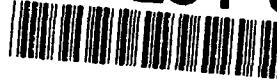


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USE OF INFRARED SPECTROMETRY TO DETERMINE
THE EFFECT OF TRICHLOROETHYLENE RESIDENT
TIME ON DESORPTION RATES FROM FLINT CLAY

THESIS

Peter LaPuma, Captain, USAF

AFIT/GEE/ENP/94S-03

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USE OF INFRARED SPECTROMETRY TO DETERMINE THE EFFECT
OF TRICHLOROETHYLENE RESIDENT TIME ON DESORPTION
RATES FROM FLINT CLAY

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In Partial Fullfillment of the
Requirements for the Degree of
Master of Science in Engineering and Environmental Management

Peter LaPuma, B.S.
Captain, USAF

August 1994

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Acknowledgments

I would like to thank my thesis advisor Major Perram who was instrumental in accomplishing this thesis. I have learned a great deal about research, and many physics concepts from him and I am honored to have had the pleasure of working with him.

I would also like to thank my reader, Dr Bleckmann who provided encouragement and guidance throughout this thesis. I thank him for giving me his time in providing a different viewpoint.

I would also like to thank my fellow classmates Ben Kindt and Abdu Fares who helped make light of the long hours and frustrating times. We made a strong team as each of us brought our different talents to use. This thesis could not have been done with out them.

Most of all I would like to thank my wife, Cheryl, and my boys, Michael and Nathan for the patience and endurance over the last 15 months. Their continuous support for me in this effort was a greatly needed source of encouragement and I love them for it. Thanks Cheryl, it won't happen again.

Peter LaPuma

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Abstract

This laboratory based thesis investigated the desorption rate of trichloroethylene (TCE) from flint clay while varying the resident time of TCE exposed to the clay. It is thought that in long contaminated soil, a majority of contaminant mass will become entrained within the interior of the soil particles to slowly desorb out of the soil over long periods of time. Recent studies suggest that the longer a contaminant is resident in soil, the longer the contaminant will take to desorb from the soil. To understand more about soil desorption, this experiment was developed using infrared spectroscopy to detect TCE vapor that desorbed from clay contaminated with TCE. Several experiments involved clay samples exposed to TCE from one day up to 56 days. The samples were then allowed to desorb in enclosed glass tubes over 36 hours. There was an initial, rapid desorption that occurs in the first hour of each experiment followed by a leveling off. This initial desorption mechanism appears to be independent of resident time and may be associated with TCE desorbing from the surface sites of the clay particles. The data from clay exposed to TCE for longer times gradually increases. This may suggest a second desorption mechanism associated with the slower diffusion of TCE out of the interior of the soil matrix. However, more research is needed to confirm this theory as the data in this thesis is too limited to draw firm conclusions about the slower, long term desorption.

USE OF INFRARED SPECTROMETRY TO DETERMINE
THE EFFECT OF TRICHLOROETHYLENE RESIDENT TIME ON
DESORPTION RATES FROM FLINT CLAY

I. Introduction

1.1 Overview

1,1,2-Trichloroethylene (TCE) is a colorless, volatile organic compound (VOC) with a wide variety of uses as a solvent. TCE has been extensively used in industry as a degreaser for metal parts and electronic components, and it is used in the dry cleaning industry. TCE was once used in the medical profession as a general anesthetic, and in the food processing industry as an extraction agent to decaffeinate coffee (1:3-5). The Air Force has been using TCE to degrease aircraft, aircraft parts, cleaning electronic components, and etc. Up until the mid 1970s, TCE was thought to be a relatively safe chemical. Consequently, inadequate disposal practices and handling techniques have resulted in many areas of the country, including Air Force bases, having TCE contaminated soil and/or groundwater. In fact, TCE is present in 35% of US Superfund sites, making TCE the most prevalent volatile organic compounds (VOCs) among clean-up sites (2:4).

TCE contamination has far reaching legal, economic and political implications. According to the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), any Potentially Responsible Party (PRP) has partial or total clean-up responsibility for remediating a contaminated site listed in the National Priority List (NPL). PRPs are also legally responsible for any injury or death resulting from a contaminated site. The clean-up and litigation costs for these sites have proven to be quite costly (3:251-320). The Air Force has been identified as a PRP at many NPL sites that contain TCE as the predominant contaminant.

The Maximum Contaminant Level (MCL) set by the EPA under the Safe Drinking Water Act is 5 ppb. This is the level considered legally "safe" for human consumption according to the EPA. 5 ppb is the mathematical equivalent of only 1/2 teaspoon (8 teaspoons in a US ounce) in a 20' x 40' x 5' pool containing 100,000 gallons of pure water. Considering the amounts of TCE inappropriately disposed of in the past, the small amount of TCE required to contaminate large volumes of water above the MCL and the expensive cost to clean-up a site, one begins to appreciate the magnitude of the problem.

A great deal of attention has been directed toward the remediation and treatment of VOCs such as TCE for ground water. In fact, ground water remediation is being accomplished at many contamination sites using a "pump and treat" system. This

relatively common remediation technique involves mechanically pumping water out of the ground for treatment at the surface. The water is often treated in an air stripper where the water is cascaded down through beads or baffles as clean air is pumped upwards to volatilize the chemical out of the water via aeration. This treatment technique has been reasonably effective in treating the ground water for many compounds. Unfortunately, the efficiency of a "pump and treat" system tends to decrease with time and reaches some limiting asymptotic value (4:547).

The limitations of the system are likely due to the slow desorption of TCE from the soil in the vadose zone into the ground water (5:274). There is a growing concern over VOCs contained in the vadose zone or unsaturated zone. The vadose zone is not saturated with water and is the area between the ground surface and the water table. A strong body of evidence indicates that a majority of VOCs will become entrained in the soil particles of the vadose zone. These untreated VOCs that are immobilized in the vadose zone will be desorbed over time and can continue a steady, downward migration toward the ground water for years. This is suspected to be the major reason that ground water remediation has been limited (4:548). Ground water, treated to safe concentrations, may become re-contaminated after remediation was initially considered successful due to this migration.

Although a large volume of research has been conducted concerning ground water contamination of VOCs, little has been done to address desorption rates of VOC contamination in the vadose zone. Desorption rates are poorly understood, in part because there are so many factors suspected to influence the rate of desorption of VOCs from soils. Some of the influencing factors include the characteristics of the soil, the moisture content of the soil, the length of time (resident time) that the soil is exposed to the VOCs, the concentration of the VOCs in the water, ambient temperature, relative humidity, and the amount of organic materia in soil.

Because of the many factors that influence VOC desorption rates from soil and the difficulty in simulating field conditions in a laboratory, the effects of different factors on the rate of desorption is poorly understood. One factor that appears to strongly influence the amount of VOC entrained in the soil is the residence time of the VOC in contact with the soil. Current knowledge indicates that the longer a VOC remains in the vadose zone, the greater the percentage of the VOC will become adsorbed into the soil matrix (6:682).

This research effort evaluated the effect of TCE resident time in the soil. This laboratory based experiment was designed to hold all other variables constant and expose flint clay to liquid TCE for varied lengths of time. The desorption of liquid TCE from the clay to the vapor state in the atmosphere above the clay was

measured with an infrared spectrometry system over time. Then, the TCE vapor that desorbed from the soil was purged from the soil's atmosphere and the subsequent desorption (TCE vapor build-up) was recorded over time. The system was fully enclosed to evaluate the desorption phenomenon in a non-destructive manner so that the soil sample and its atmosphere were not disturbed during the test.

Understanding the effects of exposure time, as it relates to TCE desorption from soil adds knowledge necessary to design more efficient remediation techniques for contaminated sites. The advantages of predicting the desorption rates, relative to the contaminant resident time, enables modelers to more accurately estimate the amount of time and expense that will realistically be expected to clean a given site. Accurate modeling is important to the Air Force, which has many sites contaminated with TCE, because it allows greater accuracy in budgeting the time and cost of remediation. It also provides insight when negotiating with EPA regulators on clean-up standards and in estimating the impact on future land use. It enhances the optimization of remediation designs to address the total problem of treating the vadose zone as well as ground water contamination to prevent recontamination.

1.2 Research Objective

This study observed the effect of TCE residence time on the rate of desorption from flint clay. Liquid TCE was exposed to clean flint clay for approximately one day, one week and two months. The subsequent desorption rate, measured using infrared spectrometry, allowed us to observe changes in the rate of desorption to the surrounding atmosphere under different exposure times. The hypothesis tested was that the longer TCE contacts soil particles, the faster the desorption rate will be at first, and the greater the total amount of TCE that will be desorbed to the surrounding atmosphere. We expected to observe a fast desorption caused by the TCE molecules attached to the surface of the soil and a longer, slower desorption associated with the TCE desorbing out of the interior of the soil particles. Figure 1 graphically represents this hypothesis.

This study also evaluated the effectiveness of using the infrared spectrometry experimental method to study the phenomenon of VOC desorption rates from soil.

1.3 Terms Used In This Study

Adsorption - Surface phenomenon where molecules are assimilated to the bonding sites of a solid (7:18). In this case, bonding

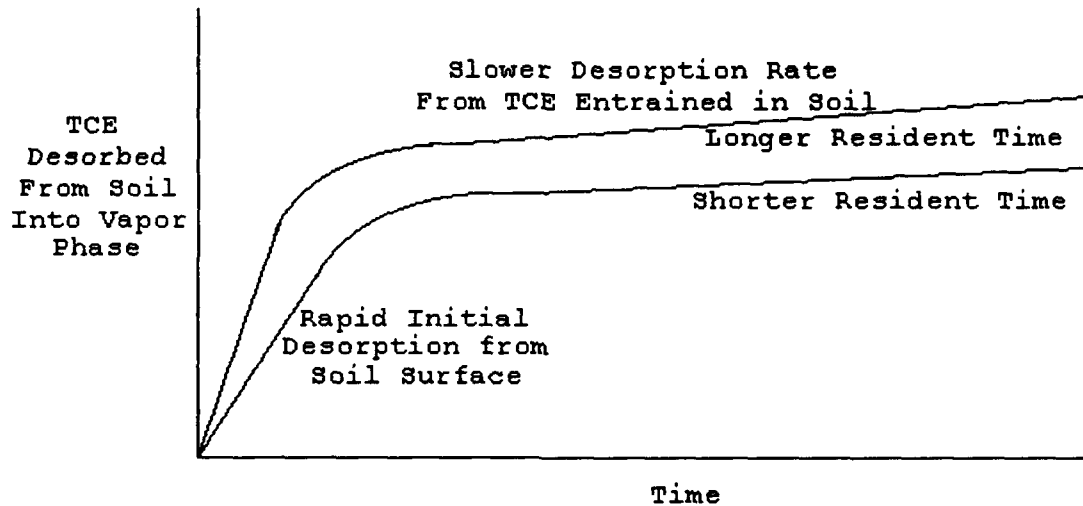


Figure 1
Expected TCE Desorption Rate Data

to the outer surface of soil particles.

CERCLA - 1980 Comprehensive Environmental Response, Compensation, and Liability Act passed by Congress to legislate clean-up responsibility and standards for pre-1980 hazardous waste and spill sites (3:267-318).

Desorption - Surface phenomenon where molecules are detached from the bonding sites of an solid surface, also used interchangeably in this thesis where molecules diffuse through the interior matrix of the soil particles and then desorb from the soil surface.

Diffusion - gradual mixing of molecules of two or more substances as a result of random thermal motion (7:368) more specifically in this thesis, movement of a TCE molecule through the interior of a soil particle

NPL - National Priority List - List of contaminated sites determined by the EPA according to the Hazardous Ranking System that are regulated under the 1980 CERCLA Act (3:277).

PRP - Potentially Responsible Parties - All parties identified to be legally liable for a NPL site. There can be one or several PRPs for a single site and if there are several, a determination must be made to the portion of clean-up costs each will be responsible for (3:289-310).

MCL - Maximum Contaminant Level - The maximum legal limit set by the EPA for National Drinking Water standards regulated under the Safe Drinking Water Standard. A maximum level determined to be safe for human consumption (3:250-259).

Organic material - Substance naturally found as a component of soil, derived from living matter (7:926).

Vadose zone - Unsaturated subsurface area between the water table and the ground surface. The vadose zone has some moisture content less than 100%. Defined as soil layers that have the three-phase system of air, water, and soil (8:90).

Volatile Organic Compounds (VOCs) - There is no precise definition of a VOC. Compounds appear to have been grouped into a class known as VOCs based on their amenability to extraction, separation and detection by a coordinated and compatible analytical procedure. In the US there are 35 organic compounds listed in the EPA Hazardous Substance List for VOCs to include TCE. Their physiochemical properties can vary over several orders of magnitude (2:5).

II. Literature Review

2.1 Background

TCE is the most prevalent VOC among clean-up sites partly due to the fact that it has been heavily used as an industrial solvent (234,000 metric tons produced annually worldwide) (9:365). Also contributing to the magnitude of TCE contamination is the fact that TCE was thought to be a safe chemical up until the mid-70s. A study performed in 1976 found TCE to be a suspected carcinogen (10:17-21). As a result of this study, EPA added TCE to the U.S. EPA's list of hazardous substances (10:17). Due to the perceived safety of TCE before this time, inappropriate and inexpensive methods were used to dispose of the product. Such methods include the dumping of TCE in landfills, drywells, or even directly on the ground. The poor historical disposal methods of TCE have contaminated much of the groundwater in the areas where TCE was dumped (10:21).

In recent years there has been increasing public and scientific concern with hazardous waste and the contamination of groundwater (11:337). Air Force bases across the country are forced to deal with TCE contamination problems and the cost of clean-up.

Some specific chemical and physical properties of TCE are listed in Table 1. Properties of interest include density (1.46 g/cm³), indicating that TCE will sink in water. TCE's relatively low

molecular weight and a relatively high vapor pressure, point to its high volatility. TCE's solubility (0.7 g/liter at 20°C) produces an equilibrium concentration of 700,000 ppb, well above the EPA's MCL of 5 ppb.

Table 1

Chemical and Physical Properties of TCE

<u>Property</u>	<u>Value</u>	<u>Units</u>
Physical State (@ 15°C and 1 atm)	Liquid	
Formula	CHCl=CCl ₂	Unitless
Molecular Weight	131.39	g/mol
Density (@20°C)	1.46	g/cm ³
Liquid Surface tension (@20°C)	0.0293	N/m
Vapor Specific Gravity	4.5	g/cm ³
Latent Heat of Vaporization	2.4x10 ⁵	J/kg
Viscosity	0.57	cP
Solubility (@ 20°C)	0.7	g/liter
Henry's Constant	0.232	Unitless
Partition Coefficient	0.199	ml/g
Vapor Pressure @ 20°C	58.0	torr
EPA's Maximum Contaminant Level	5.0	ppb
Temperatures:		
Freezing Point	-86.8	°C
Melting Point	-70.0	°C
Boiling Point	86.7	°C
Flash Point	89.6	°C
Auto ignition temperature	788.0	°F

2.2 Health Effects

The MCL for drinking water set by the EPA is 5 ppb. The World Health Organization has set a safe limit of 30 ppb (9:365). Dissolved concentrations of TCE in ground water are reported to range from 0.01 ppb to 5500 ppb. Many factors go into promulgating an MCL into EPA regulations such as technical limitations in achieving the MCL, the degree of uncertainty concerning the cancer risk, the quality of health hazard studies (human observations are generally of better quality than animal studies), or even the political climate surrounding the chemical (fear factor). Due to the number of occurrences where TCE exceeds the MCL, it is considered a major potential health hazard.

TCE is a suspected carcinogen and it may also be converted by reductive dehalogenation to more potent carcinogens such as vinyl chloride (9:365). TCE can be poisonous by inhalation, intravenous, and subcutaneous routes. In high concentrations, TCE can cause skin and eye irritation, hepatitis, or depression of the central nervous system. However, these non-carcinogenic effects result from concentrations that are far greater than values observed in drinking water (9:365). TCE's odor cannot be noticed in drinking water until its concentrations are several orders of magnitude greater than the MCL (9:365).

2.3 VOC Contamination and Treatment of Groundwater

As mentioned earlier, VOC groundwater remediation is being accomplished at many contamination sites using a "pump and treat" technique. This relatively common remediation technique involves volatilizing the chemical out of the water via aeration and has been reasonably effective in removing VOCs from groundwater.

The decrease in efficiency of a "pump and treat" system over time is likely due to the slow desorption of TCE from the soil in the vadose zone (4:547). VOC contaminants are strongly sorbed to the vadose zone soil matrix, which makes remediation by conventional aboveground treatment techniques both slow and inefficient. This is due to the fact that contaminants can persist in desorbing from soil for long periods of time (5:274). VOCs will be slowly released from the vadose soil and sink to the groundwater acting as a continuous source of groundwater contamination.

One approach to address groundwater clean-up efforts, as economically as possible, is the development of "pulsed pumping". This is where the pumps used in a "pump and treat" remediation technique are periodically cycled on and off. When the pumps are on and the contaminant is removed, the pumped groundwater generally becomes cleaner (reduced contaminant concentration) with time. After some time, the pumps are turned off to allow the soil to desorb the contaminant into the groundwater. Then, when the pumps are turned back on, the water has a higher

contaminant concentration and the effective removal of contaminant per unit of pumping time is increased because there is now more contaminant in the water to be removed. Pulsed pumping is advantageous because it enhances the removal efficiency which should reduce the overall cost. Research has been done to study the optimal "pulsed pumping" schedule to minimize cost (12). However, studies are limited due to the poor understanding of the rate and magnitude of VOC desorption from soils.

2.4 VOC Contamination of the Vadose Zone

Although a great deal of research and remediation effort has focused on the treatment of VOC contaminated groundwater, little has been accomplished in the study of vadose zone contamination. This is partly due to the fact that the desorption phenomenon in ground water is a relatively recent observation. Also, there are many variables that can influence the desorption rates of a chemical such as humidity, temperature, soil characteristics, chemical characteristics and length of exposure time. If groundwater is contaminated at a site, it is a logical assumption that the vadose zone above the groundwater is also contaminated to some degree. There is growing need to understand the effects on desorption rates of different chemicals in different soils in the vadose zone, due to its impact on groundwater remediation.

In order to clean-up Air Force sites more efficiently, we first need to understand the influences on the desorption rates of the contaminant of concern. A better understanding of desorption rates in the vadose zone will allow a more accurate pulsed pumping design cycle or indicate the need for a different clean-up method altogether. Studying the influences on soil desorption rates of TCE will help the Air Force in determining the realistic amount of time needed to remediate a site. The remediation goal of the EPA at many contaminated sites has been to get TCE groundwater concentrations below the MCL of 5 ppb (9:365). A better understanding of desorption rates will allow the Air Force to more accurately estimate the time and money it will take to remediate a site.

2.5 Remediation of Vadose Zone for VOCs

TCE, like all other VOCs, will exist in the vadose zone in five different locations. TCE may exist as:

1. a vapor trapped in the air of the soil's void spaces
2. a free liquid in the soils void spaces
3. a dissolved solvent in the soil's water
4. adsorbed to the surface of soil particles
5. firmly entrained within the interior of the soil

(13:1886)

The Vapor Extraction System (VES) is the predominant remediation method to recover VOCs in the vadose zone (14). The VES involves forcing large volumes of fresh air through the contaminated area to extract the trapped contaminant. This system is quite effective for the upper three phases (shown above), but is relatively ineffective for the last two phases. (13:1886)

Recent research indicates that the slow desorption of the VOCs entrained in the soil particles is impervious to the VES treatment method (15:1107-1108). Under equilibrium conditions, the majority of VOCs will be present in the solid portion of the vadose zone (2:5-7). Recent studies indicate that the remaining VOCs can represent up to 90% of the total amount of VOCs in the contamination area, particularly if the contaminant has been in contact with the soil for long periods of time (13:1887). A graphical representation of the distribution of 30 liters of TCE in one m³ soil at equilibrium can be seen in Figure 2. The numbers 1 - 5 on the graph correspond to the five locations listed above that TCE may reside in. Figure 2 illustrates that on a volumetric basis, a significant fraction of the total VOCs reside in solids to be released over long time periods (16:5).

2.6 Poor VOC Measurement Techniques

Another complication in remediation of the vadose zone is caused by poor measurement techniques. The current EPA measurement method called purge and trap (17) is used to measure the

effectiveness of the remediation effort. This method significantly underestimates the VOCs that remains in the soil particles (13:1887). Studies have demonstrated measurement errors of the purge and trap method to range from -100% to +25%. The significant negative bias is to a large degree caused by the inability of this method to account for the contaminant that is entrained in the soil matrix (2:11). A study intended to evaluate measurement methods determined that in long-term TCE contaminated soil, the purge and trap method detected only 11% (-89% bias) of the total TCE in the soil (18:149). Another contribution to the negative bias is the loss of VOCs due to volatilization when exposed to air (19:1387).

Alternative measurement techniques are currently under investigation. One promising method called the dynamic head space relies on the apparently strong correlation between the amount of VOC present in the sample and the head space or air gap in the sample container (20:5). Another study confirms the quality of this method indicating that direct head space analysis of soil sample/water slurry with equilibration time of one hour at 95°C was found to provide recovery and precision superior to that obtained with purge and trap with most soil types (21:709).

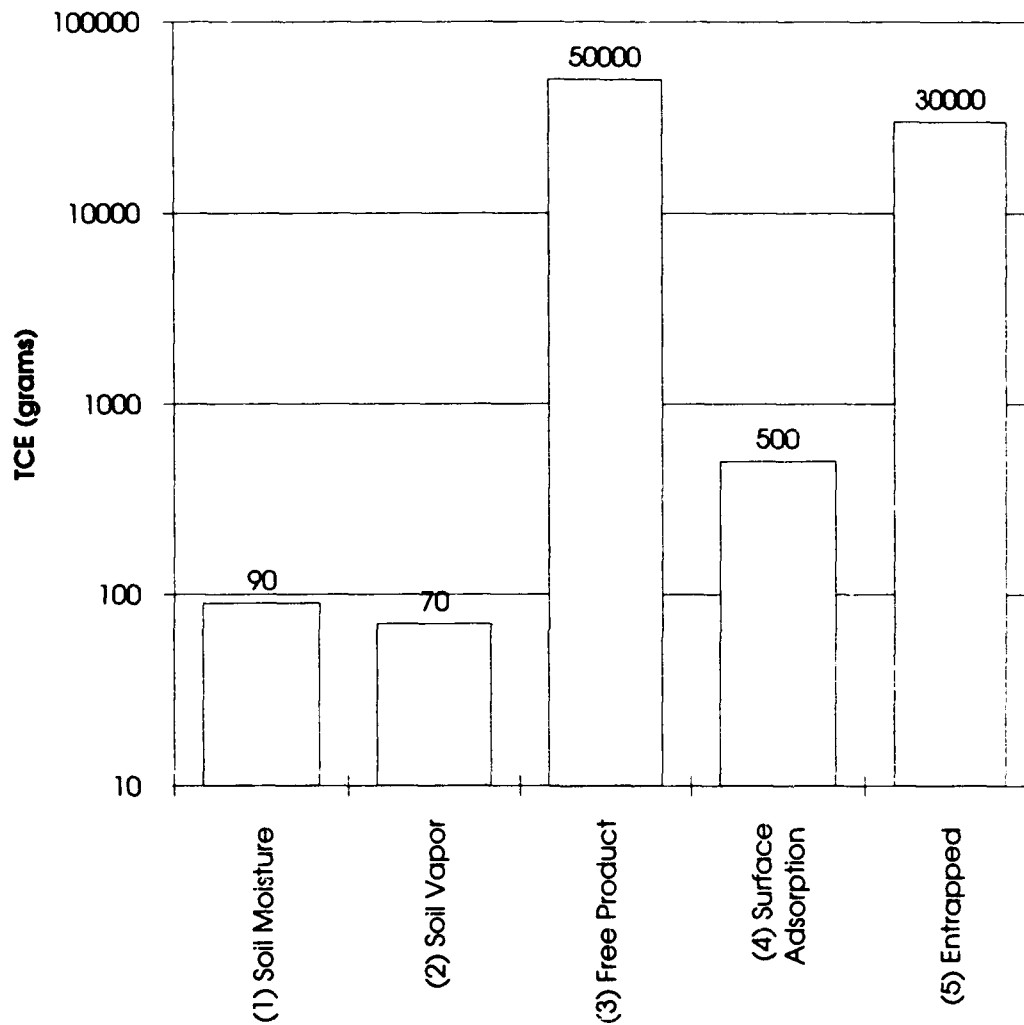


Figure 2
 Distribution of 30 Lit of TCE in one m³ of soil
 (13:1887)

2.7 TCE Partitioning in Vadose Zone

As mentioned above, VOCs such as TCE can be partitioned into several phases in the vadose zone. A significant degree of research has been done in determining the partitioning of volatile organic compounds that can be observed at equilibrium in all phases. The partitioning of VOCs among the gas, liquid, and solid (surface sorption to solids) phases involves several complex factors. Such factors include environmental conditions (humidity, hydrodynamics, surface features, temperature), VOC properties (boiling point, Henry's constant, organic carbon content, partition coefficients, solubility, vapor pressure), soil properties (bulk density, classification, conductivity, moisture content, organic carbon content, particle size, permeability), and microbiological factors (bacterial population, activity, bacterial type). The distribution of VOCs among the gas, liquid and surface sorption to solid phases is often described by the following equilibrium model (2:3):

$$C_T = aC_v\rho_b + \theta C_L/\rho_b + C_S \quad (1)$$

where:

C_T = total VOC concentration per weight of dry soil ($\mu\text{g/g}$)

C_v = vapor phase concentration ($\mu\text{g/cm}^3$)

C_L = solution concentration ($\mu\text{g/cm}^3$)

C_S = sorbed concentration ($\mu\text{g/cm}^3$)

a = soil air content (cm^3/cm^3)

ρ_b = soil density (g/cm^3)

θ = soil water content (cm^3/cm^3)

In this distribution, the sorbed concentration can be related to the solution concentration via the Freundlich isotherm:

$$C_s = K(C_L)^{1/n} \quad (2)$$

where K is the partition coefficient of the VOC in question. K , is linearly related to the soil organic matter content and is also dependent on the water solubility of the organic content (2:3). The term $1/n$ is an empirical constant, usually equal to one. When $1/n$ is close to unity, it implies that the amount sorbed to the soil is linearly related to increasing solution concentrations in the liquid phase (22:458).

In unsaturated soils, it was found that the liquid and vapor phase concentrations are related by Henry's law:

$$C_v = K_H C_L \quad (3)$$

where K_H is Henry's constant

The sorbed concentrations and gas phase concentration are related by the Langmuir Isotherm (23:260-262):

$$\beta = K_L C_V / (1 + K_L C_V) \quad (4)$$

where:

β = fraction of the surface area covered by TCE

K_L = ratio of adsorption to desorption rate coefficients

The sorbed concentration can be related to the surface fraction β through the geometry of the soil particle. However, the Langmuir Isotherm does not account for diffusion of TCE through the interior of the soil matrix.

2.8 TCE Desorption in the Vadose Zone

Organic chemicals exhibit a two-phase desorption pattern. An initial, rapid phase (hours) associated with chemicals sorbed to the surface of the soil particles followed by a subsequent longer, slow phase (days). Soils contaminated for long periods of time exhibit a more pronounced biphasic desorption pattern (5:274).

A recent study (24:173) showed that batch desorption of TCE from long-contaminated soil reached an apparently steady-state within one day (24 hours) and sorption reached an apparent steady-state in three days (72 hours). The same study indicated that the time necessary to attain equilibrium decreases with a decrease in the average grain size. In other words, the smaller soil particles, required less time to reach equilibrium. TCE desorption has been found to depend on soil moisture content, soil type, distribution

of the porous medium, temperature, and on the initial concentration of TCE (24:175).

2.9 Factors that Effect TCE Desorption

2.9.1 Soil Moisture's Effect on TCE Desorption

Water in soil suppresses the uptake of non-polar organic solvents into the soil minerals. In fully saturated soil, the soil mineral uptake approaches zero and almost all of the uptake is due to organic matter in the soil. This adsorptive behavior of water is due to the strong polar interactions of water with soil minerals. However, under dry conditions the soil matrix sorption predominates over organic matter uptake (25:112).

In the vadose zone, the effects of relative humidity, which effects the moisture content of the soil, is a significant influence on the amount of vapor phase sorption (25:111). A study conducted using pesticides demonstrated that when soil is perfectly dry, a large amount of pesticide sorption into the soil matrix is observed. However, when the relative humidity is high (90%) there is virtually no adsorption, because the water competes for adsorption into the soil matrix (25:149-152). The addition of water to soil will actually remove the surface sorbed organic contaminant. In fact, solvent-like odors have been observed at contaminated sites where a heavy rainfall occurs

after a long period of drought. However, the odors are not as prevalent if the soil was moist before the rainfall (25:156).

A study done in 1991 showed that the moisture effects on the sorption of vapor phase TCE on a variety of different soils can be broken into three regions as shown in Figure 3. K_d' is the partition coefficient of soil to atmosphere. A larger K_d' indicates that a larger portion of material will be sorbed to the soil. Region 1 is from no moisture (oven-dried soil) to a moisture content corresponding to a monolayer (one molecule thick) of water on the soil's surface. In this region, large amounts of TCE are adsorbed to available surface "sites" on the soil because there is little competition with water. Region 2 is from a monolayer of water to a moisture content corresponding to five (5) layers of water molecules on the soil surface. In region 2, TCE sorption will decrease to a minimum value as moisture increases, because water is a more powerful competitor for the available surface "sites". Finally, in region 3, which is above five layers to fully saturated soil, there is a gradual increase in sorption mainly due to TCE dissolution into the water (26:182-184).

Another study used inverse gas chromatography to demonstrate that a small amount of water vapor added to the carrier gas, which contained a certain concentration of VOCs, dramatically decreased the amount of VOC adsorbed to a sandy soil (27:883).

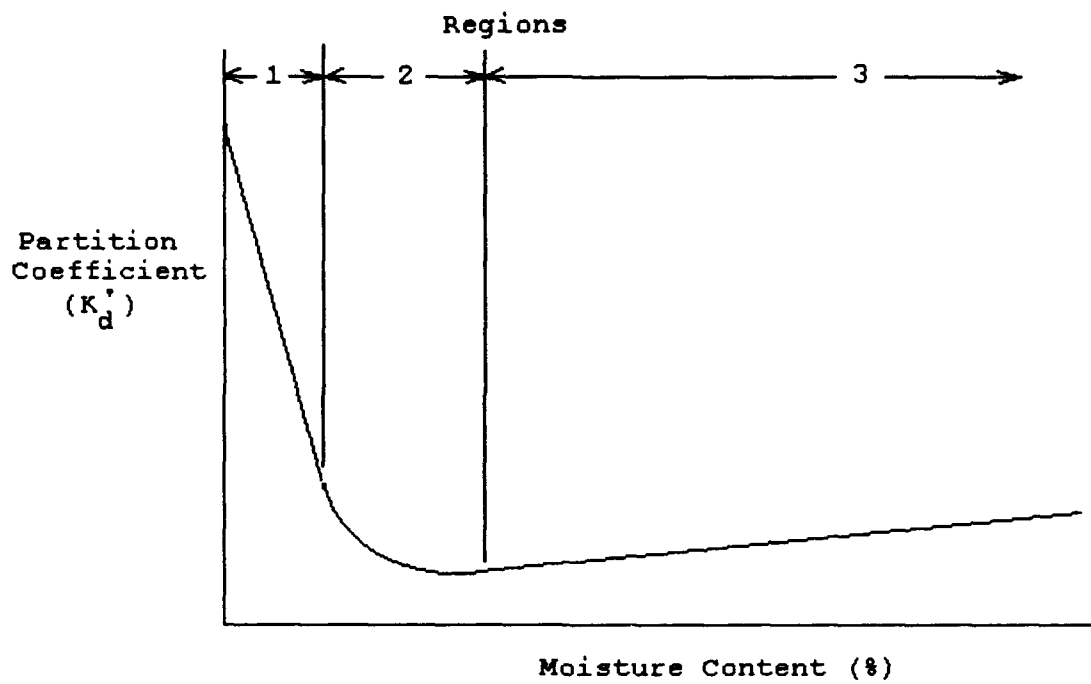


Figure 3
Moisture Versus Adsorption
(26:182)

2.9.2 Effect of pH on TCE Desorption

Research evaluating the influence of pH on soil sorption and desorption rates indicates conflicting results. A study performed at Clarkson University, NY, using soil contaminated with TCE for over 18 years, indicates that modifications to the pH has a negligible effect on desorption rates over a 24 hour period. The study evaluated effects of pH in the range of 3 - 13 and the soil was 56% sand, 32% silt and 12% clay. The study concluded that this result is expected because TCE is a non-polar hydrocarbon and therefore should not be effected by changes in pH. However, the study indicates that only surface adsorption was evaluated and that the slower, long-term desorption caused by the TCE entrained within the soil matrix was not evaluated. It is suspected that long-term desorption from within the soil particles is not significantly effected by pH (5:274).

However, another study evaluating the pH effects on sorption of TCE in pure montmorillite clay found a strong correlation between pH and sorption over a 36 hour period. This study found that a pH of 4 resulted in a maximum amount of TCE sorbed to the clay and at pH values above and below 4, the amount of sorbed TCE dropped off significantly. It is important to note that this study used pure clay treated with sodium citrate-bicarbonate-dithionite (CBD) to remove the surface coating of amorphous metal oxides on the clay particles. The same clay that was untreated did not demonstrate a correlation with pH (11:378).

This result indicated that the alteration of the normal surface charge caused by metal oxides present in clays enhances the sorption of TCE near a pH of 4. This study was unable to fully explain this phenomenon without a better understanding of the relative contribution of surface charge to the overall absorption process. Another distinction between the two studies is that one used soil with a small amount of clay that had been contaminated for a long period of time and the latter study used pure clay that was treated with TCE for only 4 days. Similar to the first study by Clarkson University, the short-term nature of this study only permits the evaluation of surface desorption, not the slower, long-term desorption caused by the TCE entrained within the soil matrix (11:377-380).

2.9.3 Other Effects on Desorption From Soil

2.9.3.1 Chemical Make-Up: The chemical make-up of soil seems to influence the rate of sorption. Al^{+3} saturated clay adsorbed benzene at a rate of three times greater than Ca^{+2} saturated clay for unexplained reasons (22:382).

2.9.3.2 Solubility: There also seems to be general relationships between adsorption/desorption kinetics involving a chemical's solubility in water. Compounds with low aqueous solubility generally tend to adsorb more strongly to soil.

However, electrostatic interactions between the chemical and the soils surface can be the more predominant influence over soil adsorption (28:27).

2.9.3.3 Surface Area: Another effect on VOC sorption is the amount of available surface area in the soil. A smaller grain size, increases the surface area and this allows for a larger amount of VOC that can be adsorbed. This effect is even more pronounced in very dry soils where water is not competing for available sorption sites (26:183).

2.9.3.4 Temperature: There is strong evidence that the desorption rate of contaminants is influenced by temperature. A study conducted on loamy sand over a 180 day period evaluated the desorption of four polycyclic aromatic hydrocarbons (PAHs) to the atmosphere at temperatures of 10°C, 20°C and 25°C. The study concluded that all four PAHs desorbed at a faster rate when the temperature was higher and that desorption for all four PAHs asymptotically approached 100% (29:15-16).

A more complex evaluation concerning the effects of temperature on adsorption in an aqueous environment was done by Mingelgrin and Gerstl in 1983. They postulated that the effect of temperature on a given solute can have a positive or a negative influence on soil sorption depending on whether the solutes (i.e. TCE) heat of "adsorption" from the solution is endothermic or exothermic with respect to the solvent (i.e. water). In an

experiment evaluating parathion uptake in partially hydrated soil, the parathion (a weaker adsorbate) competes with water (a more powerful competitor). An increase in temperature weakens the energetic interaction of soil minerals with water to a greater extent than with parathion (heat of adsorption is greater for water). Therefore, the increase in temperature allows the water to compete more favorably for adsorption than the parathion. A detailed study on TCE concerning this relationship was unavailable at the time of this writing (25:142).

2.9.4 Effect of Resident Time in Soil

This final section on factors that effect desorption will discuss the effects of contaminant resident time in the soil, which is the focus of this thesis. The kinetics of desorption of a sorbed compound appears to be related to its resident time or "age" in the soil (5:274). Evidence suggests that the longer a contaminant remains in the vadose zone, the greater the percentage of the contaminant that will be adsorbed or entrained within the soil particle (6:382).

To date, the most comprehensive experiment to evaluated the effects of TCE resident time on desorption behavior was done at Clarkson University, NY. TCE desorption was evaluated from clean soils exposed to water treated with TCE for 2.5, 5.5 and 15.5 months. The curves that resulted from a 12 day desorption period are similar to those found in other studies where there is a fast

desorption rate presumed to be associated with the surface sorbed TCE and a slower desorption rate associated with the TCE sorbed to the internal soil matrix (Figure 4).

It was demonstrated that the TCE remaining in the soil was 10% for 2.5 months of resident time and 45% for 15.5 months of resident time after a desorption period of 12 days. These results indicate that when TCE is in contact with the soil for a longer period of time, a larger portion of TCE will be taken up by the soil in the form of the desorption resistant fraction entrained in the soil matrix. It also demonstrates that a longer amount of desorption time is required to desorb an equivalent amount of TCE from soil that was contaminated for a longer period of time (30:536). The study noted that there was little influence from the soil type used. Over the longer periods of time, the desorption resistant fraction retained by the soil was similar for different soil types (30:535).

2.10 Summary

The remainder of this thesis will focus on the experiment used to study the effects of TCE residence time in flint clay. As mentioned above, some experimentation has been done on this phenomenon and it is generally accepted that the longer the soil

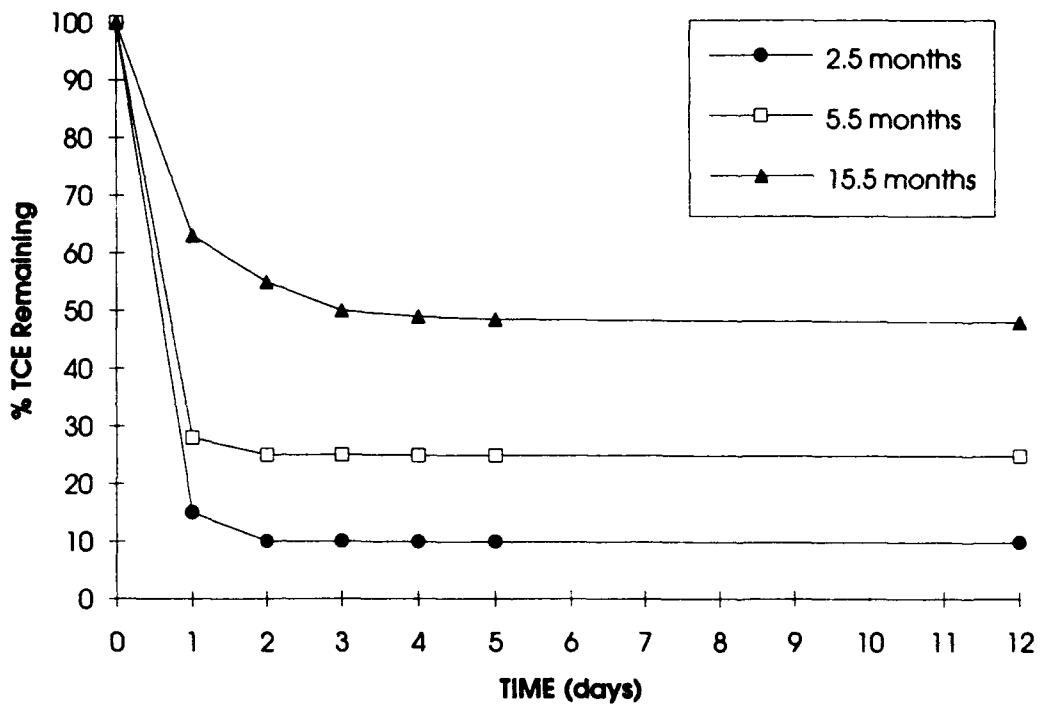


Figure 4
Percentage of TCE Remaining in Soil Over Time

is contaminated with a VOC such as TCE, the longer it remains in the soil matrix. The Clarkson experiment examined time dependent TCE desorption in an aqueous environment. However, it is likely that desorption rates may behave differently when nearly 100% liquid TCE is exposed to dry clay (atmospheric humidity may add some soil moisture). The results may be more dramatic because water is not present in any appreciable amount to compete with TCE. It is therefore the intent of this thesis to examine the time resident effects on TCE desorption in a non-aqueous environment.

III. Experimental Design and Methodology

3.1 Overview

An optical design using infrared absorption will be used in this thesis to examine the desorption rate of TCE from flint clay while varying the amount of time the clay was exposed to liquid TCE. The design of the experimental apparatus entailed shining an infrared source through two enclosed glass tubes. Detectors were placed at the end of the tubes opposite the infrared source to record changes in intensity. The detectors had narrow bandpass filters placed over them that filter out all detectable frequencies except a frequency range of 3040 - 3140 cm^{-1} . TCE will absorb a large amount of the light intensity in this frequency range. The principle used in this design is that the change in intensity between the 3040 - 3140 cm^{-1} range will correspond to a change in the TCE vapor concentration. An explanation of how this was done will follow in the next few sections of this chapter. This design allowed us to track the atmospheric TCE concentrations over time without disturbing the soil or the atmospheric concentrations of TCE. The resulting data allowed us to plot the desorption rate of TCE from the flint clay over time.

Both of the glass tubes were drawn down to a vacuum to eliminate atmospheric interferences and evaporate the remaining liquid TCE surrounding the soil particles. Whatever TCE that was adsorbed

by the soil was then allowed to desorb over a 36 hour time period and the desorption rates were recorded using the infrared detectors. Pressure and temperature readings were also recorded in each cell as a quality control check on the intensity readings. Several control experiments were done with no soil to determine sorption and desorption of TCE from the glass or O-rings due to previous TCE exposures.

The rest of this chapter is divided into two sections: theories behind the experiment and a description of the experiment itself.

3.2 Theories Behind Experiment

3.2.1 General Theory

All molecules will absorb and emit electromagnetic frequencies (EMF). Molecules that are chemically different will absorb and emit more efficiently at some frequencies than others. A particular molecule, such as TCE, strongly absorbs at one frequency and exhibit nearly no absorption at another frequency.

The reason that a particular molecule will absorb or emit more efficiently at different frequencies is the result of: the molecular structure of the molecule, the atoms that are bonded within the molecule and the types of bonding within the molecule. The different atoms and bonds determine the movement associated with the molecule. The atoms within the molecule rotate and

vibrate in various directions and frequencies. The frequencies that are efficiently absorbed by the molecule correspond to the vibrational frequencies of the atoms that make-up the molecule. Many molecules, including TCE, have both vibrational and rotational resonance in the infrared (IR) and are therefore good absorbers in the IR region of the spectrum (31:357).

Each molecule has a certain ground state energy level associated with it and the molecule can move to a higher energy level when excited by a specific frequency range. When IR radiation is absorbed by a molecule, the energy state of the molecule is generally increased to a higher energy state and when IR radiation is emitted the energy state will generally be reduced. The degree to which a chemical absorbs at a specific frequency is repeatable and is the principal used in chemical detection techniques using IR spectroscopy (31:359). This thesis will use this principal in quantifying the concentration of TCE vapor.

3.2.2 TCE Absorption Spectrum

The specific frequency range of 3040 - 3140 cm^{-1} wave numbers that TCE absorbs readily was experimentally determined. This soil desorption experiment was designed around the above frequency range in order to determine the TCE concentration in the vapor state within the glass tubes. Because TCE absorbs in this frequency range, a change in transmitted signal intensity will correspond proportionally to the concentration of TCE in the

atmosphere of the glass tubes. In deciding upon this frequency range, a low resolution IR absorption spectrum of TCE done by Sadtler Research Laboratories was evaluated (Stadtler). We then performed our own low resolution spectral analysis on TCE using a BOMEM DA-8 Fourier Transform Spectrometer accompanied with software to analyze the data. A brief discussion of this task will be discussed later in this section. The resulting low resolution spectral analysis is shown in Figure 5.

Using Figure 5, it was determined that TCE absorbs very effectively at a frequency near 3090 cm^{-1} . A frequency range where TCE strongly absorbs is desired to increase the sensitivity of the detectors and to reduce any interference from other chemicals by isolating a frequency range absorbed by TCE only. Also, the absorption feature near 3090 cm^{-1} was chosen because the indium antimonide (InSb) detectors that will be used in the soil desorption experiment can detect intensity changes most efficiently in this frequency range.

In order to define a more accurate frequency range for the filters on the detectors, a more detailed graph of the absorption spectrum of TCE near 3090 cm^{-1} was necessary. Therefore, another similar study was performed to determine

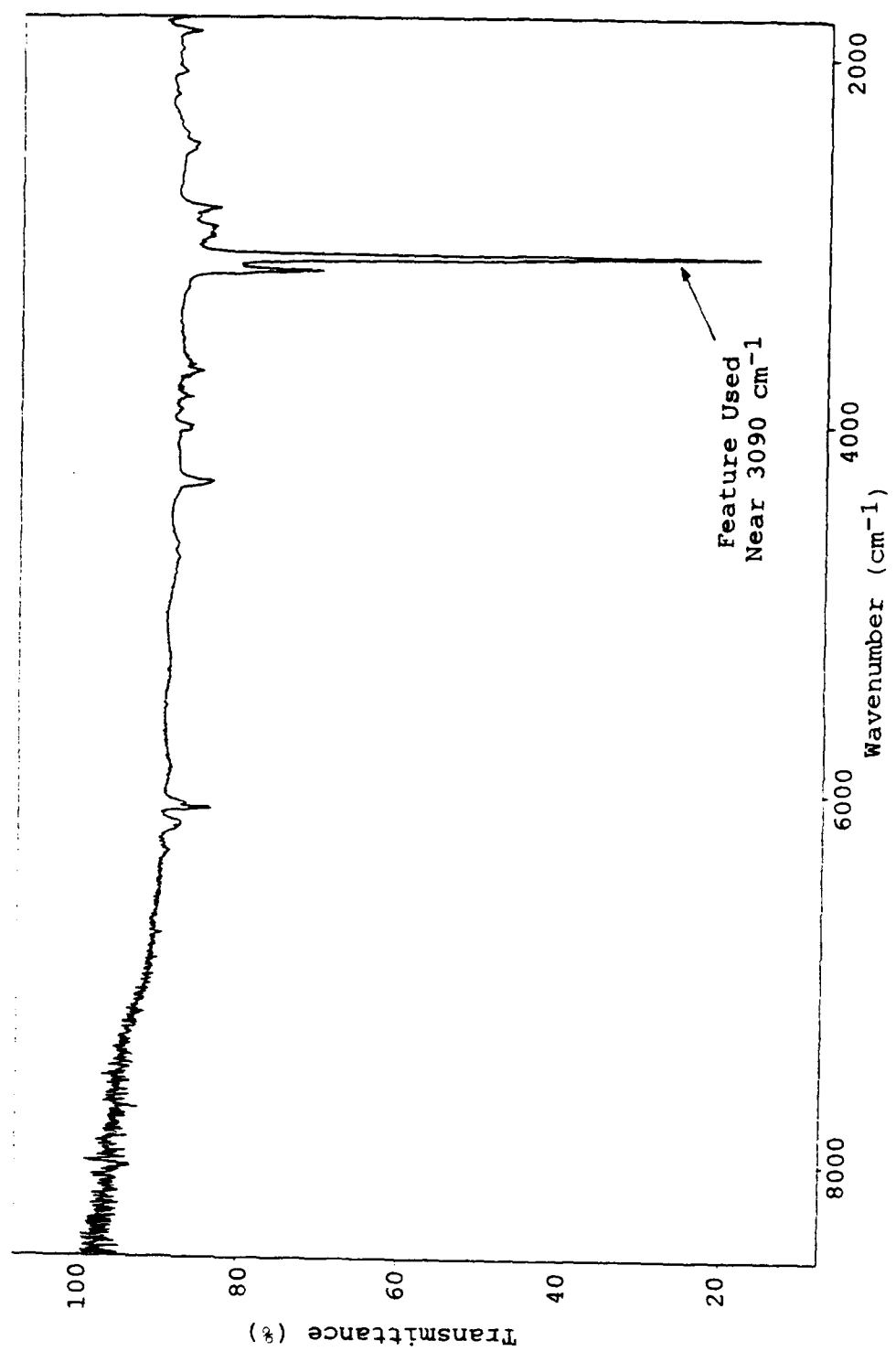


Figure 5
Low Resolution Infrared Absorption Spectrum of TCE

a more precise IR absorption spectrum of TCE near 3090 cm^{-1} at high resolution (0.02 cm^{-1}). This task was done using the same Bomem Fourier Transform Spectrometer.

Both the low and high resolution experiments were performed by designing a 2 inch in diameter by 1 inch thick custom-made cell constructed with the same material (Calcium fluoride (CaF_2) windows) that was used in the soil desorption experiment. CaF_2 windows on the cell and in the experiment had to be used because glass will absorb some of the IR frequency in the range that we were working with. The CaF_2 windows were attached to the ends of the cells and the tubes to allow the IR signal to pass through.

This custom-made cell was evacuated to $< 10^{-4}$ torr to eliminate atmospheric interference and then refilled with TCE vapor up to its vapor pressure. The cell was then placed in the optical line of the Bomem spectrometer and for the high resolution study, the signal intensity losses were measured within the frequency range of 3000 to 3200 cm^{-1} . An empty sample cell with no TCE was also evacuated down to vacuum and analyzed in the same manner to subtract any signal intensity losses caused by the CaF_2 windows or any other part of the system. The difference between the background sample and the sample filled with TCE is the resulting high resolution TCE absorption spectrum shown in Figure 6.

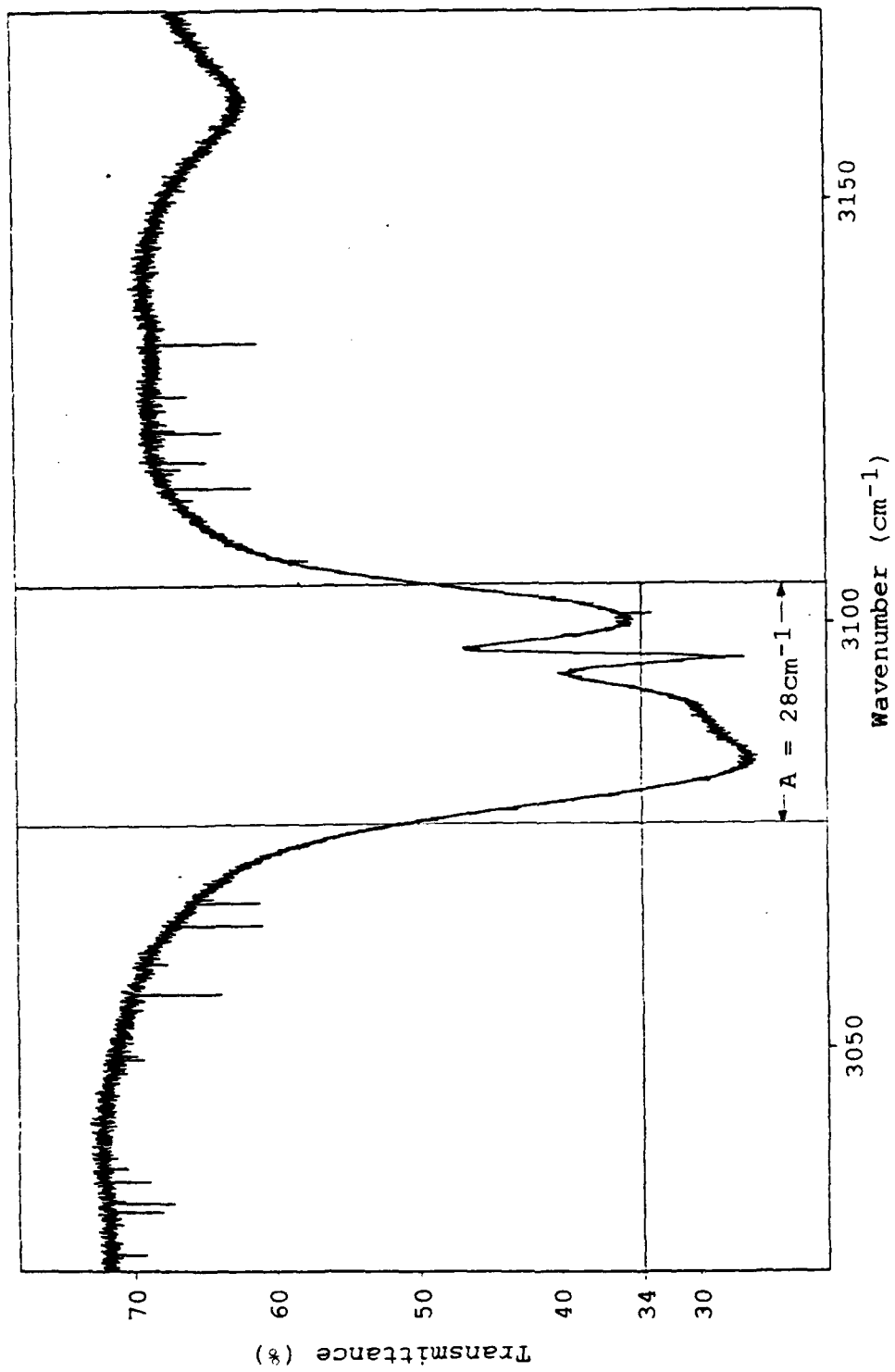


Figure 6
High Resolution Infrared Absorption Spectrum of TCE

This graph shows a more detailed representation of the absorption spectrum for TCE and it confirmed that TCE absorbs at a frequency near 3090 cm⁻¹. From this graph, we ordered custom-made band pass filters that would filter out all other detectable frequencies and allow only a range of 3040 - 3140 cm⁻¹ wave numbers to pass through. This range captures the entire feature near 3090 cm⁻¹ that TCE absorbs readily (see Figure 6) and this range extends beyond either side of this feature to include frequencies not readily absorbed by TCE. This wider frequency range was chosen due to cost considerations.

3.2.3 Beer's Law

In this section, the mathematical relationship between changes in signal intensity and changes in TCE concentrations will be discussed. When a beam of photons is incident on a medium, its intensity decreases exponentially with increasing depth of penetration into the medium. This attenuation of the beam is also caused by increasing concentration of an absorbing chemical. This phenomenon is mathematically expressed in Beer's Law, which states: (33:183)

$$I = I_0 e^{-\sigma l N} \quad (5)$$

where:

I = transmitted intensity on the detectors (mVolts)

I₀ = initial intensity (mVolts) - maximum intensity with no TCE absorption

σ = cross-sectional area of the molecule ($\text{cm}^2/\text{molecule}$)

l = path length (cm) - length of glass tube 43.5 cm

N = concentration of TCE ($\text{molecule}/\text{cm}^3$)

In order to use this relationship to convert transmitted intensity (I_0) to the concentration of TCE (N), we first had to determine the absorption cross-section (σ) of TCE near 3090 cm^{-1} .

3.2.4 Cross-Sectional Area (σ)

The cross-sectional area (σ) was obtained experimentally by adding TCE vapor into each of the glass tubes of the soil desorption experiment. The glass tubes were initially under vacuum to avoid atmospheric interferences. TCE vapor was slowly added until it reached its vapor pressure (58 torr at 20°C). Then the pressure in each cell was slowly released until it reached vacuum again. As the TCE was added and released, the pressure, temperature and transmitted intensity were continuously recorded within each glass tube. Solving for the cross-sectional area (σ) of TCE required the use of Beer's Formula (equation 5) and the ideal gas law which states:

(34:141)

$$PV = nRT \quad (6)$$

where:

P = pressure (torr)

V = volume (cm^3)

n = number of molecules

R = Gas Constant (0.0821 $\frac{\text{lit-atm}}{\text{mol-}^\circ\text{K}}$)

or upon conversion R = $1.0356 \times 10^{-19} \frac{\text{cm}^3\text{-torr}}{\text{molecule-}^\circ\text{K}}$

T = temperature ($^\circ\text{K}$)

The reason that the ideal gas law is needed to find the cross-sectional area is because in Beer's formula (5) we must know the concentration of TCE (N) in order to solve for the only other unknown, which is the cross-sectional area (σ). The ideal gas law will allow us to calculate the TCE concentration ($N = \frac{n}{V}$) using the temperature and pressure data. Rearranging the ideal gas formula (6) to solve for concentration yields:

$$N = \frac{n}{V} = \frac{P}{(R)(T)} = \frac{P}{(1.036 \times 10^{-19})(T)} \quad (7)$$

where: $N = \frac{n}{V} = \text{TCE Concentration in } \frac{\text{molecules}}{\text{cm}^3}$

P = pressure (torr)

T = temperature ($^\circ\text{K}$)

The concentration of TCE (n/V) calculated using the ideal gas law corresponds to the concentration (N) needed in Beer's Law.

Now that a value for N can be determined with the temperature and pressure data, the cross-sectional area can be calculated from Beer's Law. Rearranging equation 5 to solve for the cross-sectional area (σ) yields:

$$\sigma = -\frac{\text{Ln}\left[\frac{I}{I_0}\right]}{(l)(N)} \quad (8)$$

Substitute equation (7) for N into equation (8):

$$\sigma = -\frac{\text{Ln}\left[\frac{I}{I_0}\right]}{P} \frac{1.036 \times 10^{-19} (T)}{l} \quad (9)$$

This equation is the generic solution for the cross-sectional area (σ) in units of $\text{cm}^2/\text{molecule}$. In this cross-sectional area experiment the temperature (T) was held constant at 300°K and the path length (l), which is the length of the glass tube, is known to be 43.5 cm. Because T and l in equation 9 are held constant, we would expect the relationship of pressure (P) versus $\text{Ln}\left[\frac{I}{I_0}\right]$ to be linearly proportional with a negative slope if we assume the cross-sectional area (σ) is constant at a fixed temperature. All that is needed to solve for the cross-sectional area (σ) is the slope of the line between pressure (P) versus $\text{Ln}\left[\frac{I}{I_0}\right]$. However, the graph showing the results of the experimental data in cell 1 (both cells 1 and 2 have similar results), indicates that the slope is not constant as seen by the apparent curvature in the graph (see Figure 7). The appearance of two curves in Figure 7 is due to a difference in equipment lag time when the cell was evacuated down to vacuum and then back up to atmosphere.

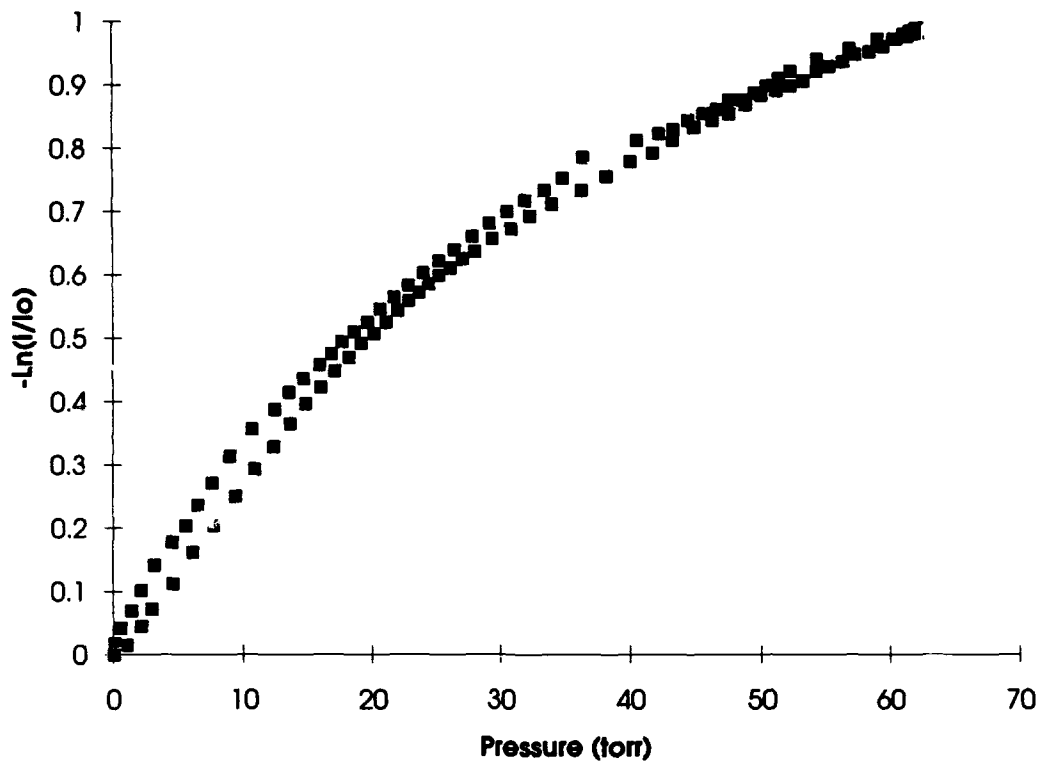


Figure 7
Pressure vs. $\ln(I_t/I_0)$
Uncorrected

The reason this graph is curved is because the broad-band frequency filters on the detectors allows some transmission of frequencies that are not absorbed by the TCE. As mentioned earlier, because TCE does not efficiently absorb the entire range of frequency allowed through by the filters, there is always a component of unabsorbed intensity which is unaffected by any concentration of TCE. This component of the intensity must be mathematically accounted for in the experimental data to evaluate the changes in total intensity that are caused only by TCE concentrations. A detailed mathematical correction needed to produce a straight line (constant slope) from the experimental data (Figure 7) can be found in appendix A. The corrected cross-sectional area (σ) for TCE (at 300°K) from appendix A is:

$$\sigma = 3.335 \times 10^{-20} \text{ cm}^2/\text{molecule} \quad (\text{A.13})$$

It is suspected that the cross-sectional area (σ) of TCE is dependent on temperature. However, this study will only vary residence time of TCE in soil and the temperature will remain fixed at room temperature of approximately 27°C (300°K). Therefore, it is unnecessary to evaluate the temperature dependence of the cross-sectional area for this study.

3.2.5 TCE Concentration using Beer's Law

Now that the cross-sectional area (σ) for IR absorption of TCE has been computed, the TCE concentration in the gas phase can be

determined using the changes in transmitted intensity (I) and Beer's Law.

$$I = I_0 e^{-\sigma l N} \quad (5)$$

Solve Beer's equation (5) for the concentration of TCE (N)

$$N = -\frac{\text{Ln}\left[\frac{I}{I_0}\right]}{(\sigma)l} \quad (10)$$

This generic equation can be used to determine TCE vapor concentrations based on the changes in intensity. The mathematical correction to the experimental intensity data $\left[\frac{I}{I_0}\right]_{\text{exp}}$ which is needed due to the transmitted frequency that is unaffected by TCE is as follows. Calculations are detailed in appendix A.

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \left[\left[\frac{I}{I_0}\right]_{\text{exp}} - 0.37\right] * 1.59 \quad (\text{A.14})$$

where $\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}}$ = the desired I/I₀ influenced only by TCE.

It is desirable to calculate TCE concentrations in units of: molecules/cm³ and torr (pressure). Again, due to the laborious math involved, the detailed calculations can be found in appendix B and C, respectively. The conversion formulas are as follows:

$$\text{molecules/cm}^3 \quad N = -6.89 \times 10^{17} \text{ Ln}\left[\left[\left[\frac{I}{I_0}\right] - 0.37\right] * 1.59\right] \quad (\text{B.1})$$

$$\text{torr} \quad P_i = -0.0714 (T) \ln\left[\left[\frac{I}{I_0}\right]^{-0.37}\right] * 1.59 \quad (C.1)$$

The data in chapter 4 is presented in terms of TCE pressure (torr). The equivalent of 1.0 torr of TCE pressure in terms of parts per million (ppm) is 1,315 ppm and the relationship is linearly proportional (ie. 2.0 torr of TCE is 2,630 ppm). The measurement unit of ppm is based on the quantity of contaminant versus the quantity of air. The reason the data is presented in pressure and not in units such as ppm is because this experiment was performed in a vacuum where there is no air present in the cells. Therefore, the equivalent measurements in ppm is provided only as a theoretical reference assuming there was 1.0 atmosphere of air at 25°C present in the cell.

In addition to the correction needed for the frequency transmitted that was unaffected by TCE (equation A.14), there is also a correction that was applied to the data to correct for a random drift in the intensity readings when no TCE was present in the cells (continuous vacuum was applied). The detectors were observed to slightly decrease in intensity over time for unknown reasons. The magnitude of the error was as high as an equivalent of 4 torr of TCE pressure but averaged closer to 2 torr. It was decided to correct for this apparent drift in intensity eventhough the error appears to be random because there was a general pattern to the drift. Two 36 hour tests were performed

under constant vacuum and a general pattern to the drift is described by the following formulas.

$$\text{Cell 1} \quad I/I_0 = .9425 + 0.0593 e^{-(\text{min}/239.78)} \quad (\text{E.1})$$

$$\text{Cell 2} \quad I/I_0 = .9362 + 0.0264 e^{-(\text{min}/300.33)} \quad (\text{E.2})$$

where: I/I_0 is a % degradation in the signal with respect to time in units of minutes. More detail on the methodology behind this correction can be found in appendix D. All intensity data will be corrected by multiplying the I_0 from the experimental data with the I/I_0 from the detector drift in equations E.1 and E.2.

3.3 The Experiment

3.3.1 Overview

A diagram of the experimental apparatus is shown in Figure 8. The two glass tubes with CaF_2 windows at each end will henceforth be referred to as cell 1 and cell 2. Cell 1 was lined with 2.0 grams of flint clay at the bottom of the tube. Each cell had a pressure detector and a thermocouple for temperature detection attached to them. Each tube was evacuated to approximately 10^{-3} torr. A glowbar lamp was used as an IR source to pass through the length of each cell. A chopper and a lock-in were placed in

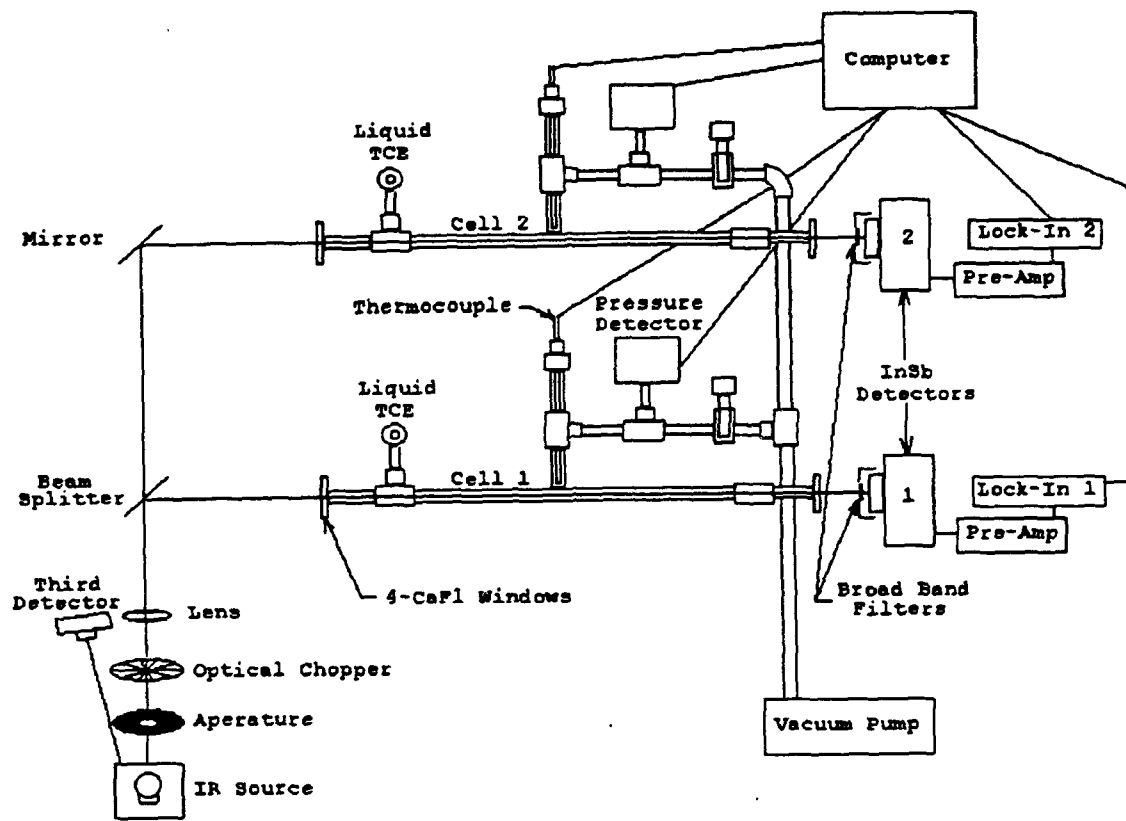


Figure 8
 Experimental Apparatus

the optical train to eliminate other sources of IR emissions. At the other end of the cells, indium antimonide detectors were placed to measure the changes in transmitted signal intensity caused by changes in TCE vapor concentrations in the enclosed atmosphere above the soil. The pressure, temperature and signal detectors converted all measurements to voltage and the voltages were transmitted to a computer workstation. A custom designed program written on the Lab Windows software on the computer then converted the voltage measurements to absolute measurements for the respective detectors and saved the data to a file.

3.3.2 Optical Train of the Experiment

A quartz-halogen glowbar lamp made by Oriel using a 12 volt, 60 Hz Oriel power source was used as the IR source. The bulb was placed in a dull, black, cylindrical holder, which is opened at one end in order to direct the IR beam toward the beam splitter. An aperture was placed in front of the IR source to limit the spatial extent of the source.

An optical chopper driven by an electric motor was placed in front of the aperture and was controlled by a Model SR-540 Chopper Controller Device made by Stanford Research Systems (SRS), Incorporated. The chopper was set at a frequency of 24 Hz. The frequency of the chopper, which essentially turns the IR source on and off, was used as the trigger for a SR-510 Lock-In Amplifier also made by SRS, Inc. The Lock-In Amplifier, which

was also linked to the output of the detectors, subtracted the intensity read by the detectors when the IR source was being blocked. The intent of this design is to eliminate stray IR emissions from other sources in the room from interfering with the detection of the IR radiation emitted only by the source. The Lock-In Amplifiers will be discussed in more detail later.

A lens is placed after the chopper to focus the IR beam through the tubes and onto the detectors.

The source is oriented in a 90 degree angle with the detectors. Therefore, a beam splitter was used to reflect approximately 50% of the IR beam through cell 1 and allow the other 50% to pass through to a front surface mirror that reflected the IR beam through cell 2.

Calcium Fluoride (CaF_2) windows were used at the ends of each cell because they allowed the transmission of the IR frequencies near 3090 cm^{-1} that passed through the cells. They were glued on using a two-part resin and hardener mix called Torr Seal which is a low vapor pressure resin designed for applications in a vacuum system.

The Band-width filters are designed to transmit up to 80% intensity transmission between $3040 - 3140 \text{ cm}^{-1}$ wave numbers ($3.21 \mu\text{m} - 3.26 \mu\text{m}$). The filters were manufactured by Barr Associates, Incorporated.

3.3.3 Data Collection System

A more detailed description for each experimental cell detailing the configuration and the data collection devices is graphically represented in Figure 9.

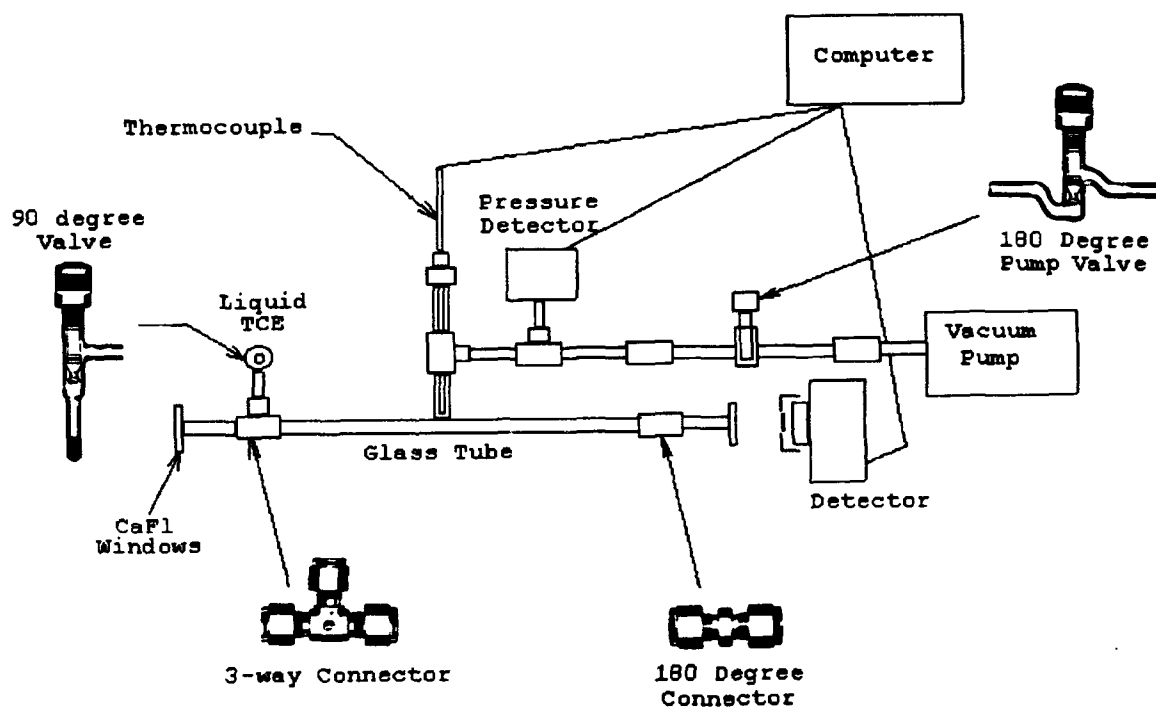


Figure 9
Data Collection System for One Experimental Cell

The data collection system is controlled by a 386 computer using Lab Windows software. A separate program was written in Microsoft QuickC so that data could be recorded to a file at a controllable time interval. All the detectors transmit a voltage to the computer where the software converts the readings into their respective units and records the data to a file.

Two (2) Photovoltaic Indium Antimonide (InSb) Detectors, which were cooled with liquid nitrogen (-77°C), were used to detect signal intensity from the IR source through the cells and the filters. The model number for each of the EE&G Judson detector units is J10D-M204-R02M-60. The detector for cell 1 is 2 mm in diameter and cell 2 is 1 mm in diameter. Each detector generates a voltage proportional to the intensity of the photons incident on the detectors. The voltages are transmitted to each respective EE&G Judson PA-9 Transimpedance Preamplifier, to boost the signal. Each of the preamplifiers is powered with two Hewlett-Packard E3611A 12 volt, DC power supplies to provide the required -12 to +12 volts. Finally, the amplified signals from the detectors along with the optical chopper frequency (24 Hz) are sent to their respective Lock-Ins. The Lock-Ins provide a continuous readout of the signal intensity and the computer reads the signal intensity output from the lock-ins at predefined time intervals.

A third detector which is a Hamamatsu brand, room temperature, silicon photo diode detector is placed next to the lens facing

the IR source. The purpose of this less sensitive detector is to measure the intensity given off from the IR source to see if there was any change in the signal over time. This data was reviewed after every experiment to see if there was a significant change in signal intensity from the source. If there were no significant changes in intensity, the data was not used as a correction to the final calculations.

A Baratron pressure transducer was connected to each cell with a Type 122A for cell 1 and type 221A for cell 2. They both were set to measure pressure in units of torr within the range of 0 to 100 torr. Changes in pressure from the cell caused a change in the deflection of a diaphragm in the detector and the deflection is converted into a voltage. The voltage is then converted to pressure in units of torr and is displayed on a readout device. The pressure transducers are also linked to the computer so that pressure readings can be recorded at predetermined time intervals.

A gas phase thermocouple was also connected to each cell to measure the temperature in the cells. A change in temperature effects the resistance and therefore the voltage in the thermocouple. The voltage was recorded by the computer at predetermined time intervals. The computer then converted the voltage output into temperature in degrees Celsius.

The main T-shaped cells that the soil was placed in along with the 2 inch extensions on either end of the cells were manufactured from a local glass-blower to standard specifications for 1/2 inch glass. The 90 degree and 180 degree valves shown in Figure 9 are under the trade name HI-VAC, Glass Valves rated for vacuum applications down to 5×10^{-7} torr. The valve stems are made of glass and there are three Kelvar O-rings on each valve stem. Kelvar (teflon) was chosen due to its high resistance to halogenated compounds such as TCE.

All connectors (see 3-way and 180° connectors in Figure 9) are all 1/2 inch Cajon Tube Fittings designed for glass tubing under vacuum down to 5×10^{-7} torr. The Cajon fittings are made of 316 Stainless Steel. The fittings compress a Kelvar O-ring to seal against the glass tubing.

A 3/4 horsepower rotary vane vacuum pump was used to draw the system down to vacuum. The manufacturing specifications for the system advertises an ultimate vacuum of less than 1.5×10^{-3} millibars (1.14×10^{-3} torr). This is the lowest pressure that this system is able to achieve.

3.3.4 Experimental Procedures

3.3.4.1 Soil Sample Preparations

Flint clay was chosen for this thesis in part because all the soil samples were crushed to a consistent grain size most closely resembling clay. Therefore, it was thought that choosing a clay soil type will more realistically resemble the true behavior of clay because the sample's grain size is similar to that of natural clay. The chemical characteristics of the flint clay sample, which is certified by the National Institute of Standards and Technology (NIST) is given in appendix F.

Two grams of flint clay, measured on a Mettler PM300 digital balance, was placed into small plastic containers. Then, spectro-analysed, lab-grade liquid TCE was added to the top of the container and the container was capped. The bottles were then marked with the date and times that they were exposed to TCE. The bottles were refilled periodically as the TCE slowly evaporated from the containers, so that the clay was continuously soaked in TCE.

The soil was prepared at specific times so that the soil resident time in liquid TCE was on the order of one day, one week and two months. The actual resident times used in this thesis are:

19 hours (< 1 day)

20 hours (< 1 day)

120 hours (5 days)
240 hours (10 days)
1320 hours (55 days)
1344 hours (56 days)
Controls (no soil)

3.3.4.2 Before Each Experiment

In preparation for each experiment, the vacuum pump was allowed to continually pump down on the cells for at least 12 hours (overnight) prior to each test run to eliminate any TCE sorbed to the cells from the previous test run. Just before each experiment, the detectors were cooled with liquid nitrogen, everything was turned on and the alignment of the cells and the detectors were checked. Then, the vacuum pump was turned off and each cell was exposed to atmosphere by removing the CaF_2 window extension closest to the IR source. The soil sample was then placed into cell 1, by allowing it to dry in front of a fan to a point where the clay was beginning to fall apart. However, the clay was still damp with TCE. Then a plastic straw with a 2 inch slit cut in the end was used to scoop out the soil and insert it into cell 1. The straw was then turned 180 degrees so that the clay would fall to the bottom of the cell. This was repeated until all the soil was in the cell and evenly spread out in the bottom of the cell. Any residual clay that fell out was caught on a piece of paper and added to the cell to reduce losses. This

procedure took about 15 minutes and both cells were exposed at atmospheric pressure the entire time.

To simulate conditions in cell 2 (control cell), the cell was opened for the same time and the finger of liquid TCE was opened to allow the TCE to evaporate into cell 2. This was done to simulate the TCE evaporating from the soil sample in cell 1. After the first few experiments, the control cell was discontinued and cell 2 was used as an experimental cell with actual soil samples in it. Four control tests indicated that no detectable levels of TCE were being desorbed from the apparatus.

After the soil was loaded, the CaF_2 window extension was then screwed back onto the ends of the cells and the valves to the vacuum pumps were opened to bring both of the cells back to vacuum. A continuous vacuum was held on each cell for 60 seconds, which was determined to be the time needed to dry the clay particles from any remaining liquid TCE in the clay.

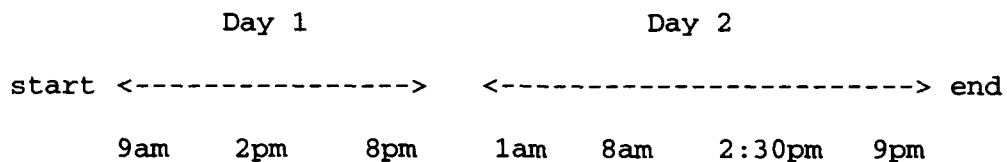
3.3.4.3 Starting Each Experiment

At the end of the 60 seconds under continuous vacuum, the computer was started to begin collecting data and the vacuum valves were promptly closed to seal the cells. The first data point was taken immediately after the 60 second period to obtain the lowest pressure reading and the highest intensity reading, which became the maximum intensity (I_0). At this point, when the

cells were sealed, the TCE vapor was allowed to build up in the cells reducing the intensity readings and increasing the pressure readings. Data was taken every 60 seconds for a total period of 36 hours or less if the TCE was exhausted before 36 hours.

3.3.4.4 During Each Experiment

During each experiment, the detector's dewers had to be replenished with liquid nitrogen at least every 7 hours. This was because the nitrogen in the dewers holding the detectors would evaporate in 7 hours and the detectors would rapidly reach room temperature, which adversely effected the data and could possibly burn-out the detectors. Therefore, the following 36 hour cooling schedule was developed and adhered to during the test:



The intensity data was temporarily effected for a period of about 2 minutes following the addition of liquid nitrogen, but then the intensity settled back to its previous level. Because of this, care had to be taken to keep from adding liquid nitrogen to the detectors at critical times in the desorption process.

When the intensity readings appeared to level out during the experiment, reaching some asymptotic value, the cells were re-evacuated back down to vacuum for 30 seconds and data collection was allowed to continue every 60 seconds. This was done because the most informative portion of the data, with respect to determining a desorption rate, occurs as the TCE pressure changes with time and it was thought to be less informative to allow the data to reach a perfectly finite equilibrium value. The times at which the cells were brought back to vacuum varied with each experiment depending upon when equilibrium was reached.

3.3.4.5 After Each Experiment

Finally, the data was collected in data files on the computer and transferred to Microsoft Excel. Graphs of the total pressure determined by the baratron pressure detector (P_{tot}) and the pressure induced by TCE determined by the intensity readings (P_{tce}) were constructed and will be analyzed in chapter 4. All P_{tce} data was corrected for frequency transmission unaffected by TCE (equation A.14), and intensity drift (equation E.1 and E.2).

IV. Findings and Analysis

4.1 Data Analysis

The graphs which relate the total baratron pressure P_{tot} and the intensity pressure P_{tce} over each experiment are illustrated in Figures 10 - 16. These figures correspond to resident times of 19 hours, 20 hours, 5 days, 10 days, 55 days, 56 days, and the control experiments. The P_{tce} for each experiment (except the suspect 10 day resident time) are summarized in Figures 17, 18 and 19. A brief discussion about each experiment precedes the graphs.

4.1.1 19 Hour Resident Time

The data for flint clay exposed to liquid TCE for 19 hours is illustrated in Figure 10 and shows an initial (first hour) rapid rise in both the P_{tce} and the P_{tot} followed by an approach to steady-state. After five hours, it was determined that a steady-state had been reached and the cell was brought back down to vacuum. As mentioned before, this was done by opening the valve to the vacuum pump for 30 seconds. The exact times that this was done can be seen on all graphs by the sharp drop in the P_{tot} and P_{tce} . In this experiment, after the second evacuation to vacuum at 5 hours, a more gradual increase in both P_{tot} and P_{tce} is apparent up to 15 hours. However, after the third evacuation to vacuum at 15 hours the P_{tce} appears to drop off from 1.0 torr to

-1.0 torr. It is unlikely that TCE was lost from the enclosed system. The drop is more likely due to movement causing poor alignment or random drift in the detector's response (see appendix D). The data after 15 hours was not further evaluated.

4.1.2 20 Hour Resident Time

In Figure 11, the 20 hour resident time, the TCE desorption rate also appears to rise rapidly in the first hour and then reach an equilibrium. After the cell was drawn back down to vacuum at 13 hours, there appears to be a very slight increase in P_{tce} indicating that there was very little (if any) TCE to desorb. The data collection was ended after only 24 hours because it appeared that there was no more TCE. The rise in P_{tce} after the second evacuation in this experiment appears less pronounced than the rise in the 19 hour resident time experiment. However, it should be noted that in this experiment the second evacuation to vacuum occurred after 13 hours where as the 19 hour experiment evacuation occurred after only 5 hours. It is possible that the extended time until the second evacuation in this experiment exhausted the TCE sorbed to the soil more so than in the 19 hour experiment where the soil may not have reached a steady-state condition.

4.1.3 5 Day Resident Time

Figure 12, again illustrates a rapid initial pressure increase. After the first few hours, there still appears to be a slow increase in the next 24 hours whereas in the 19 and 20 hour experiments, the TCE appeared to have been exhausted after 15 hours. However, the data in this experiment after 10 hours is suspect due to a leak in the adjacent cell. While the leak in the other cell was being fixed, some movement to this cell had occurred. This was suspected because at some points P_{tce} exceeded P_{tot} , which is impossible, and there were sharp changes in the P_{tce} , which indicates movement in the alignment of the cells. The I_o in this cell was adjusted to align the data if a sharp change in the intensity was obvious. This may have introduced error in the data after 10 hours and before 27 hours (second evacuation) where the movement had occurred. Also, there was a period of 2 hours before the second evacuation where data was not collected. However, tampering did not occur after 27 hours and because of the evacuation to vacuum an accurate determination of I_o could be reestablished. Therefore, the initial increase up to 10 hours and the data after 27 is considered reliable.

4.1.4 10 Day Resident Time

This experiment (Figure 13) was considered invalid but it was included in this section to illustrate some complications that

occurred in this thesis work. When the P_{tce} before the first evacuation near 5 hours (7.5 torr) is added to the ending P_{tce} at 36 hours, the total P_{tce} in 36 hours is 28 torr. This P_{tce} is far above the 2 to 5 torr increase in P_{tce} observed in all the other experiments. Identical times ranged from one day to 56 days. It is possible that the finger of liquid TCE attached to the cell added TCE by leaking slowly into the cell or that there was some liquid TCE left in the soil which did not evaporate during the initial 60 seconds at vacuum. It is more likely that the finger of TCE leaked slowly into the cell because the evaporation of liquid in the soil under vacuum is normally very rapid (on the order of seconds). The increase in P_{tce} in this experiment is gradual over the 36 hours suggesting a slow leak from the TCE finger. This leak from the TCE finger does not appear to have effected any other experiment because all other experiments reached some point where there was no increase or decrease in TCE pressure. If there was a leak in the system, it was observed in previous experiments to be a very consistent, linear change over time until the problem was corrected.

Another less serious problem that occurred during this experiment is that there was an atmospheric pressure leak into the cell. The P_{tot} increased much more rapidly than the P_{tce} . While there is typically some pressure leak into the cell (generally 2-8 torr in 36 hours), causing P_{tot} to be slightly higher than P_{tce} , it is normally not of this magnitude (85 torr in 36 hours). However, prior testing indicates that the influence of atmosphere leaking

into the cell on the P_{tce} is negligible because atmosphere has a very small effect on intensity in the frequency range that we are detecting. A more detailed analysis of atmospheric interference will be discussed in the section on experimental error. This 10 day experiment will not be further evaluated due to the suspected inaccuracy in P_{tce} .

4.1.5 55 Day Resident Time

In Figure 14, there is a similar initial increase in the first hour but the data still levels off. We expected to see a larger increase due to the longer exposure time to TCE. There was a slight atmospheric pressure leak in this experiment but as mentioned before, this is expected to have a negligible effect. This experiment was stopped after 22 hours because of some equipment problems that did not adversely affect the previous data and because it appeared to have reached an equilibrium. However, after review of the following 56 day experiment in the next section, this experiment may have been stopped prematurely. A gradual increase similar to the 56 day exposure may have become evident.

4.1.6 56 Day Resident Time

This final experiment (Figure 15) appears to be similar to all others with the possible exception that it appears to continue to increase after the second evacuation for a longer period of time

than the others. However, due to the limited length of time in data collection and the relative magnitude in experimental error, it is difficult to tell if this gradual increase in P_{tce} is caused by desorption from the clay or if it is primarily experimental error.

4.1.7 Control Experiments

Four separate 36 hour control experiments were accomplished to determine if the effect in P_{tce} is actually caused by the flint clay or if there is some residual TCE in the cell from previous experiments. As mentioned in chapter 3, under experimental procedures, the controls were treated exactly the same as experimental runs except that no soil was added to the cell. Also, while both cells were at atmospheric pressure during soil loading in the experimental cell, the finger of liquid TCE was opened in the control cell to simulate the evaporation of TCE from the soil in the experimental cell. Then, both cells were sealed and vacuumed for 60 seconds and data was collected at time intervals equivalent to the experiments. Of the four controls, two of the control experiments are illustrated in Figure 16. There was essentially no detectable increase in P_{tce} demonstrating that previous exposures to TCE had no apparent effect on the experiments.

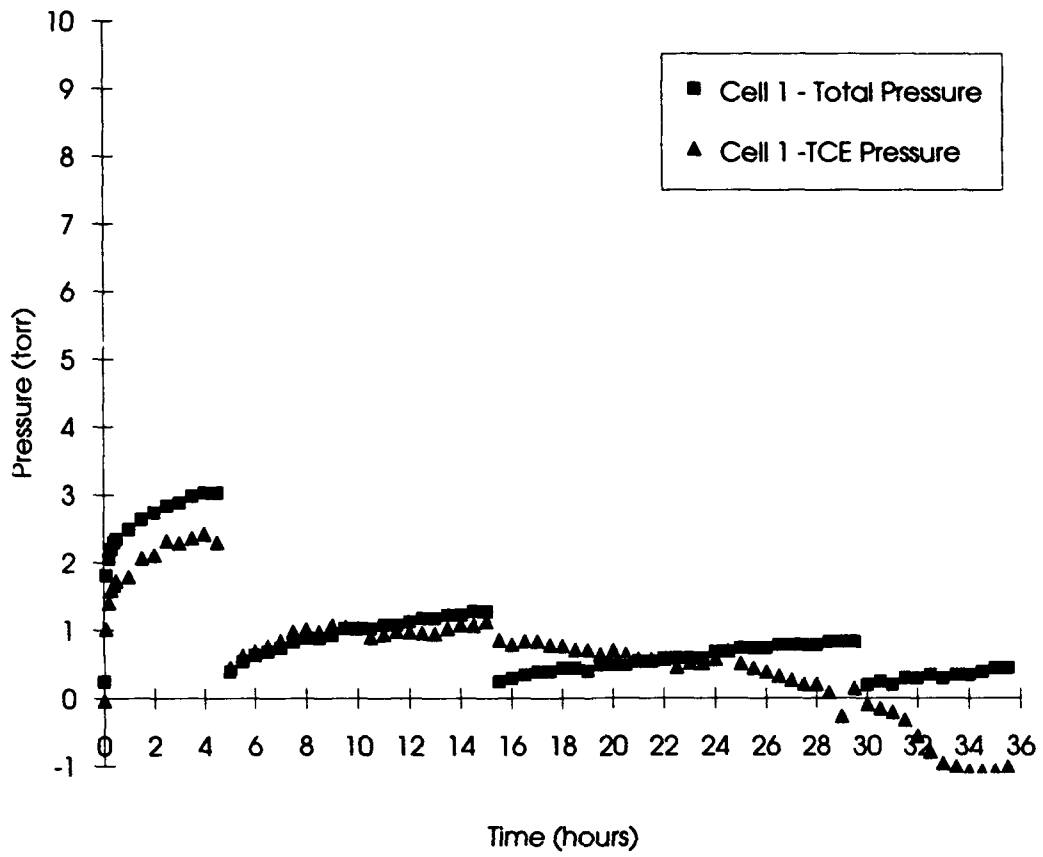


Figure 10
 P_{tot} and P_{tce} for 19 Hour Resident Time

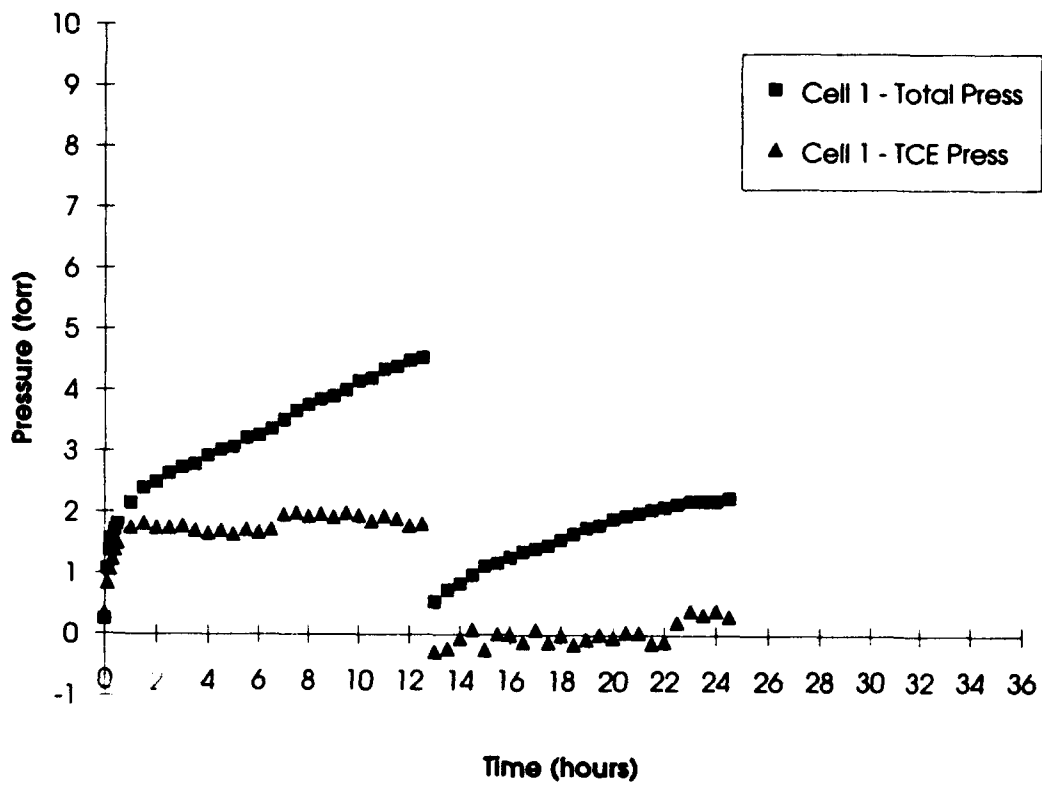


Figure 11
 P_{tot} and P_{tce} for 20 Hour Resident Time

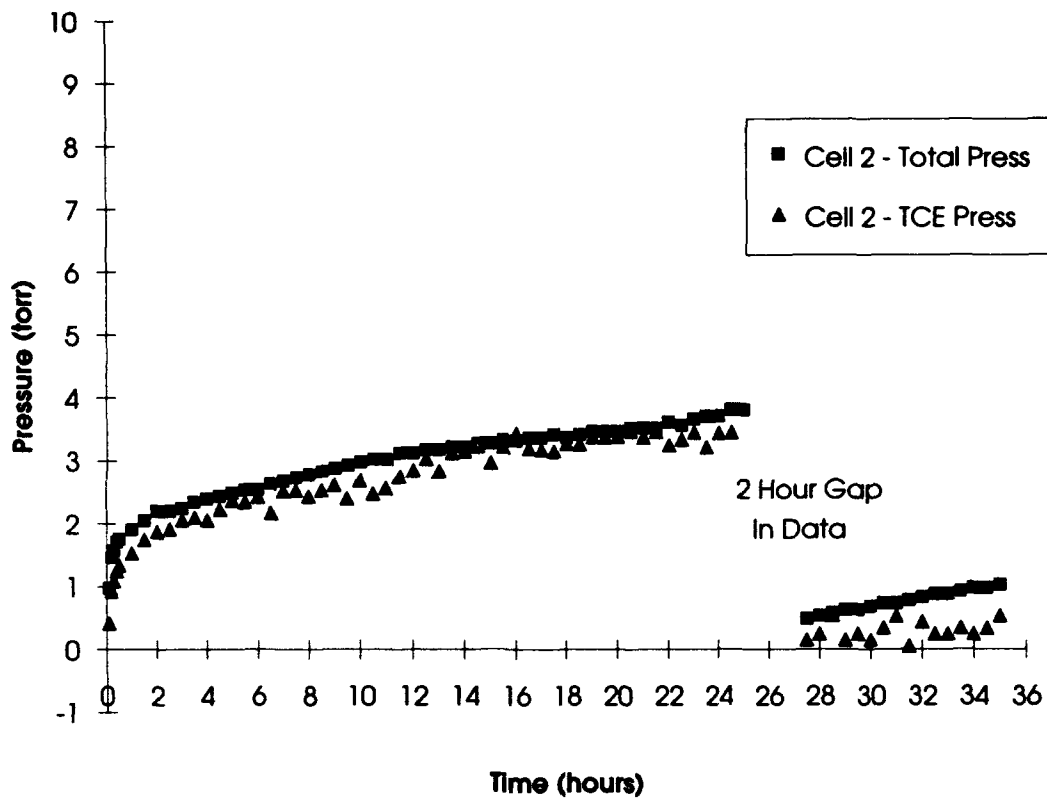


Figure 12
 P_{tot} and P_{tce} for 5 Day Resident Time

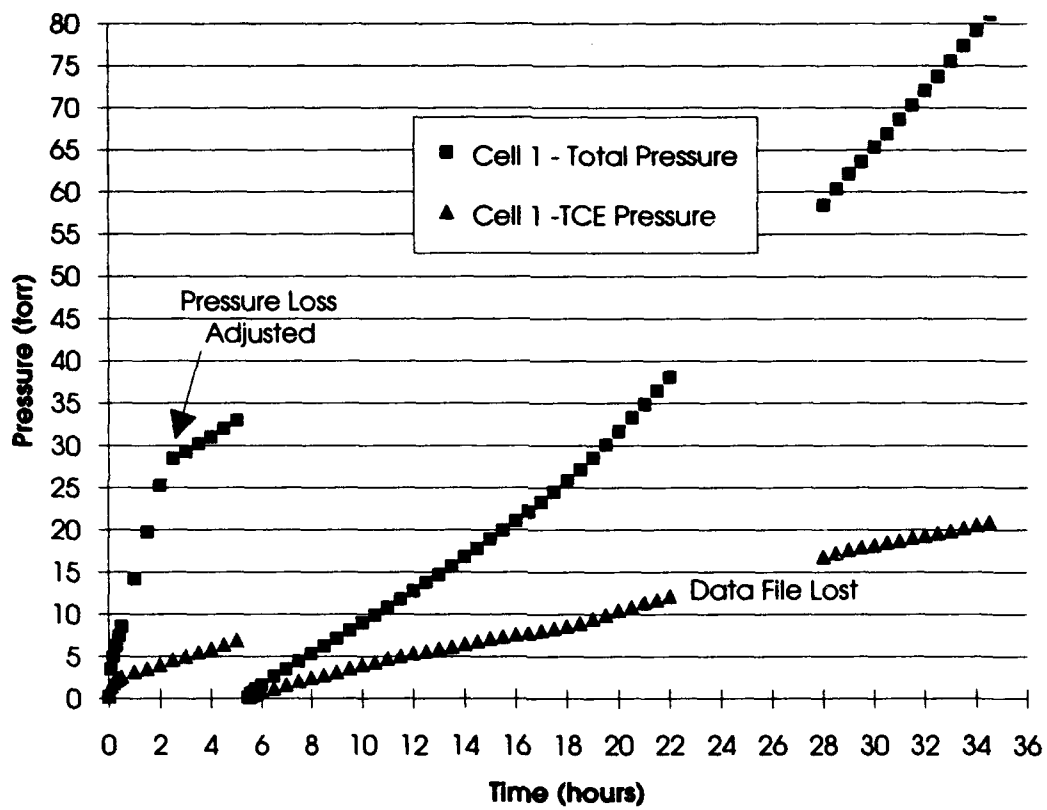


Figure 13
 P_{tot} and P_{tce} for 10 Day Resident Time

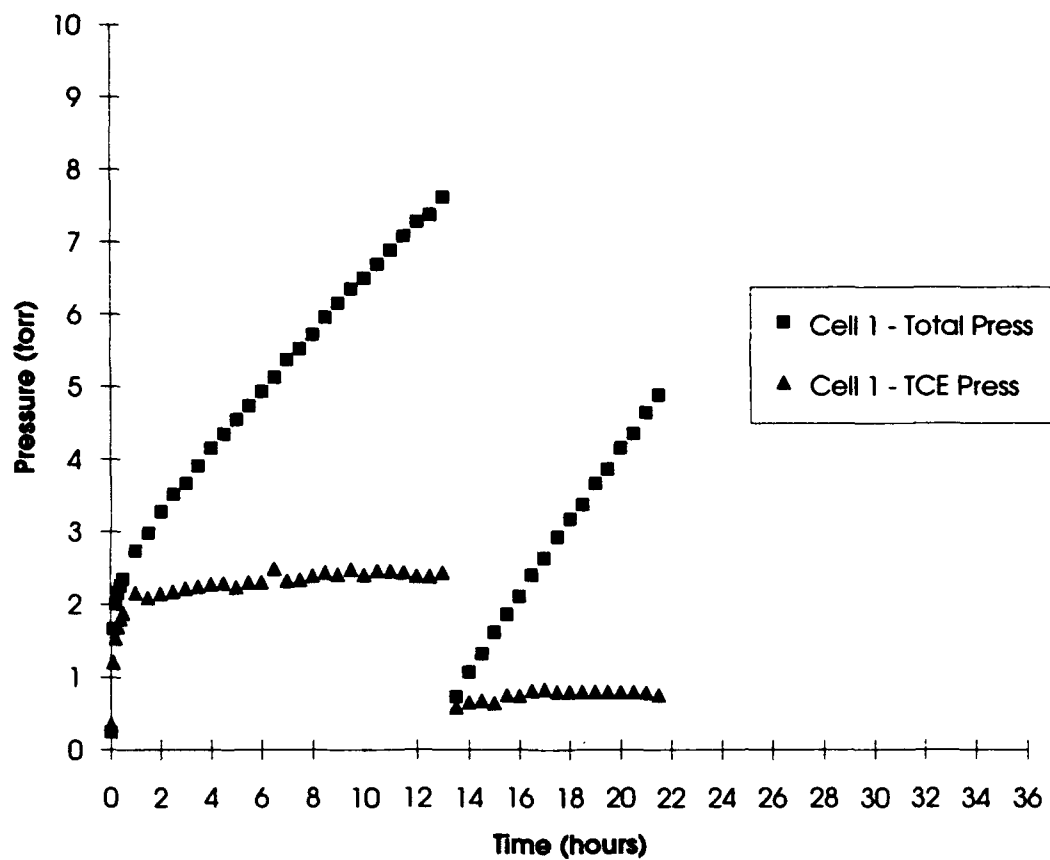


Figure 14
 P_{tot} and P_{tce} for 55 Day Resident Time

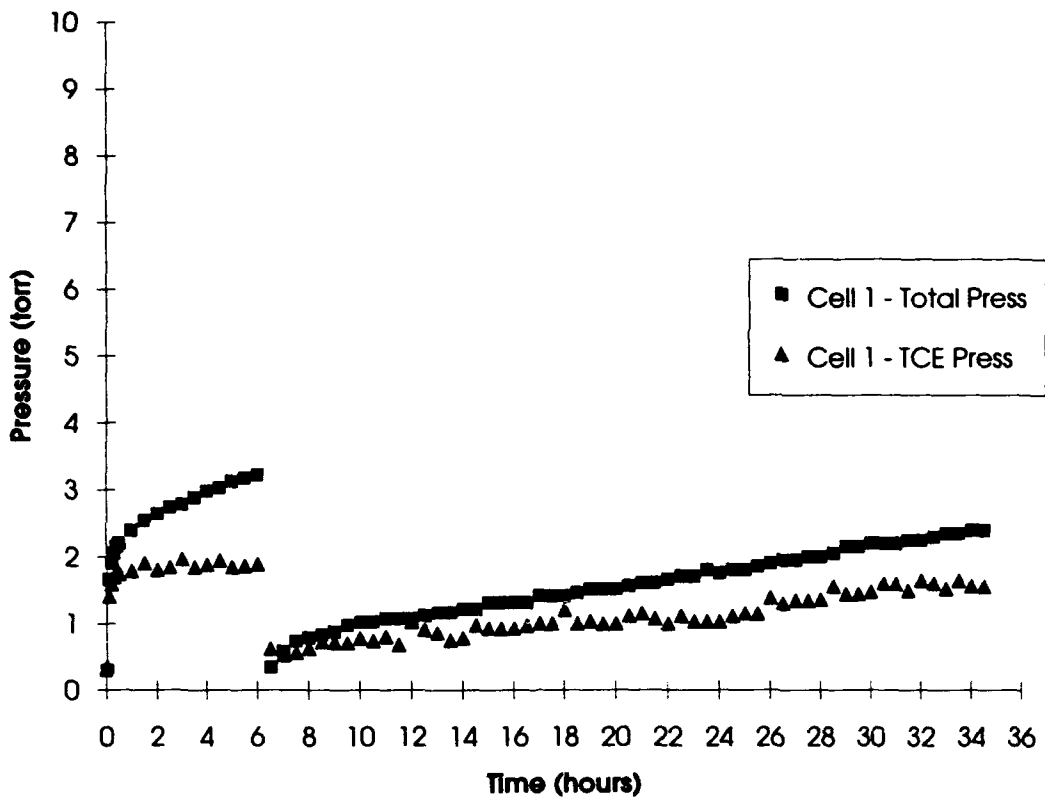


Figure 15
 P_{tot} and P_{tce} for 56 Day Resident Time

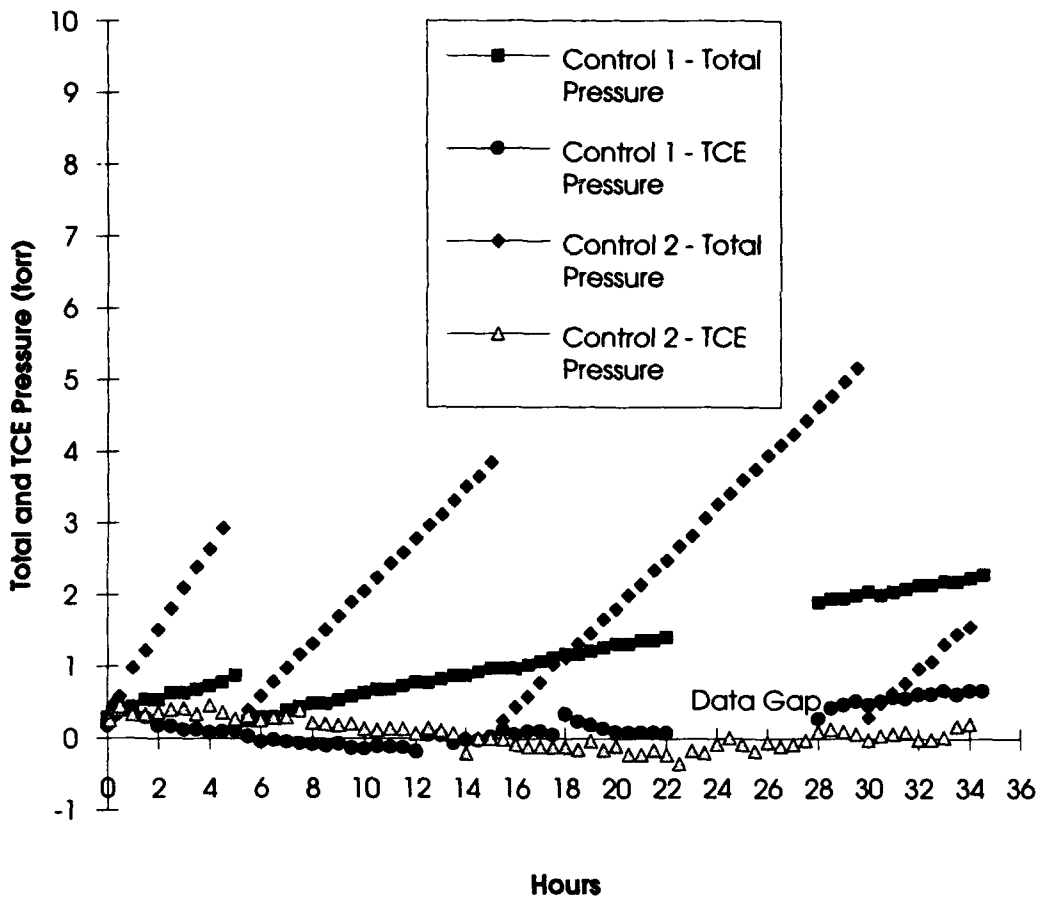


Figure 16
 P_{tot} and P_{tce} for Two Control Experiments

4.1.8 Summary of All P_{TCE} Curves Over 36 Hours

The summary of the results illustrated in Figure 17 does not clearly prove the hypothesis that there is a greater mass of TCE desorbed with increasing resident time. However, there are a few noteworthy observations that can be made about the data. The fact that there is an initially rapid rise of the same magnitude in all the experiments suggests that there is a common desorption mechanism that is independent of resident time. To observe the initial rise more closely, Figure 18 is a close-up graph during the first 4.5 hours of each experiment. This figure demonstrates more clearly that there is a repeatable pattern that appears independent of resident time. Each experiment exponentially reached an apparent equilibrium of 1.5 to 2.0 torr in the first hour.

Furthermore there appears to be similarities in the desorption rates after the second evacuation. A close-up of the time periods after the second evacuation of each experiment is illustrated in Figure 19. Figure 19 is a graph that translates the time of the second evacuation in each experiment to time zero so that the desorption patterns can be observed more clearly. Although it is more difficult to observe an increase in P_{TCE} after the second evacuation in Figure 19 as opposed to the initial rise in Figure 18, there does appear to be a generally similar rise in P_{TCE} in all the experiments. In this case the data rises approximately 0.5 to 1.0 torr in the first few hours

after the second evacuation. It can also be argued that there is a very gradual rise in P_{TCE} even after these first few hours. This gradual rise is most apparent in the 56 day exposure, which was allowed to continue desorbing longer than most other experiments and also had the longest resident time. It is possible that this gradual rise would have continued but the data collection time was not long enough to confirm this observation. The more gradual increase could be a second desorption mechanism where TCE diffuses slowly out of the clay particles. It is more likely that this mechanism is dependent on resident time. However, because the magnitude on this gradual increase is on the same order as the random drift observed in the detectors over this time period, it can not be confirmed whether the gradual increase is a real phenomenon or random drift.

4.2 Experimental Error

This section discusses some of the potential sources of experimental errors and human errors in this experiment. A lengthily discussion of the random drift in the InSb detectors, which is likely the largest source of error can be found in Appendix D, along with the formulas that were used to reduce the error. Also, a discussion of the correction required due to the filter's transmission of frequencies not effected by TCE can be found in appendix A along with the formulas to correct this

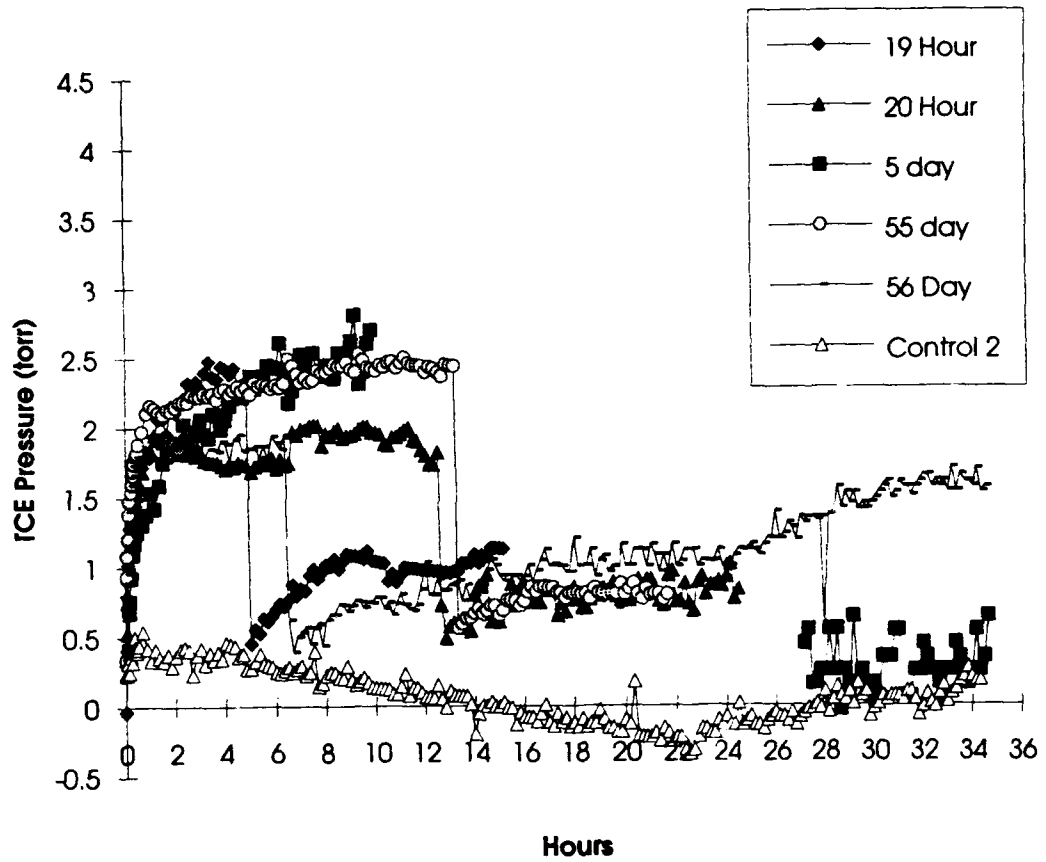


Figure 17
 P_{tce} for All Experiments Over 36 Hours

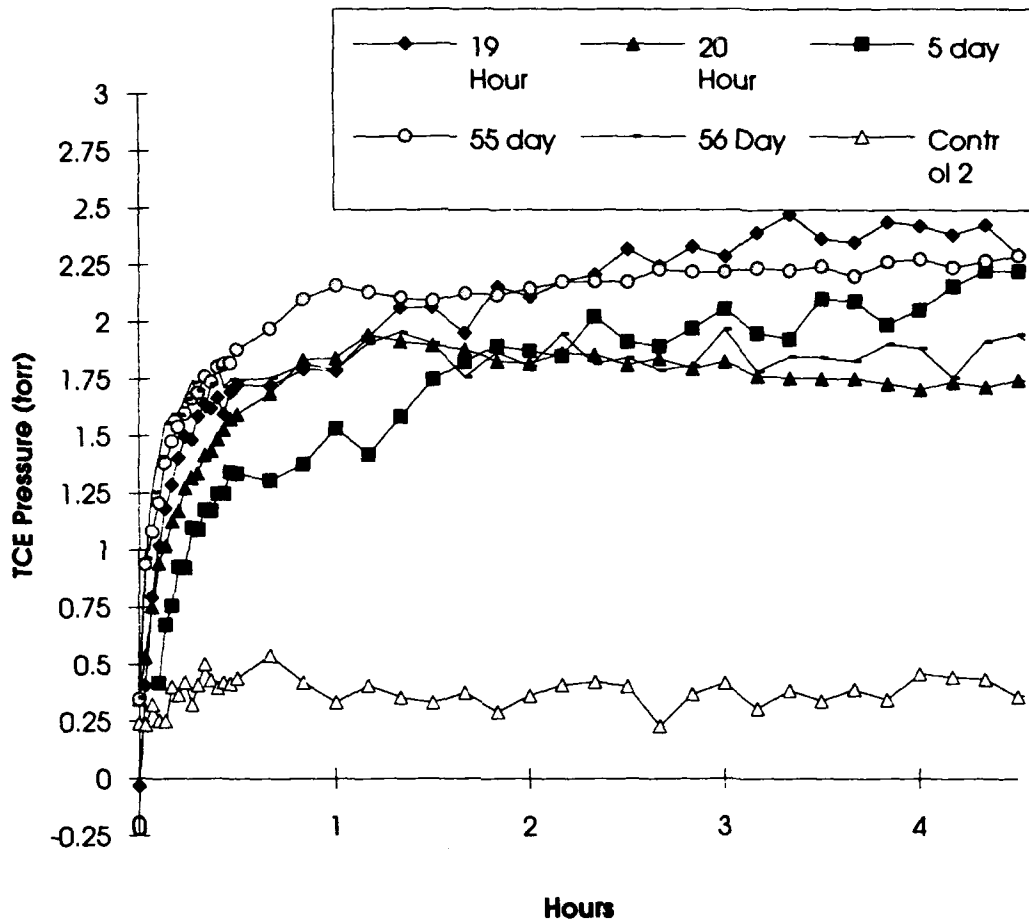


Figure 18
 P_{tce} for All Experiments Over 4.5 Hours

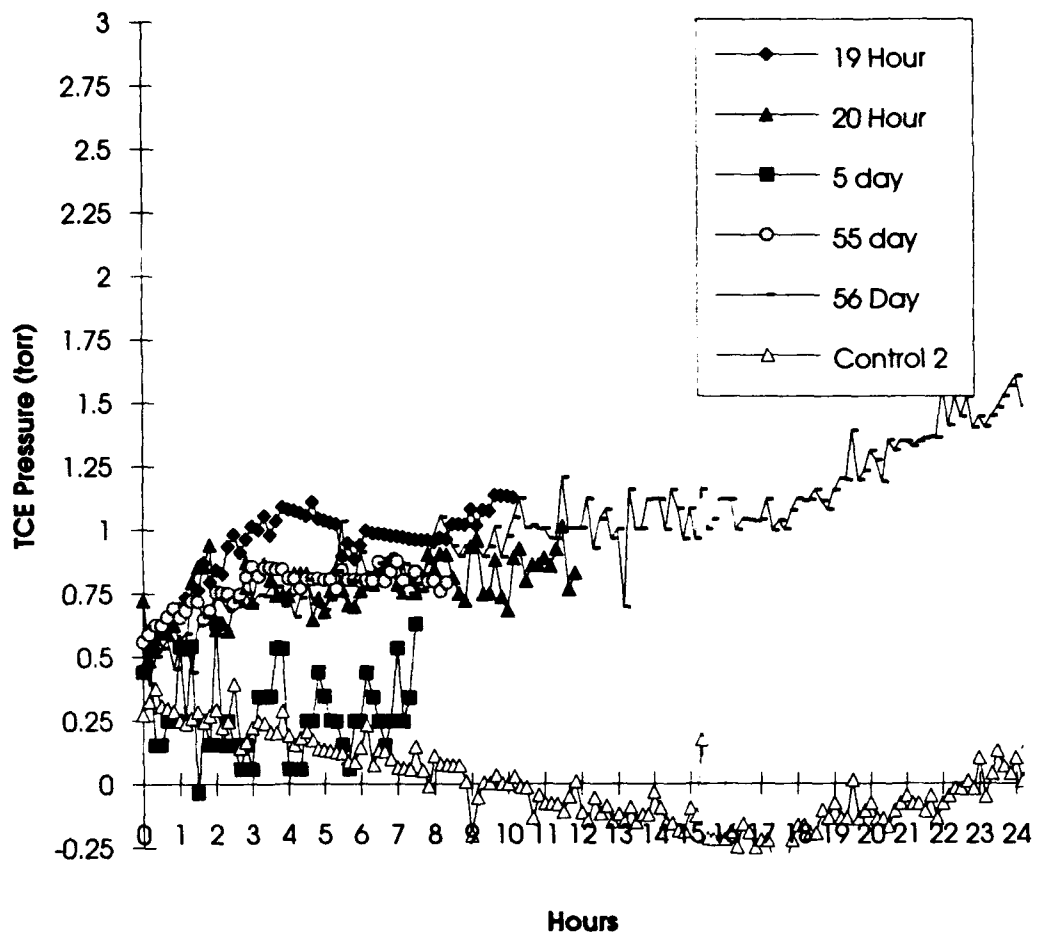


Figure 19

P_{tce} for All Experiments Starting From Second Evacuation

error. Other sources of experimental and human error includes the following:

4.2.1 Movement in the Optical Train

Because the InSb detectors are only 1 and 2 mm in diameter, any movement in a component of the optical chain will result in a rapid shift in the intensity readings and therefore the P_{tce} . Care was taken not to touch anything during an experiment. The time that posed the greatest risk of movement occurred when the detectors were being filled with liquid nitrogen. In all the above experiments there was only a few occasions when movement was detected. However, this error was easily identified and corrected because the data shift was generally obvious and the maximum intensity (I_0) was simply adjusted to line back up with the previous data points.

4.2.2 TCE Losses During Continuous Vacuum

Another source of potential error was due to differences in the amount of TCE lost during the 60 second and 30 second time periods when the cells were under continuous vacuum. When the valves to the vacuum pumps were opened during these times, atmospheric gases and TCE vapors were rapidly pulled out of the cell. Although the vacuum times (60 and 30 seconds) were held constant, there was no control on the initial amount of TCE moisture in the clay. This may have introduced some differences

in the amount of liquid TCE pulled out of the clay and perhaps some differences in the amount of TCE sorbed to the surface of the clay.

However, this was not expected to have caused any major interference with the data because the initial desorption rates from all the experiments were all very similar. If there had been large differences among the amount of TCE sorbed to the surface of the clay, we would have expected to see larger differences in the initial desorption rates. Also, the time scale of the periods under vacuum (seconds) is much shorter than the amount of time the clay took to desorb to an equilibrium from the surface sites (minutes). The initial 60 second period under vacuum was judged to have eliminated all liquid TCE from the clay. It was quite apparent that as soon as the vacuum valves were opened the clay would appear to instantly dry-up, based on its change in color. The 60 second time frame was decided upon to be sure all liquid TCE had evaporated from the soil so that only TCE sorbed to the surface sites and diffusion from the interior of the soil which occur more slowly than evaporation can be observed.

4.2.3 Atmospheric Interference

The cells leak a small amount of atmosphere into the cells over time; on the order of 2 to 8 torr in 36 hours. The amount of leakage was found by subtracting P_{TCE} from the P_{TOT} . This

increase in pressure caused by leakage mainly effected P_{tot} and it had only a small influence on P_{tce} . This is due to the fact that the band-pass filter allows a frequency through that is strongly absorbed by TCE but not strongly absorbed by atmospheric gases. There was only a maximum of a 2% reduction in intensity in going from vacuum (near 0) to one atmosphere (760 torr), which correlates to an increase of only 0.65 torr of equivalent TCE pressure. The excessive leak rate in the 10 day resident time experiment, where the leak reached about 10% of atmospheric pressure, correlates to an increase of 0.065 torr (10% x 0.65 torr) in equivalent TCE pressure. In all other experiments the P_{tot} increased by less than 1% of atmospheric pressure over 36 hours.

4.2.4 Losses in Mass of Clay

The amount of clay is expected to have an impact on the number of sorption sites and therefore the desorption rate due to a difference in the initial number of sorbed TCE molecules. The greatest source of error in the mass of clay added to the cell is losses to the container, the straw used to load the clay and spillage to the paper used to catch any clay that fell out during soil loading. These losses were estimated to be on the order of less than 0.05 grams based on initial and final weighing of each piece. Each container was filled with 2.05 grams of clay to account for these losses.

4.2.5 Microbial Activity

The degree of microbial activity in the clay was not evaluated, however the clay is oven-dried from the NIST and during the experiments it was held under vacuum with near zero moisture. Under these conditions, it is highly unlikely that there was any microbial activity.

4.3 Limitation of Experimental Design

4.3.1 Resolution and Lower Detection Limit

The lower detection limit of the system is correlated to the smallest change in the intensity readings from the InSb detectors. The Lock-Ins connected to the detectors were set to millivolts and were able to measure out to the thousandth digit. For example, we were able to measure a change from 2.000 mV to 2.001 mV. This level of resolution corresponded to a change of 0.017 torr of TCE pressure. The lower detection limit based on the limits of resolution is at least 0.02 torr of pressure. However, this level of resolution is outweighed by 3 orders of magnitude by the random drift error observed in the system (see appendix D). This random drift error over the 36 hour period is on the order of 1 to 2 torr of TCE pressure. Therefore, the lower detection limit and the resolution of the system is negligible in comparison to the random drift error.

4.3.2 Effects From Glass and O-Rings

Adsorption and desorption of TCE caused by the apparatus (glass and Kelvar O-rings) was taken into account with the control experiments. It is possible that TCE may remain sorbed into the apparatus if not enough time is allowed to off-gas the TCE. This may have caused variations in a follow-on experiment.

Preliminary experiments demonstrated that holding the system under continuous vacuum for at least 3 hours prior to a new experiment was enough to eliminate all detectable levels of TCE in the system. Therefore, before each experiment the system was held under vacuum for at least 12 hours to assure that the system did not add TCE during an experiment. Also, the control experiments confirmed that TCE was not added due to sorption in the apparatus.

However, it is expected that TCE was sorbed to the glass and O-rings as TCE desorbed from the clay to the atmosphere in the cell during the experiment. Because the inherent design of the system was common to all experiments, the comparison among the experiments was still considered useful but the equilibrium values would likely be different if there were any changes to the surface area or volume of the system.

4.3.3 Vacuum Versus Atmosphere

This study was performed under vacuum to eliminate the effects of atmospheric interferences and to accelerate the evaporation of liquid TCE. The sorption behavior of TCE may be different under vacuum than in normal atmospheric conditions. However, the trade-off in performing the experiment in a vacuum will reduce the variability that different atmospheric conditions would introduce.

V. Conclusions and Recommendations

5.1 Conclusions

5.1.1 Theory To Initial Desorption Rates

The theoretical explanation that could be used to describe the first hour of data for each experiment is that when the clay was soaked in liquid TCE, all of the surface sorption sites on the clay particles were quickly saturated. This would explain the similar initial desorption rates in each experiment even when the clay was soaking in liquid TCE for only 19 hours. This theory suggests that virtually all of the TCE pressure was caused by desorption from the surface sites on the clay particles. The reason that they all reached a similar equilibrium may be because the quantity of clay was held constant and due to the homogeneous nature of the samples there was roughly the same number of sorption sites on the clay particles for the TCE to attach to. In this case, the initial conditions of each experiment would be the same where there is no TCE in the atmosphere of the cell and there is a large amount of sorbed TCE saturating the sorption sites on the clay. With similar TCE concentration gradients in each experiment, it is conceivable that the TCE molecules desorbed at the same rate across all experiments. The fact that each experiment reached a similar equilibrium could be explained by the fact that the TCE was depleted from the surface sites on the clay. The adsorption rate back onto the clay would have to

be very small (near zero) and the desorption rate from the clay's surface would be relatively rapid.

5.1.2 Diffusion From The Soil Interior

The initial intent of this thesis was to examine the magnitude and the rate of desorption that occurs from the interior of the clay particles. However, the data is too limited to draw any solid conclusions. In general, the TCE pressure seems to gradually increase in all the experiments even after the second evacuation. This suggests that there may be a second desorption mechanism influencing the data because it is not nearly as rapid and distinct as the initial desorption rate. The data from the 56 day experiment is the most apparent data set that this gradual increase can be observed. It is possible that if the data were to be collected over a much longer time frame, perhaps weeks, this gradual increase would continue. It may also demonstrate that the clay exposed to TCE for longer time frames would continue to increase longer than clay exposed for shorter times. This could be attributed to the TCE entrained within the clay particles slowly diffusing out of the clay and desorbing into the atmosphere. However, the 36 hour time frame used in this study did not allow enough time to clearly observe this phenomenon.

5.1.3 Using This Evaluation Technique

With improvements to the system to reduce human and experimental error, it is this author's opinion that this technique is a viable way to study soil desorption. Spectrometry is a common technique used in contaminant identification and quantification. The use of infrared detection through the atmosphere surrounding the soil appears to be reliable, as indicated by the reasonable consistency in the data. Most of the limitations discussed in chapter 4 can be reduced or eliminated with improvements to the system or experimental technique.

5.2 Recommendations

5.2.1 Identify Cause of Detector Drift

Time did not allow the proper identification of the source of the drift error in the detectors (appendix D). This error was a significant hindrance to data analysis because the data did not exceed the magnitude of the error by an appreciable amount. When the cell is under continuous vacuum the intensity should not change over the length of time of the actual experiments. The source of this error should be identified and corrected perhaps by changing the type of detectors, as suggested below.

5.2.2 Use Room Temperature Detectors

Longer data collection times may have revealed the slower desorption caused by diffusion of the TCE through the interior of the soil. In order to make longer data collection periods more practical, use room temperature detectors instead of liquid nitrogen cooled InSb detectors. This would eliminate the need to continuously cool the detectors every 7 hours. The loss of sensitivity is expected to be a small trade-off in a longer experiment. This may also eliminate the detector drift problem if the source of the drift was inherent in the InSb detectors.

5.2.3 Increase the Diameter of Glass Cells

Optical alignment of the cells proved to be a tedious task and many data runs were lost to bad alignment as it is difficult to tell if there is an alignment problem until the experiment has progressed for some time. Also, alignment may become a problem during an experiment if there is any movement to the cell. Increasing the cells diameter from 1/2 inch to perhaps 1 inch would reduce the precision required to align the cell and reduce the impact of cell movement. The trade-off will be less sensitivity as more TCE molecules would be needed to produce the same change in the intensity. However, longer data collection periods may allow a larger amount of TCE to desorb out of the soil and this may reduce the impact of a loss in sensitivity. An increased cell diameter would also allow easier soil loading and

it would allow more soil to be added to the cell as there is not as much blockage of the IR beam caused by the soil. The additional soil may be more than enough to off-set the loss in sensitivity by increasing the amount of TCE molecules to desorb.

5.2.4 Firm Mounting System

Standard laboratory clamps were used to support the system which proved to be prone to movement even if touched lightly. A firm mounting system to support the cells and the detectors would reduce error caused by cell movement. A firm mount such as a long aluminum block with a V-notch in the top to rest the cell into would permanently mount the cells in the proper alignment with the detectors. Mounts for other components should be firmly in place with some fine tune adjustment capability. Fine tune adjustment is particularly important for the detectors, the beam splitter and the mirror.

5.2.5 Reduce Pressure Leaks

Over a longer experimental time frame, pressure leaks will become a greater concern. It was discovered well into this thesis that lab hygiene is very important. The soil created a fine dust in the atmosphere of the system which adhered to the O-rings and significantly reduced their ability to hold a vacuum. It was found that the best defense against this problem is to clean and re-grease each O-ring with vacuum grease after every experiment.

This practice significantly reduced the magnitude of the pressure leaks into the cell.

5.2.6 Better Materials

A complication in this experiment is that TCE is sorbed and desorbed from the glassware and O-rings in the system. Originally, Viton rubber O-rings were used and found to be a significant part of this problem. So Kelvar O-rings were used to replace the Viton O-rings. Although the new O-rings reduced TCE adsorption and desorption to the system by over 50%, there was still a significant amount of TCE being adsorbed and desorbed. In fact, preliminary experiments demonstrated that after 12 hours of vapor TCE exposure (near 65 torr) to the apparatus, the system reached an asymptotic value of 16 torr in 10 hours of desorption time after evacuation. With the better Kelvar O-rings, the system reached 10 torr in 10 hours under the same conditions. However, when the system was held at vacuum for a few hours after the vapor TCE exposure, no detectable levels of TCE were desorbed from the system. It is suspected that the glass cells were a significant part of this desorption problem from the system. Another material such as stainless steel or Teflon may reduce the amount of TCE adsorbed and desorbed to the walls of the cells.

5.3 Follow-On Research

5.3.1 More of the Same Data

The amount of time left to run experiments was short after all the problems were worked out of the system. A pattern in the data was apparent but more data is needed to confirm some of the conclusions made earlier. More of the same type of data using flint clay on an improved system may not only confirm this data but it may make some other patterns in the data easier to interpret.

5.3.2 Longer Data Collection Times

Part of the original intent of this thesis was to observe desorption of TCE from the interior of the soil particles. It is suspected that the data collected over 36 hours was too short to observe this slow desorption. Data collection on an improved system should be extended for perhaps weeks to observe this slower desorption mechanism. A problem that may be encountered in a longer desorption time period is that the magnitude of pressure losses may be more severe. However, it was demonstrated that atmospheric effects on intensity are negligible (section 4.2.3). Also, the detector drift in this thesis was analyzed over a 36 hour time period. The drift for an experiment that had a longer time frame may drift more severely or it may level off. In addition to longer experiments, more experiments should be

performed over a wider range of resident times to add validity to the data.

5.3.3 Simulate Field Conditions

In order to get closer to applying the data from this technique to actual field conditions, some adjustments can be made to simulate the sub-surface vadose zone or even the saturated zone conditions. Soil can be soaked in a water/TCE mixture and the moisture content of the soil can be determined gravimetrically before each experiment. This will allow a mass balance to be done knowing the percentage of TCE in the mixture. Water vapor will interfere to some extent in the frequency range used in this experiment but it may have a very small effect that can be corrected. To eliminate immediate evaporation, instead of a full evacuation to vacuum, a partial pressure can be allowed in the cell because atmospheric gases have been found to have a minimal effect on the intensity readings.

5.3.4 Use other Chemicals or Other Soils

It is desirable to learn more about TCE, not only because of its prevalent nature, but it would also make it easier to fine tune this technique. However, as more is learned this technique could be used with other VOCs or with different soil types. As this technique proves to be a viable research tool in learning about the phenomenon of soil desorption, using different soils and

different chemicals makes the prospects for follow-on research seemingly endless.

5.4 Summary

The results of this thesis is that there appears to be an initial and rapid (minutes) desorption mechanism that is independent of TCE resident time in clay soil. It is thought that the desorption from the surface sites on the clay particles is the dominant mechanism in this initial desorption. This conclusion implies that the surface sites on the clay are fully saturated in the tested range of 19 hours to 56 days. The data also suggests that there is a long term desorption mechanism thought to be caused by the slow diffusion of the TCE molecules from the interior matrix of the soil particles. However, the data in this thesis is too limited to draw any firm conclusions about this slow, long term desorption mechanism. Finally, the infrared spectrometry experimental method used in this thesis is an effective method to study the phenomenon of VOC desorption rates from soil. With improvements this method could be used to perform further and more detailed research on soil desorption.

Appendix A

Correction For Cross-sectional Area

In order to compute a quantitative justification to correct the experimental data from the curved feature in Figure 7 to a straight line, an understanding of the absorption spectrum of TCE and the transmittance of the broad band filters is needed. The intensity $I(\lambda)$ measured by the detector, which is frequency dependent, must pass through the column of TCE and the broad band filter. So the intensity $I(\lambda)$ as measured by the detector is the intensity with no TCE or filter (I_{\max}) multiplied by the fraction allowed through by the filter, $\left[\frac{I}{I_0}\right]_{\text{filter}}$, and multiplied by the fraction allowed through by $\left[\frac{I}{I_{\max}}\right]_{\text{TCE}}$. In other words, at a specific frequency if the column of TCE transmits 10% of the intensity and the filter transmits 50%, then only 5% of the unobstructed intensity (I_{\max}) will get through to the detector. The mathematical relationship is as follows:

$$I(\lambda) = I_{\max} \left[\frac{I}{I_0}\right]_{\text{filter}} \left[\frac{I}{I_{\max}}\right]_{\text{TCE}} \quad (\text{A.1})$$

where:

$I(\lambda)$ = Intensity measured by detectors

I_{\max} = Maximum intensity (no filter or TCE)

$\left[\frac{I}{I_0}\right]_{\text{filter}}$ = Fraction transmitted through filter (no TCE)

$\left[\frac{I}{I_{\max}}\right]_{\text{TCE}}$ = Fraction transmitted through TCE (no filter)

I_0 = intensity at detector with no TCE

We know from Beer's Law that the decay in intensity caused by the concentration of TCE in the column at any given frequency is governed by equation 5:

$$\left[\frac{I}{I_{\max}} \right]_{\text{TCE}} = e^{-\sigma(\lambda)lN} \quad (5)$$

And the filter transmission is a function of its spectral transmissivity, $T(\lambda)$. Substitution into equation (A.1) yields:

$$I(\lambda) = I_{\max} T(\lambda) e^{-\sigma(\lambda)lN} \quad (A.2)$$

Because the detector measures a wide range of frequencies, equation (A.2) must be integrated from 0 to ∞ in order to get the intensity that is measured by the detector.

$$\int_0^{\infty} I(\lambda) d\lambda = \int_0^{\infty} I_{\max} T(\lambda) e^{-\sigma(\lambda)lN} d\lambda \quad (A.3)$$

Equation A.3 can be modified for the intensity measurements when TCE is not present (I_0), which is when $N = 0$ and $e^0 = 1$. The equation for the intensity at the detector becomes:

$$\int_0^{\infty} I_0(\lambda) d\lambda = \int_0^{\infty} I_{\max} T(\lambda) d\lambda \quad (A.4)$$

The mathematical solution for I/I_0 can be found by combining equation A.3 and A.4. Because I_{\max} is a constant, it will cancel.

$$\left[\frac{I}{I_0} \right]_{\text{exp}} = \frac{\int_0^{\infty} T(\lambda) e^{-\sigma(\lambda)lN} d\lambda}{\int_0^{\infty} T(\lambda) d\lambda} \quad (\text{A.5})$$

In order to simplify the mathematics in solving equation A.5, a boxed shaped approximation of the area under the curves for the transmission spectrum of TCE and the filter will be used. The filter transmission spectrum (Figure A.1) was evaluated on a Bio-Rad Fourier Transform Infrared (FT/IR) Spectrometer model number 60A and the TCE absorption spectrum (Figure 6) was evaluated on the Bomem Fourier Transform Spectrometer. Figure A.2 illustrates the approximation of the areas under the curves from Figures 6, and A.1 in order to solve equation A.5.

The heavily shaded area in Figure A.2 is the area transmitted to the detector. The areas of the transmitted intensity have been broken into 3 regions. The heights of regions 1 and 3 are only effected by the filter (t) and area 2 is effected by both TCE and the filter and is therefore the product of (t) times e^{-alN} . The variable "a" is an arbitrary place holder for the cross-sectional area. The width of regions 1 and 3 is (T-A) and the width of region 2 is A where A and T are approximations from Figures 6 and A.1, respectively. In solving equation A.5, where the numerator is influenced by TCE and the denominator is TCE free, the correction needed to convert the experimental intensity data $\left[\frac{I}{I_0} \right]_{\text{exp}}$ into the intensity effected by TCE alone is as follows:

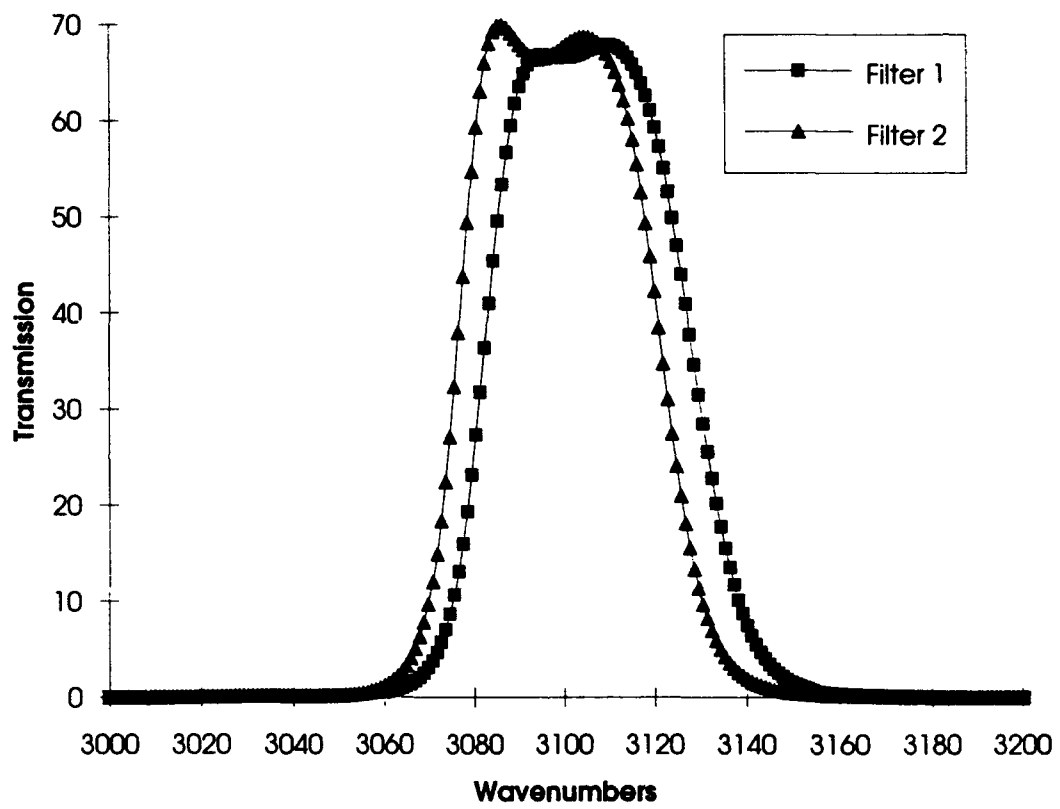


Figure A.1
Transmission Spectrum
of the Filters

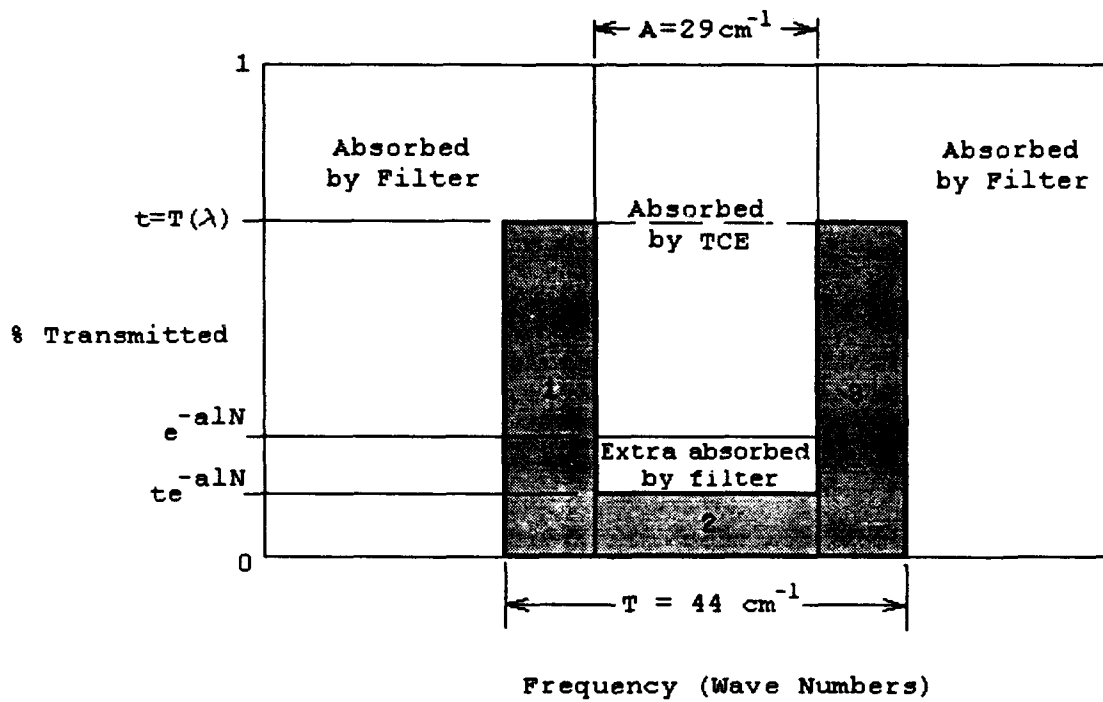


Figure A.2
 Approximation of Filters and TCE Transmission Curves

$$\left[\frac{I}{I_0}\right]_{\text{exp}} = \frac{t(T-A) + (A)(t)e^{-alN}}{Tt} \quad (\text{A.6})$$

Canceling the t's, adding equation 5 and rearranging yields:

$$\left[\frac{I}{I_0}\right]_{\text{exp}} = \left[1 - \frac{A}{T}\right] + \frac{A}{T} e^{-alN} \quad (\text{A.7})$$

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = e^{-alN} = \text{Fraction through TCE only} \quad (5)$$

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \frac{T}{A} \left[\left[\frac{I}{I_0}\right]_{\text{exp}} - \left[1 - \frac{A}{T}\right] \right] \quad (\text{A.8})$$

Therefore, in order to convert the experimental data into intensity data that is influenced by TCE alone, solve for $\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}}$ and substitute the approximated values for T and A found in Figure (A.3). The values are as follows:

$$T = 43 \text{ cm}^{-1} \quad (\text{from Figure A.1})$$

$$A = 29 \text{ cm}^{-1} \quad (\text{from Figure 6})$$

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \left[\left[\frac{I}{I_0}\right]_{\text{exp}} - \left[1 - \frac{29}{43}\right] \right] \frac{43}{29} =$$

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \left[\left[\frac{I}{I_0}\right]_{\text{exp}} - 0.33 \right] * 1.5 \quad (\text{A.9})$$

Formula A.9 is needed to correct our experimental intensity data to intensity data influenced only by TCE. When this formula is applied to the experimental data for each tube, the slope of the pressure versus $\ln(I/I_0)$ become constant to yield a constant

cross-sectional area. The slope of the corrected graph of Pressure vs. $\ln(I/I_0)$ (from Figure 7) is illustrated in Figure A.3.

The slope for filter 1 is -0.04755 at a temperature of 27°C (300°K). The linearity of the curve was computed using regression analysis where the R-squared values was 0.996. The slope can now be used to compute the cross-sectional area (σ) from equation (9).

$$\sigma = -\frac{\ln\left[\frac{I}{I_0}\right]}{P} \frac{1.036 \times 10^{-19} (T)}{l} \quad (9)$$

Solving for cross-sectional area at 300°K:

$$\sigma = -(-0.04755) \frac{1.036 \times 10^{-19} (300^\circ\text{K})}{43.5 \text{ cm}}$$

$$\sigma = 3.27 \times 10^{-20} \text{ cm}^2/\text{molecule} \quad (\text{A.10})$$

For a more accurate method in determining the correction formula in equation A.9 and the cross-sectional area (σ) in A.10, we used software called Table Curve to curve fit actual data. The formula that was used in the curve fitting was equation 9 combined with the correctional formula A.8:

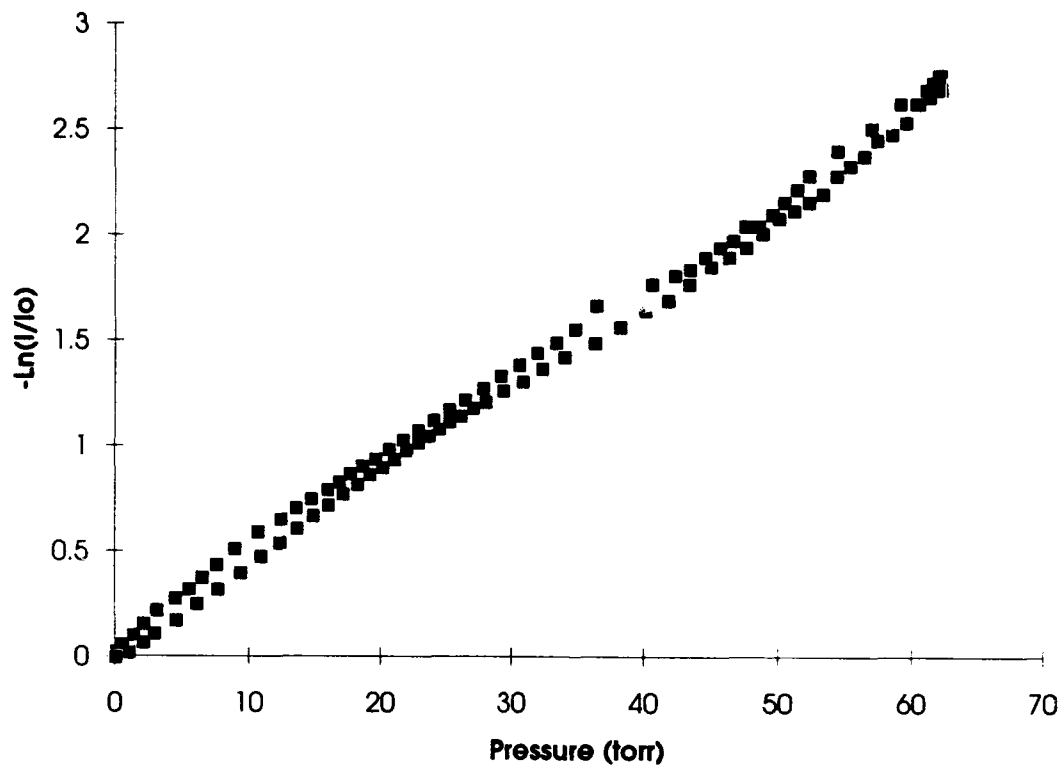


Figure A.3
Corrected Pressure Vs. $-\ln(I/I_0)$ in Filter 1

$$\sigma = -\frac{\text{Ln}\left[\frac{I}{I_0}\right]}{P} \frac{1.036\text{E}-19 (T)}{1} \quad (9)$$

$$\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \frac{T}{A} \left[\left[\frac{I}{I_0}\right] \exp - \left[1 - \frac{A}{T}\right] \right] \quad (\text{A.8})$$

where $\left[\frac{I}{I_{\text{max}}}\right]_{\text{tce}} = \text{Ln}\left[\frac{I}{I_0}\right]$ because both assume no filter and both I_0 and I_{max} assume no TCE

$$\sigma = -\frac{\text{Ln} \frac{T}{A} \left[\left[\frac{I}{I_0}\right] \exp - \left[1 - \frac{A}{T}\right] \right]}{P} \frac{1.036 \times 10^{-19} (T)}{1} \quad (\text{A.11})$$

Let:

$$Y = \frac{I}{I_0}$$

$$X = P$$

$$B = -\frac{\sigma}{T} \frac{1}{R}$$

$$C = \frac{A}{T}$$

Substitution and rearranging equation A.11 becomes:

$$Y = C e^{-Bx} + (1-C) \quad (\text{A.12})$$

This reduced form of the equation was evaluated with actual I/I_0 and pressure values for Y and X in both cells. The variables B and C were found with a best fit from the Table Curve program. The values for B , C and the R-squared values for each cell are as follows:

	B	C	R-Squared
Cell 1	0.0464	0.638	0.995
Cell 2	0.0469	0.623	0.996

Solving for the cross-sectional areas and the corrective formula with the values for B and C from above definitions will yield:

	σ	Corrective Formula
Cell 1	3.32×10^{-20}	$\left[\frac{I}{I_{\max}}\right]_{tce} = \left[\left[\frac{I}{I_0}\right] \exp -0.36\right] * 1.57$
Cell 2	3.35×10^{-20}	$\left[\frac{I}{I_{\max}}\right]_{tce} = \left[\left[\frac{I}{I_0}\right] \exp -0.38\right] * 1.61$

Due to the greater accuracy of this later method and the fact that the final results between the two cells are close, the following average values for the above results will be used to correct the data from both cells.

Cross Section $\sigma = 3.335 \times 10^{-20} \text{ cm}^2/\text{molecule}$ (A.13)

Corrective Formula $\left[\frac{I}{I_{\max}}\right]_{tce} = \left[\left[\frac{I}{I_0}\right] \exp -0.37\right] * 1.59$ (A.14)

APPENDIX B

TCE Concentration in molecules/cm³

Rearranging Beer's equation (5) for the concentration of TCE, (N), yields:

$$N = -\frac{\text{Ln}\left[\frac{I}{I_0}\right]}{(\sigma)l} \quad (10)$$

Using this generic equation along with the intensity correction formulas derived in equation A.14, yields the following TCE concentrations in molecules/cm³:

$$N = -\frac{\text{Ln}\left[\left[\left[\frac{I}{I_0}\right]-0.37\right]*1.59\right]}{(\sigma)l} = -\frac{\text{Ln}\left[\left[\left[\frac{I}{I_0}\right]-0.37\right]*1.59\right]}{(3.335 \times 10^{-20} \text{ cm}^2/\text{molecule})(43.5 \text{ cm})}$$

$$N = -6.89 \times 10^{17} * \text{Ln}\left[\left[\left[\frac{I}{I_0}\right]-0.37\right]*1.59\right] \quad (B.1)$$

where:

N = concentration of TCE (molecule/cm³)

I = transmitted intensity (mVolts)

I₀ = initial intensity (mVolts) - maximum intensity with no TCE absorption

APPENDIX C

TCE Concentration in Terms of Pressure

It is desirable to convert the concentration (N) of TCE into units of pressure in torr so that a direct comparison can be made with the pressure readings from the pressure detector. In order to convert N in molecules/cm³ to units of pressure in torr, the ideal gas formula in equation (7) is substituted into equation

B.1:

$$N = \frac{P}{(1.036 \times 10^{-19})(T)} \quad (7)$$

$$\frac{P}{(1.036 \times 10^{-19})(T)} = (-6.89 \times 10^{17}) * \text{Ln} \left[\left[\left[\frac{I}{I_0} \right] - 0.37 \right] * 1.59 \right]$$

Solving for pressure:

$$P_i = -0.0714 (T) \text{Ln} \left[\left[\left[\frac{I}{I_0} \right] - 0.37 \right] * 1.59 \right] \quad (C.1)$$

where: P_i = Pressure as computed from intensity data

T = temperature in °K

Equation C.1 relate the values for intensity observed from the detectors to the concentration of TCE in terms of pressure (torr). This formula will be used to compare the P_i values with the values measured by the pressure detectors (P_D)

Appendix D

Correction for Drift in Detectors

There is a drift observed from the detectors when all conditions are held constant and the cells are under vacuum, where the intensity measured by the detectors decrease slightly over time. The cause for this drift error in the detectors is unknown and it appears to be somewhat random. The drift does follow a pattern of an initially fast decrease in intensity followed by a leveling off for the duration of the testing (up to 36 hours). The observed effect of the decreasing intensity essentially gives the illusion that there is an increasing concentration of TCE in the cell, which we know can not be true because the cells were held at constant vacuum for the entire test. The magnitude of the error was observed to be as high as the equivalent of 4.5 torr of TCE. Two separate 36 hour tests were done on each cell while under constant vacuum to determine the repeatability and trend of the drift. Figure D.1 and D.2 illustrate the equivalent pressure readings as if the intensity changes were caused by TCE for cell 1 and cell 2, respectfully.

Although, the drift in each cell appear random, it was decided that we should still correct the intensity data for the general pattern in the curves to reduce the magnitude of the error. The software Table Curve was used to fit the data as accurately as possible and the corresponding curves are shown on

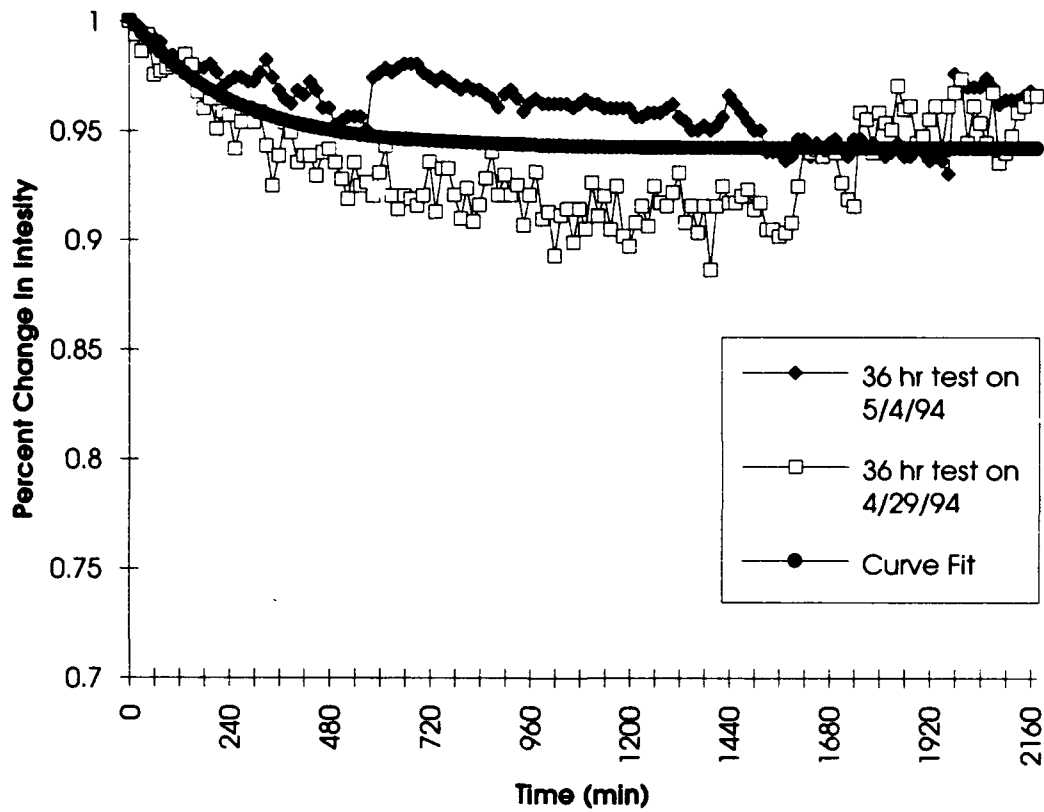


Figure D.1
 Two - 36 hour Detector Drift Tests
 Cell 1

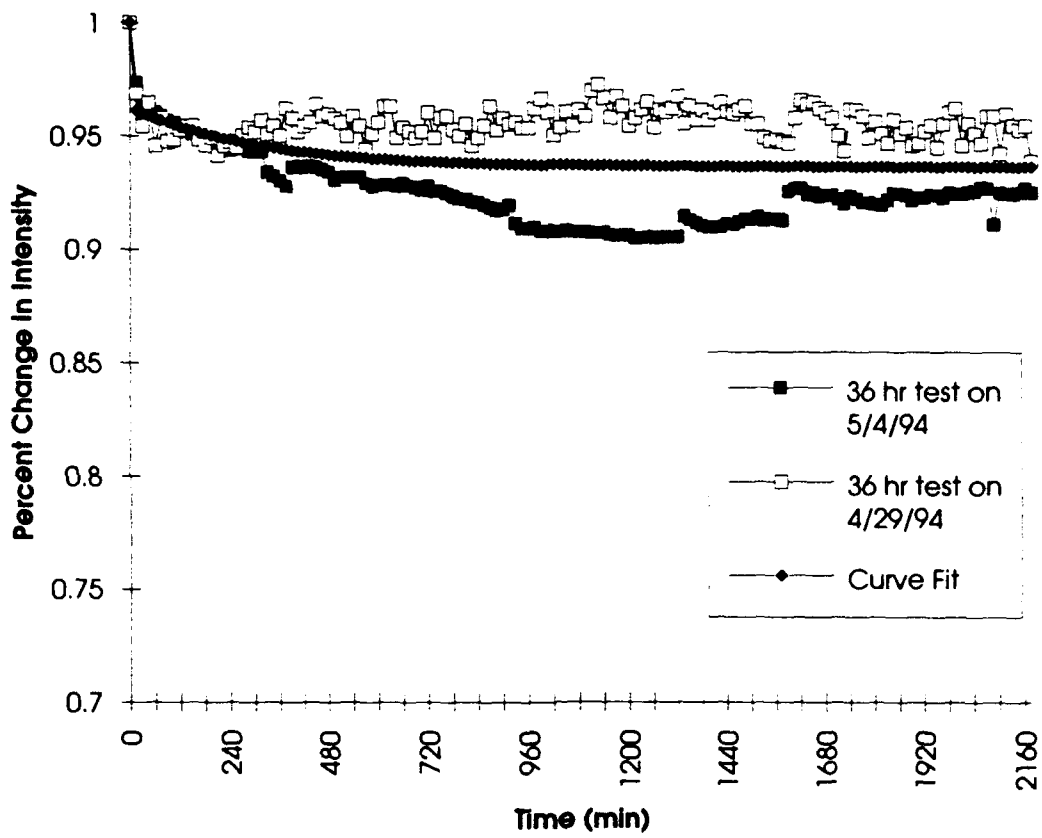


Figure D.2
 Two - 36 hour Detector Drift Tests
 Cell 2

Figures D.1 and D.2. The following algebraic formulas describe these curves with R^2 values of 0.25 and 0.08 respectively:

$$\text{Cell 1} \quad I/I_0 = 0.9425 + 0.0593 e^{-(\text{min}/239.78)} \quad (\text{D.1})$$

$$\text{Cell 2} \quad I/I_0 = 0.9362 + 0.0264 e^{-(\text{min}/300.33)} \quad (\text{D.2})$$

These curves correspond to a percent reduction in the intensity signal (I/I_0) at any point in time in units of minutes. The way the data is corrected is by multiplying the I/I_0 (% correction) in the above formulas with the I_0 in the experimental data. When correcting equation C.1 for pressure caused by TCE, the following formulas result:

$$P_i = -0.0714 (T) \text{Ln} \left[\left[\left[\frac{I}{I_0} * \% \text{ correction} \right] - 0.37 \right] * 1.59 \right] \quad (\text{D.3})$$

where the % correction is the I/I_0 in equations D.1 and D.2 with respect to time.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 97b

Flint Clay

This Standard Reference Material (SRM) is intended for use in the determination of constituent elements in clay or material of similar matrix. SRM 97b is powdered clay that was air-dried, ball-milled, and blended to ensure homogeneity.

The certified constituent elements of SRM 97b are given below in Table 1. The certified values are based on measurements made using two or more independent reliable methods or techniques. Non-certified values for constituent elements are given in Table 2 as additional information on the composition. The non-certified values should not be used for calibration or quality control. All values are based on samples that were dried for 2 hours in a conventional oven at 140 °C and a minimum sample size of 250 mg.

Table 1

Certified Values for Constituent Elements

Element ¹	Content, Wt. % ²	Element	Content, Wt. %
Aluminum ^{c,d,g}	20.76 ± 0.15	Manganese ^{b,g}	0.0047 ± 0.0005
Calcium ^{b,d,f}	0.0249 ± 0.0026	Potassium ^{b,c,f,g,i}	0.513 ± 0.023
Chromium ^{c,g}	0.0227 ± 0.0012	Silicon ^{e,i}	19.81 ± 0.04
Iron ^{c,g}	0.831 ± 0.008	Sodium ^{b,d,g}	0.0492 ± 0.0023
Lithium ^{d,f}	0.055 ± 0.001	Strontium ^{d,f,g}	0.0084 ± 0.0002
Magnesium ^{b,c}	0.113 ± 0.002	Titanium ^{b,g,h,i}	1.43 ± 0.04

¹ Methods / Techniques

- a Colorimetry (o-phenanthroline)
- b DC Plasma Spectrometry
- c Flame Atomic Absorption Spectrometry
- d Flame Emission Spectrometry
- e Gravimetry

- f Isotope Dilution Mass Spectrometry
- g Instrumental Neutron Activation Analysis
- h Spectrophotometry
- i X-ray Fluorescence

²The certified value is a weighted mean of results from two or more analytical techniques. The weights for the weighted means were computed according to the iterative procedure of Paule and Mandel (NBS Journal of Research 87, 1982, pp. 377-385). The uncertainty is the sum, in quadrature, of the half-width of a 95% expected tolerance interval and an allowance for systematic error among the methods used. The interval whose endpoints are the certified value minus and plus the uncertainty, respectively, will cover the concentration in a minimum sample size of 250 mg of this SRM for at least 95% of the samples with 95% confidence.

Gaithersburg, MD 20899
April 21, 1988

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

Table 2

Non-certified Values for Constituent Elements

<u>Element</u>	<u>Content Wt. %</u>	<u>Element</u>	<u>Content Wt. %</u>
Barium	(0.018)	Zirconium	(0.05)
Phosphorus	(0.02)		
<u>Element</u>	<u>Content $\mu\text{g/g}$</u>	<u>Element</u>	<u>Content $\mu\text{g/g}$</u>
Antimony	(2.2)	Rubidium	(33)
Cesium	(3.4)	Scandium	(22)
Cobalt	(3.8)	Thorium	(36)
Europium	(0.84)	Zinc	(87)
Hafnium	(13)		
		Loss on Ignition	(13.3 wt%)

Loss on ignition was obtained by igniting sample for 2 hours at 1100 °C after sample was dried for two hours at 140 °C.

Source and Preparation

The flint clay for SRM 97b was donated to NBS by F.J. Flanagan and J.W. Hasterman of the United States Geological Survey, Reston, Virginia. Approximately 220 kg of flint clay was collected from a stockpile near the Harbison-Walker Refractories Co. Mine on Anderson Creek, Pike Township, Clearfield County, PA. The collected clay was air-dried and processed by the same method used to prepare USGS rock standards (USGS Bulletin 1582, Flanagan, 1986). After processing, the sample was delivered to NBS, where it was again mixed in a 0.3 cubic meter "V" blender for approximately 45 minutes. After blending the clay was placed in polyethylene lined aluminum pails and subsequently bottled.

Homogeneity testing was performed using x-ray fluorescence and instrumental activation analysis on randomly selected samples from cans of bulk material. There were no significant differences among samples for any of the measured elements.

Chemical analyses were performed in the following laboratories:

- National Bureau of Standards, Center for Analytical Chemistry, E.S. Beary, D.A. Becker, W.A. Bowman III, T.A. Butler, K.A. Brletic, J.W. Gramlich, D. Mo, J.R. Moody, and T.C. Rains.
- Mineral Constitution Laboratory, Pennsylvania State University, University Park, Pennsylvania, J.B. Bodkin.
- Engelhard Corporation, Specialty Chemical Division, Edison, New Jersey, B.P. Scibek.
- Construction Technology Laboratories, Inc., Skokie, Illinois, H.M. Kanare.

The statistical analysis and evaluation of the data for certification was performed by K.R. Eberhardt and S.B. Schiller of the Statistical Engineering Division and R.L. Watters, Jr. of the Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T.E. Gills.

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Vita

I grew up in a small town in upstate New York and attended college at Clarkson University, NY where I earned a B.S. in Mechanical Engineering in 1986 and where I met my wife, Cheryl. I entered the Air Force on October 1986 at Wright-Patterson AFB, OH in the Human Engineering Division of Armstrong Laboratories where I designed research equipment for optical experiments and was program manager of an experiment in which an optical telescope flew aboard the space shuttle Endeavor on November 1990. I then changed assignments at Wright-Patterson AFB to the work for the Medical Center in the Bioenvironmental Engineering Directorate. I was Deputy Director of Industrial Hygiene and supervised 3 officers and 18 enlisted personnel to complete annual industrial hygiene surveys in over 350 facilities at WPAFB. I earned an M.B.A. at Wright-State University on May 1991 and entered AFIT on May 1993 to earn a Masters Degree in Environmental Engineering and Management.

