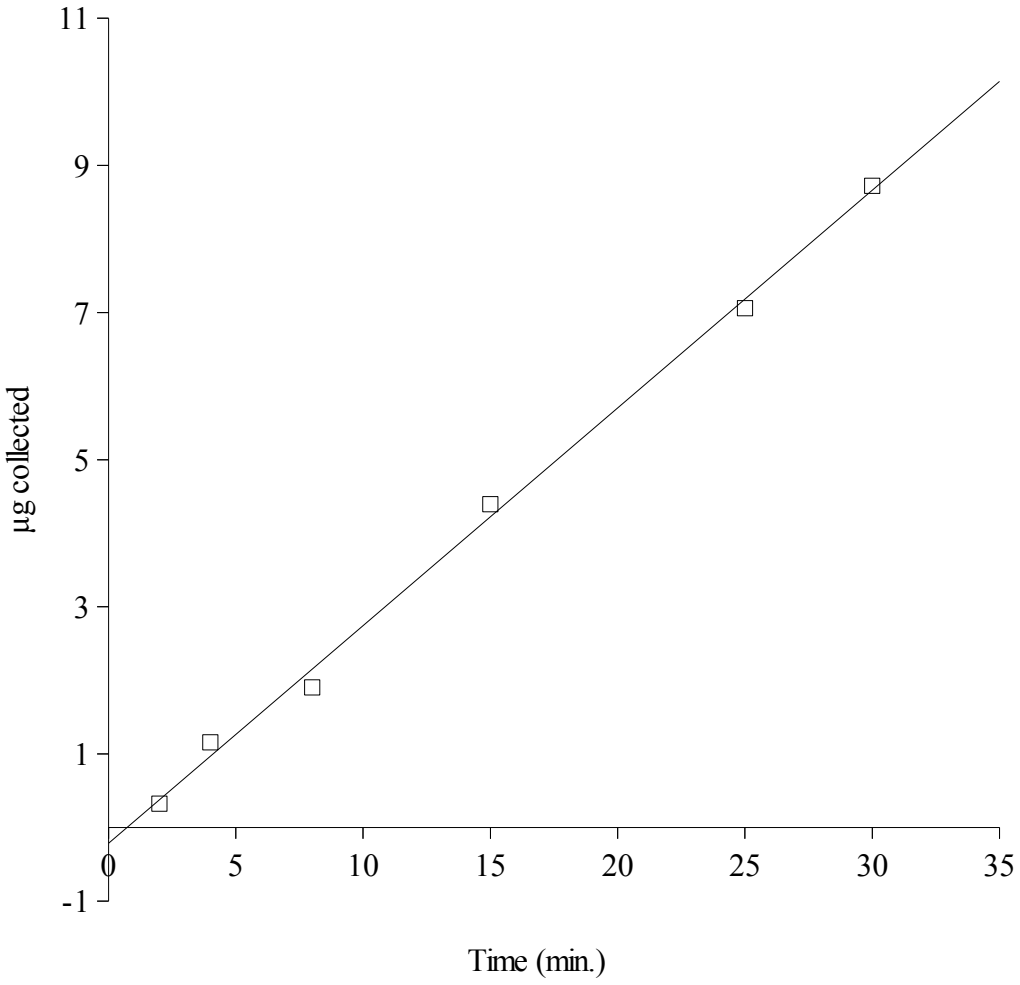


Figure 7. Example lag time plot for benzene.

Temperature Effects

The effects of temperature on the permeation rates of BTEX through the membrane were evaluated. Temperature can change the permeation rates by affecting the volatility of the components and the behavior of the membrane itself. Exposures were performed at concentrations of 6 ppb BTEX for 2 hours. A regulated circulator was used

to keep the temperature constant during the entire exposure. The temperature of the water bath was varied from 6 °C to 25 °C. Plots were made for each of the BTEX components of temperature versus amount of analyte collected, and are shown in Figure 8. An increase in the permeation constant with respect temperature is shown for all components. Table 7 shows the percentage change for each degree increase in temperature. The effects were all less than 4% per degree change.

The calibrated model could be adapted for use with a range of temperatures. The collected amount of analyte would be factored by the change in permeation rate to determine the concentration of the contaminants. Groundwater temperature normally varies less than 2°C per day (71). This small variation could be accounted for by recording the temperature once during the sampling period. This single value would be used as the correct temperature for factoring.

Table 7. Change in permeation constant due to temperature.

Component	%increase/°C	R^2
benzene	2.22	0.9836
ethylbenzene	3.34	0.9297
m,p-xylene	3.42	0.9448
o-xylene	3.20	0.9415
toluene	2.66	0.9789

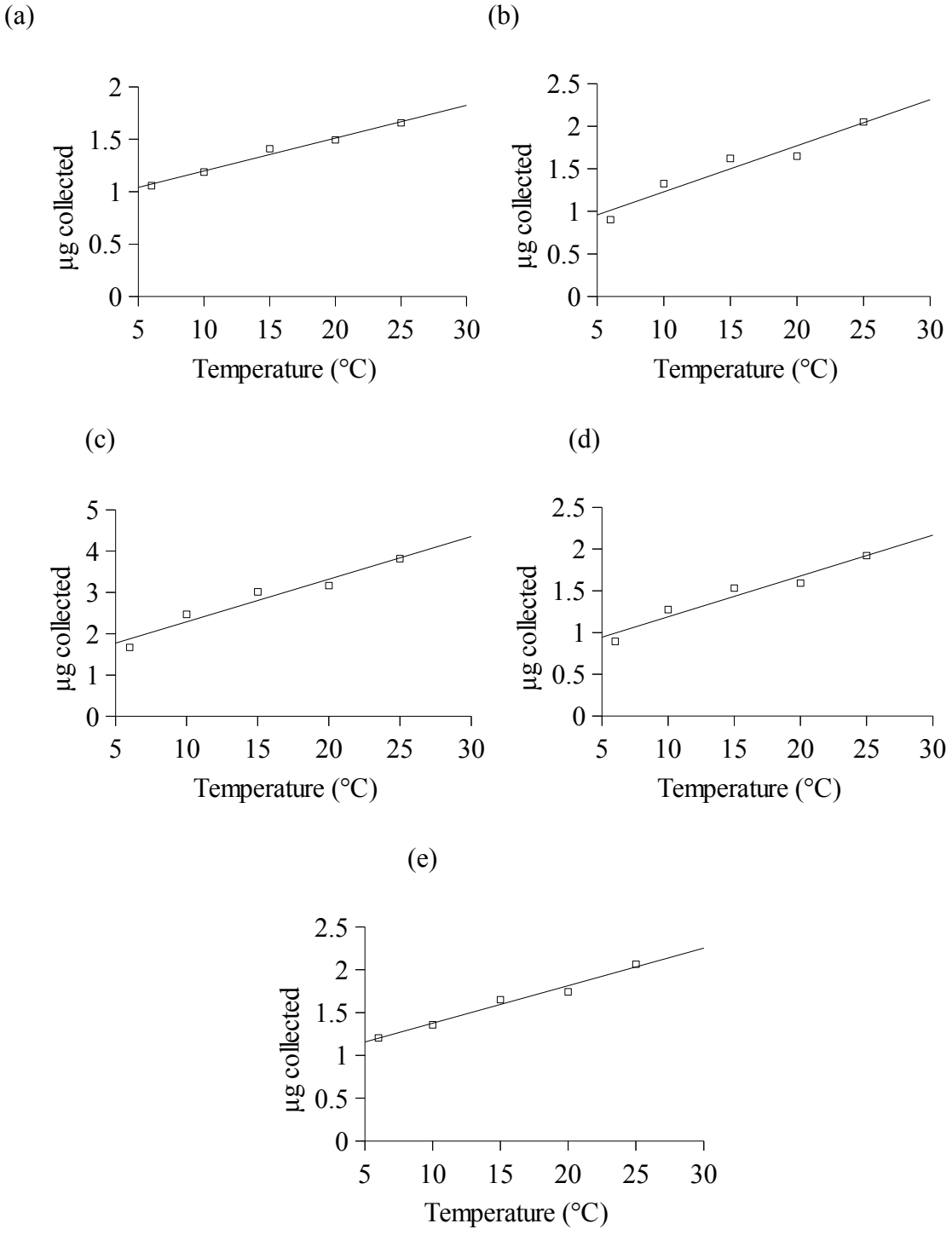


Figure 8. Temperature effect plots for: (a) benzene, (b) ethylbenzene, (c) m,p-xylene, (d) o-xylene, and (e) toluene.

Effects of Interferents

Real world groundwater often contain substances that could possibly affect the permeability of analytes through the membrane. The effect of some of the common substances found in groundwater were investigated. These substances included sodium chloride, sodium nitrate, and sodium sulfate. Solutions of 1 ppm gasoline held at a temperature of 20 °C and exposed for 1 hour were used for evaluation. This study was performed with gasoline samples to see the combined effect from both the interferents and the other gasoline components. The concentration range studied for each interferent was at normal levels found in environmental samples. Sodium sulfate and sodium chloride were examined from 2.5 to 10.0 mM. Sodium nitrate was studied in a range of 1.0 to 4.0 mM. Graphs were made showing the percent change in permeation versus the concentration of interferents. These plots are shown in Figures 9-11. No immediate trends appear due to the concentration of any of the interferents. The maximum relative deviation (MRD) from a standard solution was recorded for each interferent. Table 8 shows deviations were as high as 17%, but this is still within a normal range for gasoline. These presence of these interferents in groundwater samples should have no significant effect on the method.

Table 8. Maximum relative deviations (MRD) from environmental interferents.

Interferent	MRD (%)
sodium chloride	17
sodium nitrate	16
sodium sulfate	16

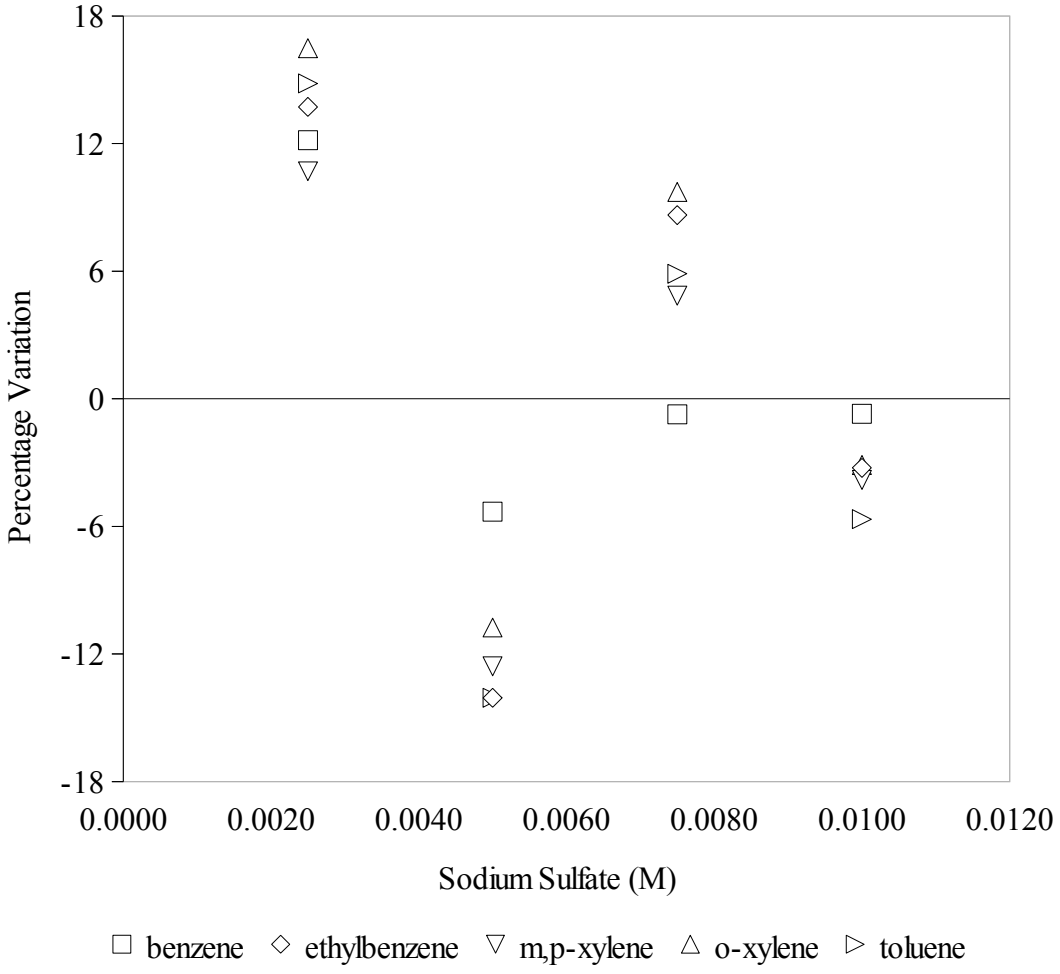


Figure 9. Variation due to the presence of sodium sulfate.

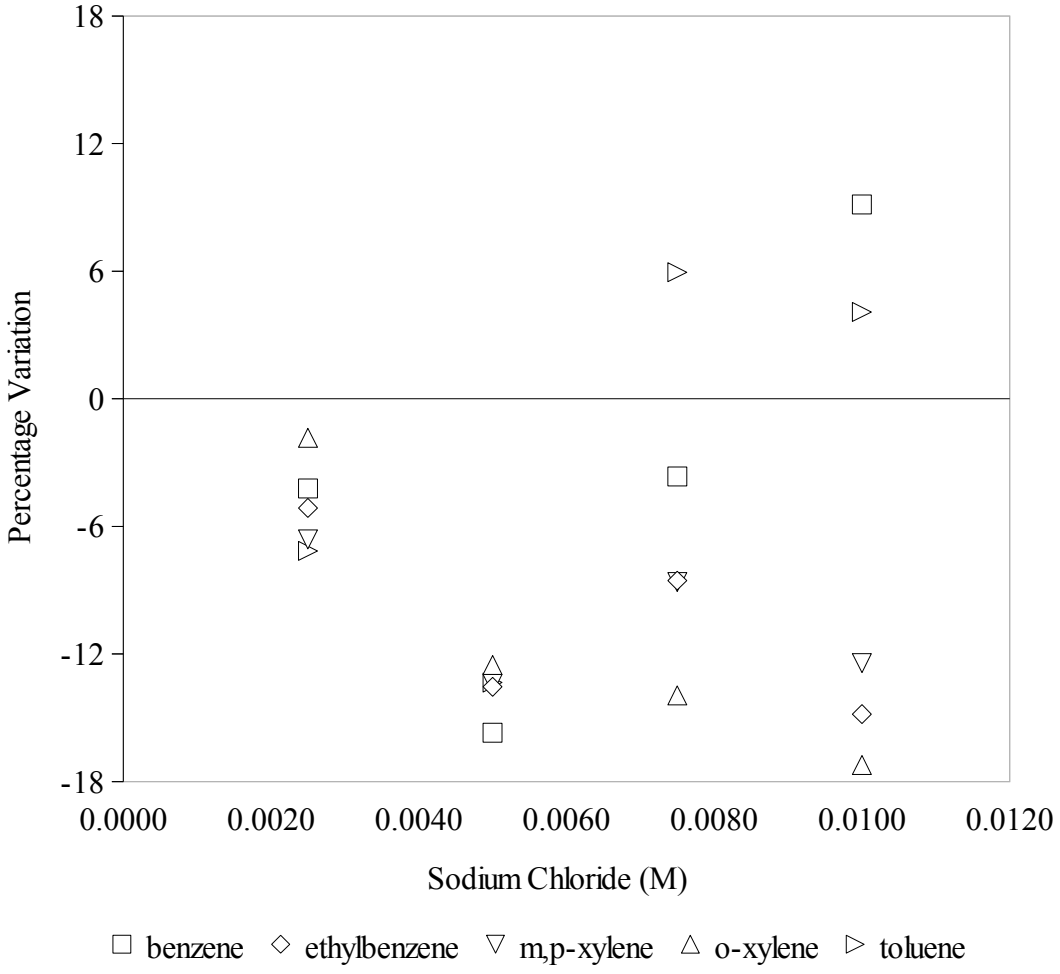


Figure 10. Variation due to the presence of sodium chloride.

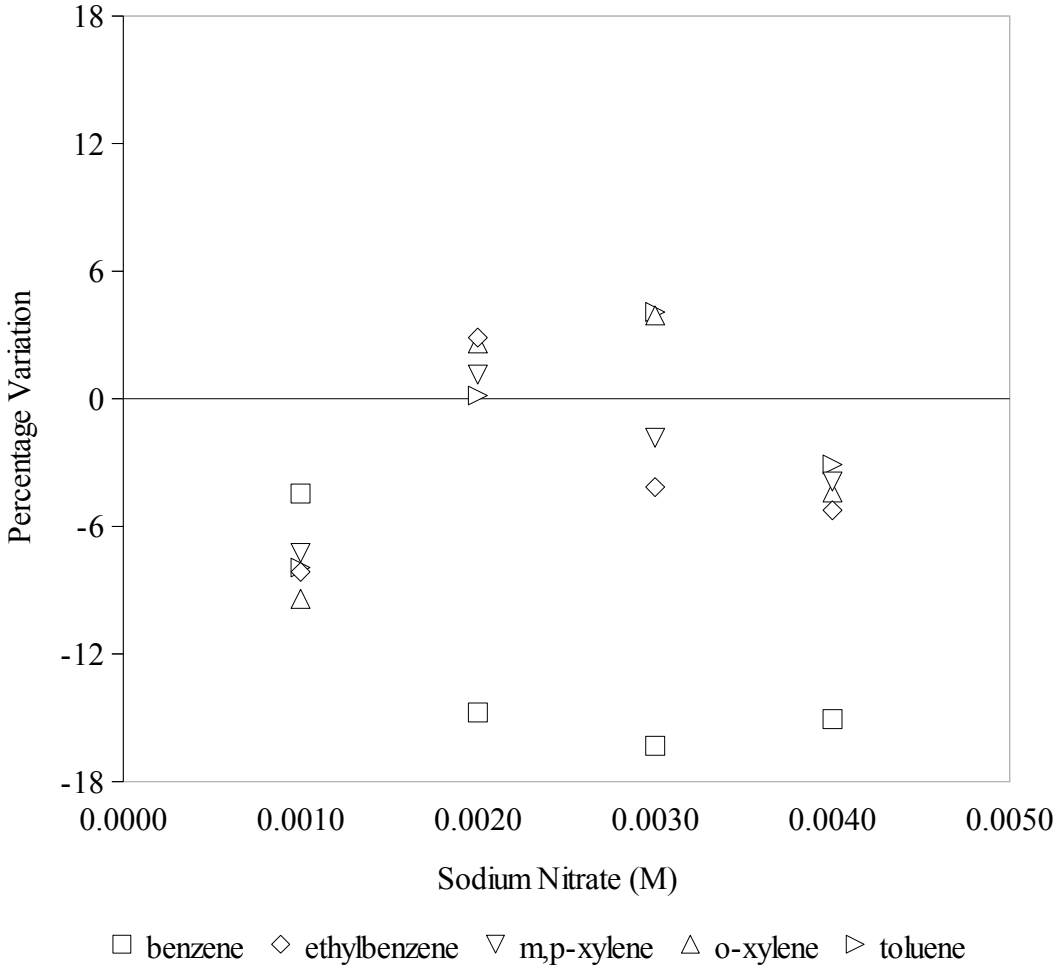


Figure 11. Variation due to the presence of sodium nitrate.

Stability

Studies were performed to determine both the stability of BTEX in stock solutions and in the sampling devices. During the construction of the calibration curves, sample exposures were repeated at different times to verify the results. Samples made immediately after creation of the standard solution were compared with samples made at later times from the same solution. It was found that samples with the same exposure level which were made more than one month after the creation of the standard solution showed at least a 10% decrease in response for benzene. Thus, fresh standard solutions of BTEX and gasoline were made on a monthly basis.

The stability of BTEX components in the sampling devices was evaluated by determining the maximum exposure time. The maximum exposure time is the point at which the method no longer gives a linear response. Exposures were performed with a solution of 15 ppb BTEX at a temperature of 20 °C. Exposure times ranged from 1 hour to 15 hours. A plot of exposure time versus amount of analyte collected was created for each of the BTEX components. The Limit of Linearity (LOL) was then determined as the point where the components began deviating from the 95% confidence interval. The resulting LOLs are shown in Table 9. Benzene began deviating from linearity after an exposure time of 9 hours. This is the maximum exposure time that should be used for calibration with this device.

Table 9. Limit of Linearity (LOL) in time at 95% confidence interval.

Component	LOL (Hours)
benzene	9
ethylbenzene	12
m,p-xylene	11
o-xylene	11
toluene	11

CHAPTER V

SUMMARY

A solventless method utilizing permeation sampling has been developed for the detection of BTEX in water. The sampling devices were constructed using a semi-permeable polymeric membrane. This membrane allows transport of organic components but not water. The components of interest were collected inside the device on an adsorbent. This adsorbent was then thermally flushed into a gas chromatograph to analyze the components.

This method resulted in time-weighted average concentration data. This data showed a linear relationship between the amount of each component collected and changes in both exposure time and concentration. Calibration curves were created to determine the concentrations of BTEX components in a water sample given the exposure time. The limits of detection for this method are all lower than the maximum contaminant levels set by the EPA for drinking water. On the other hand, the EPA requirements for detection limits of BTEX are not met under the described setup of this research.

The concentration of BTEX was also determined in gasoline contaminated water samples. The complex mixture of hydrocarbons in gasoline was seen to have an effect on the precision of the results, but the method was still able to determine concentrations for

all components. All components could be quantified from sub-ppm level concentrations of the representative gasoline sample.

Several conditions were studied which may have affected the permeation rates of the BTEX components. The lag time of each component in the membrane was determined as well as the stability of solutions in the sampling device. It was verified that calibration curves were constructed using exposure times in the linear permeation range; both significantly longer than the lag times and shorter than the maximum exposure time. Effects due to different temperatures were less than 4% per degree. These effects could be accounted for by using temperature factors for each component. The presence of environmental interferents were also studied for their affect on permeation rates. The interferents studied were sodium chloride, sodium nitrate, and sodium sulfate. It was found that none of these had a significant effect.

Use of permeation sampling has several advantages over traditional methods. These include the ability to perform extraction of components in the field. The adsorbent can then be removed and taken to the lab, making transportation and storage easier. With time-weighted average sampling, variations in concentration over time can be accounted for. This is an improvement over grab sampling techniques which only measure concentration at the point in time when the sample is taken.

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