Use of Diffuse Reflectance Spectroscopy to Determine
Desorption Coefficients of Trichloroethylene from
Powdered Soils

THESIS

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AFIT/GAP/ENP/99M-02

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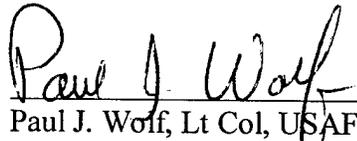Jay H. Foil, Captain, USAF

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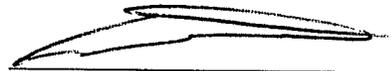Desorption Coefficients of Trichloroethylene from
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Trichloroethylene from Powdered Soils

THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science of Engineering Physics

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March 1999

Disclaimer Statement

The views expressed in this thesis are those of the author and do not reflect the

official policy of position of the Department of Defense of the United States

Government.

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Abstract

This laboratory thesis investigated the applicability of reflectance spectroscopy as a tool to measure desorption rates by directly observing the change in trichloroethylene bound to surface sites. Diffuse reflectance spectroscopy holds the promise of being a faster technique with minimal sample preparation time. Reflectance spectroscopy's dependence on the surface of the sample is its greatest advantage, as well as its greatest disadvantage. Both high and low resolution scans were made of different soil samples contaminated by trichloroethylene. After the technique of spectral subtraction was used, potential TCE signals were observed from the dolomitic limestone sample. Unfortunately, due to the low level of the signal and high amount of noise, positive identification of the signals as TCE could not be established. The low resolution scans were unable to detect any possible TCE signals. More data is required to determine the sensitivity of the device as well as prove the linearity of the signal with concentration, before this technique can be proven to be useful for studying desorption kinetics.

1 INTRODUCTION

1.1 Problem Statement

The primary emphasis of this research is to determine the applicability of reflectance spectroscopy as a tool to measure desorption rates by directly observing organic compounds bound to surface sites. In this experiment the organic compound to be studied is trichloroethylene (TCE). If diffuse reflectance proves to be an adequate technique, it may be a "quicker" method to determine desorption rates.

Contamination of the environment has become a major concern for both industry and the Department of Defense. One of the primary sources of the contamination of industrial and military sites is volatile organic compounds (VOC); the one most commonly found at contaminated sites is trichloroethylene (TCE). Within the Air Force, TCE has been widely used for degreasing mechanical parts and cleaning electronic components. This widespread use has led to the contamination of the water and soil of many superfund sites (19:3-5).

In order to determine the most effective method of site cleanup, it is important to understand the desorption process and the occurrence rate of these processes. The studies by Farres, Kindt, LaPuma, and Stager used optical absorption to measure the build up of the concentration of TCE vapor as TCE desorbes from the powdered soil over a period of time (6:42, 8:35, 9:56-59, 20:24). The main drawback to this technique is that as the vapor accumulates in the sample cell, chemical equilibrium may be reached, hampering the desorption process.

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Another approach to measuring the desorption process is to use reflectance spectroscopy to measure the changes in absorption due to changes in the concentration of TCE bound to surface sites. Reflectance spectroscopy has been widely used in many fields from agriculture, pharmacology, and environmental research, each with great success to measure chemical composition and detect the presence of organic compounds. Like transmission spectroscopy, reflectance spectroscopy can be used to determine the chemical composition of the agricultural products, pharmaceutical products, paints, and foodstuffs (11:326). The main effort of this research is to determine if reflectance spectroscopy is a suitable technique to measure desorption rates. The reflectance data will then be fitted to the Langmuir, single-site model for desorption.

1.2 Research Objectives

There are two primary objectives to this research to determine if this technique can be used to study desorption kinetics. The first objective is to determine if diffuse reflectance can be used to detect TCE bound to soil sites. Provided the first objective is successful, then the second objective is to attempt to determine desorption rates by monitoring the change in the amount of TCE bound to surface sites over time.

1.3 Overview

The remaining chapters of this thesis provide the approach and methodology to meet the research objectives. Chapter two provides the theories and concepts behind the experiment and data analysis. Chapter three describes the experimental technique, while

the results are presented in chapter four. The final chapter details my conclusions and recommendations for future experiments. The ability of the experiment to meet the research objectives will also be detailed in this section.

2 BACKGROUND

2.1 Overview

This section provides the theories and the concepts behind the experiment and the data analysis. The first section summarizes what is known about the sources of TCE contamination of the environment. The following sections will discuss TCE's behavior in the environment and previous studies' regarding it's desorption from powdered soils. Finally, the last section will discuss the theories that are needed to conduct the experiment.

2.2 Sources of TCE Contamination

TCE was a major industrial solvent from 1940 until the late 1970's, and was widely used in both private industry and in the Department of Defense. In the Air Force, TCE was primarily used as a degreaser for aircraft parts and electronic components (17:17). Until the mid 1970's, TCE was thought to be a safe product for human contact, therefore inexpensive methods were often used to dispose of the product. The dumping of TCE in landfills, drywells, and at various locations directly onto the ground, was deemed acceptable until laws and regulations stopped the practice in the late 1970's. These disposal practices have now contaminated the groundwater in the areas where TCE was dumped (Ibid:21) These unsafe disposal methods have led to extensive contamination of the soil and groundwater at many Superfund sites and Air Force Bases (2:25).

Along with the original sources of environmental contamination, secondary sources can come from the interaction of the contaminant with the environment. Even

after the original sources of contamination have been removed, secondary sources of contamination can still serve as source of environmental contamination. Once TCE is release into the soil, it can congregate as a residual in unsaturated zones or as a pool floating on or under an aquifer, thereby acting as a secondary source. TCE can also interact with the soil matrix in such a way to cause the matrix to store TCE. Over time TCE will start to desorb from the soil matrix becoming a "secondary source" (12:631).

2.3   Behavior of TCE in the Environment

Understanding how TCE interacts with the environment is another important key to site cleanup. TCE is an unsaturated, chlorinated aliphatic compound with a low molecular weight. It has a high density, low surface tension, and high vapor pressure. The specific properties of TCE are listed in Table 1. It is only slightly soluble in water, and tends to sink in water. When released into the ground, TCE migrates rapidly, especially in dry soil. Droplets of organic liquid are left in the pore spaces while some liquid will absorb to the soil particles as the liquid is pulled downward by gravity (3:359). Upon reaching a less permeable layer or the groundwater table, its descent is slowed and will collect on top of the layer, building up pressure. The pressure buildup will force the TCE to spread laterally. Once the pressure is great enough, the TCE will penetrate the groundwater, and continue downward. Any impermeable strata encountered in its pathway can cause the TCE to spread laterally. If enough pressure builds up, the TCE will spread and collect in basins and depressions, forming pools and puddles along the bottom of the aquifer. These pools can serve as secondary sources of contamination. Any water that flows over these pools and puddles will help transport the TCE horizontally across the aquifer (18:8).

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Table 1. The physical properties of TCE (10:3352-3353)

Property	Value	Units
Physical State (@ 15° C and 1 atm)	Liquid	
Chemical Formula	C_2HCl_3	
Molecular Weight	131.39	amu
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
Vapor Pressure (@ 20°C)	58.0	torr
Latent Heat of Vaporization	2.4×10^5	J/kg
Viscosity	0.57	cP
Solubility (@ 20°C)	0.7	g/liter
Henry's Constant	0.232	unitless
Partition Constant	0.199	ml/g
EPA Maximum Contaminant Level (MCL)	0.005	mg/liter
Temperature Characteristics		
Auto-Ignition Temperature	788.0	°F
Plash Point	89.6	°C
Boiling Point	86.7	°C
Melting Point	-70.0	°C
Freezing Point	-86.8	°C

2.4 Previous Desorption Studies

There is no evidence to date to show that anyone has used diffuse reflectance to measure desorption kinetics in soil samples. Previous desorption kinetics studies have either used chemical or optical absorption techniques. Previous diffuse reflectance studies have concentrated on detecting chemical composition in different sample types. The following sections will describe these efforts in more detail.

2.4.1 TCE Desortion Tests

The desorption characteristics of TCE have been detailed in many previous studies. Aside from the numerous journal articles regarding TCE and its effects in the environment, the experiments of Fares, La Puma, Kindt, and Stager specifically examined the desorption of TCE over time and tried to determine rate coefficients for both short and long-term desorption (6:4,8:6,9:1,20:7).

Each of the studies used the same method to determine the amount of TCE desorbing from the soil particles. The studies relied on measuring the change in optical absorption to determine the amount of TCE vapor leaving the soil. After their soil samples were dried in a vacuum, the TCE contaminated soil particles were placed in a cylindrical glass container. The atmosphere in the cylinder was removed before the cylinder was completely sealed. As the TCE desorbed from the soil particles, the vapor would build up in the cylinder. This build up would cause a change in the infrared spectral signal, transmitted through the cylinder and could be used to measure the change in concentration over time and determine the desorption coefficients (6:42, 8:35, 9:56-59, 20:24).

The studies by Fares, Kindt, and La Puma showed that the buildup of TCE vapor followed the Langmuir desorption model. Fares work studied the effects of temperature on desorption rates of TCE from plastic clay. The optical absorption was measured as TCE desorbed from plastic clay at fixed temperatures. His results showed that temperature influenced the desorption rate from the soil. An increase in the temperature caused an increased desorption rate as well as caused a larger amount of TCE to desorb

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from the sample (6:108). Kindt's study focused on the desorpion of TCE from multiple soils to determine the effect of soil characteristics on TCE desorption. His results showed that the magnitude and rate of desorption increased corresponding to increased total surface area of the particles. His study also showed that the elemental composition of the soil affected the desorption process. He even stated that soils with a high aluminum content could be expected to be slow desorbers (8:76). La Puma's research investigated the effect of varying the exposure time of TCE to flint clay on TCE desorption. The results indicated the initial desorption mechanism appeared to be independent of exposure time. He hypothesized that the initial desorption phase maybe associated with TCE desorbing from surface sites. His results showed that at longer times, the data increased above that expected in the Langmuir model. He hypothesized that the increase in the second desorption phase could be associated with the slower diffusion of TCE out of the interior of the soil matrix (8:92).

Stager's results did not agree well with the Langmuir model. Her research studied the long term desorption (approximately 70 hours) of flint clay. Her results showed that the long term desorption of TCE from the sample was not adequately modeled by the Langmuir model. She studied the use of model relying on a Gamma distribution of desorption coefficients, and found that the Gamma model was a more effective method of modeling her data that the Langmuir model. This led her to determine that a model that made use of more than one binding site was needed to model long-term desorption (20:59).

Other desorption research mainly relied on the results of gas chromatography. This was the method used by Pavlostathis and Mathavan in their study volatile organic

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compounds from field contaminated soils. The organic compounds used in their research were TCE, tetrachloroethylene, toluene, and xylene. The soil samples (three silty-clay and two sandy soils) were gathered from different sites in New York State. The results showed that TCE desorption from the contaminated soils following a "biphasic" pattern, meaning, a pattern characterized by two distinct phases. The biphasic pattern observed follows a rate of rapid desorption within the first 24 hours and slow desorption beyond 24 hours. The data also showed a significant portion of TCE remained sorbed to the samples after the soils were exposed to TCE for over seven days (15:532).

2.4.2 Diffuse Reflectance Tests

Diffuse reflectance studies have generally centered on either simply detecting specific chemicals or determining their concentration. Some studies have simply used the technique for spectral fingerprinting, which is to look for spectral features of a specific chemical compound. The dominant absorptions of the O-H, N-H, and C-H stretching modes are primary targets for this kind of analysis (24:11). Many researchers use statistical techniques to identify the spectral signal of the compound in question. A research group at Sandia National Laboratories has successfully used the technique to resolve the spectral signal from motor oil contaminating the soil (21:334).

Other studies use multivariate analysis of the spectroscopic data to detect and quantify the concentration of chemical components in soils. One such study detected and quantified the concentration of Diesel Fuel Marine in wet soils. The techniques of principle component analysis and partial least squares regression were used to search for

the C-H stretch near 2850 cm^{-1} and determine its relative strength compared to soil spectrum (7:984).

In the work of Burger, Kuhn, Caps and Fricke the advantages and disadvantages of diffuse reflectance are discussed. The main advantage is cited as the ability of diffuse reflectance to be a fast and nondestructive method for the analysis of powdered samples. The reflectance from the powdered samples can be used for quantitative analyses of the constituents of the powdered samples. They main disadvantage of diffuse reflectance is that the reflectance spectrum is strongly influenced by many parameters such as the particle size distribution, packing density, or the homogeneity of the powder mixture. The study points out that variations in the particle size distribution or the packing density will cause changes in the scattering coefficient and lead to different reflectance values (4:309).

One consistent aspect in the reporting to diffuse reflectance tests is the lack of specific details. In each of the studies referenced above there is no documentation of the detection limits. The signal to noise ratio of the reflectance data is also omitted. Finally, none of the studies attempt to determine the lower detectivity limits of their samples.

2.5 Theory

2.5.1 Reflectance Spectroscopy

Reflectance spectroscopy is a relatively new technique, which has found uses in many fields. Unlike transmission spectroscopy, the first serious studies were not made until the late 1930's and early 1940's (23:1). Reflectance spectroscopy does not rely upon

transmission of light through the sample; instead it relies solely upon light reflected from the sample. The reflected light is composed of both specular and diffuse components, both of which can be used independently for nondestructive testing of samples. Figure 1 shows the difference between diffuse and specular reflectance.

D = diffuse reflectance
S = specular reflectance
DS = diffuse specular
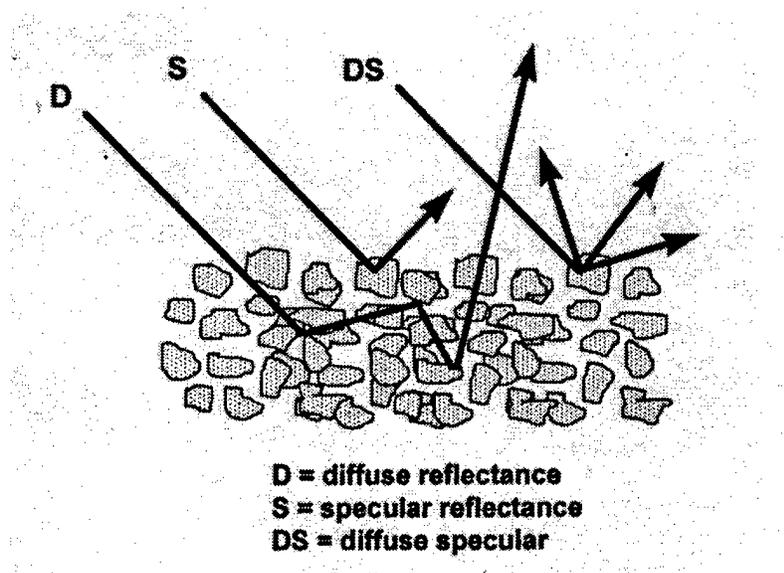
Figure 1. Diffuse and specular reflectance

Specular reflectance is caused by a mirror-like reflection of the light from the surface of the sample. It is primarily only used for flat, reflective surfaces. Its' most common applications are for the direct measurement of the absorbance of films, coatings, or surface contaminants on metal surfaces (25:70).

Diffuse reflectance is caused by the reflection of incident light from the rough surfaces of the sample. Therefore the diffuse reflectance is rich in absorption features which relate to the chemical composition of the source (1:15). Because of this, samples used in diffuse reflectance spectroscopy require relatively minimal preparation. Diffuse

reflectance can be considered the parallel technique to external reflectance. Its primary use is for studying light-diffusing surfaces, such as powders or rough surfaces. This allows diffuse reflectance to be applied in more situations than specular reflectance, and makes it suited for directly studying powdered soil samples. Unfortunately, this technique's dependence on the surface of the sample allows irregularities (peaks or troughs) in the sample surface to impact the quality of the sample spectrum. Particle size is also an important factor. Grinding the sample to reduce the overall particle size and narrowing the particle size variation, can help improve the quality of the spectrum. In the case of some organic solids, and many inorganic materials, dilution with a nonabsorbent matrix, such as potassium bromide (KBr), helps to reduce spatial distortions that originate from anomalous surface reflections (25:72).

Since the sample requires little preparation, this form of spectroscopy can easily be used in agricultural and environmental research. Reflectance spectroscopy was originally used to determine chemical composition in agricultural products (11:350). The quick response time, accuracy and minimal sample preparation has caused the use of this process to expand from agricultural science to other sciences, such as biomedicine, pharmaceuticals, cosmetics, textiles, polymer chemistry, and other areas (Ibid:326-363). Unfortunately there is no mention of the sensitivity of the technique, or the levels of contamination used in the studies.

Reflectance spectroscopy has recently found applications in the environmental sciences. Studies have been performed that show that it can be used to determine chemical composition of materials in soil samples. This process is also uniquely suited to

determine composition of organic compounds in soils. Contaminated soils can be studied quickly, accurately and with minimal sample preparation (7:984).

2.5.2 Absorbance, Concentration, and Reflectance

When incident light is directed onto a sample of material, the light must be absorbed, reflected, or transmitted. Transmitted light propagates through the material, and as it passes through the material, the portion of the light absorbed depends on the composition of the material. Diffusely reflected light enters the sample and becomes attenuated at certain absorbing wavelengths before being re-emitted. Therefore, both the transmitted light and the diffusely reflected light are rich in absorption features that can be related to chemical composition (1:14).

For gases, the amount of light absorbed depends only on the concentration of the absorbing molecules, the cross-sectional area, and the pathlength. The pathlength can be held constant through the use of a transparent cell of known thickness, and then the absorbance at a particular wavelength is proportional to the concentration. This is known as the Beer-Lambert Law (1:15).

For opaque solutions and powdered samples, the reflected light is not as easily controlled or measured. The light entering the sample will encounter not just one particle, but many particles dispersed within a surrounding medium. For samples that are more like powders, absorption is best determined by measuring the reflectance (1:15).

If transmission is prevented, then the light that is either absorbed or reflected. The absorbance (A) is defined as the logarithm of the ratio of the incident intensity (I_0) to the reflected intensity (I_r) or in terms of reflectance (R):

$$A = -\log(I_r / I_0) = \log(I_0 / I_r) = \log(1/R) \qquad (3)$$

In Aucott's study on the statistical analysis of near infrared reflectance data, it was found that for powdered samples the absorbance could be determined from the reflectance. Unfortunately, the particle sizes and the mean pathlength for absorption are not constant (1:17).

The absorbance can only be approximately linear with respect to concentration of a chemical component (24:7). Although the Beer-Lambert law does not strictly hold, measurements of the log (1/R), at characteristic wavelengths, can be recorded for a series of prepared samples with known chemical composition. The measurements are then correlated to the known chemical composition, using multiple linear regression routines. The following equation is then generated to relate the chemical composition to the measured log (1/R) values at the characteristic wavelengths of the chemical in question.

$$\% \text{ Constituent} = K_1 + K_2 \log (1/R_a) + K_3 \log (1/R_b) + \ldots\ldots \quad (4)$$

The K's represent the regression constants and the R values are the reflectances measured at the characteristic wavelengths. Once the constants have been determined, the equation can be applied to samples with unknown amounts of the chemical constituent in question (1:22, 24:7). From this equation we can see that a change in the amount of a constituent is related to a corresponding change in the log (1/R) or a change in the absorbance. Mathematically this would be stated as:

$$\Delta (\% \text{ Constituent}) \propto \Delta (\log (1/R)) \propto \Delta (\text{Absorbance}) \qquad (5)$$

where Δ represents the change in the respective variables. If we treat the TCE bonded to the soil sites as a constituent of the sample, then we can say,

$$\Delta \text{ TCE} \propto \Delta \text{ Absorbance} \qquad (6)$$

So as the TCE bonded to the surface soil sites decreases, the absorbance due to the TCE will decrease. If the TCE follows the biphasic pattern observed in other studies, we should expect to see an initial rapid decrease in the absorbance followed by a constant value for longer times.

Another way to look at this process would be to visualize how the TCE bonded to the surface affects the light reflected off the sample. Incident light reflected off a powdered soil sample is transformed into a spectral signal via the Fourier transform. If TCE is bonded to the surface sites of the soil, the TCE molecules will act like thin film, increasing the absorbance at selective wavelengths. As the TCE desorbes from the sample, there are fewer molecules to absorb, decreasing the absorbance at the select wavelengths. This decrease in absorbance can then be related the decrease in TCE molecules bonded to the surface, and to the decrease in filled bonding sites. Mathematically this is stated simply in Eqn 6.

2.5.3 Langmuir Model

The Langmuir kinetics model has been used repeatedly to model the desorption process. The TCE absorption and desorption are represented by the following equation:

$$ -\overset{|}{\underset{|}{S}}- \; + \; TCE \; \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \; -\overset{|}{\underset{|}{S}}-TCE \qquad (8) $$
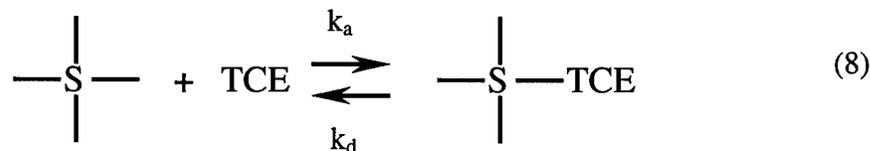
where k_a is the rate coefficient of absorption, k_d is the rate coefficient of desorption, and -S- represents a binding site on the soil. If the absorption process is prevented by gently blowing a gas across the sample, then the rate equation simply becomes:

$$\frac{d}{dt}(TCE) = k_d \cdot \theta \qquad (9)$$

where [TCE] is the concentration of TCE vapor, k_d is the desorption rate coefficient
(molecules/cm^3*hour), and θ is the ratio of the number of sites occupied by TCE
molecules to the total number of sorption sites in the soil sample. The change in the
concentration of TCE vapor can be related to the ratio of occupied sites by the following
equation:

$$\frac{d}{dt}(TCE) = -\mu \cdot \frac{d}{dt}\theta \qquad (10)$$

Where μ is the total concentration (molecules/cm^3) of TCE vapor desorbing from the soil
into a specified volume of a container. Now we can represent the change in occupied

$$\frac{d}{dt}\theta = \frac{-k_d}{\mu} \cdot \theta \qquad (11)$$

sites by:

Solving for θ at time t, we get:

$$\theta = \theta_0 \cdot e^{\frac{-k_d}{\mu} \cdot t} \qquad (12)$$

where θ_0 is the ratio of the number of sites occupied by TCE molecules to the total
number of sorption sites in the soil sample at time t = 0. Therefore if the Absorbance is

proportional to the concentration of TCE, and the change in TCE is proportional to the change in bonded sites, then

$$\frac{\theta}{\theta_0} = \frac{\text{Absorbance}}{\text{Absorbance}_0} \qquad (13)$$

2.5.4 Assumptions

As stated in the previous sections, the Beer-Lambert law is only linear with concentration for gases. Therefore, it is necessary to make certain assumptions in order to perform a quantitative analysis. The first assumption is that changes in absorbance correspond to approximately linear changes in TCE concentration. The second assumption is that any scattering is primarily due to the soil particles, and any scattering effects are removed in spectral subtraction.

3   EXPERIMENTAL PROCEDURE AND METHODOLOGY

3.1   Overview

This section provides a description of the equipment and methodology by which

the experiment was carried out. The equipment section describes the Bomem FTIR and

how it is used in spectroscopic studies. The remaining sections describe the experiments

that were performed, the experimental procedure that was followed, and the rational

behind the experiment and how they relate to the research objectives.

3.2   Equipment

The device used to perform the experiment was the Bomem MB-157s FTIR. The

spectrometer is a self-contained unit that consists of a sample compartment and sealed

instruments compartment, see Figure 2.

Sample
Compartment

Instrument
Compartment
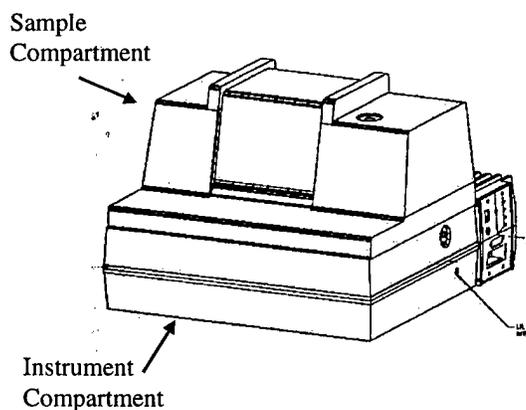
Figure 2. The Bomem Michelson Interferometer

The sample compartment is enclosed within a purge cover and houses the diffuse reflectance optical unit. The optical unit allows powders, fibers, and rough surface to be scanned without extensive sample preparation. Figure 3 shows how the optical unit optimizes the diffuse reflectance energy, while minimizing the specular reflectance. The light from the IR source, reflects off the input ellipsoid and is incident onto the sample. The IR radiation reflected off the surface strikes the output ellipsoid and is then guided to the detector. The key element, the blocker, is a small baffle the blocks the specular beam but allows diffuse reflectance to pass (22:4 & 5). The purge cover allows the environment around the sample to be controlled by making use of a nitrogen gas purge to limit carbon dioxide and water vapor contamination. Studies by Ong and Lion show that water vapor competes with TCE for sorption sites. The sorption of TCE is greatly reduced by even a monolayer of water (14:180). In the current configuration, the detector in use is a Mercury Cadmium Telluride (MCT) detector, whose highest sensitivity is in the area of 800 cm^{-1}.
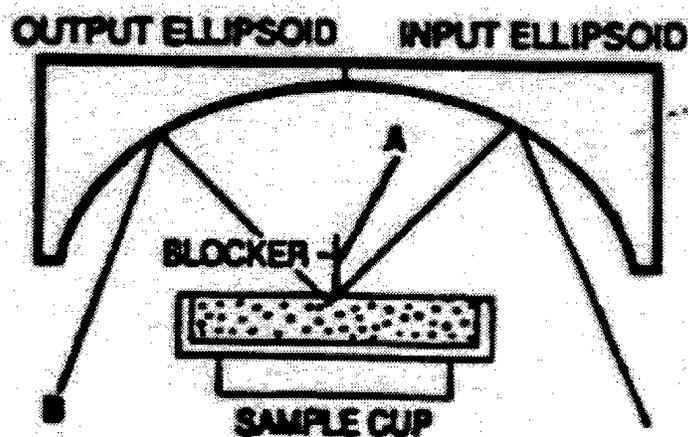
Figure 3. Optical unit configuration to minimize specular reflectance.

The instrument compartment is sealed to prevent contamination by dust, water vapor, and carbon dioxide. It is also purged with nitrogen gas to further protect against contamination. The compartment contains the Michelson interferometer, an infrared-transmitting "beamsplitter", a Helium-Neon laser for measurement of scan position, necessary power supplies and electronic assemblies.

The heart of the spectrometer is the Michelson interferometer. After a beam splitter separates the source beam into two parts, a path difference can be introduced by moving one of the mirrors. When the two beams are recombined, the interaction causes all wavelengths to be modulated simultaneously with distinct modulation frequencies for each wavelength. The intensity of the resultant waveform is a function of the optical path difference is an interferogram. Once the detector records the interferogram, its Fourier transform is computed to yield the final infra red spectrum (26:5-1 & 5-2).

The Bomem FTIR uses a variation of the standard Michelson interferometer to record the spectrum of samples. Figure 12 shows a schematic diagram of the Bomem Michelson spectrometer. The Bomem design replaces the two flat mirrors with a pair of corner cube mirrors. Both mirrors are mounted on an "L" shaped arm that rotates back and forth about a fixed pivot point allowing both mirrors to move. After the two beams have been recombined, the resultant modulated beam is focused onto the sample. The reflectance off the sample is then recorded by the detector and transformed, via the Fourier transform, into the infrared spectrum of the sample.
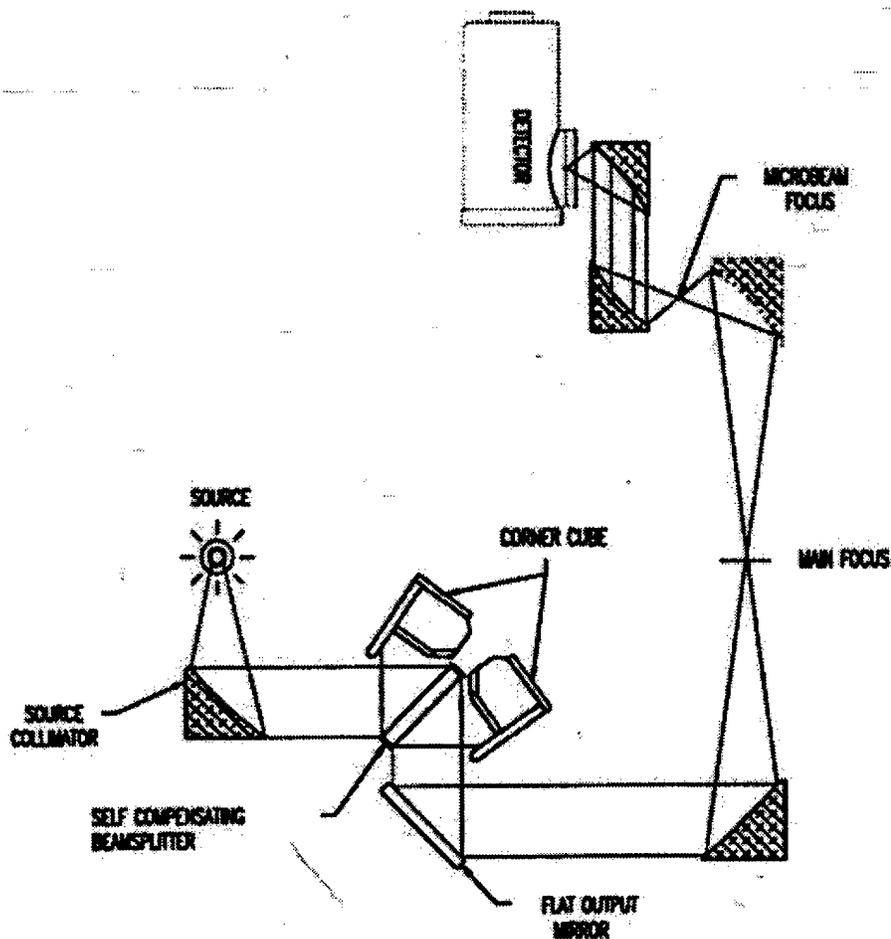
Figure 4. Schematic of the Bomem Michelson Spectrometer

The resolution and gain of the spectrometer can be manually controlled through the use of a pair of rotary dials. The resolution of the device can be changed from 1 cm^{-1} to 128 cm^{-1}. Increasing the resolution increases the path difference between the two separated beams and increases the sample scanning time. The rotary gain switch changes the preamplifier gain applied to the signal coming off of the sample. The gain switches can increase the signal by factors of 1 to 16 in steps of factors of two.

Unfortunately, increasing the gain will also increase the noise in the spectrum (26:5-10 & 5-11).

3.3   Soil Spectroscopy Experiments

3.3.1   Overview

The main objective of these experiments was to determine if the technique could be used to observe the change in the relative concentration of TCE bound to the soil over time. Preliminary studies at a resolution of 4 cm^{-1} did not show clear signs of TCE spectral signals in the soil after the soils were dry. In an effort to detect TCE bound to surface sites, a series of high resolution scans were taken of a sample of TCE contaminated powdered soil. The preliminary studies also showed that some soils after exposure to TCE, displayed a broadband change in the spectral features of the soil that appeared to behave contrary to the observed behavior of TCE exposure causing increased absorption. Soil spectral features are due to the combination of absorption lines caused by changes in the vibrational behavior of the chemical constituents. Low resolution scans were taken of various soil samples to observe how these changes spectral features behaved over time, and to determine if desorption information could be obtained. The following sections will describe how the soil samples were prepared and how the experiments were preformed.

3.3.2   Sample Preparation

In order to provide the best possible chance for success in the high resolution experiment, a soil was chosen from Kindt's study that desorbed a large amount of TCE

vapor (8:61). The NIST Standard Reference Material 88b, dolomitic limestone was chosen since its affinity for TCE was second only to Montana soil (Ibid:65). Five grams of dolomitic limestone were placed in a glass container and allowed to soak in neat TCE for three months. The sample to be studied was scooped out of the solution and placed in a Pyrex glass dish to dry to avoid possible contamination. After the soil had air dried for ten minutes, it was placed in the sample cup and the surface was smoothed as much as possible to minimize spectral anomalies due to surface features. (It is important to note that the samples were dry, but they still retained the darkened discoloration of a wetted soil sample.)

For the low resolution experiment five different powdered soils were chosen. Approximately five grams of each soil were soaked in liquid TCE for two months. The soils chosen were dolomitic limestone (NIST Standard Reference Material 88b), glass sand (NIST Standard Reference Material 81a), Montana soil (NIST Standard Reference Material 2710), plastic clay (NIST Standard Reference Material 98b), and san joaquin soil (NIST Standard Reference Material 2709). The soils were chosen due to chemical composition and average particle size. Appendix A provides the chemical composition of each of the soils. Table 2 shows the average particle size for each of the soils stated above.

Table 2. Average Particle Diameter (8:34)

Soil	Average Particle Diameter (μm)
Dolomitic Limestone	3
Glass Sand	1
Montana Soil	2
Plastic Clay	10
San Joaquin Soil	5

Each sample to be studied was handled in the same fashion described in the high resolution experiment with only a couple of exceptions. The samples air dried for only five minutes before placement in the sample cup, instead of ten minutes. When the samples were placed in the cup, they were still "wetted" and had a mud-like consistency instead of the dry consistency cited above.

The soil samples used in these experiments are all National Institute of Standards & Technology (NIST) standard reference materials. These soils have each been sifted, to minimize variation in particle diameter. Each of the soils has been baked to remove all water molecules that would be harbored in the soil matrix and in the spaces between particles. Each soil type has undergone detailed chemical analysis to determine the chemical constituents of each soil type.

In the environment, TCE binds to organic material. In the process used to prepare the NIST soils, all of the organic compounds are removed along with the water molecules. When the soil samples are exposed to TCE, there are little or no organic molecules to bond to. Given these facts, the desorption process studied in this research would be a physical process (physisorption) rather than a chemical process (chemisorption).

3.3.3 Procedure

The procedures followed for both the high and low resolution experiments were almost identical. The differences were in the resolution, number of co-added scans, and how the data was handled for analysis. In both cases, the background spectrum was recorded using the mirror reference so that effects from the atmosphere within the sample compartment could be removed from the spectrum. The spectrum of an

uncontaminated soil sample was recorded at 1 cm^{-1} resolution using 1000 co-added

scans for the high resolution experiment, and 4 cm^{-1} resolution using 100 co-added scans

for the low resolution experiment. The samples of the contaminated soils were placed in

the holder and the spectrum of the sample was recorded. The background spectrum, the

uncontaminated soil spectrum and the contaminated soil spectrum were all scanned at

the same resolution, same gain, and the same number of co-added scans. The spectrum

for each sample was recorded at intervals of one hour, four hours, eight hours, and

finally twenty-four hours. In each case, the raw spectral data was recorded. Processing

of the signal to remove the atmospheric background and place the spectrum in terms of

Reflectance was done after the scanning.

For the high resolution experiment, the spectrum of contaminated soils was

compared with the spectrum of the uncontaminated soil. The procedure of spectral

subtraction was used to remove the signal of the uncontaminated soil from the

contaminated soil. The resulting spectral signal was compared with the spectrum for

neat and condensed phase TCE to look for possible TCE spectral signals. The changes

in these possible signals were tracked over time.

For the low resolution experiment, the spectrum was divided into two separate

regions to isolate the effects to be studied. The spectral signal of both regions was

integrated to determine the area of each region. The changes in the areas of both regions

were monitored over time and compared to determine if the changes could be correlated

and desorption data inferred.

4 RESULTS & ANALYSIS

4.1 Overview

This section will give a brief statement of the general results of the soil spectroscopy experiments. How the results of the high resolution portion of the soil spectroscopy experiments were used to detect possible TCE signals will be shown. The analysis necessary to determine if the detected spectral signals are TCE spectral signals is also presented. The results and analysis of the low resolution study will also be presented.

4.2 Soil Spectroscopy Results

The Bgrams 32® software was used to record and manipulate the data from the high-resolution study. After the raw spectral data was converted into reflectance, neither the high nor low resolution experiments displayed obvious TCE spectral signals. Figure 5 compares the high and low resolution scans of dolomitic limestone samples. By comparison we see that there is little difference between the two spectra. The main difference between these two spectra appears to be attributable to water vapor, carbon dioxide, and scattering differences. This discussion will be covered again in section 4.3.
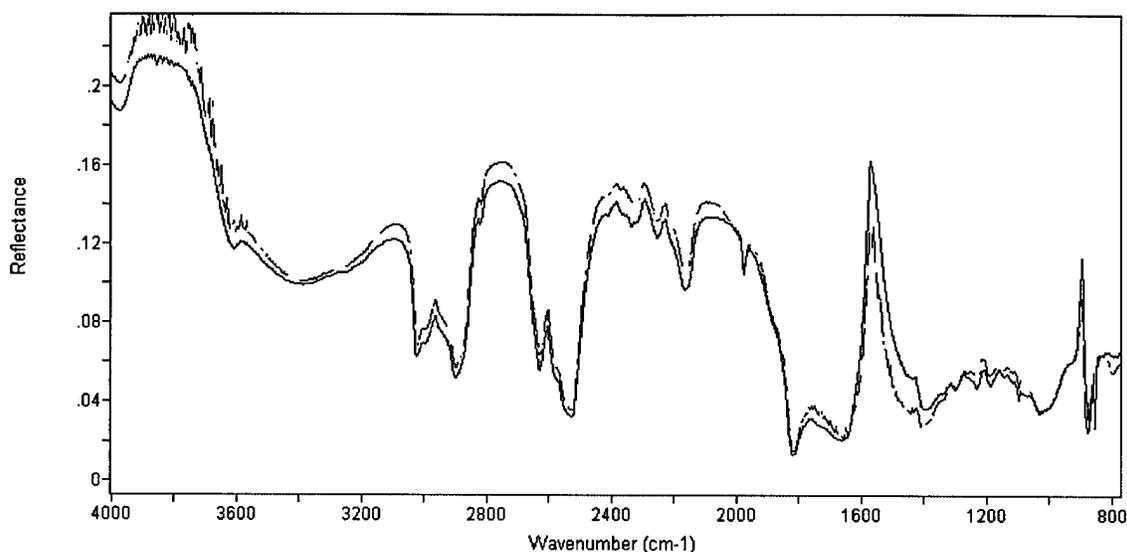
Figure 5. Comparison of High (dashed) and Low Resolution (solid) scans of Dolomitic Limestone

4.3 High Resolution Experiment

The first priority was to determine if TCE signals could be detected. The technique of spectral subtraction was used on the high resolution scans of dolomitic limestone to subtract the spectral signal of the uncontaminated dolomitic limestone from the TCE contaminated spectral signal. Figure 6 shows the result of the spectral subtraction. When compared with previous figure we can see that the spectral features from 4000 cm^{-1} to 1400 cm^{-1} are artifacts of the spectral subtraction and not actual spectral features. The resultant spectrum was compared with the spectrum of liquid TCE evaporating out of the sample cup, Figure 7. The spectral region of interest was limited to under 1350 cm^{-1} due to the spectral artifacts discussed above, and previous scans showed that water vapor blocked the TCE signal above 1350 cm^{-1} and the largest number of strong TCE spectral signals were under 1350 cm^{-1}. After comparison to the TCE liquid spectrum, there appear to be eight spectral signals, two strong and six weaker signals, in the resultant

spectrum that could be TCE signals. Figure 8 shows the resultant spectrum in the region

of interest and points out the eight possible TCE spectral signals and their location. The

letters in Figure 8 correspond to wavelengths in Table 3. Only two of these appear to be

influenced by natural spectral features of dolomitic limestone, the signal at 853.2 cm^{-1},

under a Al_2O_3 absorption band, and at 894.1 cm^{-1} which is very close to the reflectance

peak between a SiO_3 and Al_2O_3 absorption bands. Figure 9 shows the uncontaminated

dolomitic limestone spectrum in the area of interest.
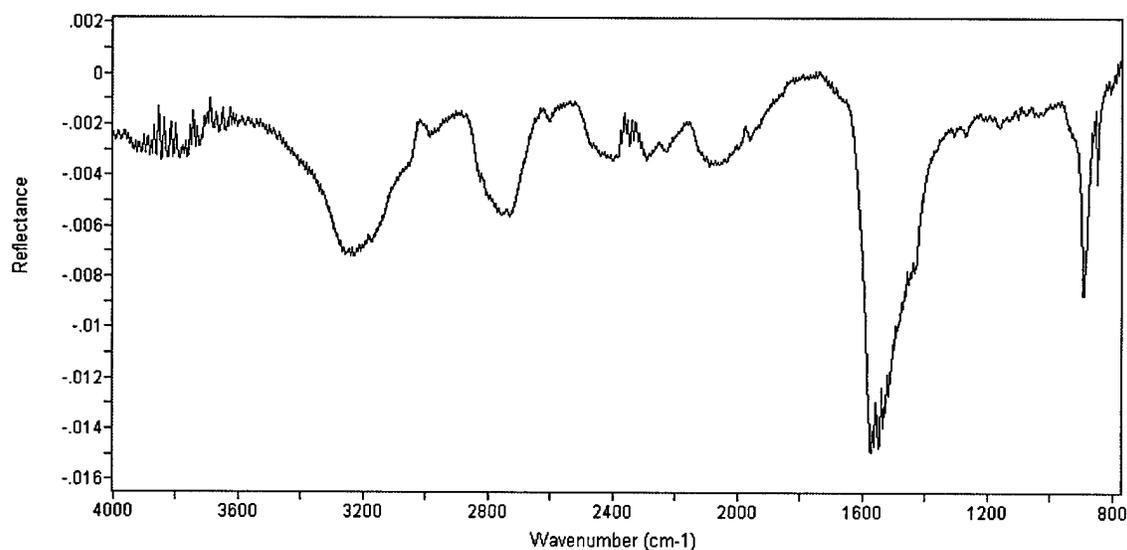
Figure 6. Result of the subtraction of the uncontaminated soil from the TCE contaminated soil.
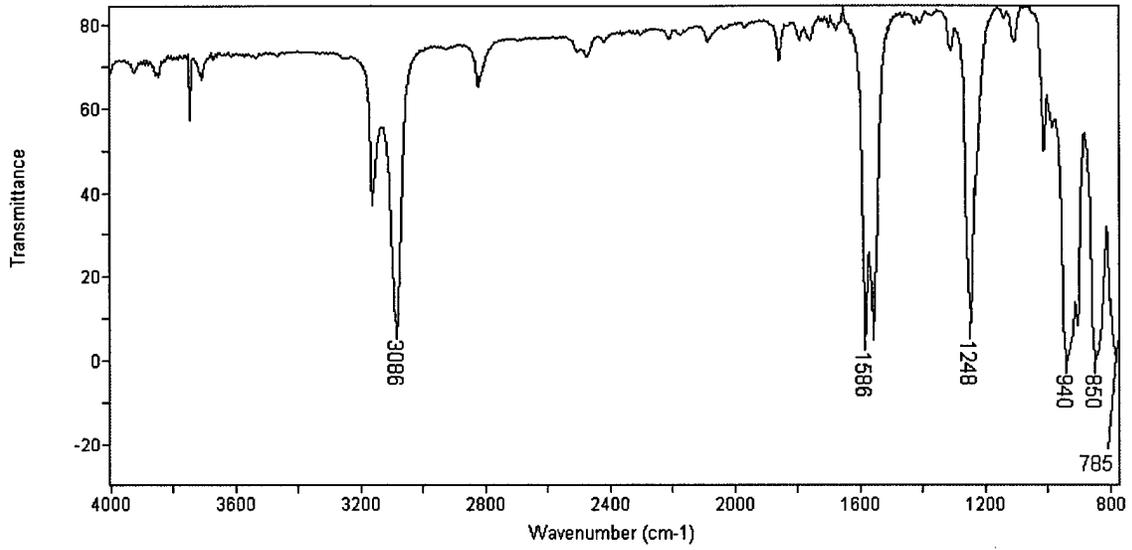
Figure 7. Spectrum of liquid TCE as it evaporates.
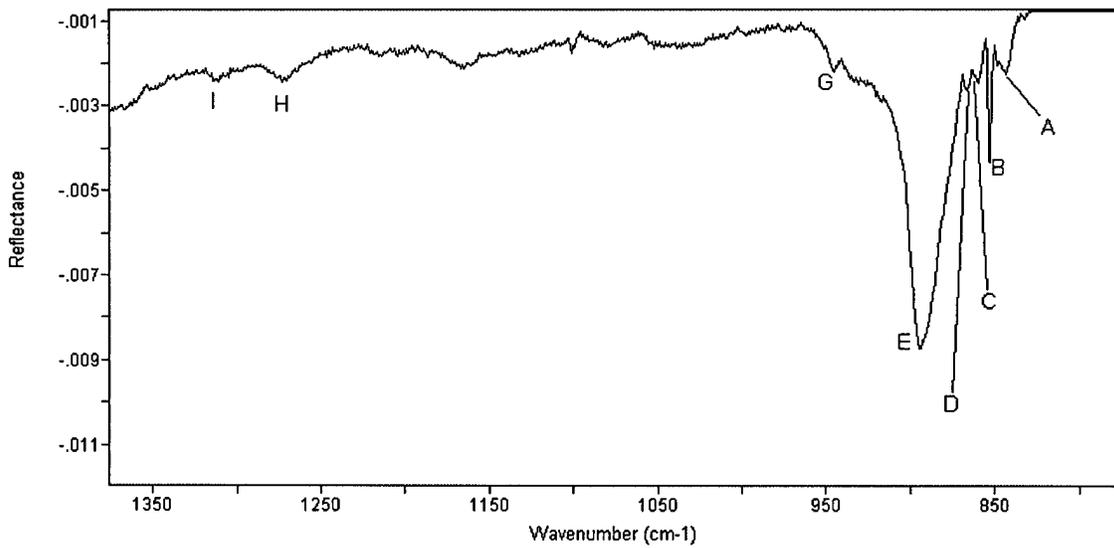
Figure 8. Candidate TCE signals from spectral subtraction.

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Table 3. Position of spectral signals

Letter	Wavelength (in cm^{-1})
A	843.5
B	853.2
C	859.7
D	866.8
E	894.1
G	945
H	1272.5
I	1310.1
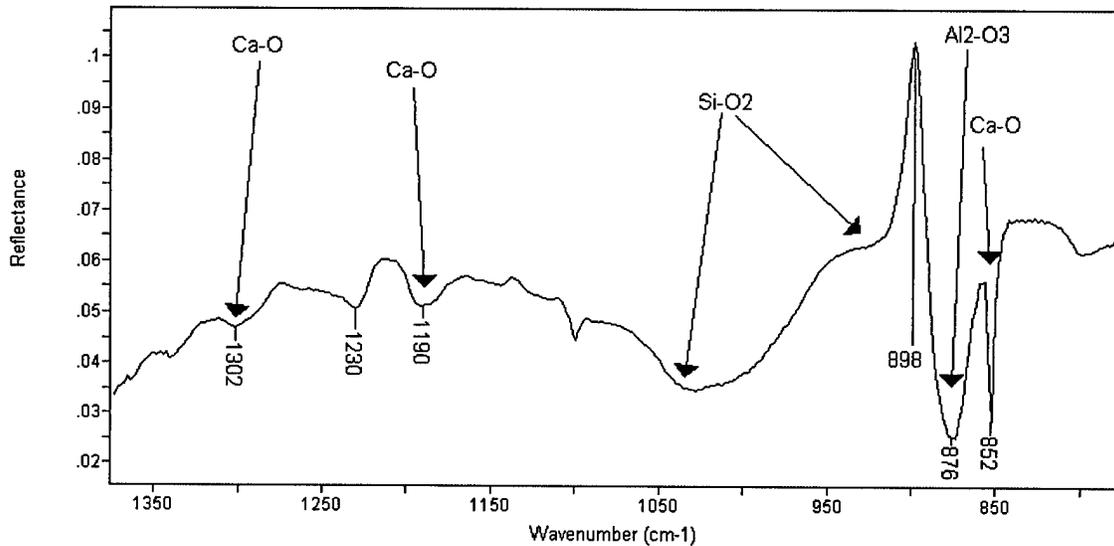
Figure 9. Spectrum of uncontaminated dolomitic limestone in region of interest

Once possible TCE spectral signals were detected, the behavior of the possible

signals over time must be studied. The results of the Langmuir model dictate that the

change in the signal intensities should follow an exponential decay. After studying the

intensity over time, it was observed that the intensity of each of the eight signals

decreased over time. The depths of the signals were recorded, and the reflectance values

of the signals were determined using the baseline method. This method is normally used

to correct for solvent background interference, but the process is the same to measure a solvent interacting with a soil sample (4,103). Once the relectance values for each signal were determined, the absorbance values, or log (1/R) was computed. The absorbance values for each data point after time t=0, was ratioed to the absorbance value at time t=0 to determine the fractional changes in the absorbance values for each signal over time. The fractional changes in absorbance for each signal were plotted with time and the data was fitted to the following exponential decay function.

$$Y = a + be^{-kx} \qquad (14)$$

Figure 10 shows the plots for three of the spectral signals. From the plot it can be seen that the three signals follow almost the same trend, the difference is in the offset and the relative amount of change in each signal. Table 4 shows the results of the curve fit for each of the spectral signals, with the following exceptions: 866.8 cm^{-1}, 945 cm^{-1}, and 1272.5 cm^{-1}. The excluded signals could not be fitted to an exponential decay function. The data in Table 4 shows the wavelength of each signal, the fit parameters and the error associated with each fitted value, and the Chi^2, which characterizes the dispersion between the data points and the values predicted by the exponential fit.
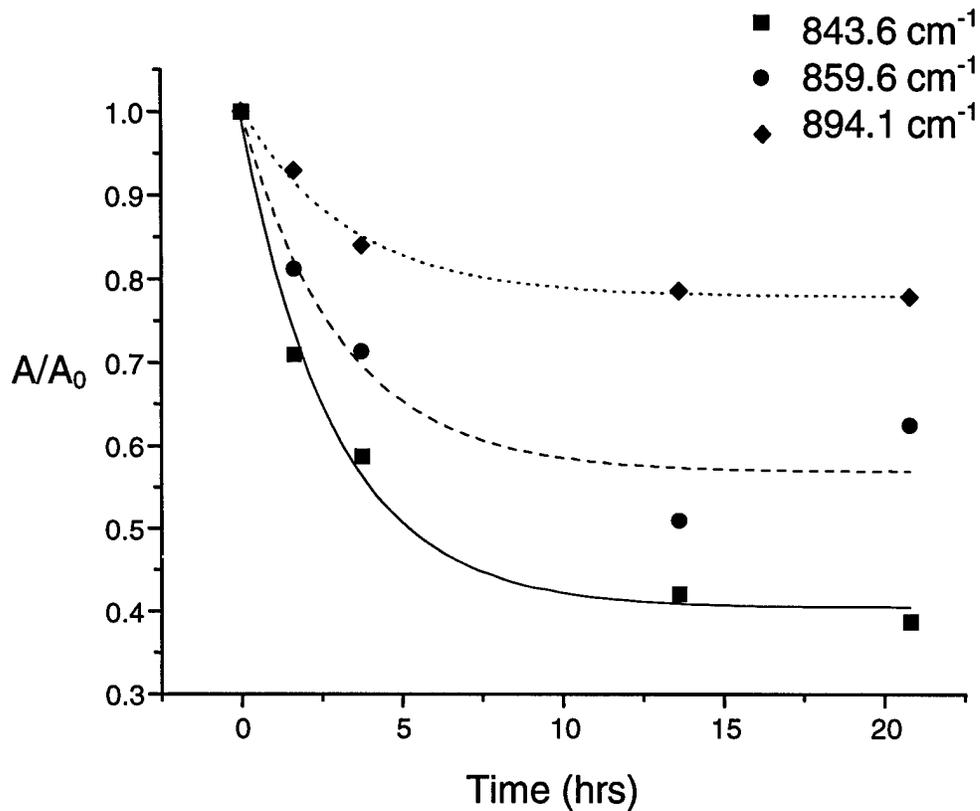
Figure 10. The ratioed change in absorbance of three of the spectral signals.

Table 4. Exponential Decay Fit Parameters of Spectral Signals

Wavelength	a	$\pm$ Error	b	$\pm$ Error	k (hour^{-1})	$\pm$ Error	Chi^2
843.5	0.40418	0.02193	0.58705	0.0353	0.34847	0.04971	0.00089
853.2	0.69775	0.06725	0.32115	0.06139	0.12212	0.07443	0.0013
859.7	0.56844	0.04624	0.43006	0.07306	0.3242	0.13288	0.0038
894.1	0.77842	0.01004	0.22603	0.01557	0.30463	0.0516	0.00017
1310.1	0.44474	0.30728	0.54162	0.29943	0.03893	0.03265	0.00036

After the behavior of the signals over time has been established, the possible

explanations for the spectral signals must be explored. The first possibility is that the

signals are just due to changes in the dolomitic limestone soil spectrum over time. If this

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is the explanation, then the reflectance values of uncontaminated dolomitic limestone

should behave in the same manner as the signals. Figure 11 shows a plot of the

reflectance of uncontaminated dolomitic limestone at the 875.85 cm^{-1}, the Al_2O_3 feature,

over time. The figure clearly shows that the signal is basically flat over time and does not

exhibit the same behavior as the signals. Thus, it can be concluded that the behavior

observed in Figure 10 is not due to changes in the dolomitic limestone spectrum over

time.
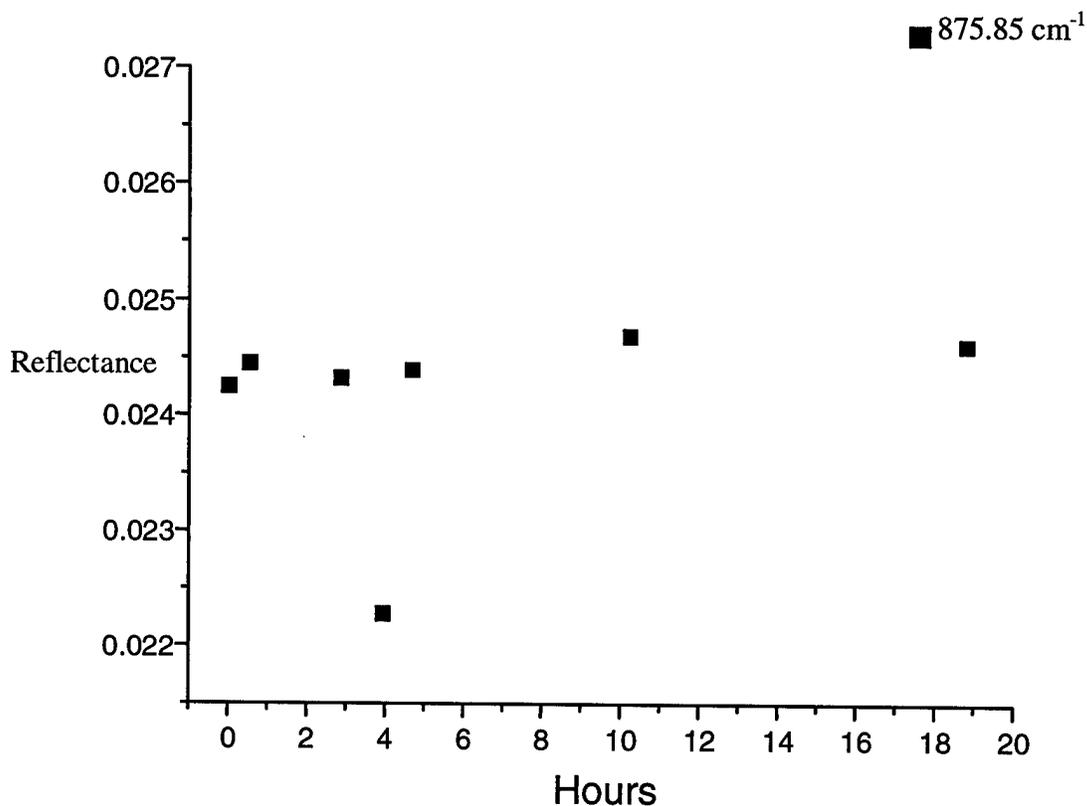
Figure 11. Reflectance of uncontaminated dolomitic limestone over time.

The second possibility is that the signals are from TCE bonded to the surface. We know that over time the amount of TCE bonded to the surface decreases in an exponential fashion. Equation 12 shows that the fractional change in the occupied sites exhibits an exponential decay. As stated earlier, the signals at 866.8 cm^{-1}, 945 cm^{-1}, and 1272.5 cm^{-1} could not be fitted to an exponential decay. It is possible that these signals are not from TCE, but are just artifacts from the spectral subtraction. The other possibility is that the TCE signal is so small that the error due to noise obscures the signal. The remaining signals at 843.5 cm^{-1}, 853.2 cm^{-1}, 859.7 cm^{-1}, and 1310 cm^{-1} can be fitted to an exponential decay, with three signals exhibiting similar k values. These signals have the best chance of being TCE signals. If the ratio of $A/A_0 = \theta/\theta_0$, then the b values should be one (or unity) for the signals at 843.5 cm^{-1}, 859.7 cm^{-1}, and 894.1 cm^{-1} if they are TCE signals. The b values for each of these signals is less than one. This could either be due to an offset error that has not been accounted for, the signals are not TCE, or noise is starting to induce error in the measurements. The closest TCE gas phase signals occur at 783 cm^{-1}, 842 cm^{-1}, and 934 cm^{-1}, see Figure 12. Thus the resultant signal at 843.5 cm^{-1} is the only one that closely corresponds to a known TCE spectral peak. The signals at 859.7 cm^{-1} and 894.1 cm^{-1} kinetically behave as expected, but they do not correlate to a TCE spectral feature. The remaining signals at 853.2 cm^{-1} and 1310.1 cm^{-1} have such different k values that they are probably not TCE or are also effected by noise.

If the signal at 843.5 cm^{-1} is from TCE then there are two questions that must be asked. The first question is if the signal is from TCE why is it not detectable at a resolution of 4 cm^{-1}? Most spectral studies are conducted at this resolution, and even

looking at a vapor phase transmission spectrum of TCE, Figure 12, it is clear that many

of the spectral features are wider than 4 cm^{-1}. It is possible that the signals from the high

resolution scans are from a very small amount of TCE on the surface, or from TCE vapor

escaping from the soil sample. Vapor phase signals have smaller widths than liquid phase

signals. If the signal at 843.5 cm^{-1} is a signal from TCE vapor escaping from the soil,

then that could explain why no signals could be detected at 4 cm^{-1} resolution. It is also

possible that it is not from TCE. The second question is if the spectral signal from the

high resolution scans is from TCE why is one of the TCE spectral peaks present and

others are not? It is possible that if the signal is from a very small amount of TCE on the

surface, then some TCE spectral signals may be lost in the noise.
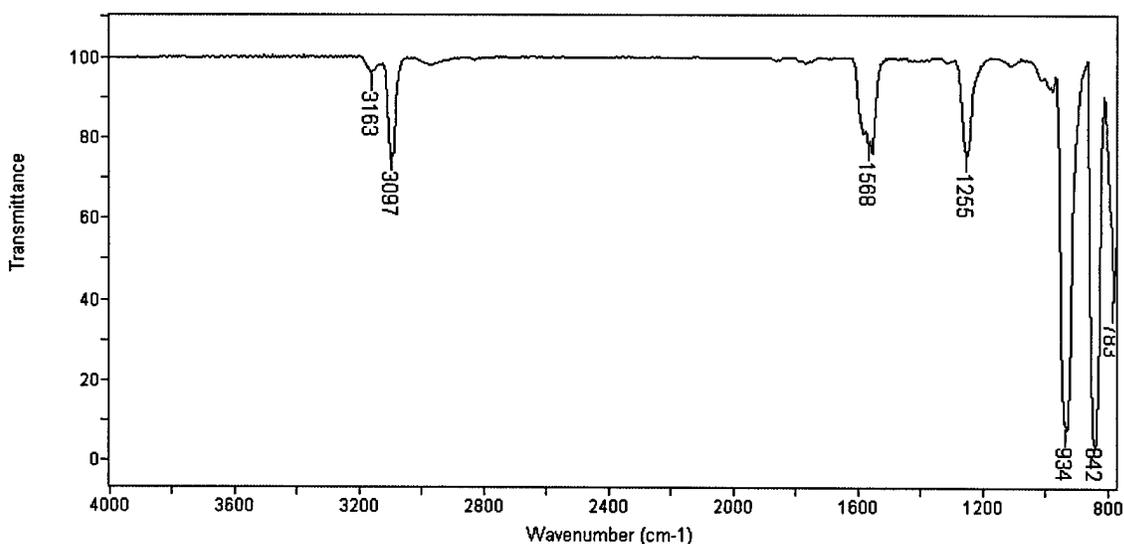
Figure 12. Gas phase spectrum of TCE

Unfortunately noise had a significant impact on the measured reflectance. Many of

the signals have a noise level that is approximately 1-10% of the measured reflectances.

This is the main source of error in the measurements. Another source of error comes

from using digitally stored background spectrum and uncontaminated soil spectra. The

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environment within the sample compartment does change. This will effect the reflectance calculation. The uncontaminated sample can also change. Different scans of the same sample yield slightly different results. The general form of the spectrum is the same, but certain spectral features will have higher intensities. Another source of error could be scattering from the soil particles.

It is unfortunate that possible TCE signals in the flint clay and plastic clay could not be detected. It is possible that La Puma's results are correct and any TCE on the surface evaporated away very quickly, in under one hour, and any TCE that remains is the TCE attached to the soil matrix and in the pores of the soil. This would mean that any perceived long term desorption would actually be a capillary action, as the TCE works its way out of the pores in the soil. This could also explain the need for a model that uses a distribution of rate coefficients to model desorption. This type of action would not be detected by diffuse reflectance spectroscopy.

This same procedure was tried on both NIST Standard Reference Material 97b, flint clay, and NIST Standard Reference Material 98b, plastic clay. The results of the spectral subtractions did not provide any clearly definable TCE signals.

4.4 Low Resolution Experiment

After the low resolution raw spectral data was converted into reflectance, the spectrums of the contaminated soils were compared with the spectrum of the corresponding uncontaminated soils. Appendix B shows the spectra of each of the uncontaminated soils used in the low resolution experiment. Figure 13 shows the result of spectrally subtracting the uncontaminated plastic clay soil spectrum from the TCE

contaminated plastic clay soil spectrum. The broad spectral feature around 1064 cm^{-1} is

only present in the spectrum of plastic clay after its contamination of TCE. This same

type of feature appears in TCE contaminated glass sand, as can be seen in Figure 14.

Figure 15 shows the result of spectrally subtracting the uncontaminated San Joaquin soil

spectrum from the TCE contaminated San Joaquin soil spectrum. It is readily apparent

that the increased signals in this spectrum are due to water vapor and carbon dioxide and

not from exposure to TCE like in plastic clay or glass sand.
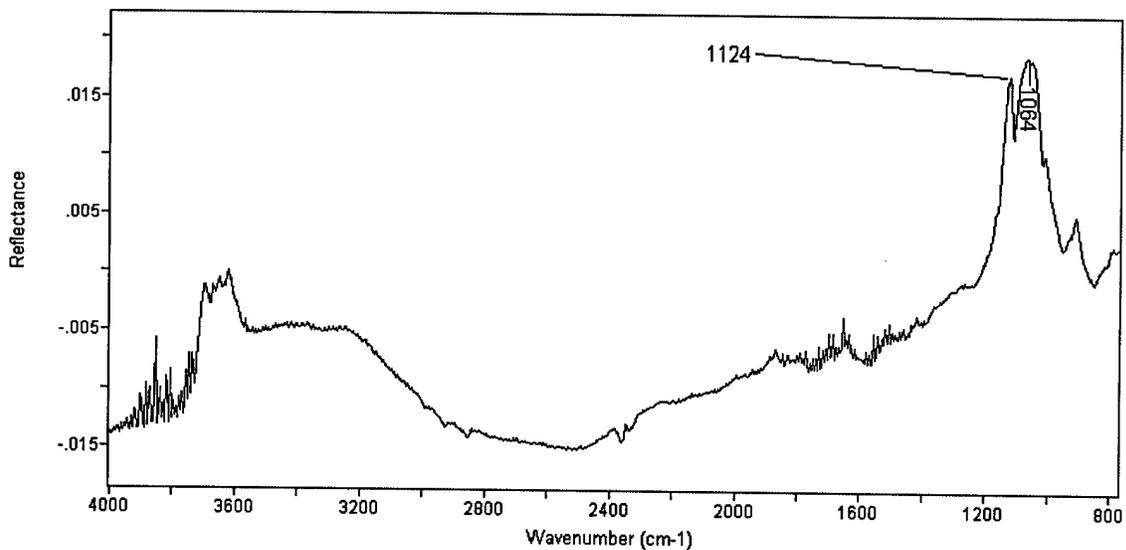
Figure 13. Spectral subtraction of uncontaminated plastic clay from TCE contaminated plastic clay.
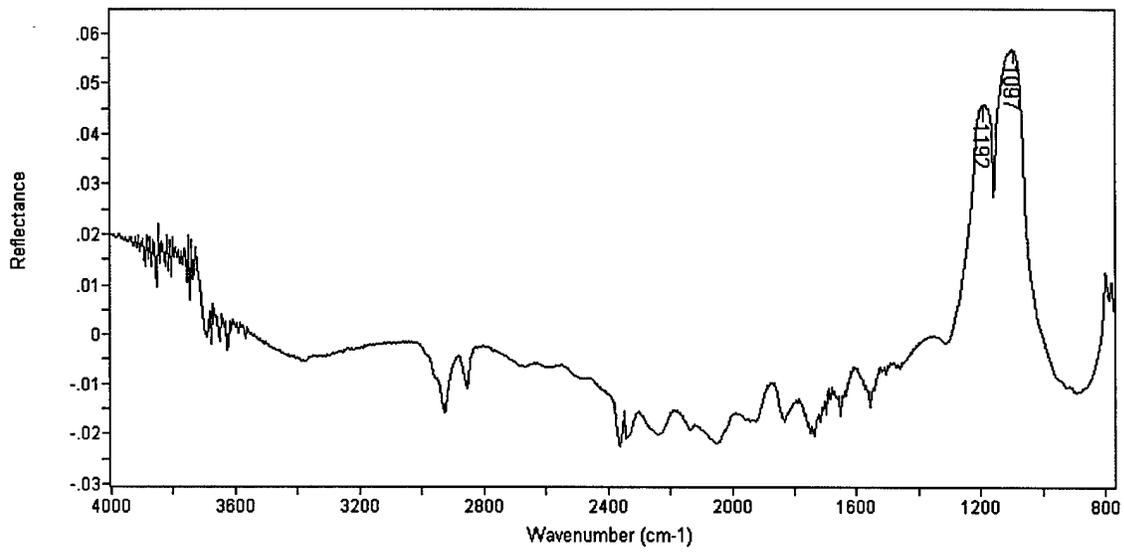
Figure 14. Spectral subtraction of uncontaminated glass sand from TCE contaminated glass sand.
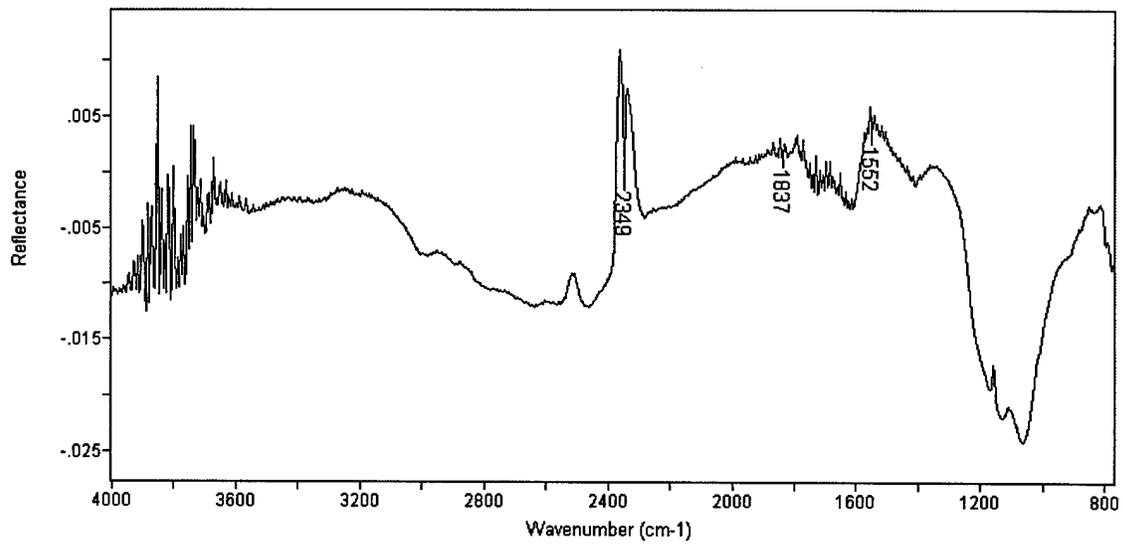
Figure 15. Spectral subtraction of uncontaminated San Joaquin soil from TCE contaminated San Joaquin soil.

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The spectral signals of each of the contaminated soils were divided into two areas, as shown in Table 5, and integrated. The changes in the two areas were monitored over time, and the spectrum in both regions of all the soil samples, behaved in the same manner. Instead of the first region of each soil growing while the second region decreased, both sections grow initially and then reached a constant area. Unfortunately, this does not give us any information regarding the desorption of TCE from the soil samples.

Table 5. The separate spectral regions for study.

Soil	Region 1 (in cm^{-1})	Region 2 (in cm^{-1})
Dolomitic Limestone	3612 - 2000	2000 - 780
Glass Sand	3612 - 2000	2000 - 780
Montana Soil	3699 - 1628	1628 - 780
Plastic Clay	3616 - 1866	1866 - 780
San Joaquin Soil	3695 - 1810	1810 - 780

Unfortunately, no information could be obtained by comparing changes in two spectral areas over time. It also did not help answer the simple question of what causes the enhanced spectral intensity. Current theory indicates that the addition TCE to the soil should increase the absorbance, and decrease the reflectance. The addition of TCE to the soil should not increase the reflectance in a spectral region. Searching through the literature reveal no answers that could satisfactorily explain the cause of the feature.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Several conclusions can be made from the results of the experiments. This chapter will describe the conclusions from the experiments and discuss the applicability of this technique to desorption kinetics.

5.1.1 Soil Spectroscopy Experiments

None of the soil spectroscopy experiments provided clear, obvious TCE spectral signals. The high resolution scans of dolomitic limestone provided a spectral signal that may be due to TCE bound to the surface site or in a vapor phase above the sample. The signal is clearly not due to just dolomitic limestone over time. But the lack of signals in the same regions as some of the key TCE spectral signals and the large error due to noise cast doubt on identity of the signal being from TCE.

The presence of a broad increase in the reflectance of the plastic clay and glass sand soil samples could not be explained. The addition of the solvent, TCE, to the soils should produce reduced reflectance values due to the higher absorbance caused by the addition of TCE. What was observed was the opposite, a region where the reflectance was actually increased. A search of the literature failed to provide any satisfactory explanations for this occurrence. The low resolution experiments were also unable to determine any connection between changes in this phenomena and the desorption of TCE from the soil sites.

5.1.2 Applicability of Diffuse Reflectance to Desorption Kinetics

The data from the experiment fails to prove that the technique of Diffuse Reflectance can be used to measure the desorption of TCE from the powdered soils. The data shows that possible TCE signals were detected, but failed to prove conclusively that the signals were from TCE bound to the surface. The technique was also unable to produce the same type of spectral signals from Flint or Plastic Clay soil samples. It is unclear if this technique would only be valuable to soils with significant organic content, or if the chemical composition of the samples used cause the TCE to be harbored within the soil particles causing a gradual diffusion process. If this is the case, the diffusion process would explain the behavior that observed in previous studies and the need for using the continuum of desorption rates that is used in the Gamma model.

5.2 Recommendations

Future experiments are needed to answer important questions regarding the applicability of this technique.

The main issue that needs to be addressed is to try to repeat the experiment with other soils. The first soil that should be tried is Montana soil. This soil has the next highest affinity for TCE compared to dolomitic limestone (8:62). Other soils can then be tested to see if the results can be duplicated. To obtain the best results, these tests would need to conducted under the purge cover, with the compartment continuously purged with nitrogen gas. The background spectrum and the spectrum of the uncontaminated soil should be scanned each time with the contaminated soil sample. Although this is extremely time consuming at $1cm^{-1}$ resolution, it would be very helpful in reducing

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errors. The scans also need to be conducted at 1cm^{-1} resolution, and at least 400 scans to help maximize the signal.

Other issues that still need to be addressed are the sensitivity of the instrument, and the linearity of the signal to concentration. The sensitivity study would involve creating a chemical solution of TCE and water. By varying the concentration of TCE in the solution and scanning the solution to determine the lower limit of delectability, the lower limit of the FTIR's ability to detect TCE could be established. These tests could also be used to determine if the measured spectral signals are linear with respect to the concentration of TCE in the solution. This would also answer a fundamental question regarding the ability to predict the concentration of TCE based solely on measured reflectance values.

Another possible way to use this technique could be to study absorption instead of desorption. After the uncontaminated soil sample is scanned, a TCE mist is allowed to coat the sample. The sample is then scanned and then compared to the uncontaminated soil. The process is repeated over time to determine the kinetics involved in the absorption process. Since the sample is never moved, errors due to the movement of the sample will not effect the experiment. Since the sample area would be purged with nitrogen gas and could remain sealed any changes in the spectral signal would be due to absorption of TCE onto surface sites.

Appendix A: NIST Reference Material Data Sheets

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 81a
Glass Sand

(In Cooperation with the American Society for Testing and Materials)

This SRM is issued in the form of a ground powder (95% less than 106 μm) blended to ensure homogeneity. It should be dried for 2 hours at 105 °C before use.

Constituent	Recommended Value Percent by Weight	Range	s
Al_2O_3	0.66	0.62 - 0.69	0.011
Fe_2O_3	.082	.075 - .089	.0024
TiO_2	.12	.10 - .14	.0064
ZrO_2	.034	.025 - .042	.0026
Cr_2O_3	46 μg/g	33 - 58	3.9

Certification - The recommended value listed for each oxide is the best estimate of the true value based on the analytical data from both cooperators and NBS. The range of values listed is the tolerance interval, constructed such that it will cover at least 95% of the population with a probability of 0.99. It is computed as $X \pm Ks$: where s is the standard deviation, K is a factor that depends on n (the number of samples measured), p, the proportion of the total sample covered (95%), and γ, the probability level (99%). In all cases none of the n values used exceeded the range specified. Thus, it includes variability between laboratories and between samples.

The overall direction and coordination of the round-robin analysis leading to certification were performed by Paul Close, Chairman of ASTM Subcommittee C-14.02 on Chemical Analysis of Glass and Glass Products.

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 W. P. Reed.

Washington, D.C. 20234
January, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Chemical analyses for certification were performed in the following laboratories:

Anchor Hocking Corp., Lancaster, Ohio, R. E. Carr
Brockway Glass Co., Inc., Brockway, Pa., E. L. McKinley.
Corning Glass Works, Corning, N.Y., Y. S. Su.
Ford Motor Co., Lincoln Park, Mich., T. O. LaFramboise.
National Bureau of Standards, Analytical Chemistry Division, E. J. Maienthal, J. D. Messman and T. C.
    Rains.
Kimble Div. Owens-Illinois, Vineland, N. J., H. S. Moser.
Owens-Illinois, Inc., Toledo, Ohio, P. Close.
Penn State Univ., University Park, Pa., J. B. Bodkin.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 98b

Plastic Clay

This Standard Reference Material (SRM) is intended for use in the determination of constituent elements in clay or material of similar matrix. SRM 98b is powdered clay that was air-dried, ball-milled, and blended to ensure homogeneity.

The certified constituent elements of SRM 98b 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]	14.30 ± 0.20	Manganese [b,g]	0.0116 ± 0.0005
Calcium [b,d,f]	0.0759 ± 0.0035	Potassium [b,c,f,g,i]	2.81 ± 0.07
Chromium [c,g]	0.0119 ± 0.0005	Silicon [e,i]	26.65 ± 0.16
Iron [c,g]	1.18 ± 0.01	Sodium [b,d,g]	0.1496 ± 0.0066
Lithium [d,f]	0.0215 ± 0.0003	Strontium [d,f,g]	0.0189 ± 0.0008
Magnesium [b,c]	0.358 ± 0.012	Titanium [b,g,i]	0.809 ± 0.012

[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

[2] The 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

Element	Content, Wt%	Element	Content, Wt%
Barium	(0.07)	Rubidium	(0.018)
Phosphorus	(0.03)	Zinc	(0.011)
		Zirconium	(0.022)

Element	Content, µg/g	Element	Content, µg/g
Antimony	(1.6)	Hafnium	(7.2)
Cesium	(16.5)	Scandium	(22)
Cobalt	(16.3)	Thorium	(21)
Europium	(1.3)		

Loss on Ignition   (7.5 wt.%)

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

Source and Preparation

The plastic clay for SRM 98b was donated to NBS by F.J. Flanagan and J.W. Hasterman of the United States Geological Survey, Reston, Virginia. Approximately 220 kg of plastic clay was collected from the underclay of the Clarion coal bed at the Harbison-Walker Refractories Co. plant at Clearfield, 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 samples randomly selected samples from cans of bulk material. There were no significant differences between 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.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 88b

Dolomitic Limestone

This Standard Reference Material (SRM) is intended for use in the analysis of rocks, ores, minerals, and materials of similar matrix. SRM 88b is a powdered limestone that was passed through a No. 60 sieve (nominal sieve opening of 250 μm). Limestone is a major industrial raw material for the cement and refractory materials industries (including the steel industry). The control of constituents in limestone is essential to the quality control of the product and product additives.

The certified constituents for SRM 88b are given in Table 1. The certified values are based on measurements using two or more independent reliable methods or techniques. Noncertified values for constituent elements are given in Table 2 as additional information on the composition. The noncertified values should not be used for calibration or quality control. For user convenience gravimetric factors for converting the oxides to elements are given in Table 3. All values are based on samples that were dried for 2 hours at 110 °C and a minimum sample size of 250 mg.

Table 1
Certified Values for Constituents

Constituent[1]	Content, Wt. %[2]	Constituent	Content, Wt. %
Al_2O_3[c,g,h,k]	0.336 ± 0.013	MgO[c,g,h]	21.03 ± 0.07
CaO[c,g]	29.95 ± 0.05	Na_2O[a,e,f,k]	0.0290 ± 0.0007
CO_2[d,g,i]	46.37 ± 0.12*	P_2O_5[b,h]	0.0044 ± 0.0003*
Fe_2O_3[a,b,e,h,j]	0.277 ± 0.002	SiO_2[e,g,h]	1.13 ± 0.02
(Total Fe as Fe_2O_3)		SrO[a,e,f,j]	0.0076 ± 0.0003
K_2O[a,e,f,j]	0.1030 ± 0.0024		
MnO[a,b,h]	0.0160 ± 0.0012		

[1] Methods/Techniques
[a] Atomic Absorption Spectrometry
[b] Colorimetry
[c] Complexometric Titration
[d] Coulometry
[e] DC Plasma Emission Spectrometry
[f] Flame Emission Spectrometry
[g] Gravimetry
[h] Inductively Coupled Plasma Atomic Emission Spectrometry
[i] Inert Gas Fusion
[j] Isotope Dilution Mass Spectrometry
[k] Neutron Activation Analysis

[2] The listed uncertainty, unless otherwise noted, is ± two standard deviations of the certified value. The uncertainty primarily reflects differences between the various methods of analyses.
* The statistically derived uncertainty was extremely small for this constituent. The uncertainty is based on judgment and approximates ± two standard deviations.

October 9, 1987
Gaithersburg, MD 20899
(Revision of Certificate
dated April 21, 1986)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Table 2
Noncertified Values for Constituents

Constituent	Content, μg/g	Constituent	Content, wt. %
CeO_2[k]	(4.7)	TiO_2[e,f]	(0.016)
CoO[k]	(1.3)		
Cr_2O_3[k]	(3.4)		
Cs_2O[k]	(0.17)	LOI[g] (1000 °C for 18 hrs)	(46.98)
Eu_2O_3[k]	(0.15)		
HfO_2[k]	(0.16)	H_2O[g] (110 °C for 2 hrs)	(0.24)
Sc_2O_3[k]	(0.56)		
ThO_2[k]	(0.35)		

Table 3
Gravimetric Factors Used for Conversion of Oxides to Elements
(Compiled from International Atomic Weights of 1985)

Constituent	Gravimetric Factor	Constituent	Gravimetric Factor
Al_2O_3	0.52925	K_2O	0.83015
CaO	.71469	MnO	.77446
CeO_2	.81408	MgO	.60304
CO_2	.27292	Na_2O	.74186
CoO	.78648	P_2O_5	.43642
Cr_2O_3	.68420	Sc_2O_3	.65196
Cs_2O	.94323	SiO_2	.46743
Eu_2O_3	.86361	SrO	.84559
Fe_2O_3	.69943	ThO_2	.87881
HfO_2	.84798	TiO_2	.59941

PLANNING, PREPARATION, TESTING, AND ANALYSIS:

The material for this SRM was provided by Material Service Corporation, Chicago, Illinois. The source of the material was a mine near Skokie, Illinois. The material was received at NBS as a fine powder, 80 to 100 percent passing a 200 mesh sieve. At NBS the material was sieved with a No. 60 sieve, blended, and placed in polyethylene lined aluminum cans for bulk storage.

Samples from the top and bottom of each can were analyzed, using x-ray fluorescence, to establish homogeneity of the material. Seven elements, Mg, Fe, Ti, Cu, Si, K, and Al were determined in 18 randomly selected samples of SRM 88b and no significant differences between samples were found for any of the measured elements.

Homogeneity testing was performed by G.A. Sleater of the Gas and Particulate Science Division.

Chemical analyses for certification were performed in the following laboratories:

National Bureau of Standards, Center for Analytical Chemistry, Gaithersburg, MD, D.A. Becker, T.A. Butler, Mo De-Ming, B.I. Diamondstone, R.C. Gauer, J.W. Gramlich, Yie Guirong, J.D. Fassett, J.R. Moody, P.A. Pella, T.C. Rains, T.A. Rush, G.A. Sleater, R.L. Watters, Jr., and Y.Z. Zhang.

Mineral Constitution Laboratory, Pennsylvania State University, University Park, Pennsylvania, J.B. Bodkin, J.C. Devine and H. Gong.

The statistical analysis of the data for certification was performed by R.C. Paule, National Measurement Laboratory.

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.

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 2710

Montana Soil

Highly Elevated Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. SRM 2710 is a highly contaminated soil that was oven-dried, sieved, and blended to achieve a high degree of homogeneity. A unit of SRM 2710 consists of 50 g of the dried material.

The certified elements for SRM 2710 are given in Table 1. The values are based on measurements using one definitive method or two or more independent and reliable analytical methods. Noncertified values for a number of elements are given in Table 2 as additional information on the composition. The noncertified values should not be used for calibration or quality control. Analytical methods used for the characterization of this SRM are given in Table 3 along with analysts and cooperating laboratories. All values (except for carbon) are based on measurements using a sample weight of at least 250 mg. Carbon measurements are based on 100-mg samples.

NOTICE AND WARNINGS TO USERS

Expiration of Certification: This certification is valid for 5 years from the date of shipment from NIST. Should any of the certified values change before the expiration of the certification, purchasers will be notified by NIST. Return of the attached registration card will facilitate notification.

Stability: This material is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser.

Use: A minimum sample weight of 250 mg (dry weight - see Instructions for Drying) should be used for analytical determinations to be related to the certified values on this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., Hg, As, Se) are to be determined, precautions should be taken in the dissolution of SRM 2710 to avoid volatilization losses.

Statistical consultation was provided by S.B. Schiller of the NIST Statistical Engineering Division.

The overall direction and coordination of the analyses were under the chairmanship of M.S. Epstein and R.L. Watters, Jr., of the NIST 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 Standard Reference Materials Program by T.E. Gills and J.S. Kane.

Gaithersburg, MD 20899
October 30, 1992

William P. Reed, Chief
Standard Reference Materials Program

(over)

Instructions for Drying: When nonvolatile elements are to be determined, samples should be dried for 2 h at 110 °C. Volatile elements (i.e., Hg, As, Se) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture is to be made to the data for volatile elements before comparing to the certified values. This procedure ensures that these elements are not lost during drying. The weight loss on drying has been found to be in the range of 1.7 to 2.3 %.

Source and Preparation of Material: The U.S. Geological Survey (USGS), under contract to the NIST, collected and processed the material for SRM 2710. The soil was collected from the top 10 cm (4 in) of pasture land located at Longitude 112° 47' and Latitude 46° 01' along Silver Bow Creek in the Butte, Montana area. The site is approximately nine miles east of the local Anaconda plant and 6.5 miles south of settling ponds that feed the creek. The creek periodically floods, depositing sediment with high concentrations of copper, manganese, and zinc at the collection site. The material was shoveled from a 6.1 m x 6.1 m (20 ft x 20 ft) area into polyethylene bags in cardboard cartons for shipment to the USGS laboratory for processing.

The material was spread on 30.5 cm x 61 cm (1 ft x 2 ft) polyethylene-lined drying trays in an air drying oven and dried for three days at room temperature. The material was then passed over a vibrating 2-mm screen to remove plant material, rocks, and large chunks of aggregated soil. Material remaining on the screen was deaggregated and rescreened. The combined material passing the screen was ground in a ball mill to pass a 74-μm screen and blended for 24 h. Twenty grab samples were taken and measured for the major oxides using x-ray fluorescence spectrometry and for several trace elements using inductively coupled plasma atomic emission analysis to provide preliminary assessment of the homogeneity of the material prior to bottling. The material was bottled into 50-g units and randomly selected bottles were taken for the final homogeneity testing.

Analysis: The homogeneity, using selected elements in the bottled material as indicators, was assessed using x-ray fluorescence spectrometry and neutron activation analysis. In a few cases, statistically significant differences were observed, and the variance due to material inhomogeneity is included in the overall uncertainties of the certified values. The estimated relative standard deviation for material inhomogeneity is less than 2 % for those elements for which homogeneity was assessed.

Certified Values and Uncertainties: The certified values are weighted means of results from two or more independent analytical methods, or the mean of results from a single definitive method, except for mercury. Mercury certification is based on cold vapor atomic absorption spectrometry used by two different laboratories employing different methods of sample preparation prior to measurement. 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 stated uncertainty includes allowances for measurement imprecision, material variability, and differences among analytical methods. Each uncertainty is the sum of the half-width of a 95 % prediction interval and includes an allowance for systematic error among the methods used. In the absence of systematic error, a 95 % prediction interval predicts where the true concentrations of 95 % of the samples of this SRM lie.

Table 1. Certified Values

Element	wt. %			Element	µg/g		
Aluminum	6.44	±	0.08	Antimony	38.4	±	3.0
Calcium	1.25	±	0.03	Arsenic	626	±	38
Iron	3.38	±	0.10	Barium	707	±	51
Magnesium	0.853	±	0.042	Cadmium	21.8	±	0.2
Manganese	1.01	±	0.04	Copper	2950	±	130
Phosphorus	0.106	±	0.015	Lead	5532	±	80
Potassium	2.11	±	0.11	Mercury	32.6	±	1.8
Silicon	28.97	±	0.18	Nickel	14.3	±	1.0
Sodium	1.14	±	0.06	Silver	35.3	±	1.5
Sulfur	0.240	±	0.006	Vanadium	76.6	±	2.3
Titanium	0.283	±	0.010	Zinc	6952	±	91

Noncertified Values: Noncertified values, shown in parentheses, are provided for information only. An element concentration value may not be certified if a bias is suspected in one or more of the methods used for certification, or if two independent methods are not available. Certified values for some of these elements will eventually be provided in a revised certificate when more data is available.

Table 2. Noncertified Values

Element	wt.%	Element	µg/g
Carbon	(3)	Bromine	(6)
		Cerium	(57)
		Cesium	(107)
		Chromium	(39)
		Cobalt	(10)
		Dysprosium	(5.4)
		Europium	(1)
		Gallium	(34)
		Gold	(0.6)
		Hafnium	(3.2)
		Holmium	(0.6)
		Indium	(5.1)
		Lanthanum	(34)
		Molybdenum	(19)
		Neodymium	(23)
		Rubidium	(120)
		Samarium	(7.8)
		Scandium	(8.7)
		Strontium	(240)
		Thallium	(1.3)
		Thorium	(13)
		Tungsten	(93)
		Uranium	(25)
		Ytterbium	(1.3)
		Yttrium	(23)

Table 3. Analytical Methods Used for the Analysis of SRM 2710

Element	Certification Methods [*]	Element	Certification Methods [*]
Ag	ID ICPMS; RNAA; INAA	Mo	ID ICPMS
Al	XRF1; XRF2; DCP; ICP	Na	INAA; FAES
As	RNAA; HYD AAS; ICP; INAA	Nd	ICP
Au	INAA; FAAS	Ni	ID ICPMS; ETAAS; INAA
Ba	XRF2; FAES	P	DCP; COLOR; XRF1; XRF2
Br	INAA	Pb	ID TIMS; POLAR; ICP
C	COUL	Rb	INAA
Ca	XRF1; XRF2; DCP	S	ID TIMS
Cd	ID ICPMS; RNAA	Sb	RNAA; ETAAS
Ce	INAA; ICP	Sc	INAA; ICP
Co	INAA; ETAAS; ICP	Si	XRF1; XRF2; GRAV
Cr	INAA; DCP; ICP	Sm	INAA
Cs	INAA	Sr	ID TIMS; INAA; ICP
Cu	RNAA; FAES; ICP	Th	ID TIMS; INAA; ICP
Dy	INAA	Ti	XRF1; XRF2; DCP
Eu	INAA	Tl	ID TIMS; LEAFS
Fe	XRF1; XRF2; DCP; INAA; ICP	U	ID TIMS; INAA
Ga	INAA; ICP	V	INAA; ICP
Hf	INAA	W	INAA
Hg	CVAAS	Y	ICP
Ho	INAA	Yb	INAA
In	INAA	Zn	ID TIMS; ICP; INAA; POLAR
K	XRF1; XRF2; FAES; ICP		
La	INAA; ICP		
Mg	XRF1; ICP		
Mn	INAA; DCP; XRF2		

[*]Methods in **bold** were used to corroborate certification methods or to provide information values.

ID TIMS - Isotope dilution thermal ionization mass spectrometry; mixed acid digestion.
ID ICPMS - Isotope dilution inductively coupled plasma mass spectrometry; mixed acid digestion.
INAA - Instrumental neutron activation analysis.
RNAA - Radiochemical neutron activation analysis; mixed acid digestion.
XRF1 - Wavelength dispersive x-ray fluorescence on fused borate discs.
XRF2 - Wavelength dispersive x-ray fluorescence spectrometry on pressed powder.
ICP - Inductively coupled plasma atomic emission spectrometry; mixed acid digestion.
DCP - Direct current plasma atomic emission spectrometry; lithium metaborate fusion.
ETAAS - Electrothermal atomic absorption spectrometry; mixed acid digestion.
CVAAS - Cold vapor atomic absorption spectrometry.
HYD AAS - Hydride generation atomic absorption spectrometry.
FAAS - Flame atomic absorption spectrometry; mixed acid digestion except for Au, leached with HBr-Br$_2$.
FAES - Flame atomic emission spectrometry; mixed acid digestion.
COLOR - Colorimetry; lithium metaborate fusion.
GRAV - Gravimetry; sodium carbonate fusion.
COUL - Combustion coulometry.
LEAFS - Laser enhanced atomic fluorescence spectrometry; mixed acid digestion.
POLAR - Polarography.

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National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 2709

San Joaquin Soil

Baseline Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. SRM 2709 is an agricultural soil that was oven-dried, sieved, and blended to achieve a high degree of homogeneity. A unit of SRM 2709 consists of 50 g of the dried material.

The certified elements for SRM 2709 are given in Table 1. The values are based on measurements using one definitive method or two or more independent and reliable analytical methods. Noncertified values for a number of elements are given in Table 2 as additional information on the composition. The noncertified values should not be used for calibration or quality control. Analytical methods used for the characterization of this SRM are given in Table 3 along with analysts and cooperating laboratories. All values (except for carbon) are based on measurements using a sample weight of at least 250 mg. Carbon measurements are based on 100-mg samples.

NOTICE AND WARNINGS TO USERS

Expiration of Certification: This certification is valid for 5 years from the date of shipment from NIST. Should any of the certified values change before the expiration of the certification, purchasers will be notified by NIST. Return of the attached registration card will facilitate notification.

Stability: This material is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser.

Use: A minimum sample weight of 250 mg (dry weight - see Instructions for Drying) should be used for analytical determinations to be related to the certified values on this Certificate of Analysis .

To obtain the certified values, sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., Hg, As, Se) are to be determined, precautions should be taken in the dissolution of SRM 2709 to avoid volatilization losses.

Statistical consultation was provided by S.B. Schiller of the NIST Statistical Engineering Division.

The overall direction and coordination of the analyses were under the chairmanship of M.S. Epstein and R.L. Watters, Jr., of the NIST 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 Standard Reference Materials Program by T.E. Gills and J.S. Kane.

Gaithersburg, MD 20899
October 30, 1992

William P. Reed, Chief
Standard Reference Materials Program

(over)

Instructions for Drying: When nonvolatile elements are to be determined, samples should be dried for 2 h at 110 °C. Volatile elements (i.e., Hg, As, Se) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture is to be made to the data for volatile elements before comparing to the certified values. This procedure ensures that these elements are not lost during drying. The weight loss on drying has been found to be in the range of 1.8 to 2.5 %.

Source and Preparation of Material: The U.S. Geological Survey (USGS), under contract to the NIST, collected and processed the material for SRM 2709. The soil was collected from a plowed field, in the central California San Joaquin Valley, at Longitude 121° 25' and Latitude 36° 55'. The collection site is in the Panoche fan between the Panoche and Cantu creek beds. The top 7.5-13 cm (3-5 in) of soil containing sticks and plant debris was removed, and the soil was collected from the 13 cm level down to a depth of 46 cm (18 in) below the original surface. The material was shoveled into 0.114 m³ (30-gal) plastic buckets and shipped to the USGS laboratory for processing.

The material was spread on 30.5 cm x 61 cm (1 ft x 2 ft) polyethylene-lined drying trays in an air drying oven and dried for three days at room temperature. The material was then passed over a vibrating 2-mm screen to remove plant material, rocks, and large chunks of aggregated soil. Material remaining on the screen was deaggregated and rescreened. The combined material passing the screen was ground in a ball mill to pass a 74-µm screen and blended for 24 h. Twenty grab samples were taken and measured for the major oxides using x-ray fluorescence spectrometry and for several trace elements using inductively coupled plasma atomic emission analysis to provide preliminary assessment of the homogeneity of the material prior to bottling. The material was bottled into 50-g units and randomly selected bottles were taken for the final homogeneity testing.

Analysis: The homogeneity, using selected elements in the bottled material as indicators, was assessed using x-ray fluorescence spectrometry and neutron activation analysis. In a few cases, statistically significant differences were observed, and the variance due to material inhomogeneity is included in the overall uncertainties of the certified values. The estimated relative standard deviation for material inhomogeneity is less than 1 % for those elements for which homogeneity was assessed.

Certified Values and Uncertainties: The certified values are weighted means of results from two or more independent analytical methods, or the mean of results from a single definitive method, except for mercury. Mercury certification is based on cold vapor atomic absorption spectrometry used by two different laboratories employing different methods of sample preparation prior to measurement. 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 stated uncertainty includes allowances for measurement imprecision, material variability, and differences among analytical methods. Each uncertainty is the sum of the half-width of a 95 % prediction interval and includes an allowance for systematic error among the methods used. In the absence of systematic error, a 95 % prediction interval predicts where the true concentrations of 95 % of the samples of this SRM lie.

Table 1. Certified Values

Element	wt. %			Element	μg/g		
Aluminum	7.50	±	0.06	Antimony	7.9	±	0.6
Calcium	1.89	±	0.05	Arsenic	17.7	±	0.8
Iron	3.50	±	0.11	Barium	968	±	40
Magnesium	1.51	±	0.05	Cadmium	0.38	±	0.01
Phosphorus	0.062	±	0.005	Chromium	130	±	4
Potassium	2.03	±	0.06	Cobalt	13.4	±	0.7
Silicon	29.66	±	0.23	Copper	34.6	±	0.7
Sodium	1.16	±	0.03	Lead	18.9	±	0.5
Sulfur	0.089	±	0.002	Manganese	538	±	17
Titanium	0.342	±	0.024	Mercury	1.40	±	0.08
				Nickel	88	±	5
				Selenium	1.57	±	0.08
				Silver	0.41	±	0.03
				Strontium	231	±	2
				Thallium	0.74	±	0.05
				Vanadium	112	±	5
				Zinc	106	±	3

Noncertified Values: Noncertified values, shown in parentheses, are provided for information only. An element concentration value may not be certified if a bias is suspected in one or more of the methods used for certification, or if two independent methods are not available. Certified values for some of these elements will eventually be provided in a revised certificate when more data is available.

Table 2. Noncertified Values

Element	wt.%	Element	μg/g
Carbon	(1.2)	Cerium	(42)
		Cesium	(5.3)
		Dysprosium	(3.5)
		Europium	(0.9)
		Gallium	(14)
		Gold	(0.3)
		Hafnium	(3.7)
		Holmium	(0.54)
		Iodine	(5)
		Lanthanum	(23)
		Molybdenum	(2.0)
		Neodymium	(19)
		Rubidium	(96)
		Samarium	(3.8)
		Scandium	(12)
		Thorium	(11)
		Tungsten	(2)
		Uranium	(3)
		Ytterbium	(1.6)
		Yttrium	(18)
		Zirconium	(160)

Table 3. Analytical Methods Used for the Analysis of SRM 2709

Element	Certification Methods [*]	Element	Certification Methods [*]
Ag	ID ICPMS; RNAA	Mo	ID ICPMS
Al	XRF1; XRF2; INAA; DCP; ICP	Na	INAA; FAES; ICP
As	RNAA; HYD AAS; INAA	Nd	ICP
Au	INAA; FAAS	Ni	ID ICPMS; ETAAS; INAA
Ba	XRF2; FAES	P	DCP; COLOR; XRF2
C	COUL	Pb	ID TIMS
Ca	XRF1; XRF2; DCP	Rb	INAA
Cd	ID ICPMS; RNAA	S	ID TIMS
Ce	INAA; ICP	Sb	INAA; ETAAS
Co	INAA; ETAAS; ICP	Sc	INAA; ICP
Cr	INAA; DCP; ICP	Se	RNAA; HYD AAS
Cs	INAA	Si	XRF1; XRF2; GRAV
Cu	RNAA; FAES; ICP	Sm	INAA
Dy	INAA	Sr	ID TIMS; INAA; ICP
Eu	INAA	Th	ID TIMS; INAA; ICP
Fe	XRF1; XRF2; INAA; DCP	Ti	INAA; XRF1; XRF2; DCP
Ga	INAA; ICP	Tl	ID TIMS; LEAFS
Hf	INAA	U	ID TIMS; INAA
Hg	CVAAS	V	INAA; ICP
Ho	INAA	W	INAA
I	INAA	Y	ICP
K	XRF1; XRF2; FAES; ICP; INAA	Yb	INAA
La	INAA; ICP	Zn	ID TIMS; ICP: INAA; POLAR
Mg	INAA; XRF1; ICP	Zr	INAA
Mn	INAA; ICP		

[*]Methods in bold were used to corroborate certification methods or to provide information values.

ID TIMS - Isotope dilution thermal ionization mass spectrometry; mixed acid digestion.
ID ICPMS - Isotope dilution inductively coupled plasma mass spectrometry; mixed acid digestion.
INAA - Instrumental neutron activation analysis.
RNAA - Radiochemical neutron activation analysis; mixed acid digestion.
XRF1 - Wavelength dispersive x-ray fluorescence on fused borate discs.
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FAAS - Flame atomic absorption spectrometry; mixed acid digestion except for Au, leached with HBr-Br$_2$.
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COLOR - Colorimetry; lithium metaborate fusion.
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COUL - Combustion coulometry.
LEAFS - Laser enhanced atomic fluorescence spectrometry; mixed acid digestion.
POLAR - Polarography.

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Appendix B: NIST Powdered Soil Spectroscopy

The following IR spectra were taken of the NIST powdered soils that were used in the low-resolution soil spectroscopy experiment. All of the spectra were taken with the Bomem FTIR. Some of the more prominent features have been correlated with the chemical compound responsible for the spectral absorption. All spectra are presented in terms of reflectance and in the spectral bandwidth of 4000 cm^{-1} to 775 cm^{-1}. All IR spectra of chemical compounds are taken from the book, Inorganic Spectra of Inorganic Compounds, by Nyquist and Kagel (13:207,209, 217, 219).
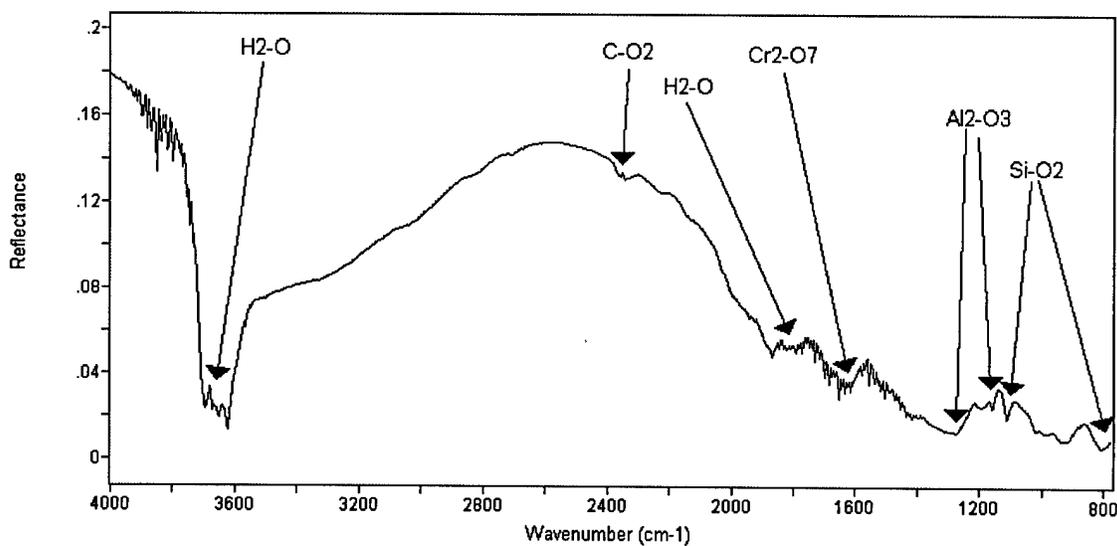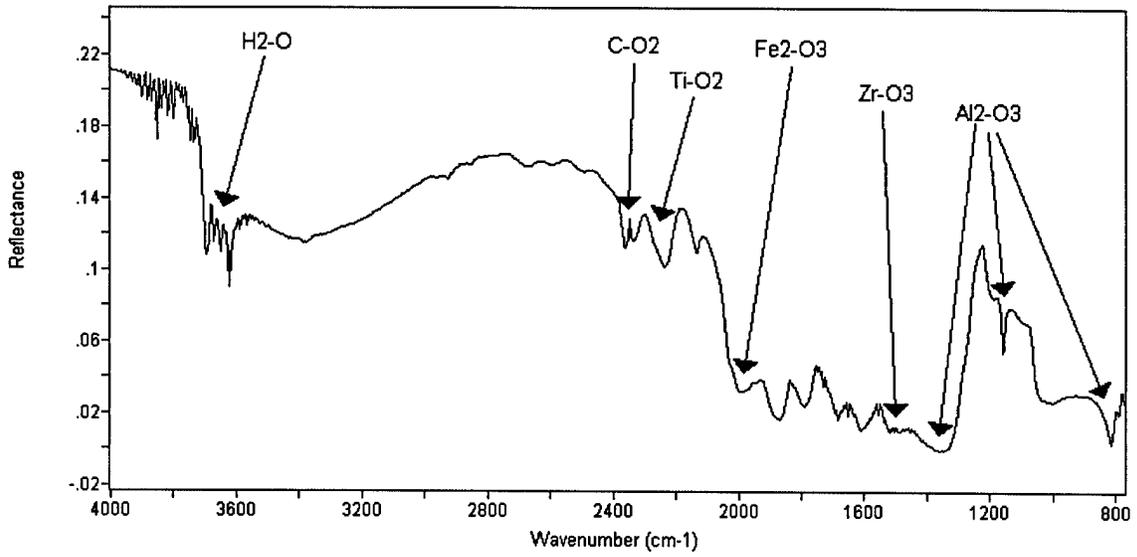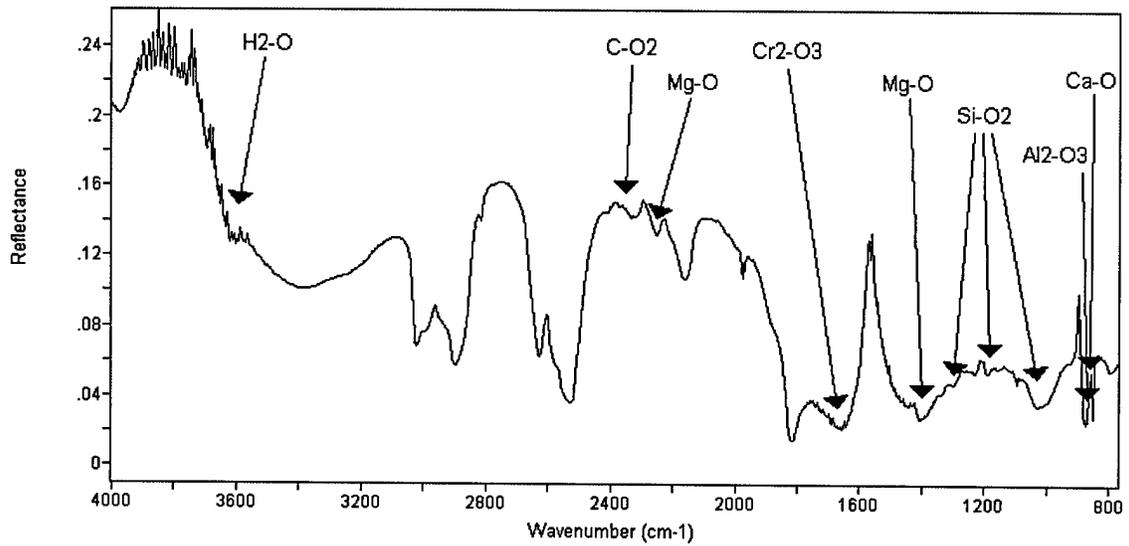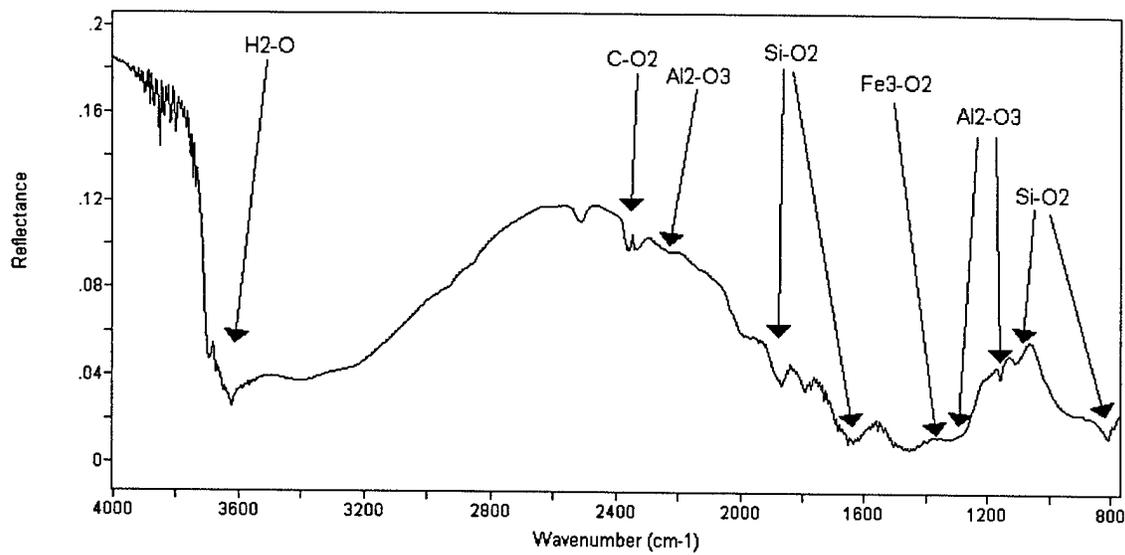

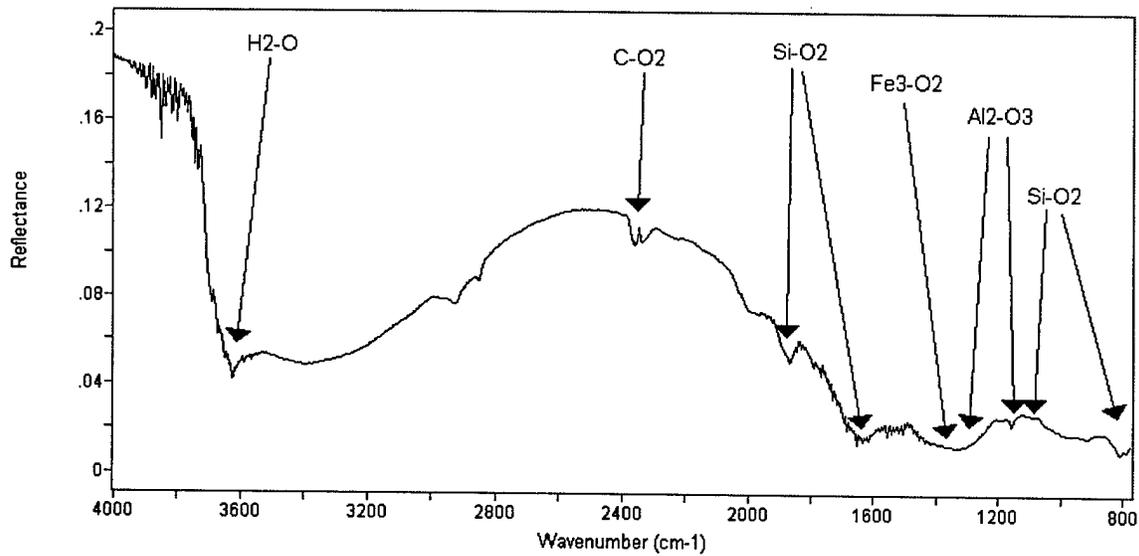**Figure 16. Plastic Clay**

Figure 17. Glass Sand

Figure 18. Dolomitic Limestone

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Figure 19. San Joaquin Soil

Figure 20. Montana Soil

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Vita

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 1999	

4. TITLE AND SUBTITLE

Use of Diffuse Reflectance Spectroscopy to Determine Desorption coefficients of Trichloroethylene from Powdered Soils

5. FUNDING NUMBERS

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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2750 P Street
WPAFB OH 45433-7765

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

Approved for public relsease; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This laboratory thesis investigated the applicability of reflectance spectroscopy as a tool to measure desorption rates by directly observing the change in trichloroethylene bound to surface sites. Diffuse reflectance spectroscopy holds the promise of being a faster technique with minimal sample preparation time. Reflectance spectroscopy's dependence on the surface of the sample is its greatest advantage, as well as its greatest disadvantage. Both high and low resolution scans were made of different soil samples contaminated by trichloroethylene. After the technique of spectral subtraction was used, potential TCE signals were observed from the dolomitic limestone sample. Unfortunately, due to the low level of the signal and high amount of noise, positive identification of the signals as TCE could not be established. The low resolution scans were unable to detect any possible TCE signals. More data is required to determine the sensitivity of the device as well as prove the linearity of the signal with concentration, before this technique can be proven to be useful for studying desorption kinetics.

14. SUBJECT TERMS

TCE Desorption, Diffuse Reflectance Spectroscopy, Trichloroethylene (TCE)

15. NUMBER OF PAGES

66

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL