ARSON ACCELERANT ANALYSIS BY ATTENUATED TOTAL REFLECTANCE SPECTROSCOPY

by

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Abstract

Arson is a serious problem both locally and nationally. In 1994, the National Fire Protection Association reported over 100,000 arson fires with over $1.2 billion in damages and 550 deaths. Locally, in 1996, Youngstown had 326 arson fires with almost $4.0 million in damages and five deaths. Often these fires are accelerated by flammable materials. Organic, petroleum-based, non-water soluble solvents, such as gasoline, can be detected at very low concentrations after an intense fire by several well developed techniques. However, water soluble solvents, such as methyl (wood), ethyl (grain), and isopropyl (rubbing) alcohol have proven to be difficult to analyze. Not only does the water used to extinguish the fire wash away the accelerant by convection, it also disperses it by dissolution. Additionally, most techniques used for analysis require organic solvents to dissolve the materials to be analyzed. Since the accelerants to be studied are in water, they would need to be extracted with organic solvents reducing their concentration further. Attenuated Total Reflectance Spectroscopy (ATR), a relatively sensitive and selective technique, was used to perform analysis on these water-soluble accelerants. Concentration gradient experiments, time controlled burn experiments, and field-controlled burns were performed with detectability in more than 75% of the samples. Most tests were on carpet samples, but some tests were on cloth samples as well. Using ATR has proven to be an ideal way to handle those situations where a water-soluble accelerant needs to be detected.

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List of Symbols and Abbreviations

Symbol	Definition
ATR	Attenuated Total Reflectance
IR	Infrared
I	Moment of Inertia
m	molecule
r_I	axis of rotation
mm	millimeters
IRS	Internal Reflection Spectroscopy
α_I	angle of incidence
θ_c	critical angle
μm	micrometers
n	refractive index
v	propagation velocity
R	reflectivity
I_D	incident identity
I_R	reflected intensity
FTR	Frustrated Total Reflection
IRE	Internal Reflection Element
a	adsorption parameter
FT-IR	Fourier Transform-Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
v:v	volume to volume

mL	milliliters
nm	nanometer
L/min	Liters per minute
psi	Pounds per square inch
°C	Degree Celsius
kHz	kilohertz
sec.	seconds
hrs.	hours
min.	minute(s)

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Chapter One

Introduction

The characterization of water soluble accelerants used in arson fires is difficult to accomplish by commonly used techniques in a forensic lab. Of other possible techniques, the one used in this study was Attenuated Total Reflectance (ATR) Infrared Spectroscopy. ATR occurs when radiation passes through a prism made up of a substance with a high refractive index relative to aqueous solutions and reaches the interface of the prism where the sample is in contact with it. The radiation penetrates the sample to the depth of a few micrometers and then suffers total reflectance. An accelerant is any substance that is used to accelerate (and sometimes direct) the spread of a fire. The accelerants of interest in this study were those that are water-soluble and readily available to an arsonist. They include simple alcohols such as methanol (wood alcohol), ethanol (grain alcohol), isopropanol alcohol (rubbing alcohol) and acetone.

Statistics of Arson

Arson is the intentional setting of a fire. Arson is a crime that kills people and destroys property and life. In 1994, The National Fire Protection Association reported over 100,000 arson-related fires, with over $1.2 billion and 550 lives lost.[1] Locally, in 1996, Youngstown had 326 arson fires that resulted in $3,805,805 in losses and 5 deaths.[2] The arson fires were not only to residential structures but also commercial structures and vehicles. In the period from 1990-1997, Youngstown has averaged 326 arson fires per year with $2,238,797 in damages and 4.7 deaths[2]. This is a serious problem that will not get better until there is not anyway for an arsonist to get away.

Arson Investigation

An arson investigation usually begins immediately after the fire is brought under control. The fire battalion chief makes a preliminary cause and origin determination. If arson is suspected, an investigator is sent to the scene. The fire scene is photographed from all angles. The investigator will then do a cause and origin determination to reassert the battalion chief's assessment. Samples are then taken from selected areas throughout the scene, with emphasis at the site of origin. The evidence is recorded and sent to the crime laboratory for accelerant analysis. While the evidence is being tested, the investigation centers on motive, means, and opportunity.

Arson is one of the most difficult crimes to prosecute because there is usually little direct evidence. An arson case depends mainly upon the chemical analysis of physical evidence collected at the scene. The basic goal of chemical analysis of fire debris is to establish whether materials are present in the remnants of the fire that could have been used to start and/or accelerate the fire. Even a highly volatile fuel, such as gasoline, is detectable after an intense fire. According to Bertsch, in controlled burns, these fuels are still detectable after 90% evaporation, i.e. 90% of its mass is gone. Kerosene maintains many of its characteristic chromatographic features following 90% evaporation.[1]

IR Theory

Infrared (IR) Spectroscopy deals with the interaction of infrared radiation with matter. The infrared region of the electromagnetic spectrum lies between the visible and microwave regions. This region is divided into three categories:

Region	Range (cm^{-1})
Near-infrared	13,300-4,000
Mid-infrared	4,000-400
Far-infrared	400-10

Infrared spectroscopy theory states that a molecule may absorb infrared radiation of the appropriate frequency to excite it from one vibrational or rotational level to another. When a beam of infrared energy, covering a broad frequency range, passes through a sample, the energy is absorbed at certain frequencies by the sample. In polyatomic molecules, many kinds of vibration are possible, which gives rise to an infrared spectrum composed of many relatively sharp absorption bands. The frequencies of the molecular vibrations, and consequently the wavenumber of the absorption bands appearing in the vibrational spectra, are determined by the mass of the atoms and the forces acting between them.[3] A graph of energy absorbed versus frequency can then be plotted. This is the absorption spectrum of the sample. The spectrum is characteristic of the particular molecule and its molecular motions.[4] Most molecules absorb infrared radiation with the exceptions being homonuclear diatomics.[5]

The quantized energy uptake of substances is connected with the internal motions of the molecule. The change in energy of the molecule is composed of energy changes of three kinds, associated with electronic motion, rotation, and vibration.[6] Absorption occurring in the region of infrared radiation is caused by a change in the vibrational and rotational state of a molecule. Vibrational and rotational motions where absorption can be detected only occurs for polyatomic molecules.

The fundamental postulates upon which chemists base the utility of infrared spectroscopy in determining structural data can be stated as follows:

1. Organic substances exhibit characteristic group frequencies in the infrared region.
2. The absorption spectrum of a given substance is generally specific for that and only that substance.
3. The absorption spectrum of mixtures is generally additive, i.e. the sum of the individual spectra of the components.
4. The intensity of an absorption band is related to the concentration of the substance that absorbs the incident radiation. [7]

Quantum Mechanics of Infrared Spectroscopy

According to quantum mechanics, adsorption of radiation induces a change in the rotational state of a molecule if the dipole moment of the molecule is also changing, or, in the case of rotation combined with vibration, if a dipole moment transition occurs during vibration.[8] For polyatomic molecules, the structure of the rotational spectrum is determined by the distribution of the moment of inertia of the molecule. The moment of inertia, I, is given by the masses of the atoms forming the molecule, m_i , and their distances from the axis of rotation , r_i .

$$I = \Sigma m_i r_i^2 \qquad \text{(eqn. 1)} \qquad [10]$$

Investigating the value of I along directions starting from the center of gravity, it is found that in three mutually perpendicular directions the value of I exhibits a maximum or minimum. In vibratory motion, atoms undergo vibrations about their equilibrium position in a molecule while the center of gravity remains in the same position.

To discuss the vibrational modes of polyatomic molecules, a knowledge of normal modes and of the symmetry characteristics of the molecule is needed. For normal vibrations, each atom forming the molecule undergoes near-harmonic vibration of identical frequency in identical or opposite phase along the straight line passing through the equilibrium position.[11] The vibration of the molecules results from the superposition of the normal vibrations. According to Svehla, normal vibrations can be divided into two groups. In the first group, the displacement of the atom occurs in the direction of the valence bond, so that bond distances will increase and decrease periodically. The bond angles change only if it is necessary to ensure that the center of gravity remains the same. These vibrations are referred to as stretching vibrations. The other type is known as deformation vibrations. Here, the bond angles change periodically and the bond distance will change only if necessary to ensure the center of gravity remains the same .[11]

Infrared spectra can be taken on solids, liquids and gases. Generally, work is done at room temperature and atmospheric pressure. When measuring the IR spectra of liquids, it is very important that the cell windows and the solvent used transmit in the infrared region selected for analysis. For quantitative examination, the spectra of some substances must be taken using in solution. The interaction between solute and solvent, the so-called solvent effect, increases with increasing complexity and polarity of the solvent molecule.[12] Whenever possible, aqueous solutions should be avoided. Water dissolves most materials used to make cell windows, and moreover it has strong absorption bands, so that it can only be used below a cell thickness of 0.02 mm.[25] The spectra of aqueous solutions can be taken without putting them in a cell, by forming a capillary film on a support frame in the presence of a surfactant. Owing to the strong absorption of water, the energy of the reference beam path must also be reduced in most cases. It is best to examine substances soluble only in water in reflected light or in the form of an emulsion. The transmission spectra of attenuated total reflectance and H_2O give reasonable results. The advantages of ATR will be discussed later.

Interpretation of IR Spectra

Interpretation of an IR spectrum is done by looking at the characteristic bond and group frequencies. Characteristic bond and group frequencies depend on the atoms which form the molecule, on the nature of the chemical bonds between the atoms, and on the structural characteristics of the molecule. From the positions of the bands appearing in the spectrum and from their intensities or relative intensities, conclusions can be drawn regarding the types of bonds, atomic groups and their arrangement within the molecule.[13] Some of the physical and chemical effects that considerably affect the position, shape, and intensity of the bands appearing in the spectrum are:

1. Mass effects, due to a change in the mass vibrating with the group and to isotope exchange
2. Steric effects, among which diastereomerism, rotational isomerism, ring stretching, steric crowding and restriction, bond angle distortion, collinearity, and coplanarity should be mentioned.

3. Effect of the electron affinity of substituents, leading to hyperconjugation, inductive and mesomeric effects.
4. Tautomerization effects, e.g. giving rise to keto-enol forms. [14]

Evanescent Wave

The history of Internal Reflection Spectroscopy (IRS) began in the early 1600's when Newton observed an evanescent field in a lower index of refraction medium in contact with a higher index of refraction medium in which a propagating wave of radiation undergoes total internal reflection. According to Mirabella, the established method of the time was a transmission method in which the critical angle of refraction was located with the sample placed as a thin film between the hypotenuse face of two isosceles prisms of glass. At angles smaller than the critical angle, light was transmitted through both prisms. At angles at or above the critical angle, total internal reflection occurred at the prism-sample interface of the first prism and no light was transmitted through the second prism. For most angles of incidence above the critical angle, the reflection spectra resemble transmission spectra fairly closely; however, for angles of incidence just below the critical angle the spectra may resemble the mirror image of the dispersion in the index of refraction.

In order to discuss the theory of IRS, a description of the properties of the evanescent field is needed. Some of the basic properties of the evanescent wave are as follows:

1. The field intensity in the rarer medium is nonzero and there is an instantaneous normal component of energy flow into this medium whose time average is

zero. Thus, there is no loss of energy and the propagating radiation in the denser medium is totally internally reflected, except at those frequencies in the rarer medium where absorption occurs.

2. The evanescent field in the rarer medium is a nontransverse wave and has components in all spatial orientations.
3. The evanescent field is confined to the vicinity of the surface of the rarer medium and decreases in intensity with distances into this medium normal to the surface.
4. There is a net energy flow parallel to the surface resulting in a displacement of the incident and reflected waves. [15]

The evanescent field decays exponentially in the rarer medium as a result of the presence in an optically denser medium (one having a high refractive index) of a standing wave established at a totally reflecting interface. The exponential decay of the electric field amplitude (E/E_0) and the intensity $(E/E_0)^2$ as a function of depth into the surface Z is shown by Figure 1.1.[16] It shows that most of the absorbance information comes from the first 3 or 4 μm of depth into the surface. The fact that the evanescent wave is nontransverse, and has vector components in all spatial orientations, is significant because it permits these vector components to interact with dipoles in all orientations.

The properties of the evanescent field in the rarer medium also depend on the thickness of that medium. The interaction of the evanescent field with bulk materials and thin films can be expressed in terms of an effective thickness. The effective thickness is a measure of the strength of coupling to a sample and is useful in comparing internal reflection spectra to transmission spectra.[17] Two distinct cases can be defined. The first is the semi-bulk case which is when the electric field amplitude falls to a very low value

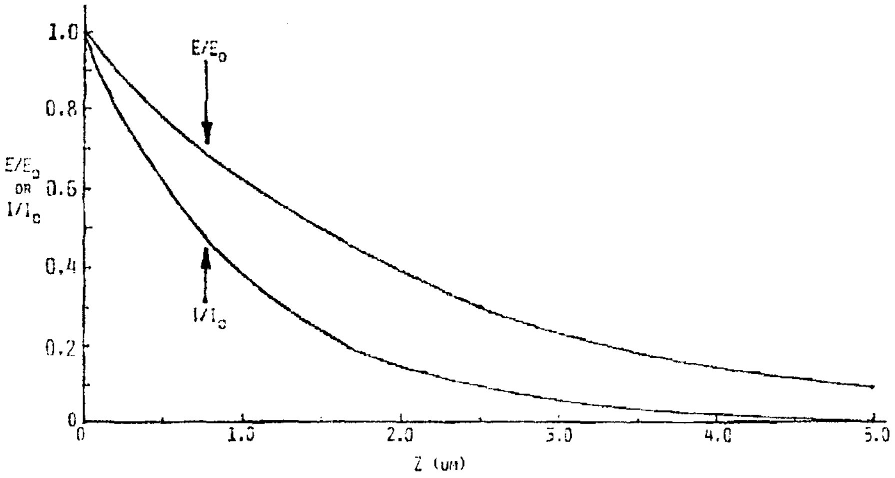


Figure 1 . 1 Ratio of intensity and amplitude of electric vector at depth Z to that at the surface versus the depth Z. The values used to calculate the curves were $n_2 = 1.50$, $n_1 = 2.38$, and $\theta = 45°$ at a wavelength of 10 μm.

within the thickness of the rarer medium. Second, the thin film case is when the electric field amplitude remains essentially constant over the thickness of the rarer medium.

Reflective and Refractive Properties of Light with Water

Before discussing the specifics of IRS, some of the basic principles governing the interaction of light with water should be established. More specifically, reflective and refractive properties of light propagating through media having distinctive optical properties are of interest because they will dictate not only the amount of energy propagating through but also the direction of propagation.[18] Light is an electromagnetic wave. When electromagnetic radiation strikes an interface between media of two different refractive indices, both refraction and reflection can occur. When the two media are in contact with each other, the path of the light will be distorted, depending on the angle of incidence (see Figure1.2).[19] According to Harrick, light is transmitted at a 90° angle of incidence and partially reflected at $\alpha_1 < \theta_c$ or totally reflected at $\alpha_1 > \theta_c$. When the angle of incidence, α_1, is greater than the critical angle,θ_c, the light is totally reflected, and this forms the basis for internal reflection spectroscopy. Under the circumstances of $\alpha_1 > \theta_c$, the amount of electromagnetic energy being put in the sample by the evanescent wave exceeds the amount coming out, and the evanescent wave will be attenuated.[20]

In spectroscopy, we start with a system in some stationary state, expose it to light, and observe whether or not the system has made a transition to another stationary state.

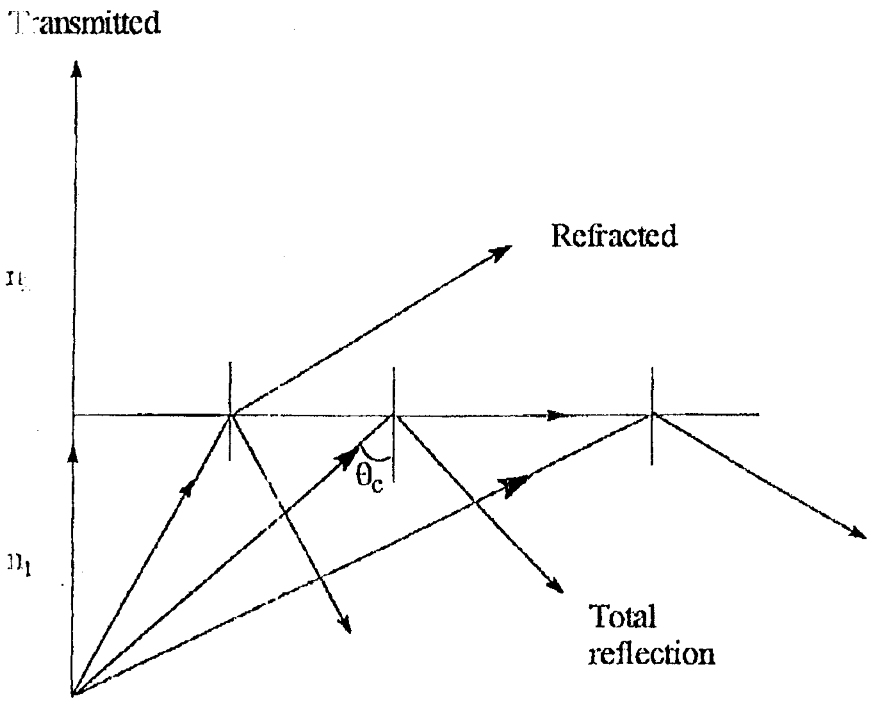


Figure 1.2 *Effect of angle of incidence on direction of propagation.*

Conditions For Internal Reflection Spectroscopy

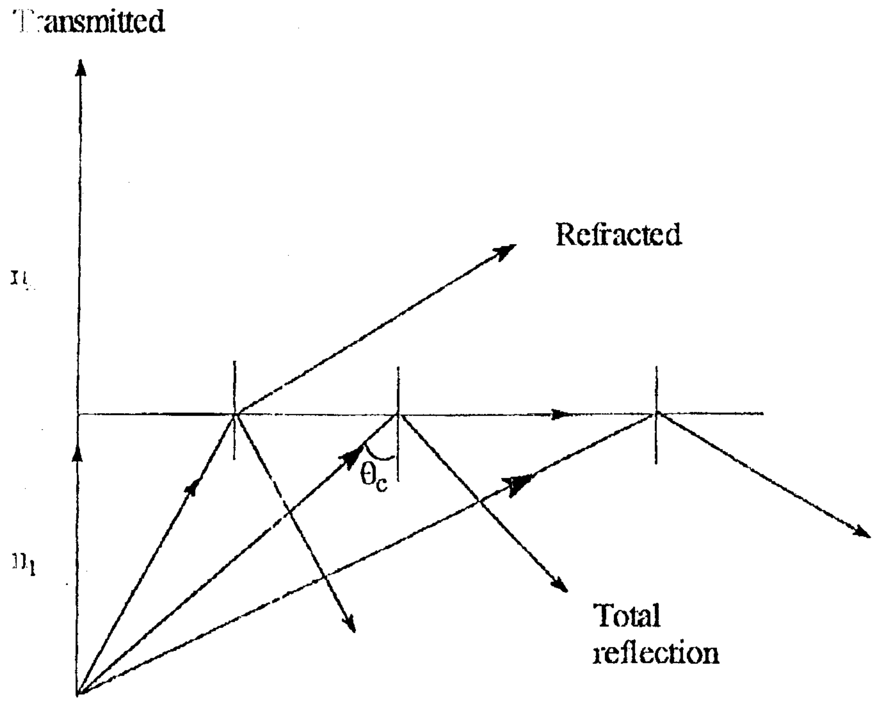
A realistic set of conditions in IRS include a medium of low absorbance and a finite diameter irradiating beam. Further, an absorbing rarer medium requires considerations of dispersion of the refractive index across an absorbing medium.[21] The refractive index is a measure of the medium's interaction with radiation. The variation of the refractive index with wavelength of radiation is referred to as dispersion. Dispersion curves usually show a gradual increase in the refractive index with decreasing wavelength. If light propagates through a medium with refractive index n_1 and enters a medium with refractive index n_2 (Figure 1.3), the light path will change, and the extent of refraction is given by

$$\sin \alpha_1/\sin \alpha_2 = n_2(\nu)/n_1(\nu) = v_1/v_2 \qquad \text{(eqn. 2)} \qquad [22]$$

where α_1 and α_2 are the angles of incidence and refraction, respectively, and v_1 and v_2 are propagation velocities in media 1 and 2, respectively. The principle of refraction, known as Snell's law, is illustrated by Figure 1.4 and is given by

$$R = I_R/I_0 \qquad \text{(eqn. 3)} \qquad [23].$$

The same results can be obtained by starting with Maxwell's equations which also clearly show the essential presence of the evanescent wave. From this mathematical treatment, the dependence of reflection on angle of incidence and polarization is obtained for non-absorbing and absorbing media. The reflection phenomenon is then treated from a physical viewpoint which is valid for low absorptions. The latter treatment gives a clear insight into the interaction mechanisms of the evanescent wave with the absorbing rarer medium.



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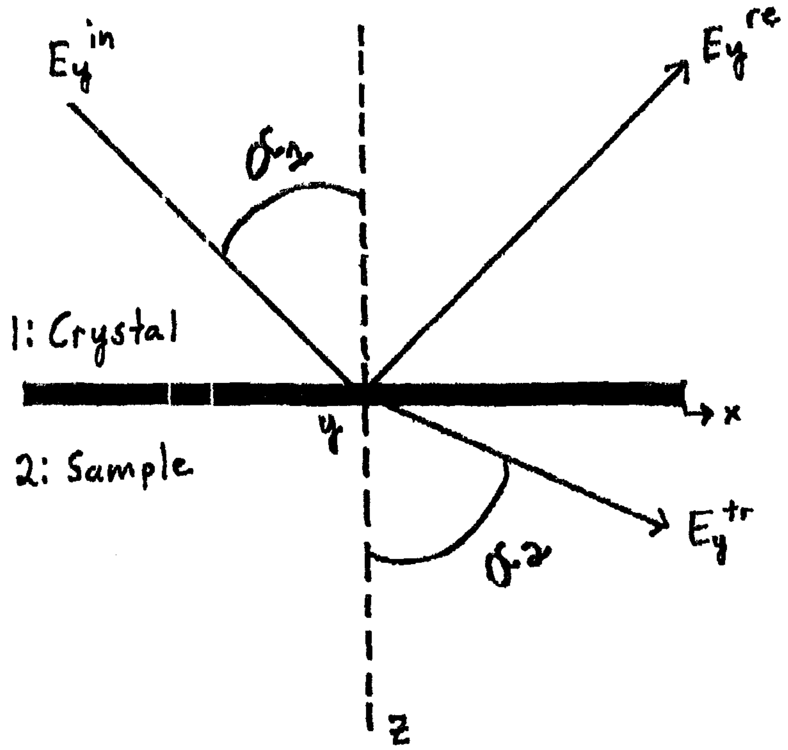


Figure 1.3: Schematic diagram of the perpendicularly polarized light beam E_y impinging on the interface between two semi-infinite media and split into two beams: one transmitted and one reflected.

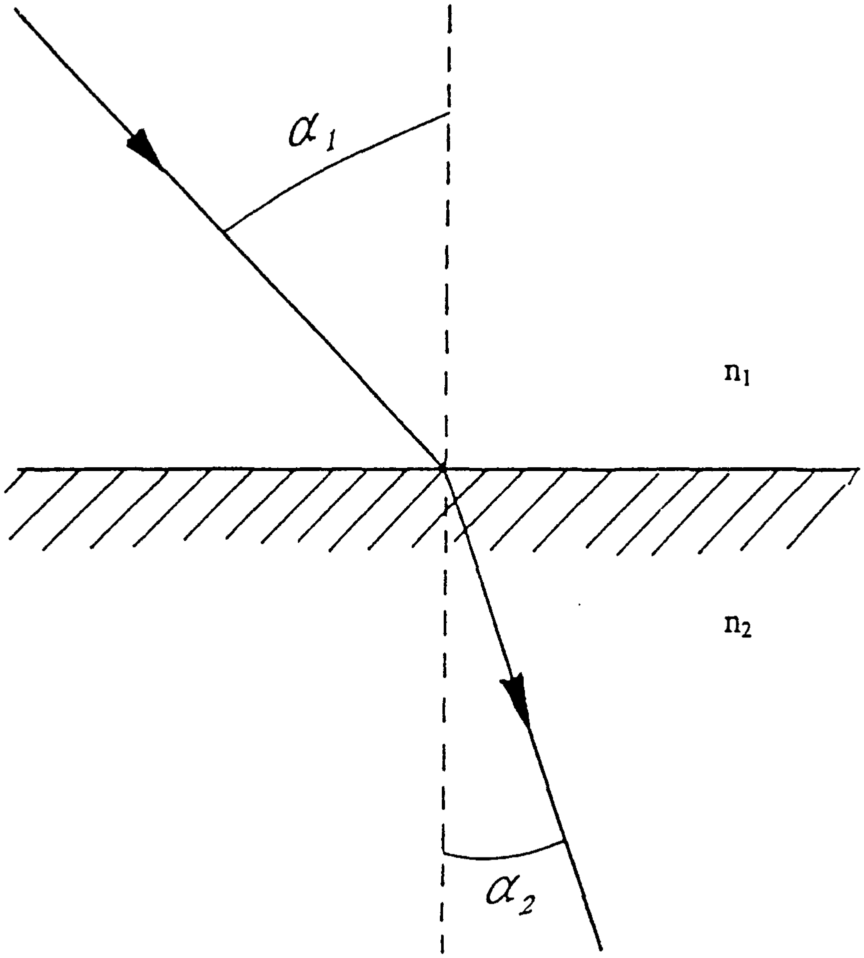


Figure 1.4 Snell's Law

For internal reflection, the electric field amplitude at the surface is nearly zero. For total internal reflection, there is still a sinusoidal variation of the electric field amplitude with distance from the surface in the denser medium; however, by selecting the angle of incidence, it is possible to obtain large electric field amplitudes.[24] It is important to note that electric fields exist in all spatial directions at the reflecting interfaces. This is one reason for the difference between IRS and transmission spectra, i.e. dipoles will absorb energy in internal reflection regardless of their orientation, whereas for transmission, dipoles oriented parallel to the direction of propagation cannot absorb energy.[25]

Newton's experiments showed, and it follows from Maxwell's equations, that an electromagnetic disturbance exists in the rarer medium beyond the reflecting interface for total internal reflection. This disturbance is unusual since it exhibits the frequency of the incoming wave, but it is an evanescent wave whose electric field amplitude falls off exponentially with distance from the surface. The depth of penetration, is defined as the distance required for the electric field amplitude to fall to e^{-1} of its value at the surface. To demonstrate the existence of the evanescent wave and to measure its depth of penetration, it is necessary to disturb it either by absorbing its energy or by redirecting it.[26]

Light escaping a medium very near the critical angle may be coupled back into this medium and reappear at a distance along the surface, considerably removed from the point of escape.[27] There are two distinctly different methods of coupling the evanescent wave and extracting energy from it and thereby making reflection less than total. In one coupling mechanism some or all of the energy is redirected and there is no energy loss, whereas in the other, energy is absorbed and there is a loss. The former is known as frustrated total reflection (FTR) while the latter is known as attenuated total reflectance

(ATR).[28] Attenuated total reflection is due to an absorbing coupling mechanism whereby the reflectivity for total internal reflection can be continuously adjusted between some value greater than 0 and 100% by placing an absorbing medium in contact with the reflecting surface.[29] Attenuated total reflection is observed when the angle of incidence is set and remains above the critical angle and the wavelength is swept through an absorption band.

When electromagnetic radiation strikes an interface between media 1 and 2 that have different refractive indices, reflection also occurs. The fraction of radiation that is reflected becomes larger with increasing differences in refractive index.[22] The case of an absorbing rarer medium can be treated in terms of the intensity loss per reflection. If I_0 is the incident intensity and I_R is the reflected intensity, then the reflectivity, R, is given by:

$$R = I_R/I_0 \qquad \text{(eqn. 3)} \qquad [23]$$

For total reflection, $I = I_0$ and $R = 1$. The dispersion in the index of refraction in the vicinity of molecular absorption bands affect the nature of the optical spectrum for transmission and reflection. For internal reflection spectroscopy, where the angles of incidence employed may be between a value somewhat below the critical angle to "grazing incidence", the dispersion in the refractive index also plays an important role in the nature of the spectrum of bulk materials, but the degree of its influence depends on the angle of incidence. For thin films, the effect of the dispersion in the refractive index is quantitatively similar to that observed in transmission spectra.[30] Physical insight into the nature of the spectrum can be obtained from a consideration of the absorption parameter equations as the refractive index in the rarer medium changes due to the dispersion near molecular resonances. Internal reflection spectra do not represent a single optical constant but are related to both the refractive index and absorption coefficients.[31] The dispersion in the refractive index affects the spectra. Furthermore, the effect of this dispersion is dependent on the angle of incidence near the critical angle for measurements on bulk materials. Total internal reflection occurs when light traveling in an optically dense medium impinges on an interface with a less dense medium.

Problems With Internal Reflection Spectroscopy

The primary problem in obtaining high quality qualitative spectra or for performing quantitative IRS work is the difficulty in obtaining good and reproducible contact of the sample to the internal reflection element (IRE). The IRE is the transparent optical element used in internal reflection spectroscopy for establishing the conditions necessary to obtain internal reflection spectra of materials.[32] The ability to obtain an internal reflection spectrum and information from the spectrum is determined by a number of characteristics of the IRE. Choices must be made regarding the working angle or range of angles of incidence, number of reflections, aperture, number of passes, surface preparation, and material from which it is made.[33] These characteristics can be determined with some knowledge of the sample to be studied, the interaction mechanisms, and a few simple considerations regarding the reflection element. In general, it is advantageous to use an internal reflection element of low reflective index, and an angle near the critical angle because a higher contrast spectrum is obtained in this manner.[31] The index of refraction changes with wavelength regardless of the material. Therefore, the degree of refraction at the entrance face of the IRE, hence the internal angle of incidence, θ, on the sampling surface is wavelength dependent for oblique incidence. Since it is desirable to maintain the same angle of incidence over the entire wavelength range under investigation, refraction should be eliminated. This is the case when light enters and exits the IRE via the aperture at normal incidence. The aperture of the IRE is thus defined as that portion of the beveled area which can be utilized to conduct the light into the IRE at the desired angle of incidence θ.

An absorbing medium may strongly affect the reflectivity for internal reflection, particularly in the vicinity of the critical angle. It should be noted that when the absorbing medium is absorbing, the critical angle loses its significance; i.e. there is no longer a sharp critical angle for the absorbing case and the reflectivity curves become less steep in this region.[34] The absorption loss is quite large near the critical angle, is greater for parallel polarization than it is for perpendicular polarization, and decreases with increasing angle of incidence for both polarizations. It is interesting to note the dependence of the reflectivity on absorption coefficient for internal reflection at angles exceeding the critical angle. The absorption parameter, a, is defined as the reflection loss per reflection and is greater near the critical angle than it is for larger angles and is also greater for $\|$-polarization than for $\perp$-polarization.[34]

Advantages of Attenuated Total Reflection Spectroscopy

The primary advantage of using internal reflection spectroscopy is that water soluble substances that are usually very difficult to look at using transmission methods can be studied. Another of the advantages is that the IRE's used, most likely Ge or ZnSe cells, are not water soluble whereas in transmission methods NaCl cells are used which are water soluble. Although AgCl could be used in transmission, transmission thin layer cells are difficult to construct.

In attenuated total reflectance spectroscopy, the sample is placed against the internal reflection crystal. Depending on the angle of incidence, the IR beam undergoes multiple internal reflections before it exits the crystal. A more detailed description, including figures, is in Chapter Three. The refractive indices of the sample and the crystal are the critical factors that determine what the obtained spectra will look like. ATR band intensity is proportional to concentration in accordance with Beer's Law.[35] This is the only difference between IR absorption spectra and ATR spectra.

The Infrared Spectrometer

The spectrophotometer has four fundamental components:

1. A stable source of energy emitting continuous radiation.
2. An interferometer.
3. A detection system capable of measuring the amount of absorption from the sample.
4. A recorder [7].

The main component of an FT-IR spectrometer is the Michelson interferometer. It contains a fixed mirror, a movable mirror, and a beamsplitter. The beamsplitter transmits half the incident radiation to a moving mirror and reflects the other half to the fixed mirror. The two beams are reflected back to the beamsplitter, where they recombine. As the moving mirror is moved away from the beamsplitter, an optical path difference is generated. This is known as retardation. The optical retardation, in a Michelson interferometer, is equal to twice the difference between the distance of the fixed mirror and the distance of the moving mirror from the beamsplitter. The two beams travel different distances before recombining. The frequency of the retardation and the position of the moving mirror are the basis for the pattern of constructive and destructive interferences that are generated. Thus, the intensity of the radiation varies in a complicated pattern, as a function of mirror movement. The output beam is a result of modulation by the interferometer. The modulated output beam is directed through the sample compartment to the detector. At the detector, it generates a continuous electrical signal called an interferogram. A beam from the He-Ne laser is also passed through the interferometer to its own detector, which generates a reference signal. This enables the spectrometer electronics to sample the interferogram at precise intervals. The computer converts the interferogram into a single-beam spectrum via a Fourier transform.

The FTS-40 (BIO-RAD Cambridge, MA) first collects the spectrum of the source (background spectrum) and stores it. The single beam spectrum of the source, modified by the absorption due to the sample, is collected and compared to the background spectrum. The difference between these gives the desired absorption spectrum.

Chapter Two

Project Information

Arson fires are a major problem for the fire investigator. Often, these fires are accelerated by flammable materials. Organic, petroleum based, non-water soluble solvents, such as gasoline, can suprisingly be detected at very low concentrations by several well-developed analytical techniques such as GC/MS. However, water soluble solvents, such as methanol, ethanol, and isopropanol , have proven to be difficult to analyze. Not only does the water used to extinguish the fire wash away the accelerant by convection, it also limits detectability of the accelerant by dissolution.

Dilution standards were run on each of the accelerants tested. These standards were 5.0% v/v accelerant:water, 2.0%, 1.0%, and 0.5%. These solutions gave an idea of how little accelerant is needed to be in the sample and still be able to be detected.

The first stage of controlled burnings were done on carpet samples. The carpet samples were discontinued floor samples that were donated by Home Carpet in Boardman, Ohio. A known amount of accelerant (10mL) was poured on the carpet, burned for various times ranging from 30 sec. to 180 sec. , and extinguished with a known amount of water (100mL). The water was collected from the carpet and run-off that went into a collection trough. An IR spectrum was then obtained for the water samples. In each trial, the accelerant being tested was detectable.

The second stage of burning was also done on carpet samples. The burning was the same as mentioned above. In this stage, The samples were left out overnight and then collected into evidence cans (Tom's Automotive Hubbard, OH). They were tested a week later for the presence of an accelerant. This stage was then repeated to ensure that the results were reproducible.

The third stage of burning was done in surroundings that were similar to those that would actually be encountered in the field. In coordination with the Youngstown Fire Department and the Arson Bureau, controlled burns were performed at a vacant house (320 E. Lucius Ave. Youngstown, OH) that was scheduled for demolition. Twenty-one samples were taken. However, only sixteen were tested because a few of the samples were too bulky to be tested.

The samples were collected using the techniques that are consistent with those used by the Youngstown Arson Bureau. The samples were placed in evidence cans (Tom's Automotive Hubbard, OH) which are the same used by the Arson Bureau. The lids were hammered on and a piece of tape was placed over the lid to ensure that the cans were not opened at any time before analysis. The samples were tested for the presence of the selected accelerant. For the interpretation of the results, only the fingerprint region (1800-750 cm^{-1}) was used.

The results of these experiments will be significant because there is currently no method that is able to accurately detect water soluble accelerants.

Chapter Three

Materials and Methods

Materials

Analytical grade methanol, ethanol, and isopropyl alcohol (Fisher Scientific, Fair Lawn, NJ) were used as accelerants. Carpet samples were discontinued floor samples (donated by Home Carpet Boardman, Ohio). A BIO-RAD FTS 40 spectrophotometer (BIO-RAD Cambridge, MA) was used to perform the analysis (see Figure 3.1). The ATR cell used is a Harrick Scientific Corp. ZnSe nine reflection prism liquid cell with a 45° incident angle (see Figure 3.2).

Methods

Attenuated Total Reflectance Spectroscopy is a very effective way to perform analysis on aqueous samples. A background can be obtained using water and then subtracted out of the sample spectra. There is very little time required to prepare samples for analysis. Samples can be collected and run without having to do the organic solvent extraction step that is necessary with other techniques, such as GC-MS. There is good contact between the sample and the crystal which gives quality spectra that are highly reproducible. A detailed list of parameters used for analysis is listed as Table 4.1.

FTS 40 Components

The FTS 40 spectrophotometer (BIO-RAD Cambridge, MA) is fitted with purge shutters, which are on both sides of the sample compartment. When the knobs are out,

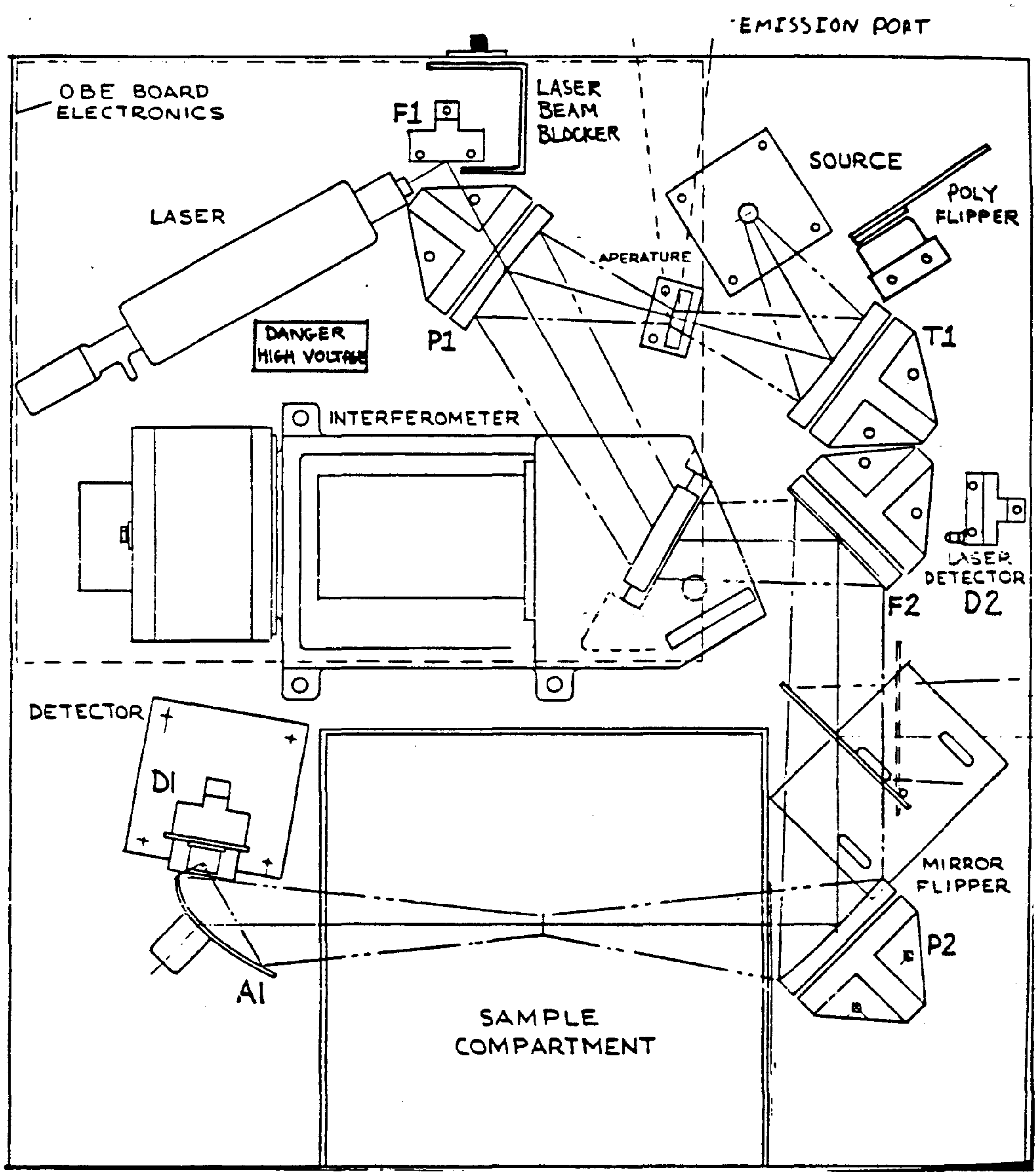


Figure 3.1: FTS-40 Optical Schematics

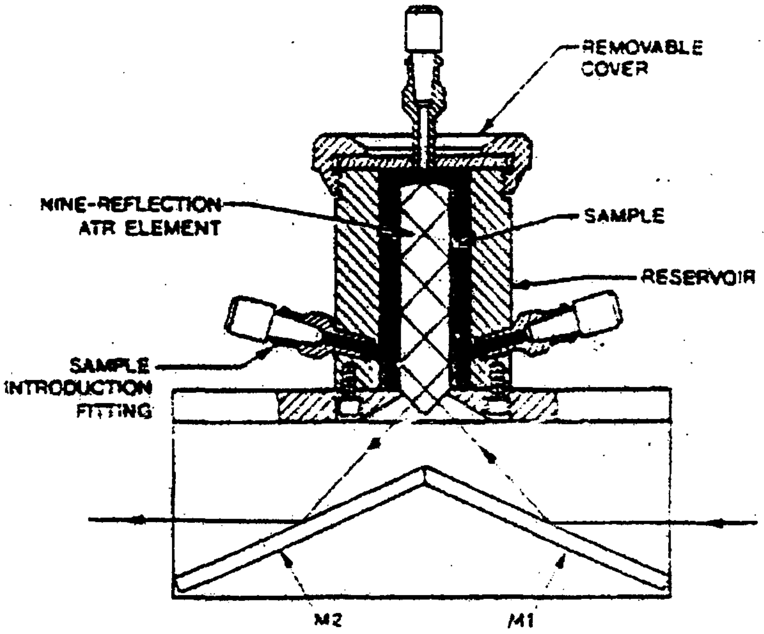


Figure 3.2: ATR Cell Reservoir

the shutters isolate the sample compartment preventing water and carbon dioxide from entering the interferometer compartment. The sample compartment has a hinged cover to isolate it from the environment. The FTS 40 (BIO-RAD Cambridge, MA) uses a He-Ne laser operating in the visible region at a wavelength of 632.8 nm. It has an aperture wheel which has four holes of different diameter. Each hole restricts the beam differently so that the desired light intensity is reached. In this study, the open aperture setting was used to allow the unrestricted beam to pass through the crystal. The FTS 40 (BIO-RAD Cambridge, MA) uses a MCT high-sensitivity narrow band detector that it cooled with liquid N_2. The IR source requires a supply of cooling water. A minimum flow of 1 L/min, with an inlet pressure no higher than 25 psi and temperature no higher than 20°C are required. The FTS-40 (BIO-RAD Cambridge, MA) has a Michelson interferometer (Figure 3.3). It contains a fixed mirror, a moveable mirror, and a beamsplitter. The beamsplitter sends half of the incident radiation to the moving mirror, and the other half to the fixed mirror. The two beams are reflected back to the beamsplitter and recombined. The resolution is able to be varied with the higher resolution giving more detailed spectra.

Absorbing Materials

Accelerants are usually poured on carpets, couches, chairs, mattresses, hardwood floors, etc. The physical and chemical characteristics of these absorbing materials play an important role in the accelerant behavior during the fire. Some of the important absorbing material characteristics include:

1. Absorb flammable liquids.

Carpets, chairs, mattresses, and hardwood floors are examples of

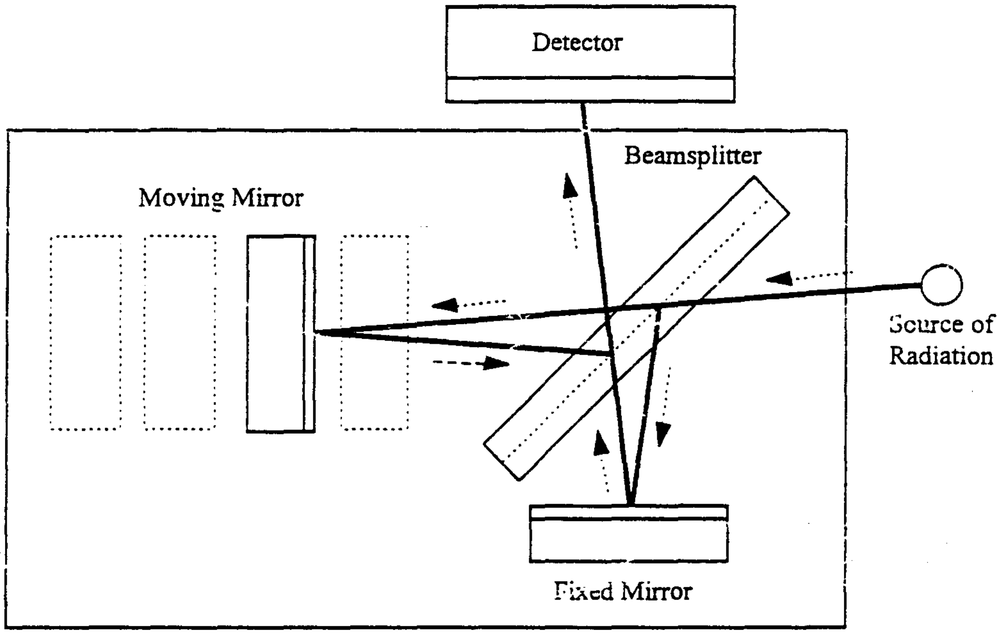


Figure 3.3: Michelson Interferometer

good absorbing materials since liquids poured on them soak in.

2. Retain absorbed liquids.

   Materials that possess little ability to absorb, will have the accelerant pass through to something that absorbs and retains them.

3. Contaminate the absorbed liquid.

   The most commonly used accelerants are composed of hydrocarbons. The hydrocarbons will dissolve and mix with many synthetic materials such as carpet rubber backing. The mixture will interfere with patterns produced by IR analysis.

4. React to heat and fire.

   The exposed surface of many absorbing materials will melt and/or char upon exposure to heat and flame.

When a liquid is poured on a porous or a semiporous material, a certain amount of the accelerant will soak into that material. The amount depends on the factors discussed above.

All of these factors were taken into account when deciding which absorbing materials to use. However, a majority of the time accelerants are poured onto carpeting. With this in mind, it was decided that carpet samples would be the best absorbing material to use for the project. It has the ability to absorb and retain a large quantity of liquid. It also will melt and bubble when burned to form air bubble pockets that will retain the accelerant so that it is easier to detect in analysis.

Chapter Four

Procedures and Results

A. Preparing Concentration Gradient Curve Solutions

Initially, a 200 mL 5.0% methanol:95.0% water v:v solution was prepared. From this solution, a 2.0%, 1.0%, and 0.5% v:v solution was prepared. Then, a 200 mL 5.0% ethanol:95.0% water v:v solution was prepared. From this solution, a 2.0%, 1.0%, and 0.5% solution was prepared. Then, a 200 mL 5.0% isopropyl alcohol:95.0% water v:v solution was prepared. From this solution, a 2.0%, 1.0%, and 0.5% solution was prepared.

Obtaining Spectra

The procedure for obtaining spectra remained the same throughout this project. Any exceptions will be mentioned when necessary. The procedure will be discussed thoroughly in this section.

The parameters used to obtain spectra were as follows:

Table 4.1: List of Parameters

Speed	5 kHz
Filter	4.5 kHz
UDR	2
Resolution	8
Aperture	open
Sensitivity	1
IR source	ceramic
Detector	Mid-IR DTGS
Beamsplitter	KBr
Apodization	triangular
Number of scans	64

The cell reservoir was filled via a needle and syringe. A background spectrum of deionized water was obtained each day that analysis was to be performed. The cell reservoir was flushed twice with the desired solution before being filled for analysis. The cell reservoir was then placed in the sample compartment. The instrument was purged for 1 min. before analysis was initiated.

B. **Initial Burning of Carpet Samples**

The carpet samples were trimmed to approximately 4" by 6". To each sample, 10 mL of methanol was poured over the carpet and ignited. The burn times were varied (30 sec., 60 sec., 90 sec., 120 sec., and 180 sec.) so that % recovery versus time could be determined. The samples were extinguished with 100 mL of water. The water that stayed in the carpet was collected, as was the water than ran-off in to the overflow trough. A sample was then burned with 10 mL *m*-xylene so that a burn comparison could be made. Also, a 10 % v:v methanol:water solution was prepared that would represent the maximum recovery possible. The spectra were obtained using the procedure previously discussed.

Another set of carpet samples were then burned using ethanol employing the same procedure as with methanol with one exception: a 150 sec. burn time was included. A third set of carpet samples were burned with isopropyl alcohol using the same procedure as ethanol.

C. Burning of Carpet Samples – Second Stage

In this stage, more realistic conditions are trying to be obtained. The procedure for burning the samples is the same as in section C. However, the collection procedure was changed. Instead of collecting the water samples immediately, the carpet was placed on aluminum foil overnight. After 24 hrs, the carpet samples were placed in evidence cans and stored for one week.

When it was time for analysis, an extraction step had to be performed. The extraction step consisted of pouring 15 mL of water on the carpet sample and squeezing the water out. The spectra were obtained using the procedure previously described.

Burning of Samples – Third Stage

This stage of burning was the most important. In this stage, the conditions are as realistic as we can get without actually setting an arson fire. The burns were done at a vacant house (320 E. Lucius Ave. Youngstown, OH) in coordination with the Youngstown Fire Department and the Arson Bureau. The accelerants used were methanol, ethanol, isopropyl alcohol, rubbing alcohol and two unknowns prepared by Dr. Curtin.

The first burn was in the upper left bedroom. An area was cleared of all debris. A pile of clothes were placed in the center of the cleared area. Approximately 300 mL of methanol was poured over the pile and ignited. The pile was burned for 25-30 sec. before being extinguished by firefighters with an minimum amount of water. Samples collected were sample 1- sweater, sample 2 – socks, sample 3 – carpet, and sample 4 – carpet.

The second burn was also in the upper left bedroom. It was done the same way as the first burn with the accelerant being unknown A. The samples collected were sample 5 – free standing water, sample 6 – clothes, sample 7 – cloth, and sample 8 – carpet.

The third burn was in the upper right bedroom. The pile burned included clothes and part of a curtain. Approximately 300 mL of commercially available rubbing (isopropyl) alcohol was poured on the pile and ignited. It was burned for 1 min. before being extinguishing with an minimum amount of water. The samples collected were sample 10 – cloth, sample 11 – curtains, and sample 12 – carpet.

The fourth burn was in the upper right bedroom. The area was cleared and a pile of clothes were placed in the center. Approximately 300 mL of unknown B was poured on the pile and ignited. It was burned for 1 min. before being extinguished with an minimum amount of water. The samples collected were sample 13 – clothes and sample 14 – clothes.

The fifth burn was done on the front porch. Approximately 300 mL of unknown B were poured on a couch cushion and ignited. It was burned for 90 sec. before being extinguished. The samples collected were samples 15,16, and 17 – cushion material and padding. Analysis of these samples required an extraction step consisting of pouring 30 mL water on the sample and squeezing it out.

The final burn was done in the third bedroom upstairs. The area was cleared of all debris. Approximately 300 mL of an ethanol and isopropyl alcohol mixture was poured on the carpet and ignited. It was burned for 120 sec. before being extinguished. The samples collected were sample 18 – free standing water and samples 19-22 - carpeting.

The spectra were obtained using the methods and parameters previously described with one exception: the number of scans was 128. The number of scans was changed to 128 instead of 64 so that the spectra would have less noise.

Results

The results from the concentration gradient curves are the first presented. For methanol, there were peaks at 781 cm^{-1}, 824 cm^{-1}, **1017 cm^{-1}**, 1113 cm^{-1}, 1472 cm^{-1}, 1506 cm^{-1}, 1558 cm^{-1}, and 1686 cm^{-1}. For ethanol, there were peaks at 877 cm^{-1}, **1045 cm^{-1}**, **1086 cm^{-1}**, 1418 cm^{-1}, and 1454 cm^{-1}. For isopropyl alcohol, there were peaks at 761 cm^{-1}, 945 cm^{-1}, **1107 cm^{-1}, 1126 cm^{-1}, 1164 cm^{-1}**, and 1558 cm^{-1}. For acetone, there were peaks at 770 cm^{-1}, 789 cm^{-1}, 1094 cm^{-1}, **1239 cm^{-1}**, 1371 cm^{-1}, 1423 cm^{-1}, and **1699 cm^{-1}**. The spectra have been included (see Figures 4.1-4.16). The wavenumbers in bold type are the characteristic peaks that were used to distinguish between the accelerants.

For methanol, the peak at 1017 cm^{-1} represents the C-O stretch. For ethanol, the peaks at 1045 cm^{-1} and 1086 cm^{-1} represents the C-O stretch. For isopropanol, the peaks at 1107 cm^{-1}, 1126 cm^{-1}, and 1164 cm^{-1} represent a C-O stretch. For acetone, the peak at 1699 cm^{-1} represents the ketone C=O stretch. The data for these characteristic peaks of each solution have been tabulated (see Table 4.2) and plotted (see Figures 4.17-4.24).

Representative spectra from section C have been included (see Figures 4.25-4.32). The results of section C have been tabulated (see Table 4.3) and plotted (see Figures 4.33-4.42). Only the characteristic peaks from the concentration gradient curves were looked at. Representative spectra have been included from section D (see Figures 4.43-4.45). The results of this section were tabulated (see Table 4.4) and plotted (see Figure 4.46).

Results – Third Stage Burns

Sample 1 was too bulky and was unable to be analyzed. Samples 2-4 show peaks at 1017 cm^{-1} and 1112 cm^{-1} (see Figure 4.47-4.49).

Sample 5, accelerant unknown A, shows a peak at 1016 cm^{-1} and at 1112 cm^{-1} (see Figure 4.50) Sample 8, accelerant unknown A, also shows a peak at 1017 cm^{-1} and 1112 cm^{-1} (see Figure 4.51). Samples 6-7 were too bulky to be analyzed.

Sample 10, accelerant rubbing (isopropyl) alcohol, had peaks at 1385 cm^{-1}, 1165 cm^{-1}, and 1128 cm^{-1}. Sample 11 showed peaks at 1698 cm^{-1} and 1129 cm^{-1}. Sample 12 had no peaks that corresponded to isopropyl alcohol (see Figures 4.52-4.54).

Samples 15, accelerant unknown B, showed peaks at 790 cm^{-1}, 1016 cm^{-1}, 1101 cm^{-1}, 1375 cm^{-1}, and 1453 cm^{-1}. Sample 16 had peaks at 748 cm^{-1}, 1107 cm^{-1}, and 1630 cm^{-1}. Sample 17 had peaks at 790 cm^{-1}, 846 cm^{-1}, and 1631 cm^{-1} (see Figures 4.55-4.57).

Sample 18 consisted of several peaks. The main peaks were at 1045 cm^{-1}, 1087 cm^{-1}, 1126 cm^{-1} and 1164 cm^{-1}. Samples 19-22 shows the same peaks as sample 18 (see Figures 4.58-4.62).

Figure 4.1: **5.0% v/v methanol/water**

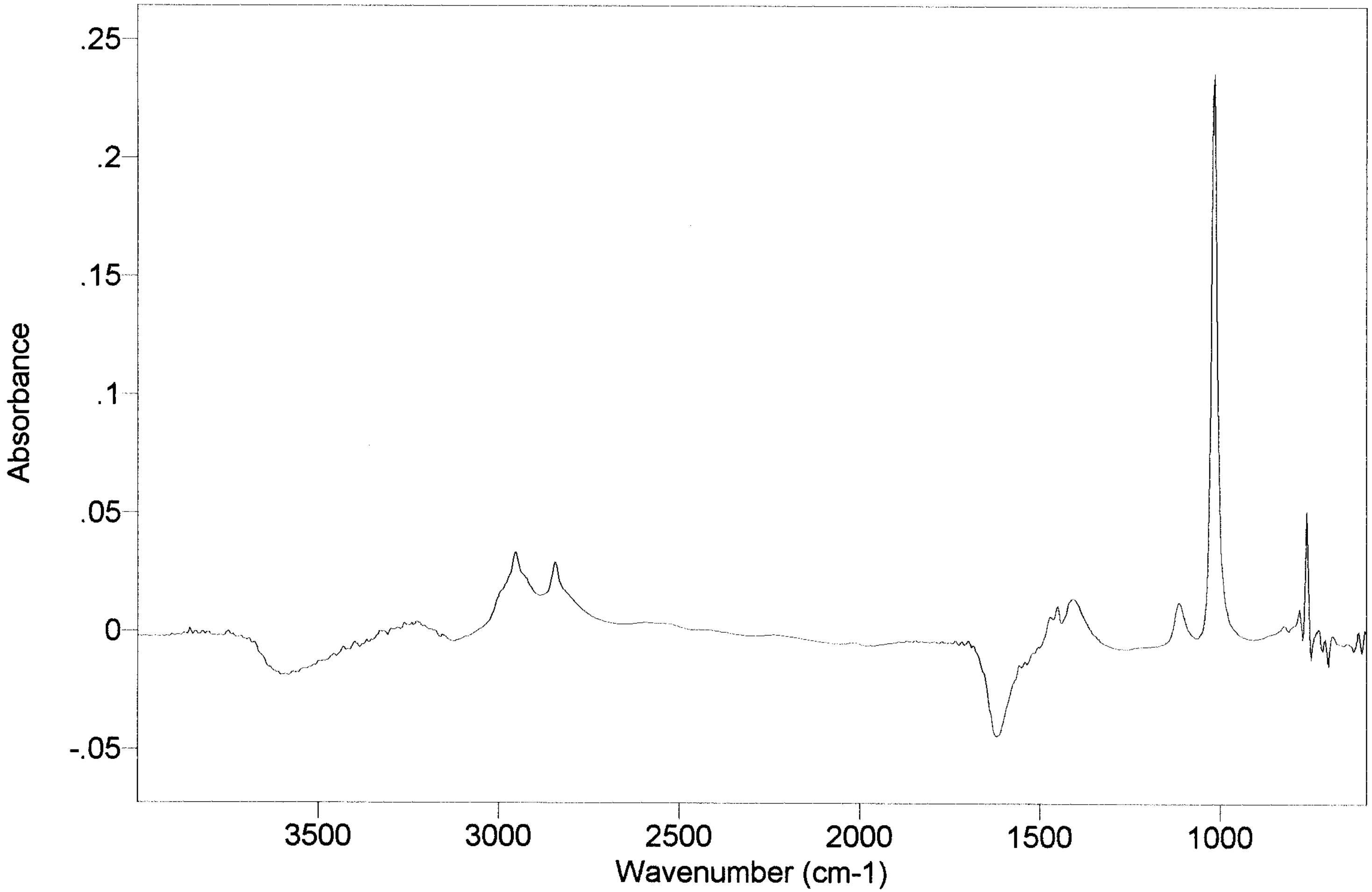


Figure 4.2: **2.0% v/v methanol/water**

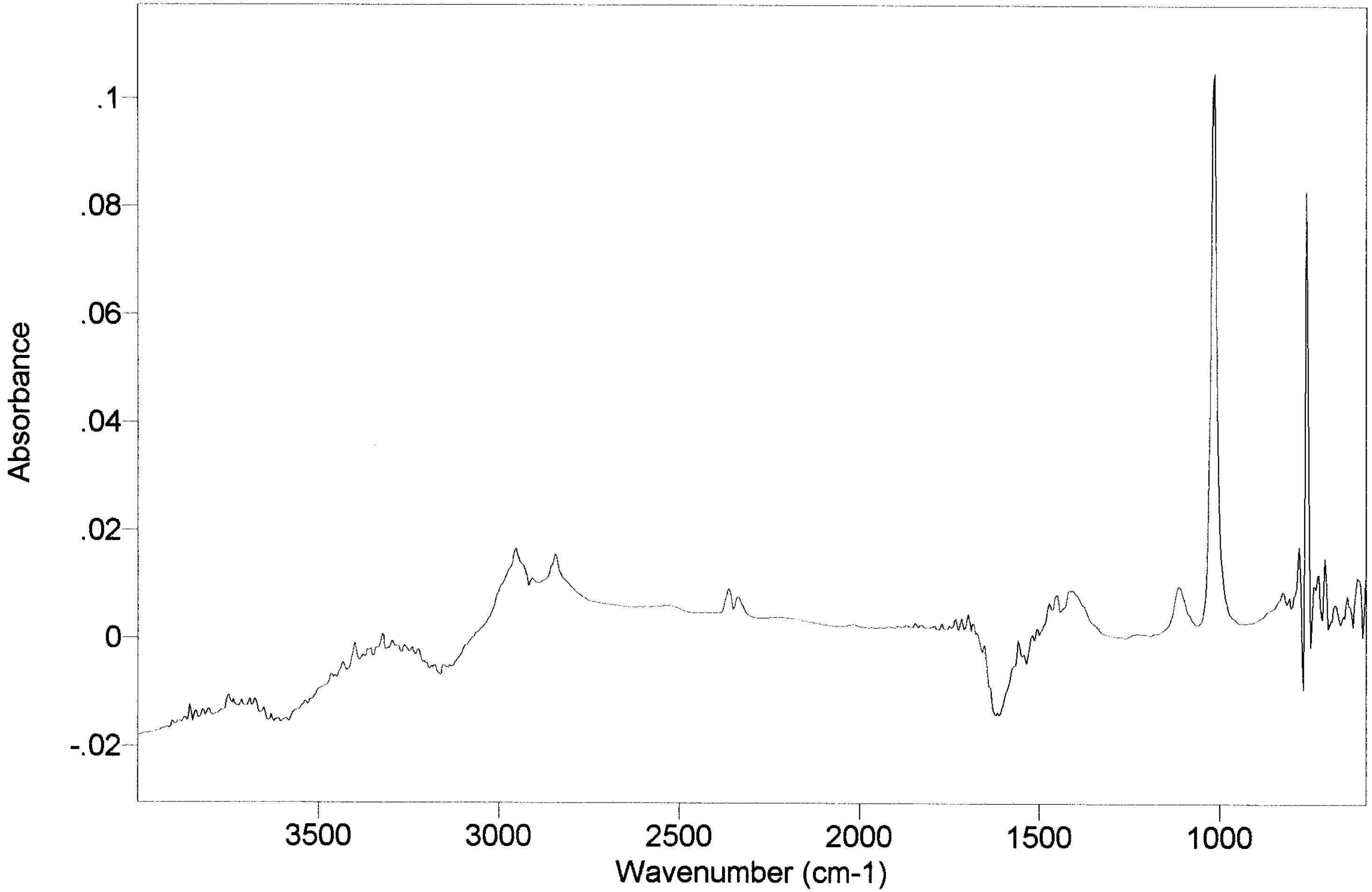


Figure 4.3: **1.0% v/v methanol/water**

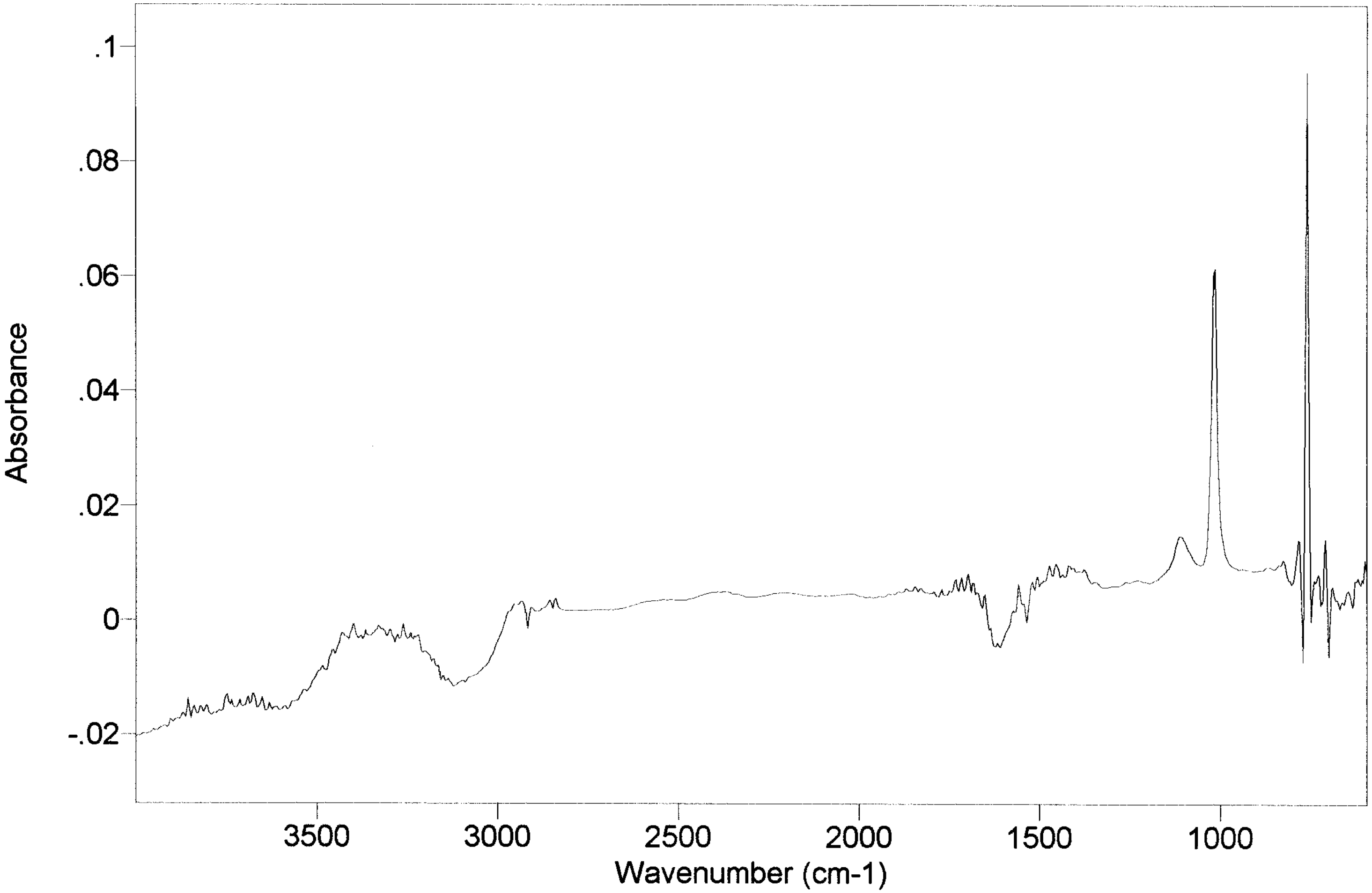


Figure 4.4: **0.5% v/v methanol/water**

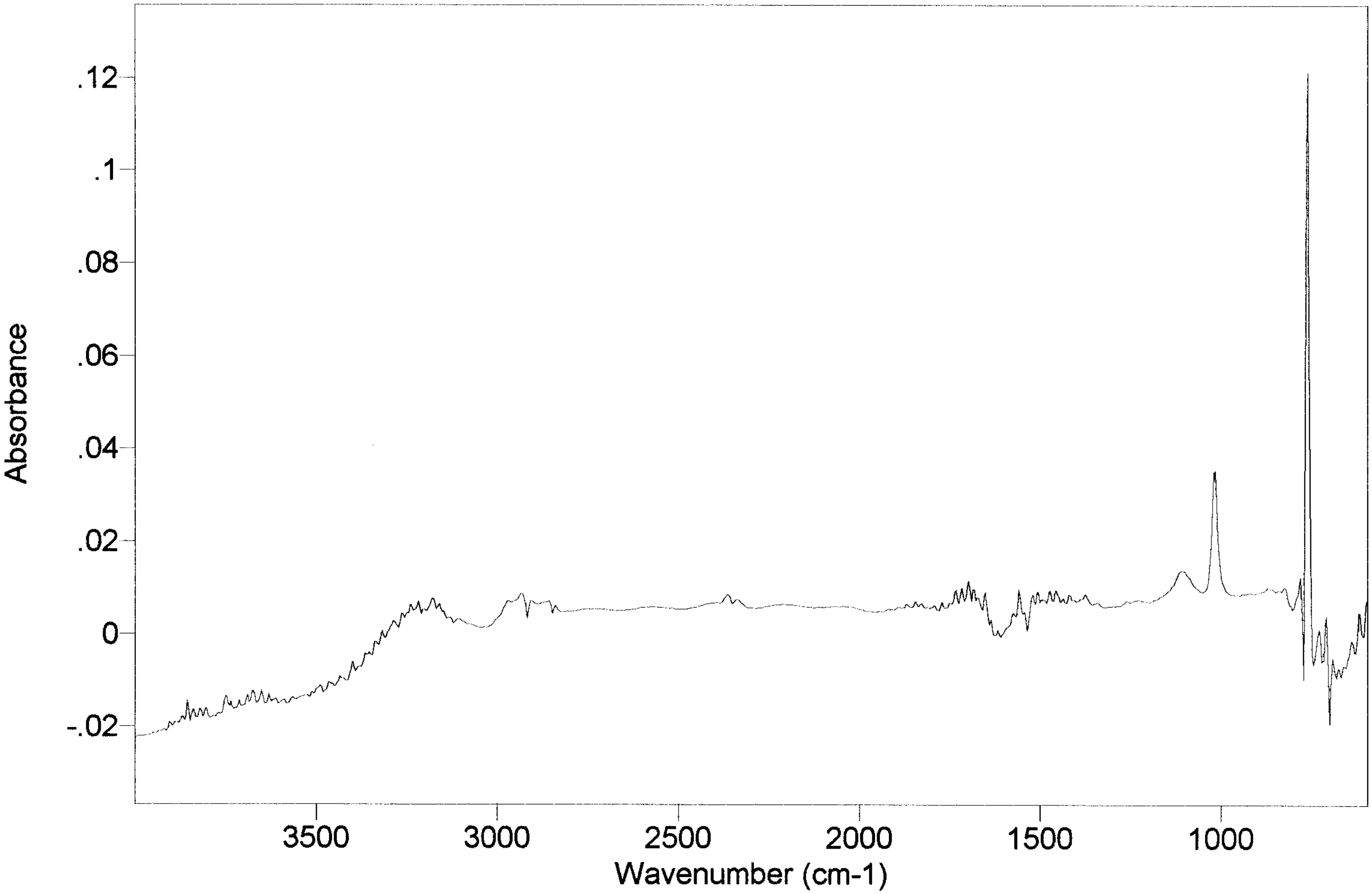


Figure 4.5: **5.0% v/v ethanol/water**

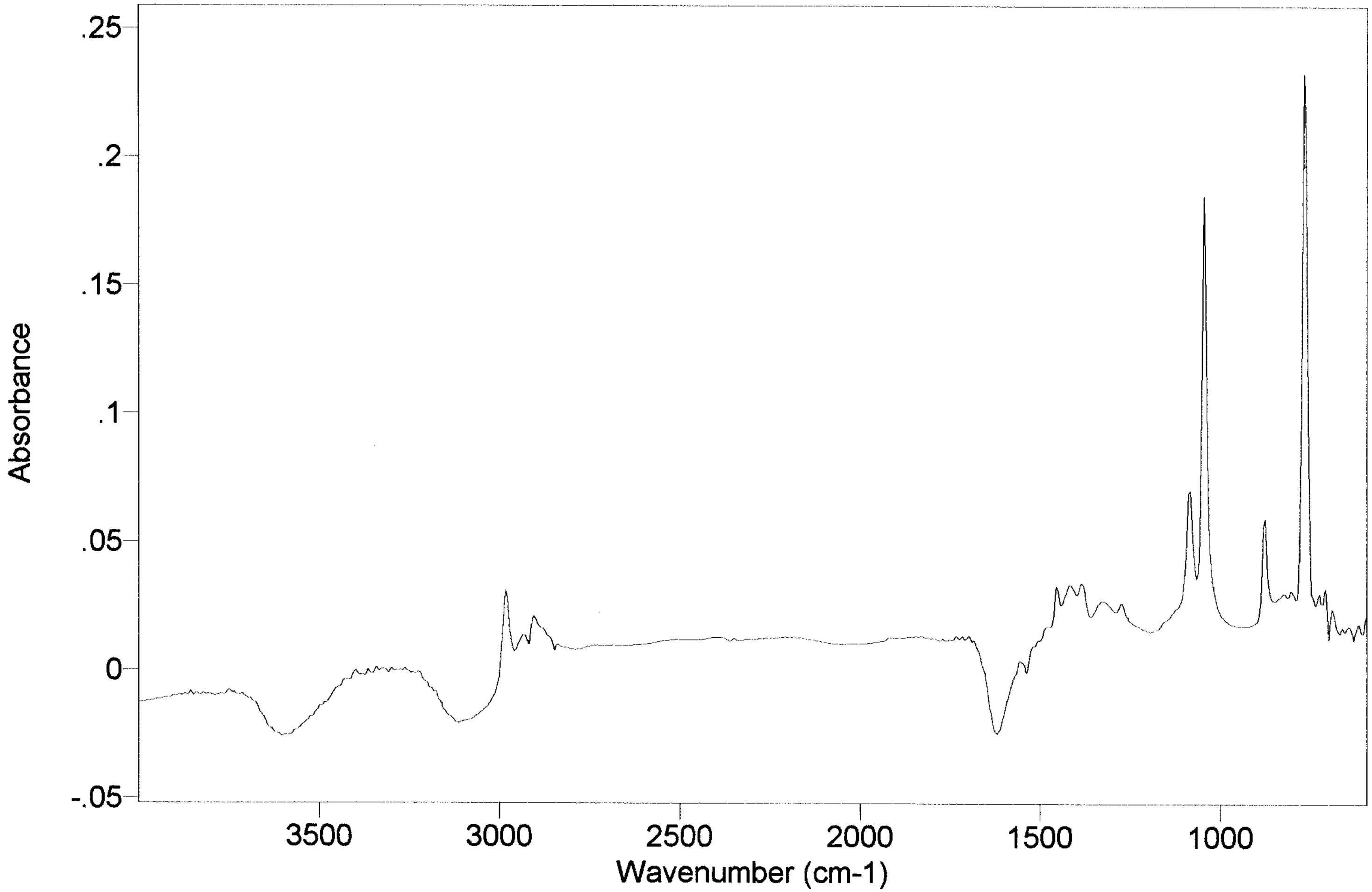


Figure 4.6: **2.0% v/v ethanol/water**

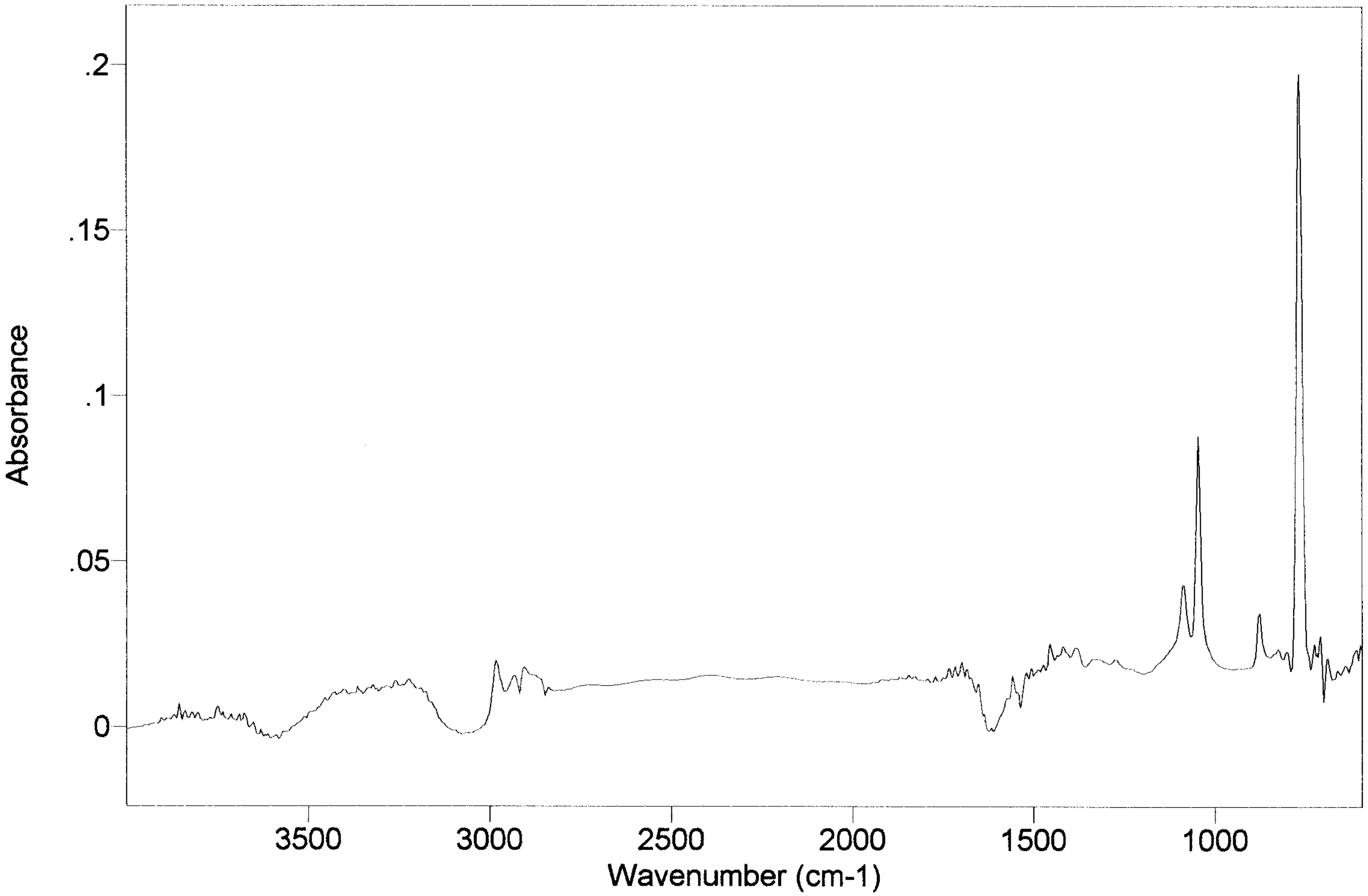


Figure 4.7: **1.0% v/v ethanol/water**

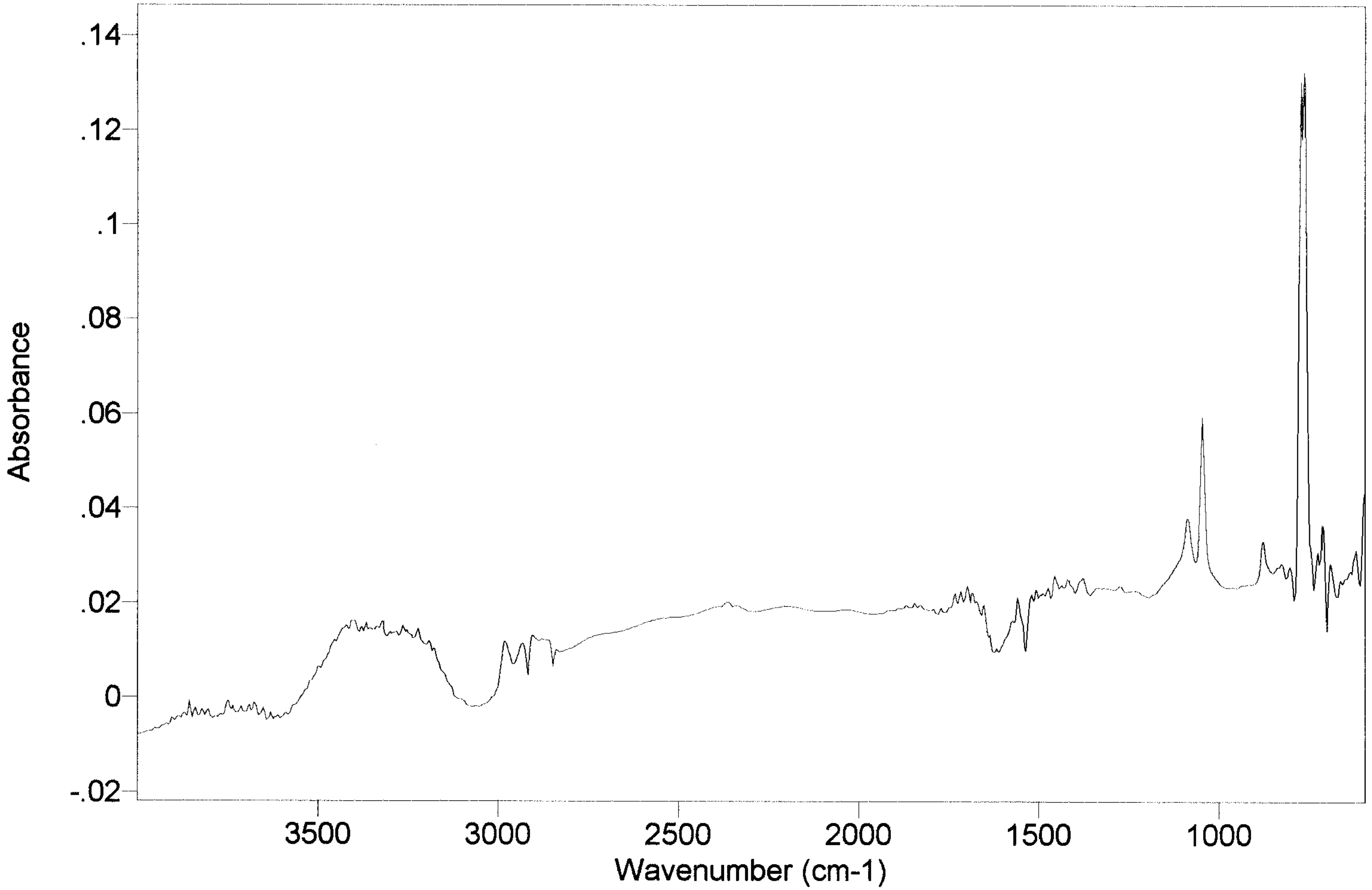


Figure 4.8: **0.5% v/v ethanol/water**

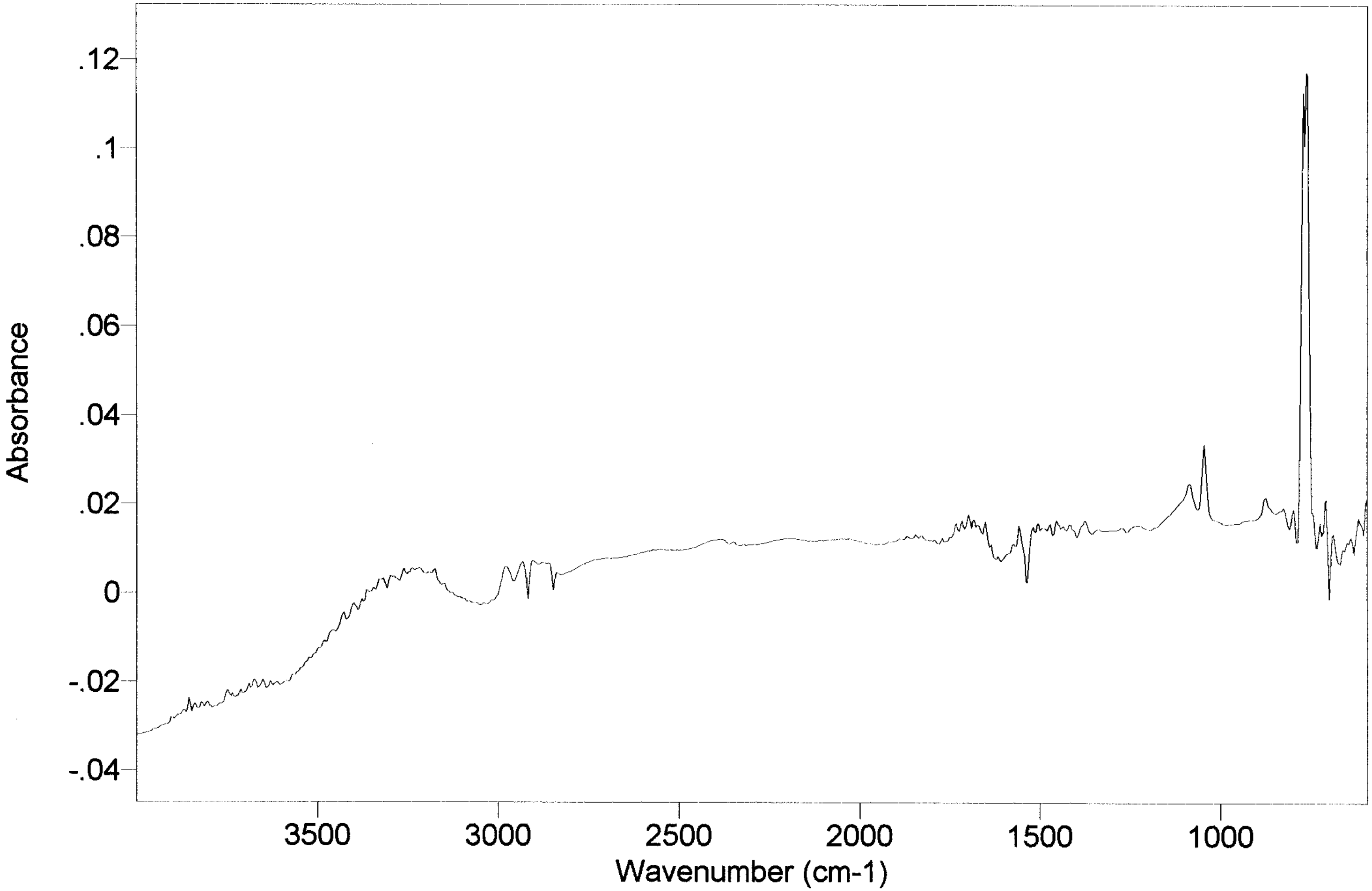


Figure 4.9: **5.0% v/v isopropyl alcohol/water**

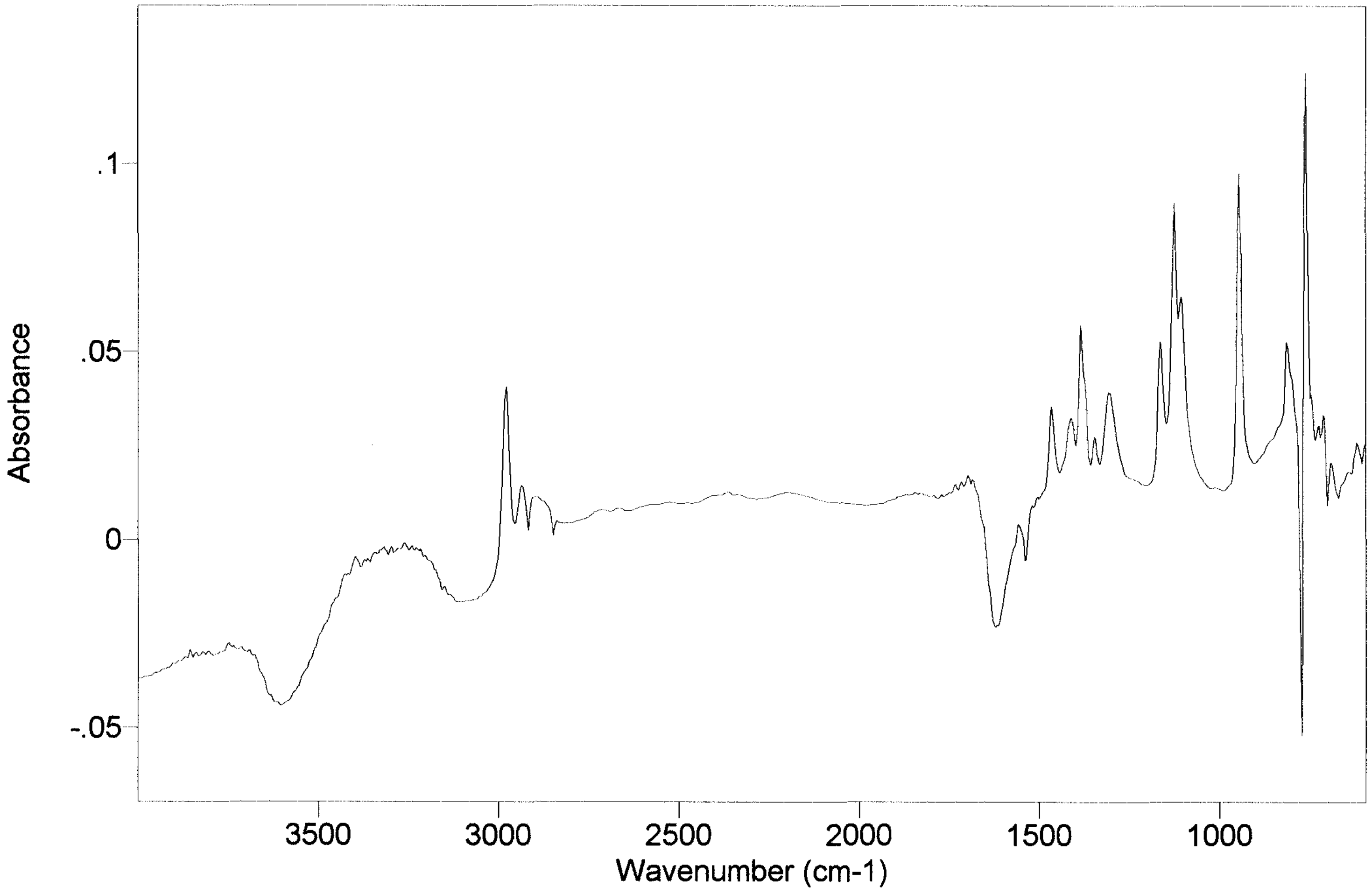


Figure 4.10: **2.0% v/v isopropyl alcohol/water**

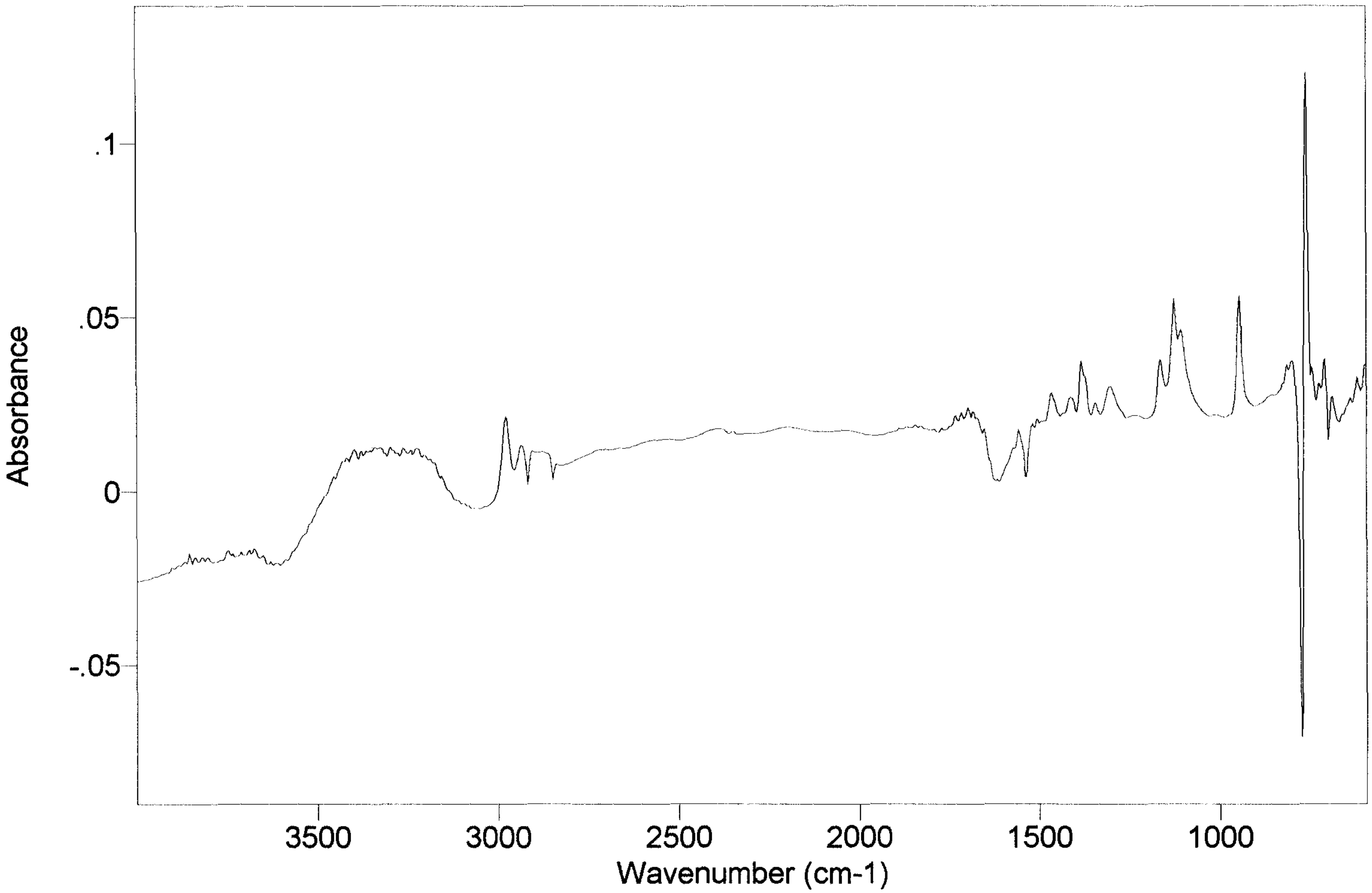


Figure 4.11: **1.0% v/v isopropyl alcohol/water**

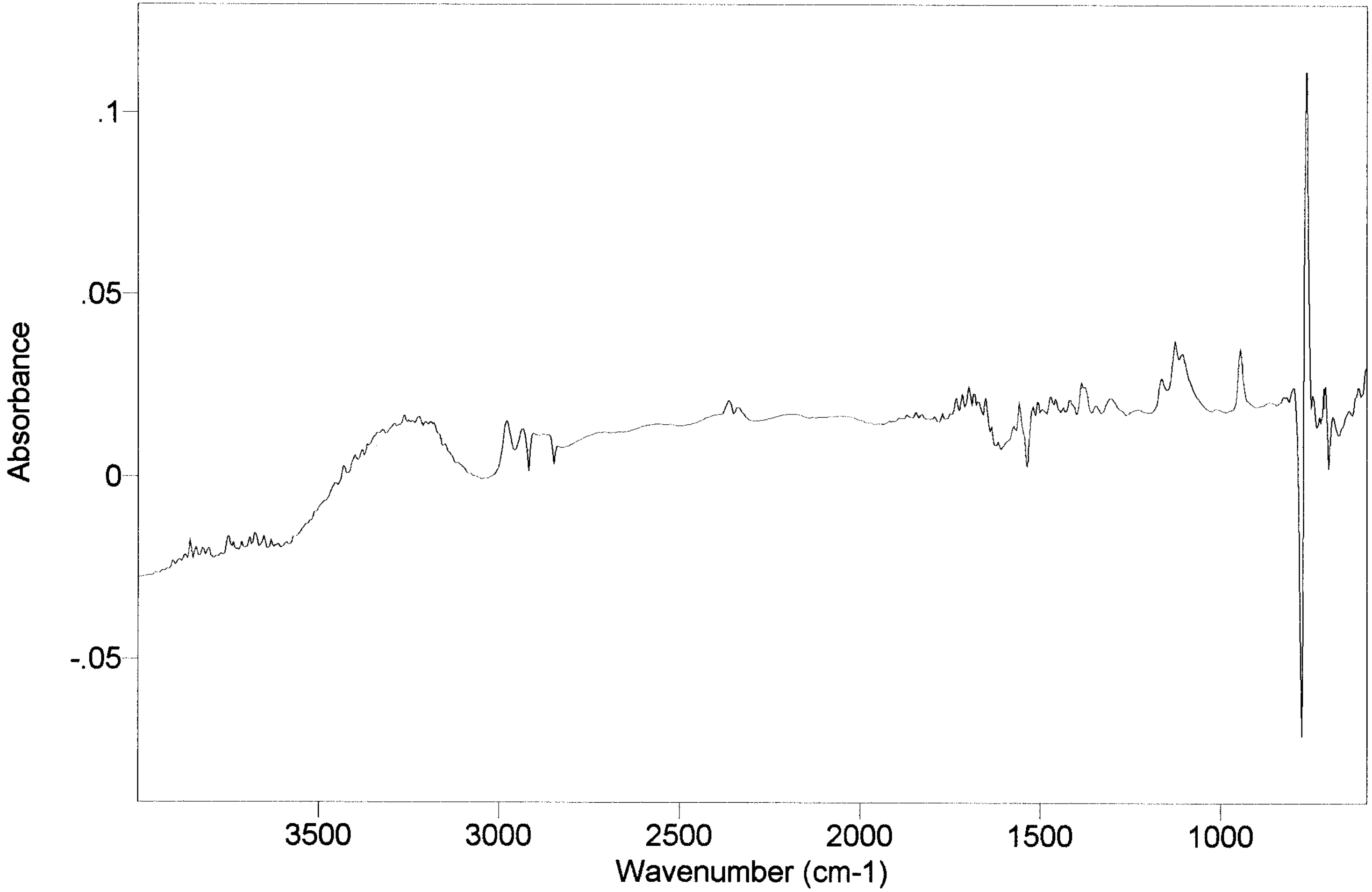


Figure 4.12: **0.5% v/v isopropyl alcohol/water**

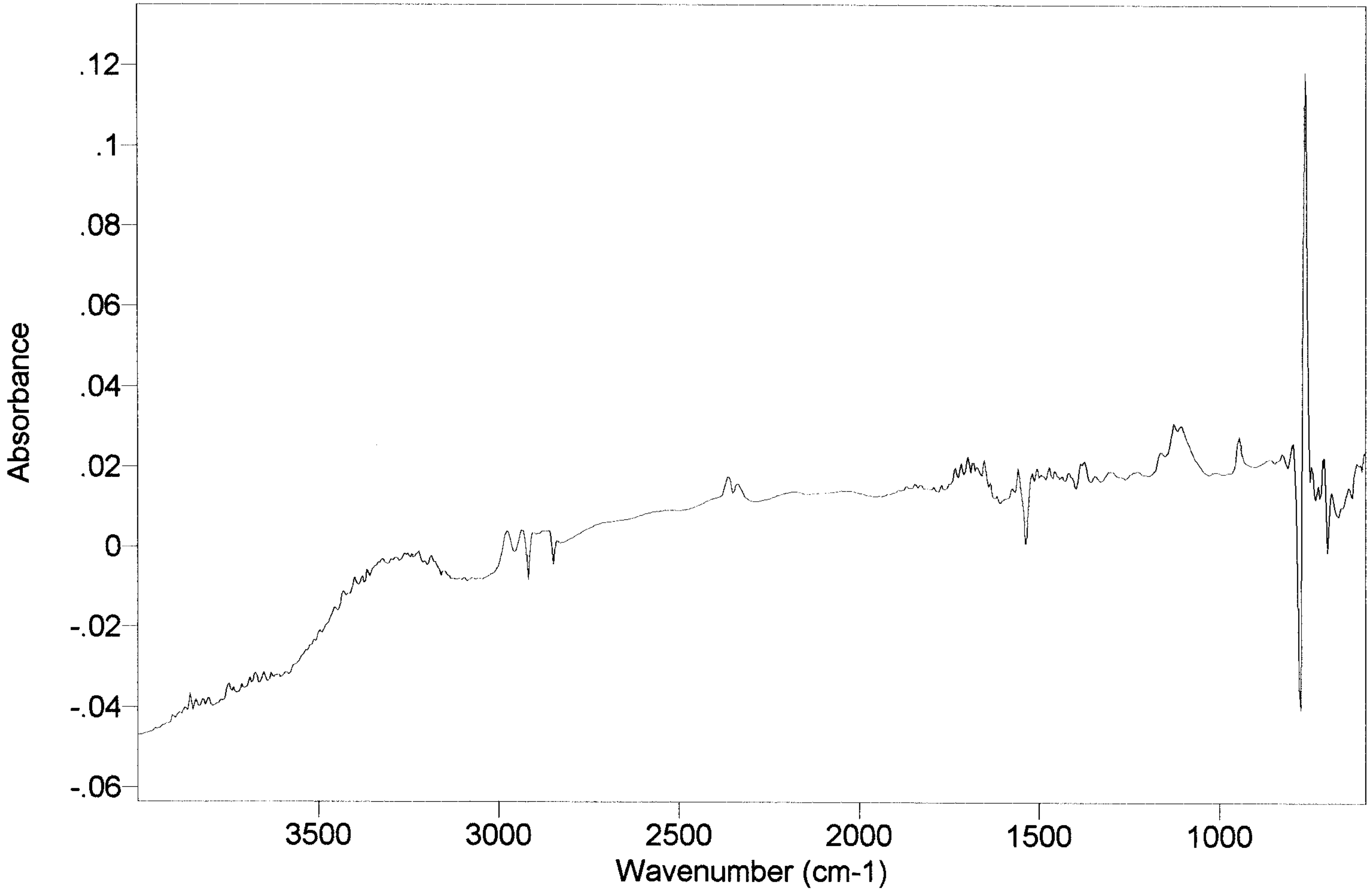


Figure 4.13: **5.0 % v:v acetone/water**

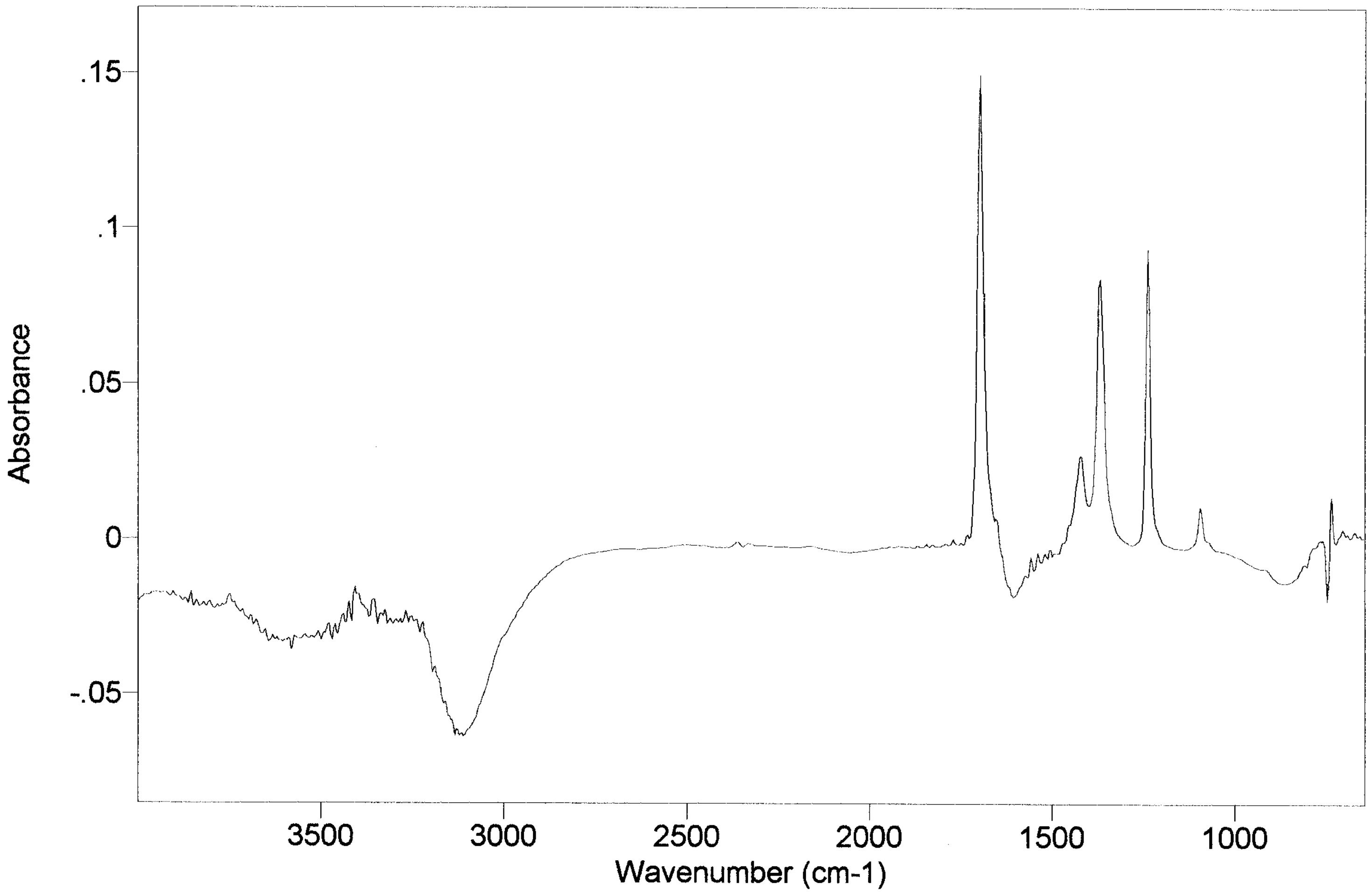


Figure 4.14: **2.0 % v:v acetone/water**

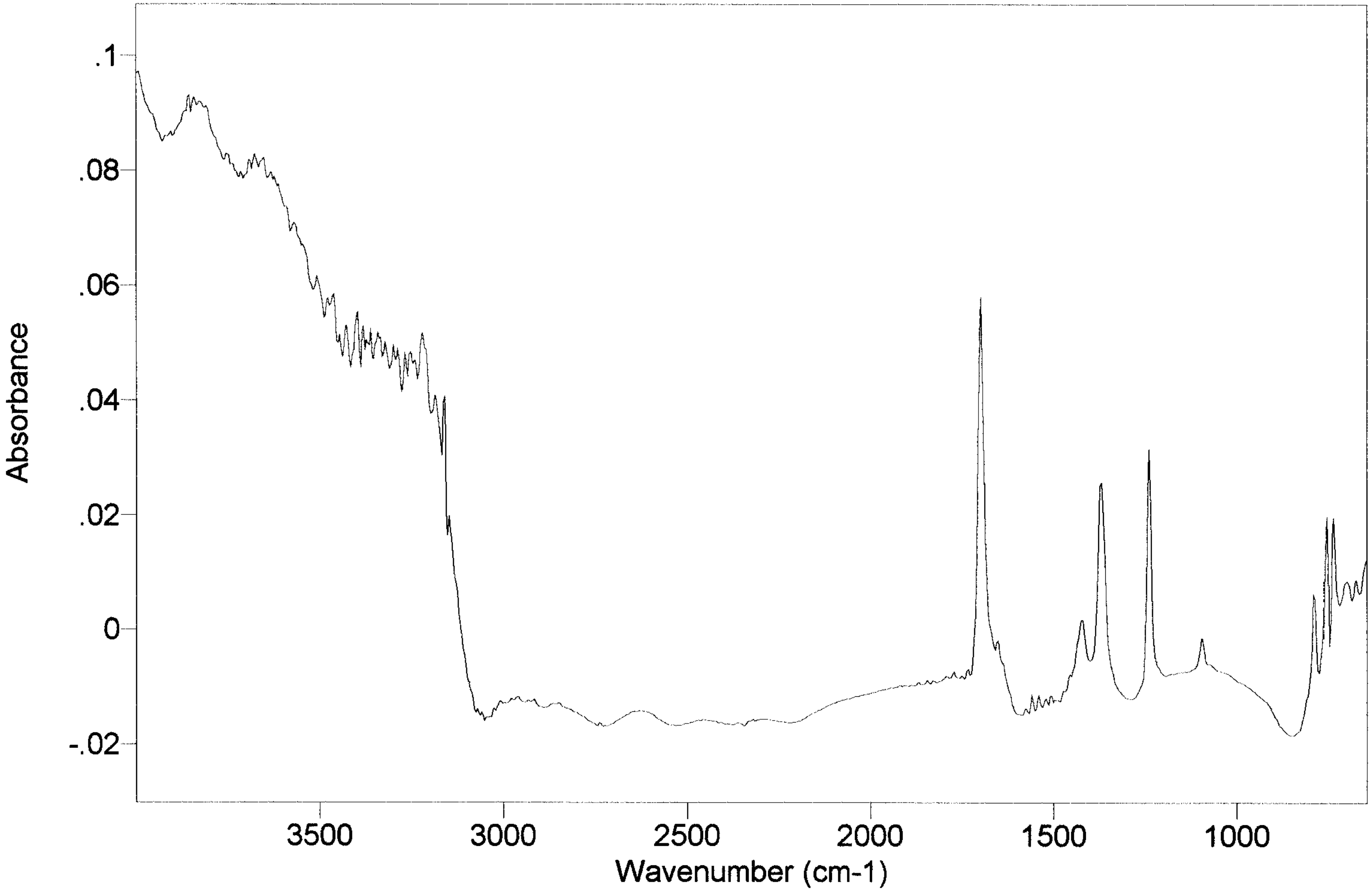


Figure 4.15: **1.0 % v:v acetone/water**

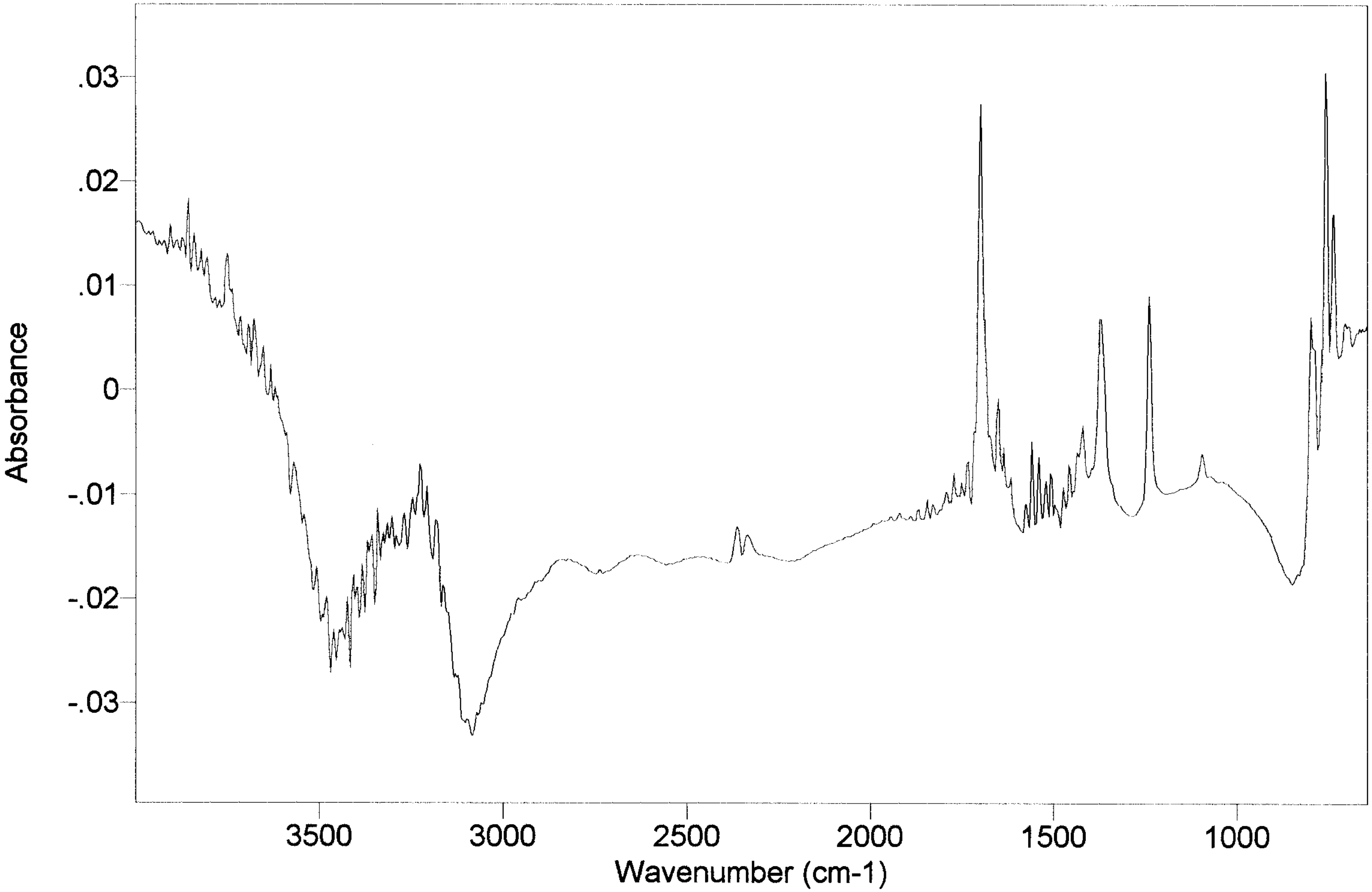


Figure 4.16: **0.5 % v:v acetone/water**

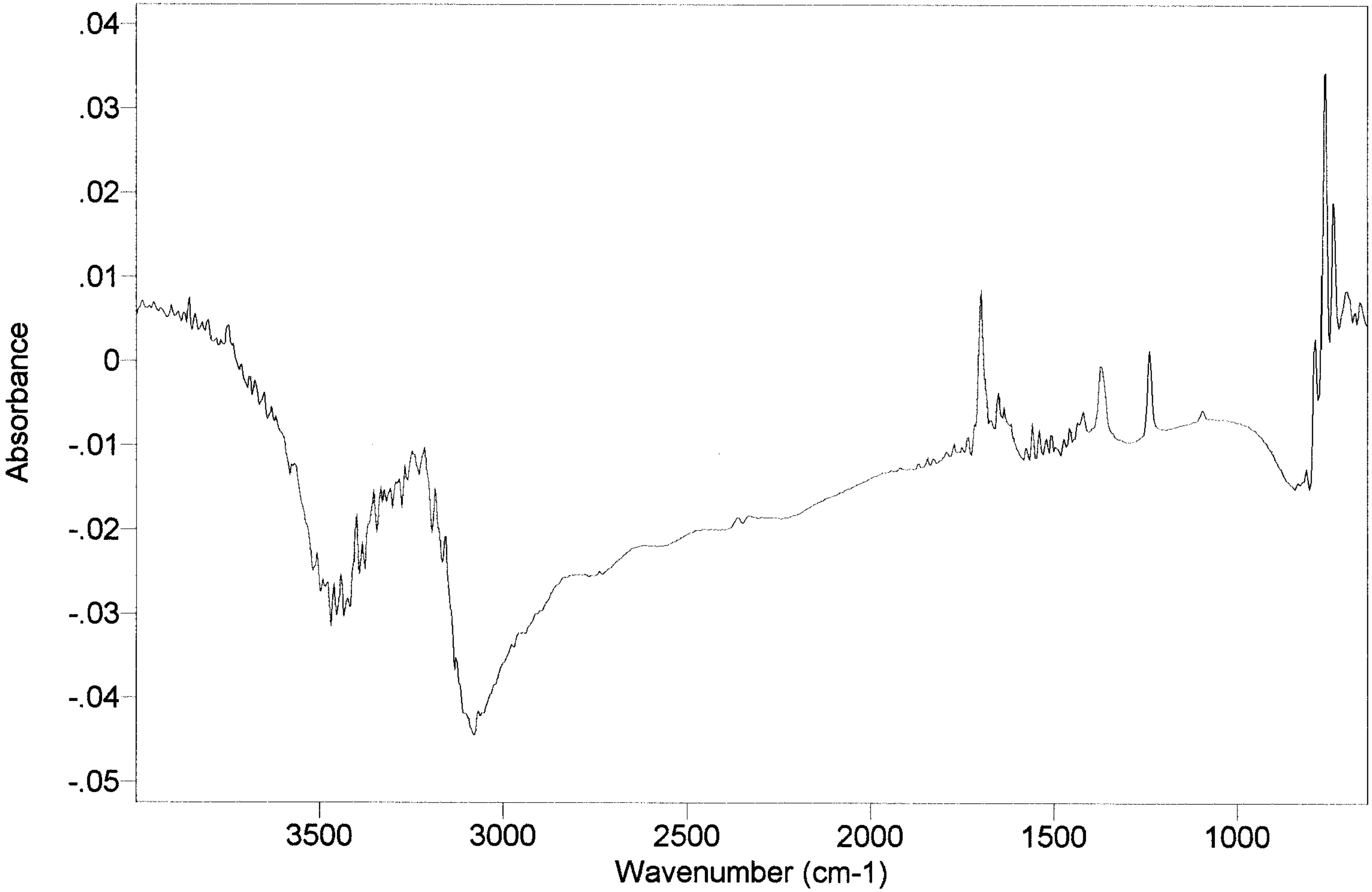


Table 4.2: Data from concentration gradient solutions

% methanol\water	1016 cm-1
0.5	0.0354
1	0.0614
2	0.105
5	0.2361

% ethanol\water	1086 cm-1	1045 cm-1
5	0.0705	0.185
2	0.043	0.088
1	0.038	0.0595
0.5	0.0249	0.0336

% isopropyl\water	1164 cm-1	1126 cm-1	1107 cm-1
0.5	0.0238	0.0308	0.0306
1	0.0273	0.0378	0.0341
2	0.0379	0.0555	0.0464
5	0.0528	0.0896	0.0647

% acetone\water	1699 cm-1	1239 cm-1
0.5	0.00854	0.00135
1	0.0275	0.00909
2	0.058	0.03149
5	0.1496	0.0936

Figure 4.17: Methanol Standards 1016 cm-1

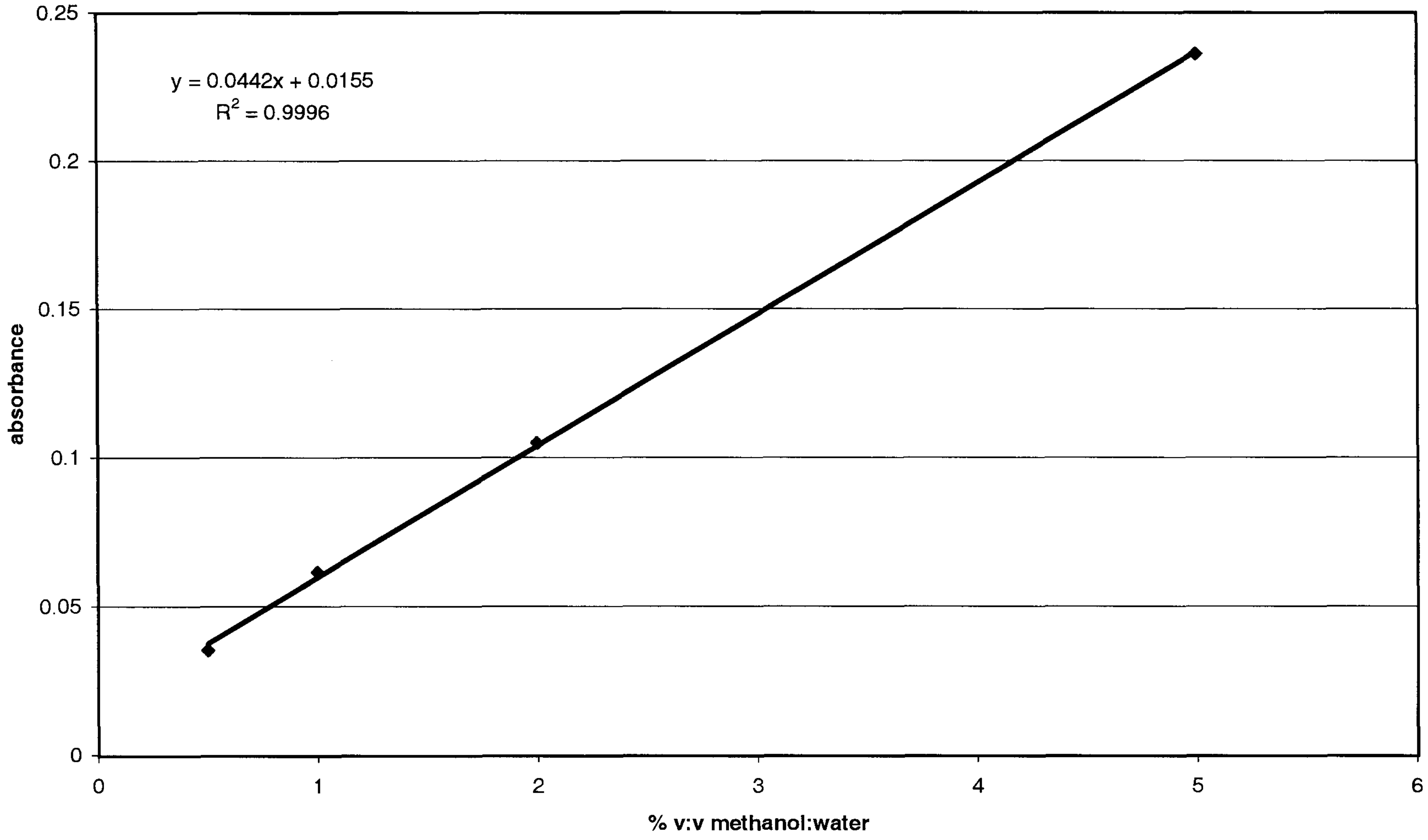


Figure 4.18: Ethanol standards - 1045cm-1

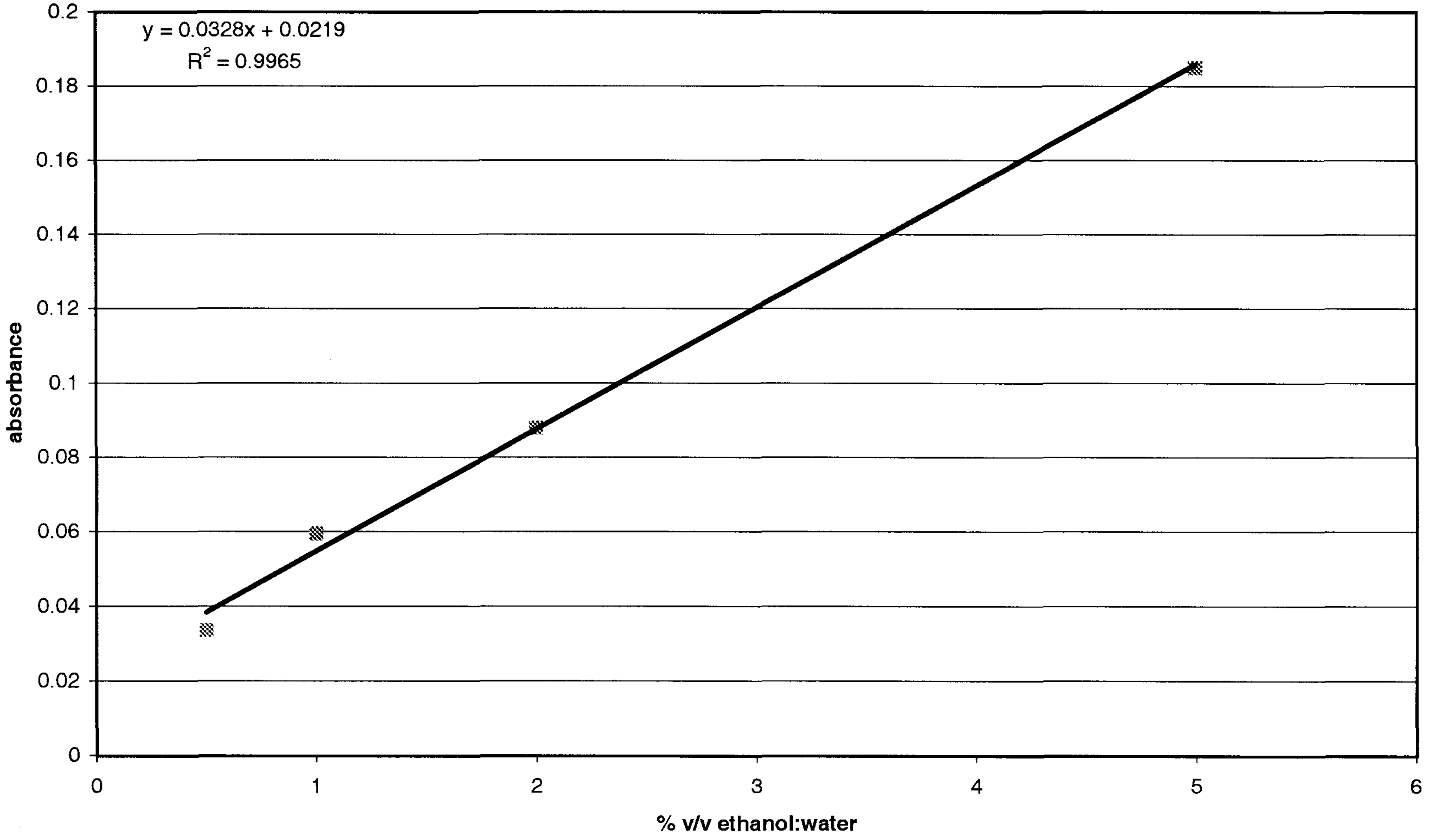


Figure 4.19: Ethanol standards - 1086cm-1

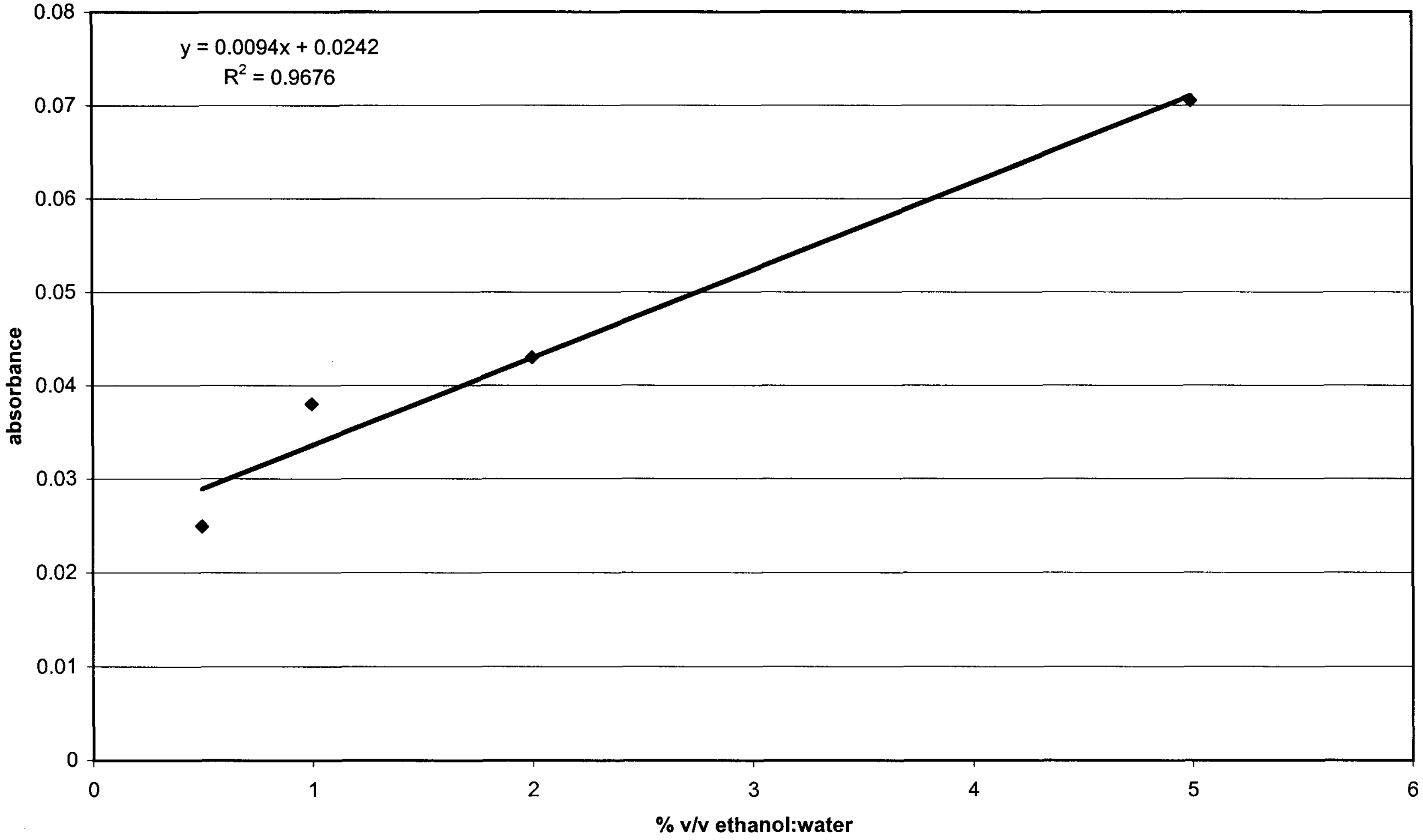


Figure 4.20: Isopropyl Alcohol Standards 1107 cm-1

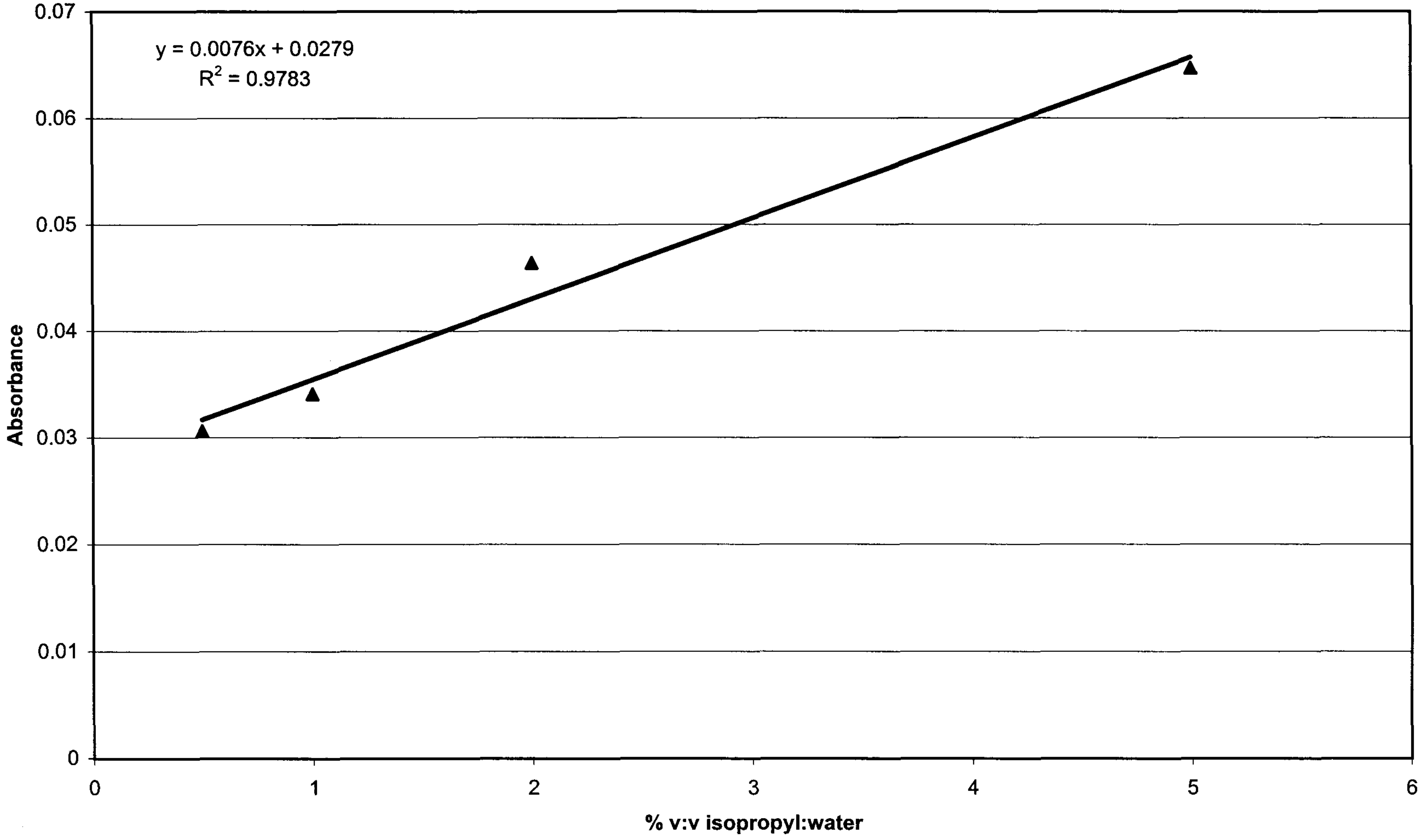


Figure 4.21: Isopropyl Alcohol Standards 1126 cm-1

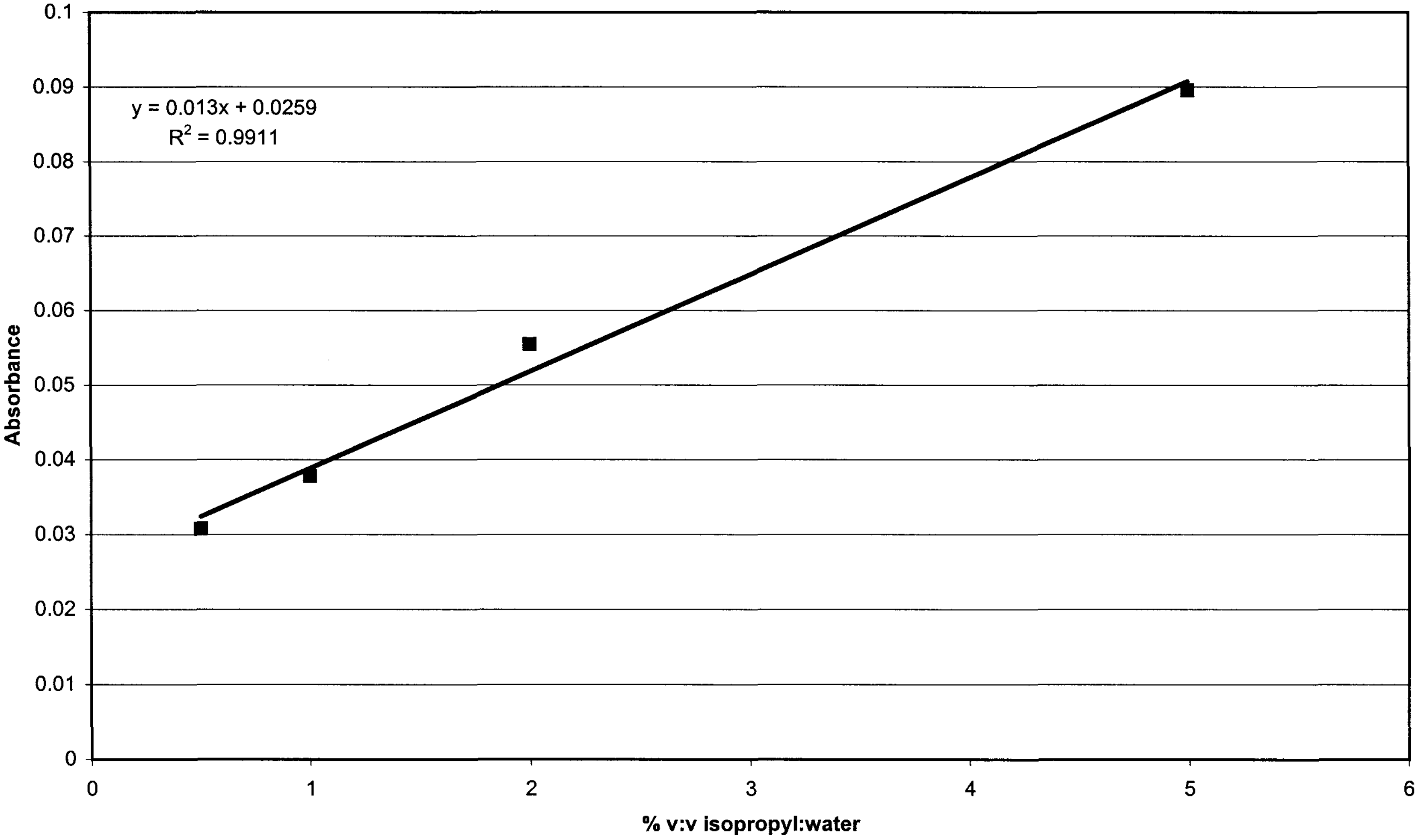


Figure 4.22: Isopropyl Alcohol Standards 1164 cm-1

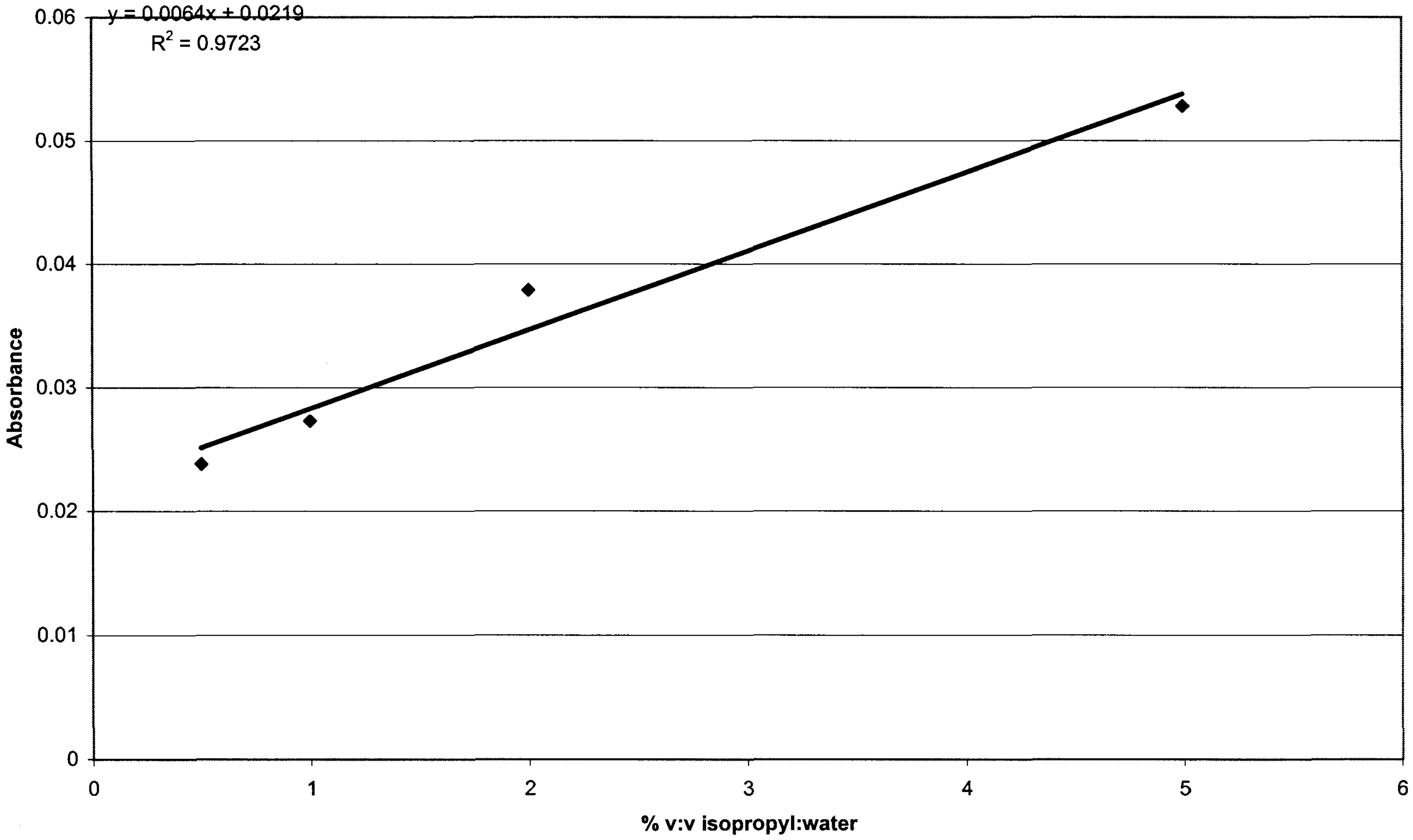


Figure 4.23: Acetone Standards 1239 cm-1

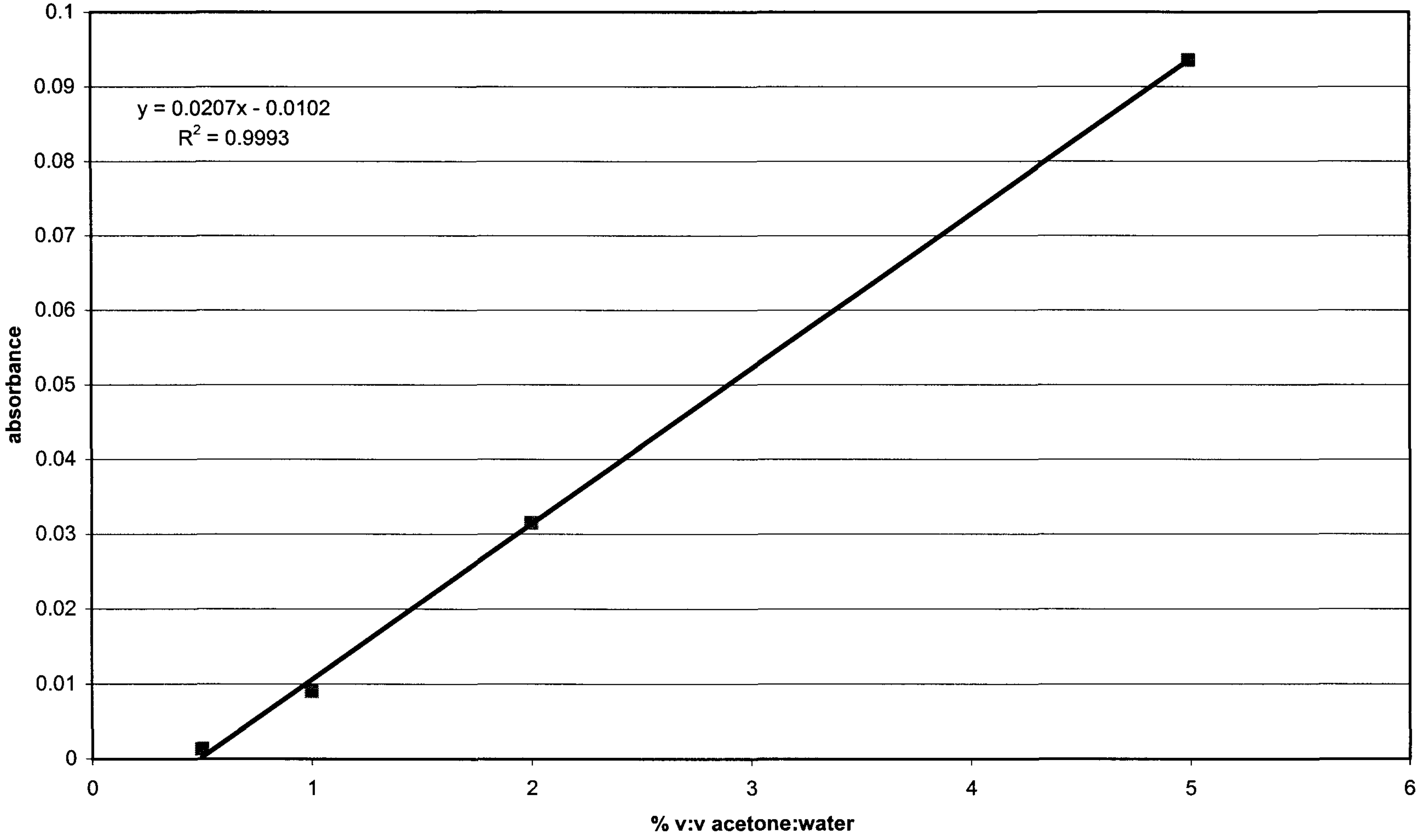


Figure 4.24: Acetone Standards 1699 cm-1

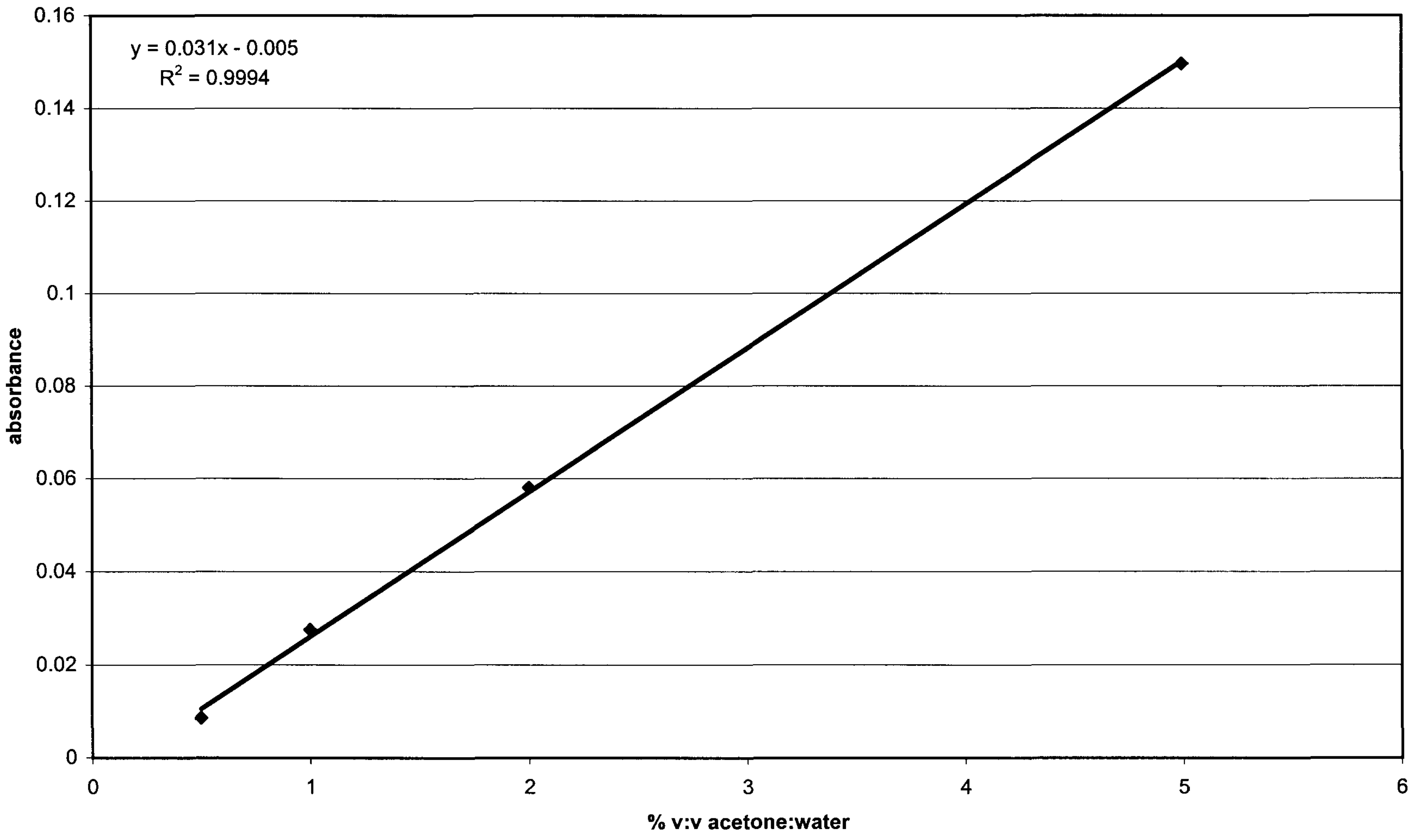


Figure 4.25: **10mL mth/100mL wtr 25 sec. burn retrieved from carpet**

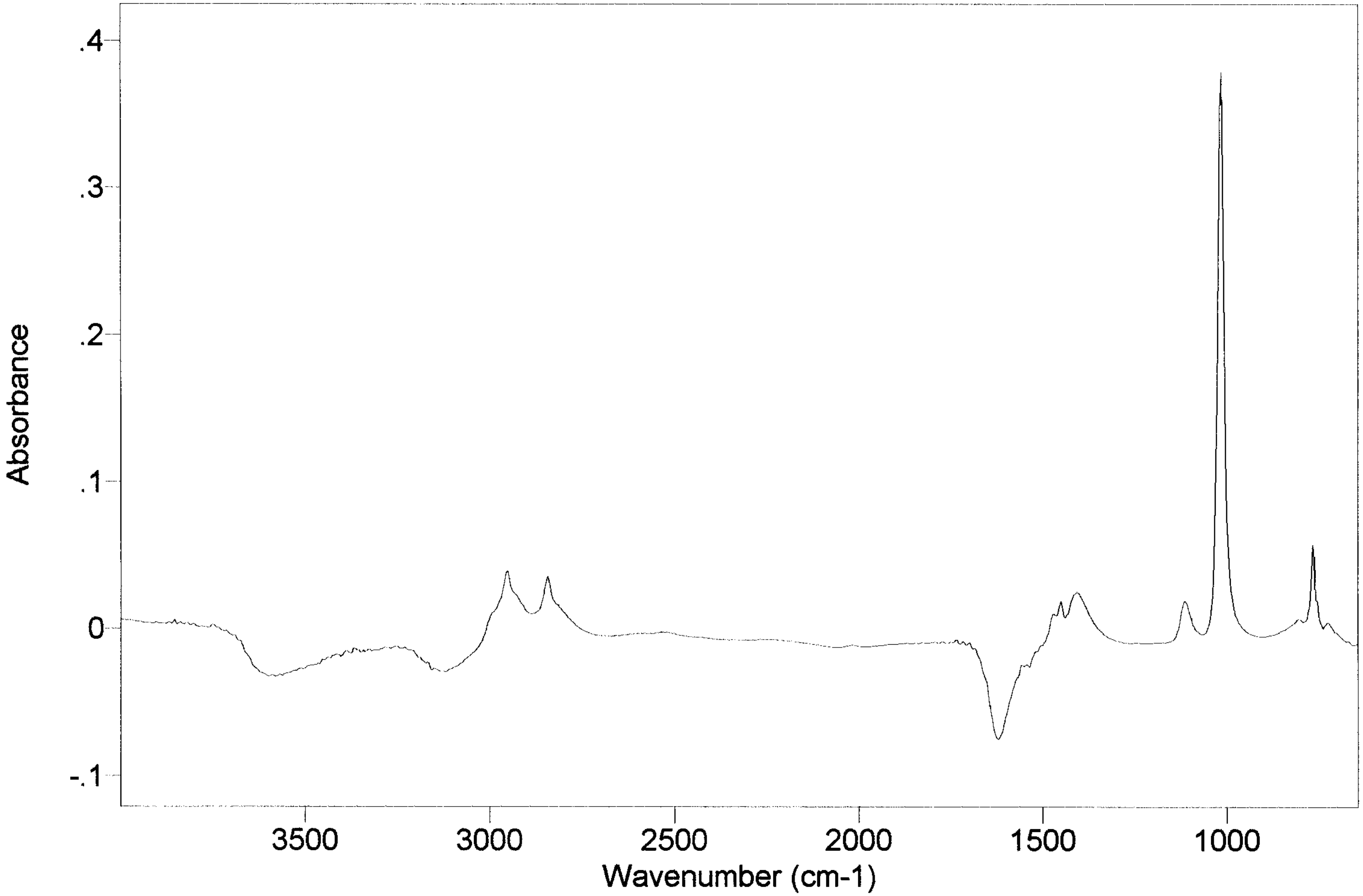


Figure 4.26: **10mL mth/100mL wtr 90 sec. burn retrieved from carpet**

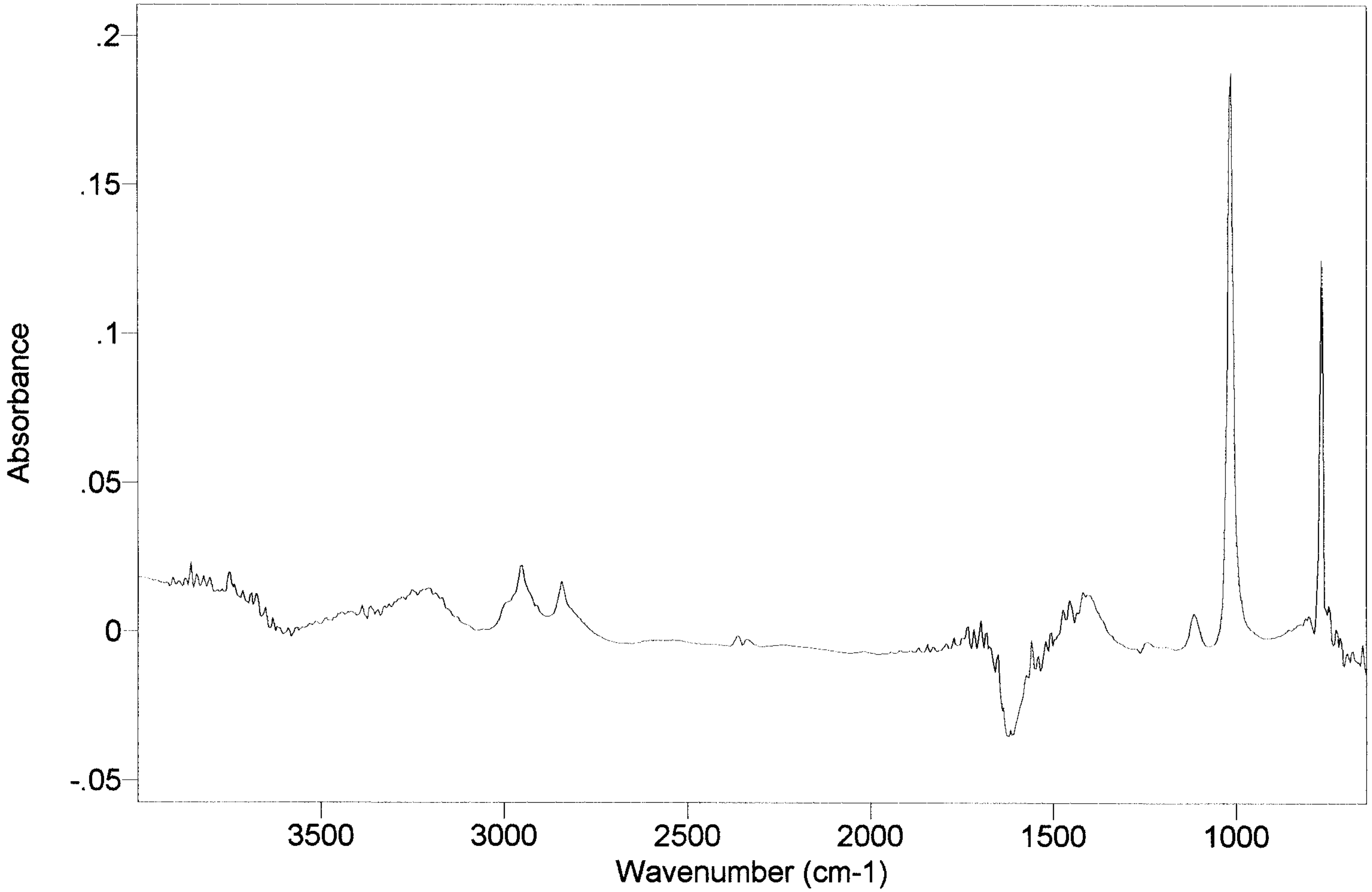


Figure 4.27: **10mL eth./100mL water - 30sec. - retrieved from carpet**

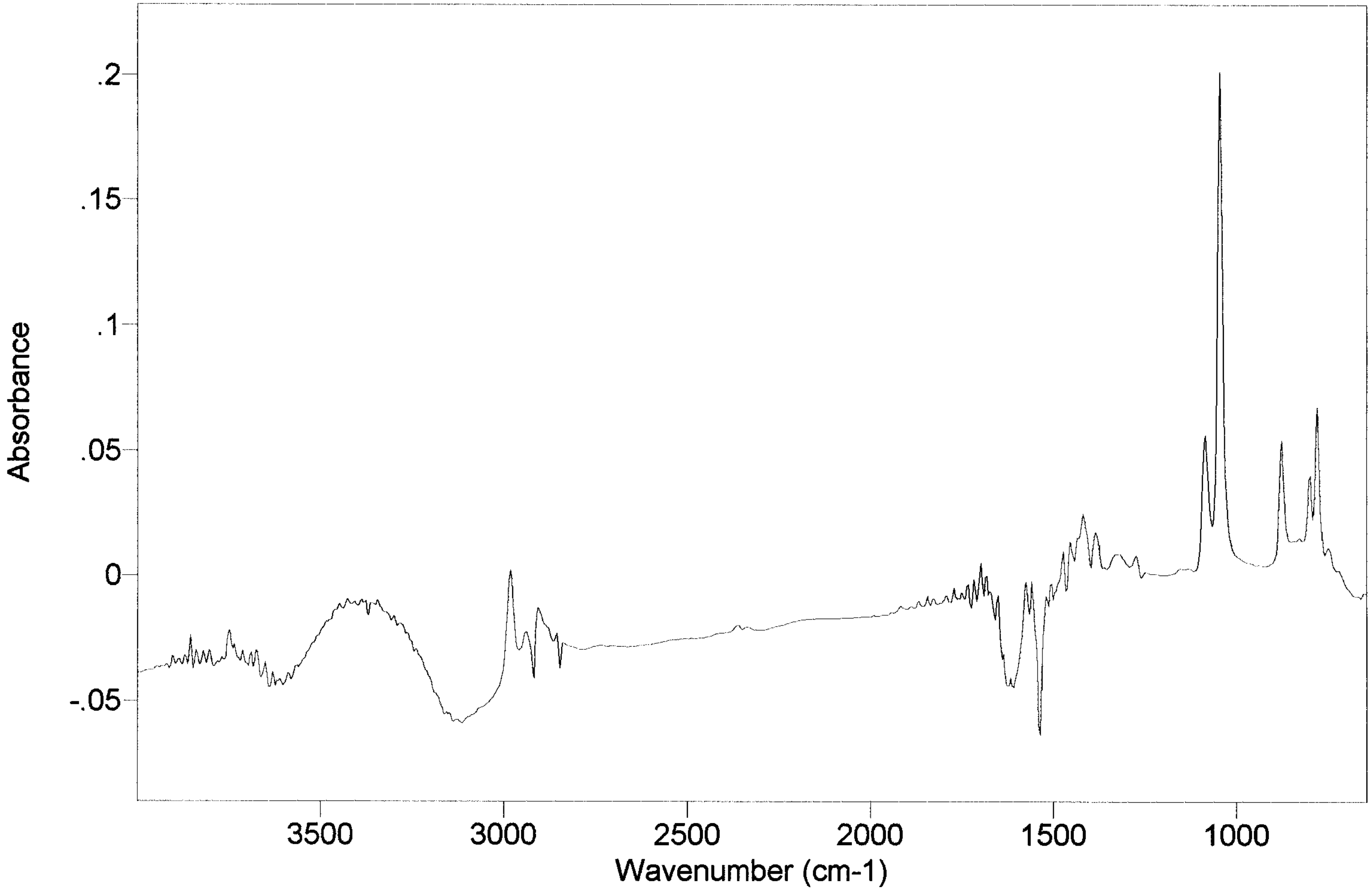


Figure 4.28: **10mL eth./100mL water - 90sec. - retrieved from carpet**

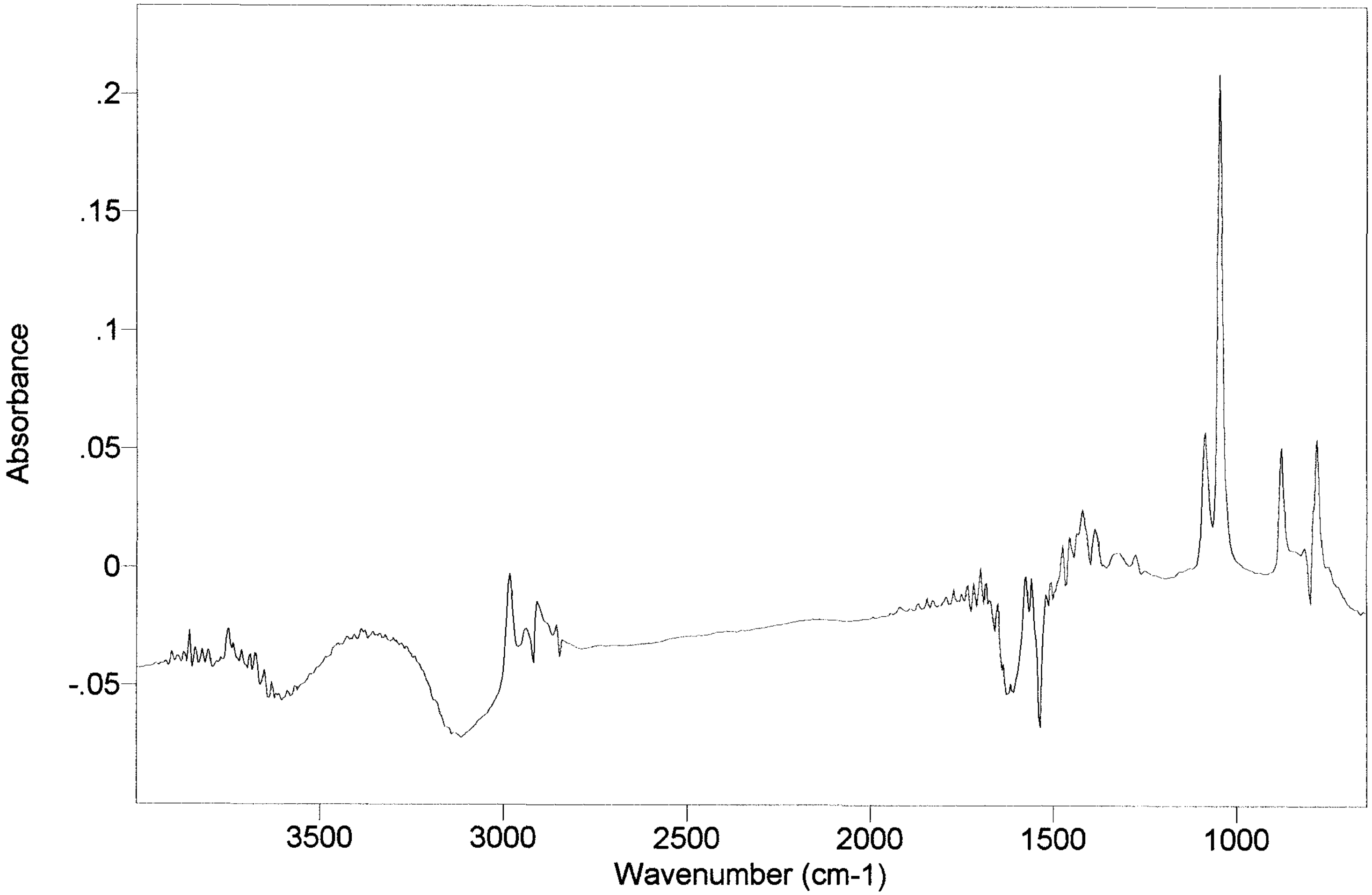


Figure 4.29: **10mL eth./100mL water - 150sec. - retrieved from carpet**

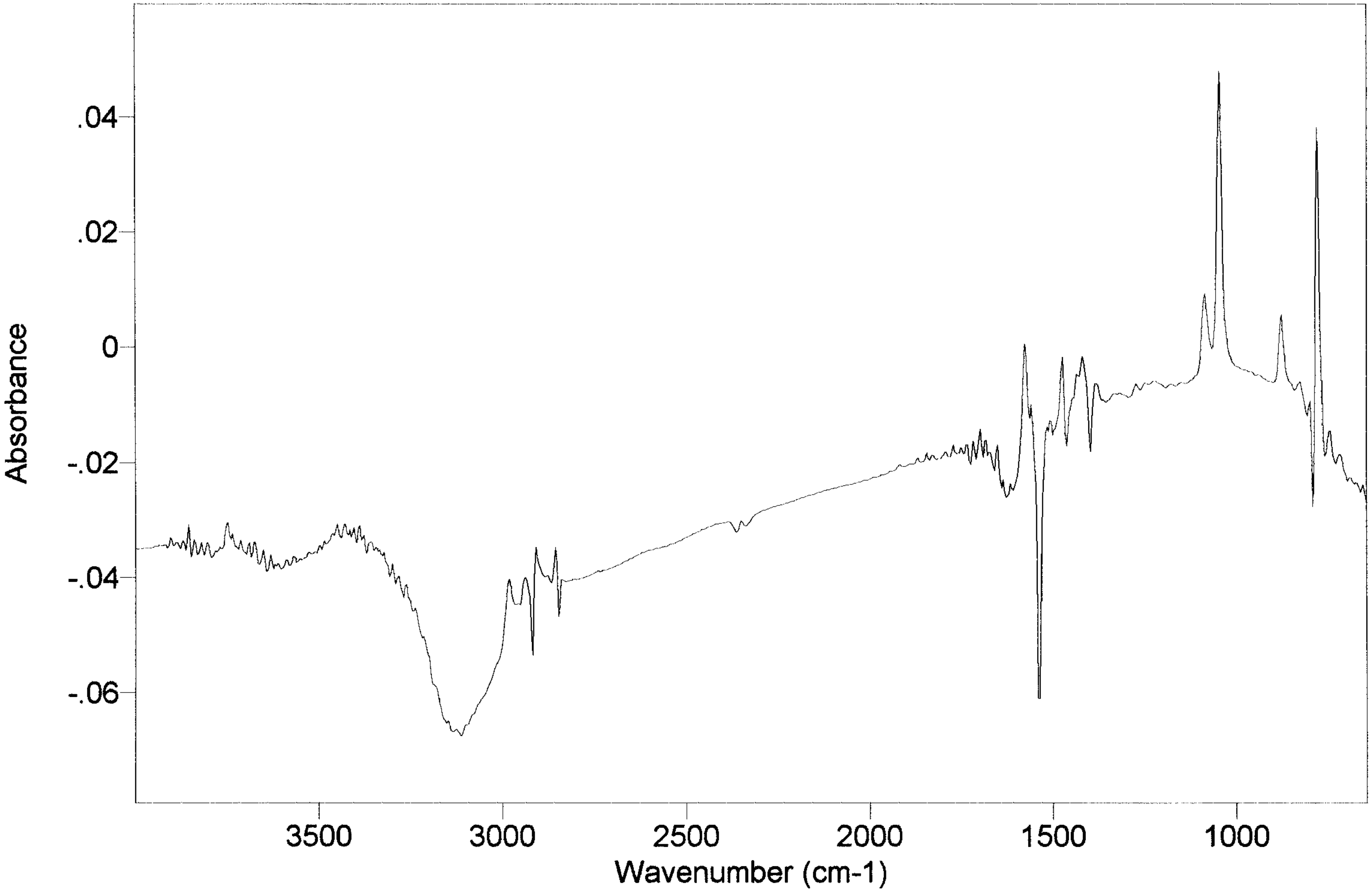


Figure 4.30: **10mL prpyl/100mL water - 30sec. - retrieved from carpet**

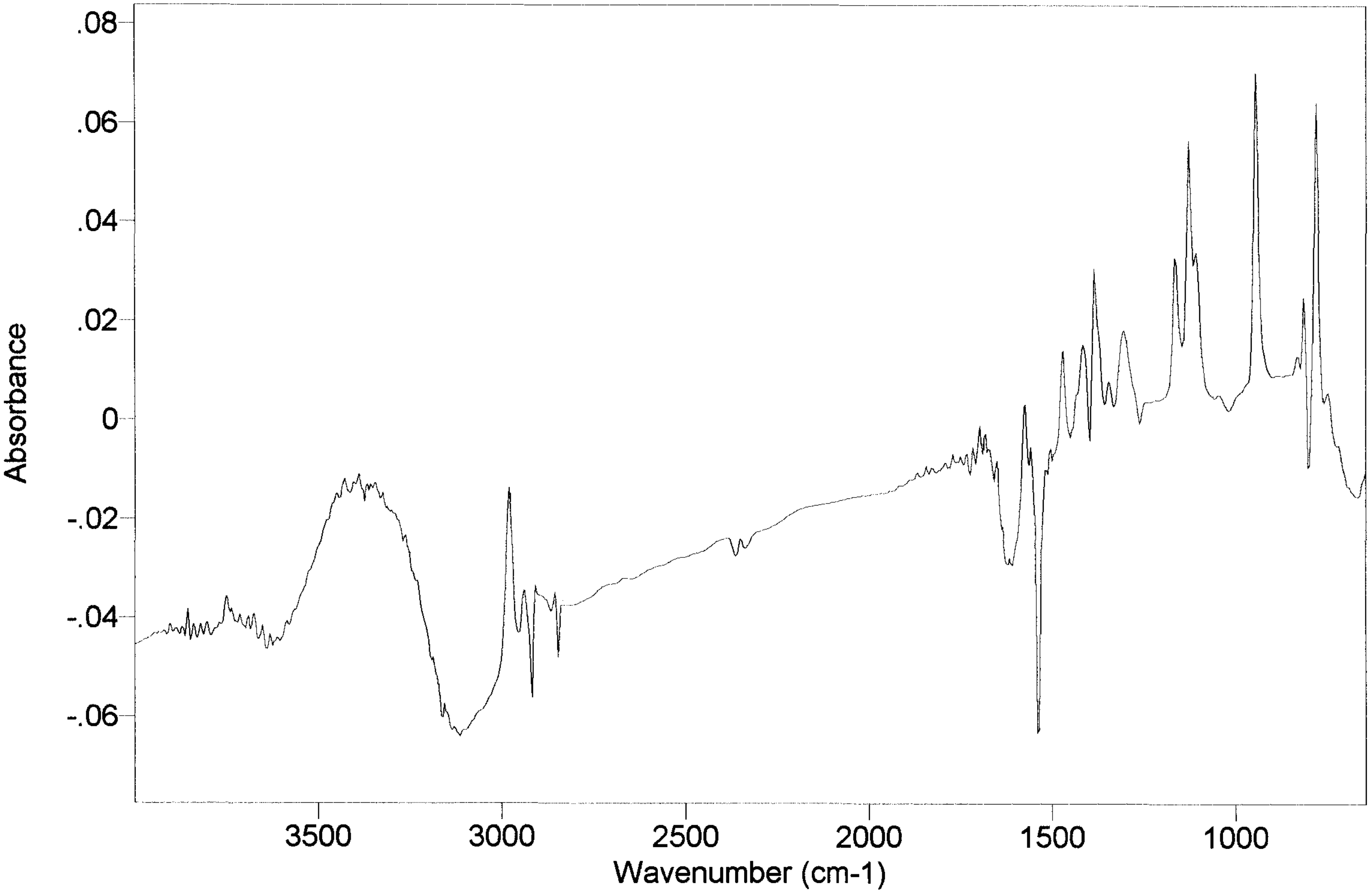


Figure 4.31: **10mL prpyl/100mL water - 90sec. - retrieved from carpet**

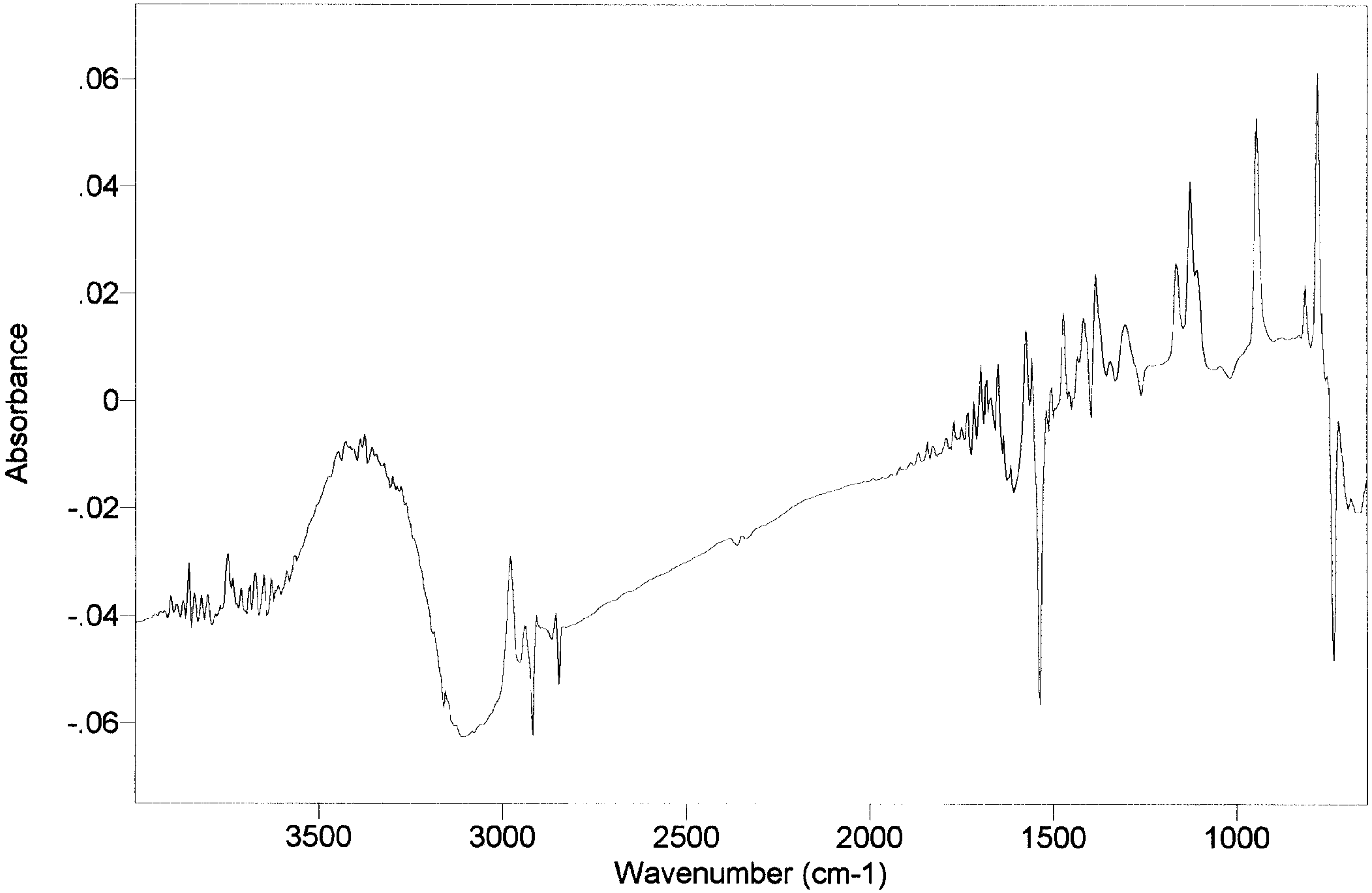


Figure 4.32: **10mL prpyl/100mL water - 150sec. - retrieved from carpet**

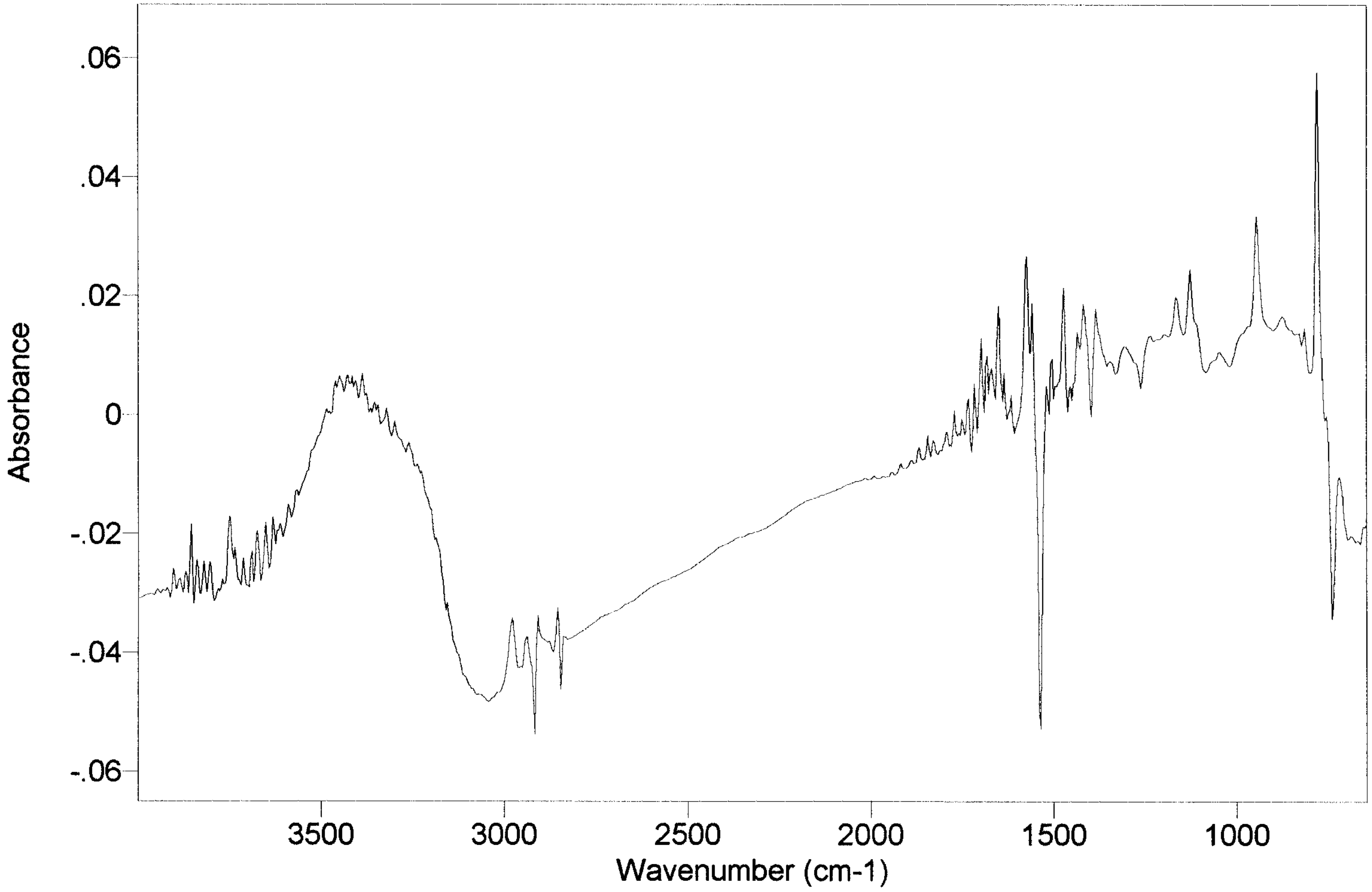


Table 4.3 Stage One Burns

Methanol 2/12/98

Burn time	1016 cm-1 absorbance	1016 cm-1 % recovery
0	0.434	100
25	0.4561	105
60	0.3082	71
90	0.2612	60
120	0.4063	94
180	0.0877	20

Burn time	1016 cm-1 absorbance	1016 cm-1 % recovery
0	0.434	100
25	0.4561	105
60	0.3082	71
90	0.2612	60
180	0.0877	20

Ethanol 2/19/98

Burn time	1085 cm-1 absorbance	1085 cm-1 % recovery	1045 cm-1 absorbance	1045 cm-1 % recovery
0	0.0948	100	0.3112	100
30	0.0856	90	0.3111	100
60	0.0636	67	0.2455	79
90	0.0646	68	0.2392	77
120	0.0456	48	0.165	53
150	0.0161	17	0.0769	25
180	0.0263	28	0.0915	29

Isopropanol 2/19/98

Burn Time	1164 cm-1 absorbance	1164 cm-1 % recovery	1126 cm-1 absorbance	1126 cm-1 % recovery	1107 cm-1 absorbance	1107 cm-1 % recovery
0	0.0739	100	0.1303	100	0.0813	100
30	0.0826	112	0.1423	109	0.0877	108
60	0.0656	89	0.1107	85	0.0669	82
90	0.0541	73	0.0811	62	0.0504	62
120	0.0528	71	0.0753	58		
150	0.0374	51	0.0429	33	Unable to detect	
180	0.0377	51	0.0416	32		

Figure 4.33: Methanol Burn 2/12

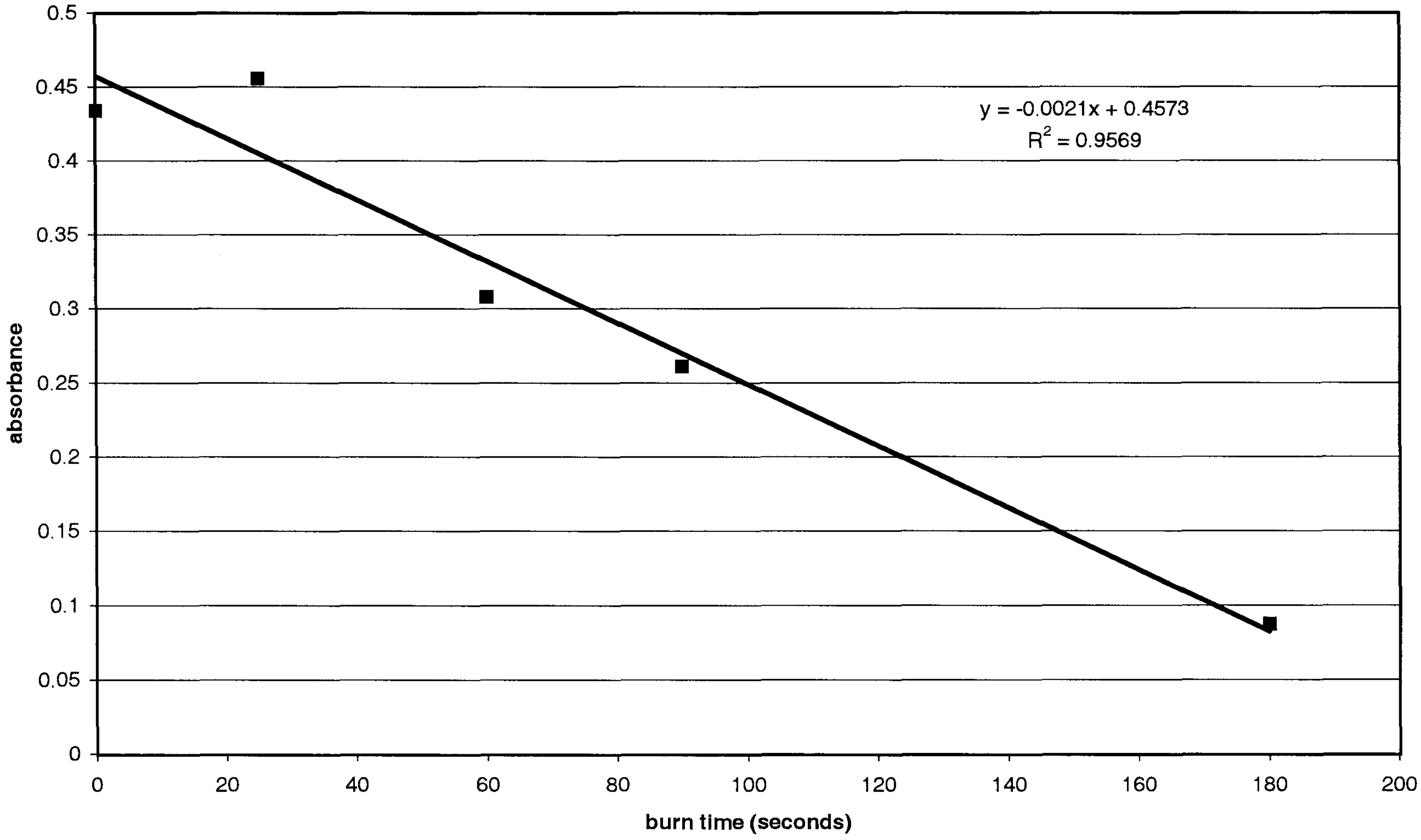


Figure 4.34: Methanol Burn 2/12

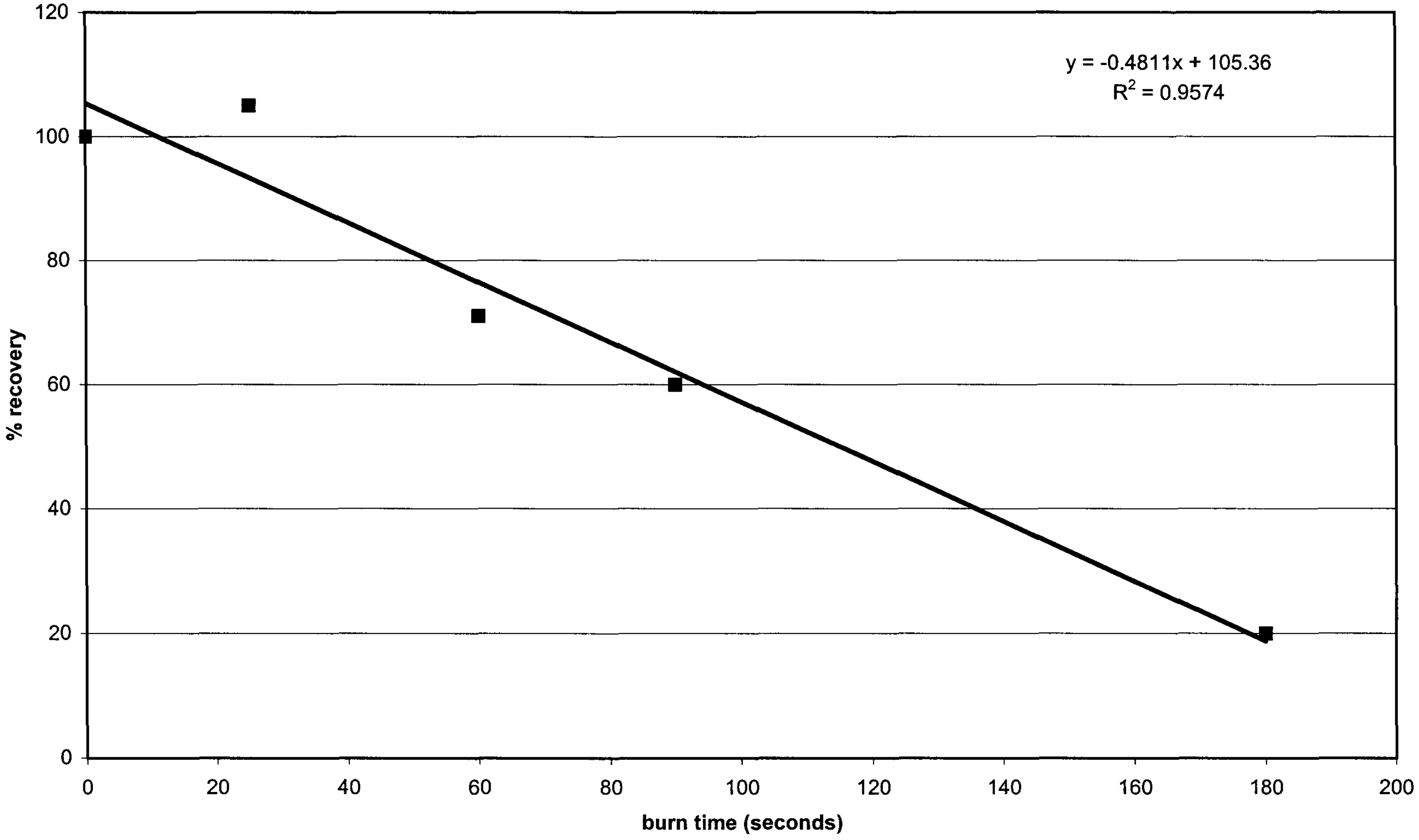


Figure 4.35: Ethanol: Absorbance(1044.9 cm^{-1}) vs. time

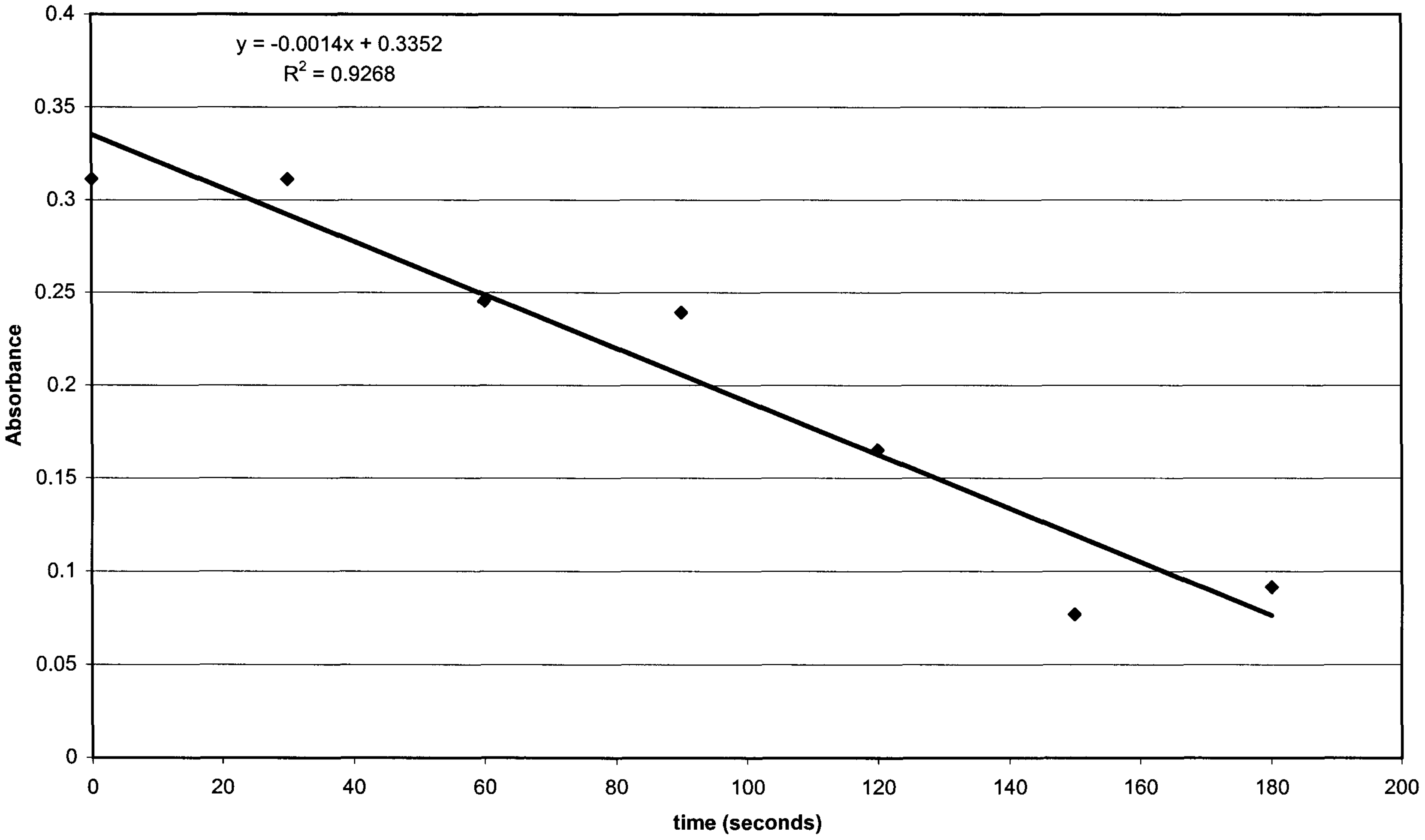


Figure 4.36: Ethanol: % recovery(1044.9cm-1) vs. time

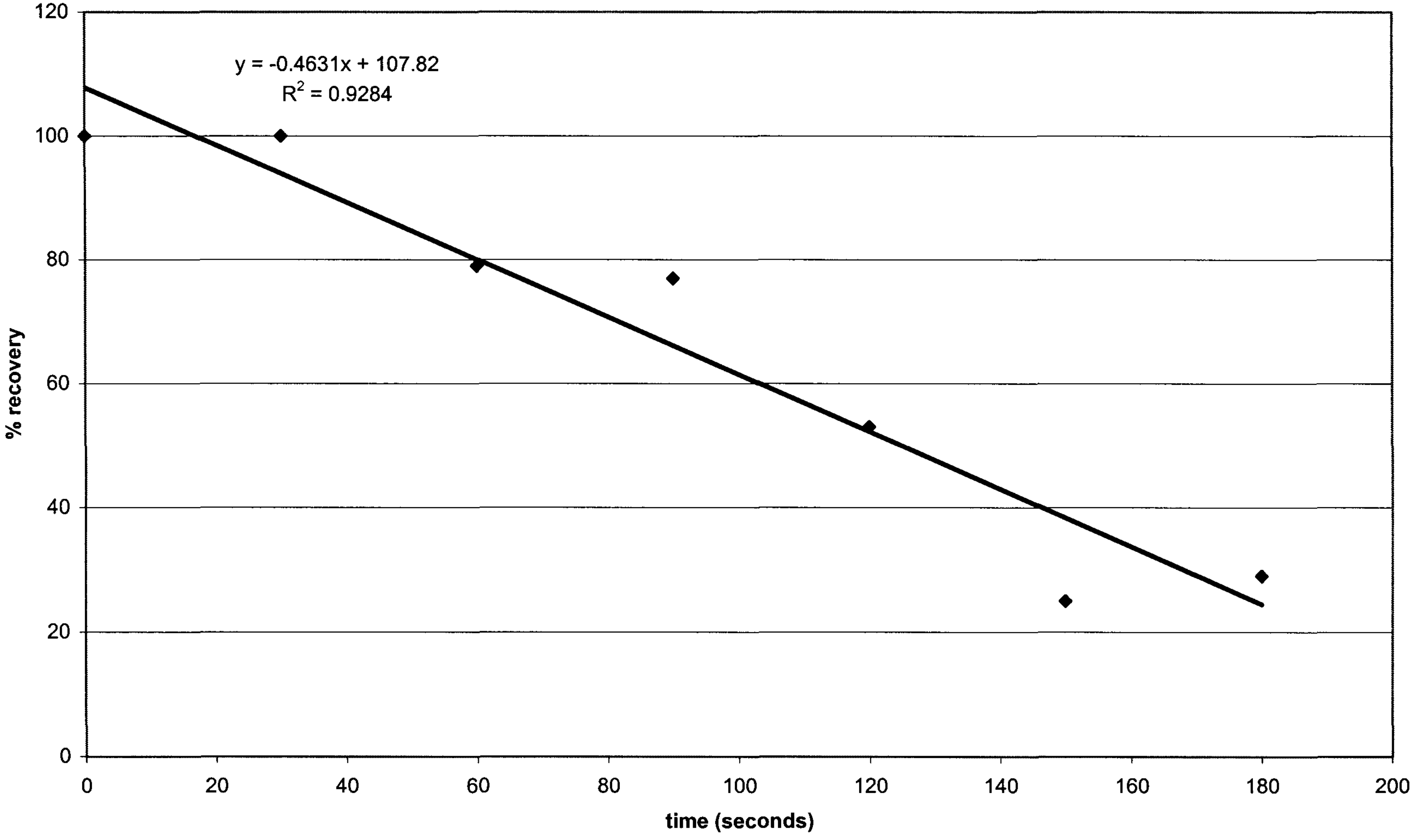


Figure 4.37: Ethanol: Absorbance(1085.7cm^{-1}) vs. time

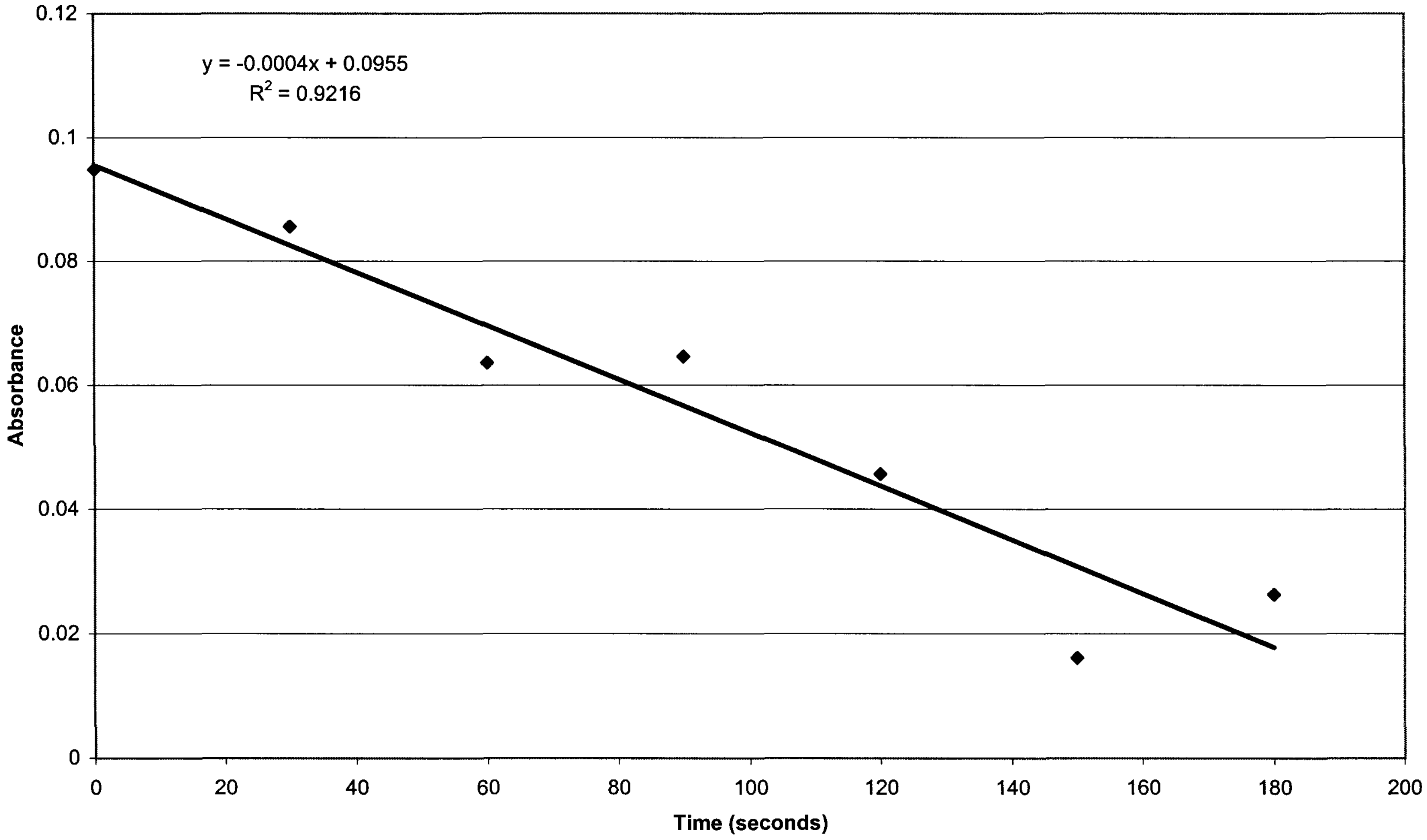


Figure 4.38: Ethanol: % recovery(1085.7cm^{-1})vs. time

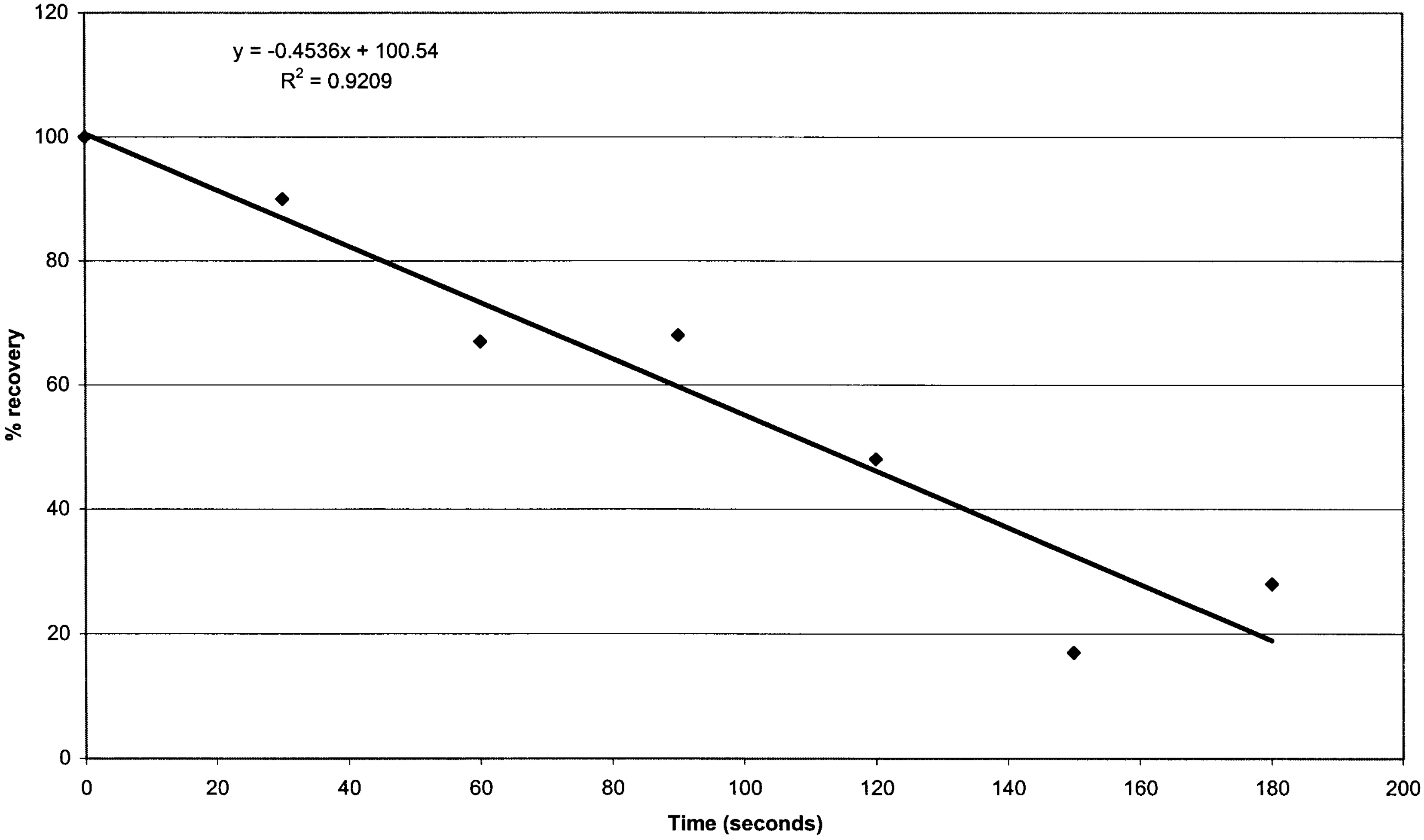


Figure 4.39: Isopropanol Burn 2/19 1126 cm-1

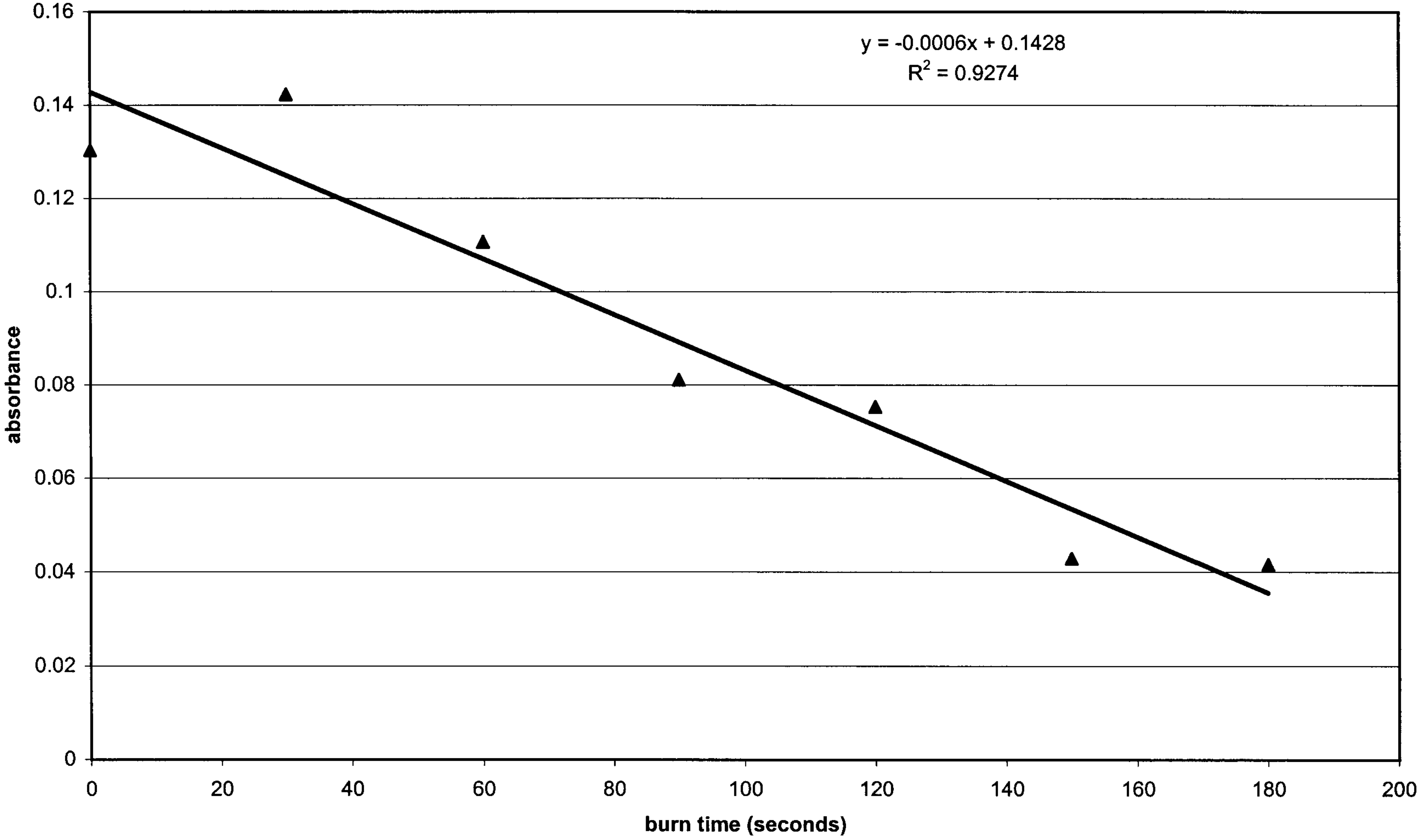


Figure 4.40: Isopropanol Burn 2/19 1126 cm-1

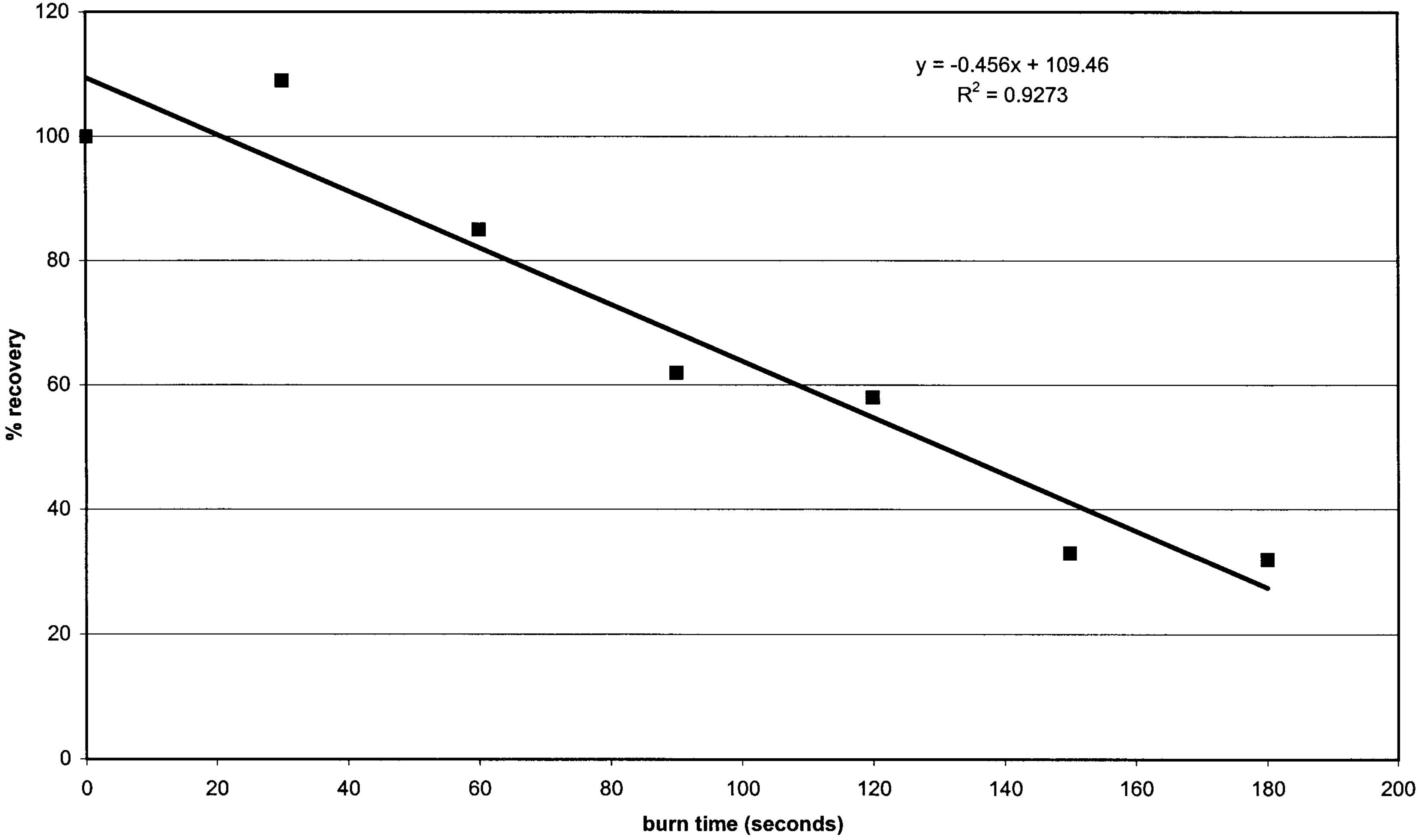


Figure 4.41: Isopropanol Burn 2/19 1164 cm-1

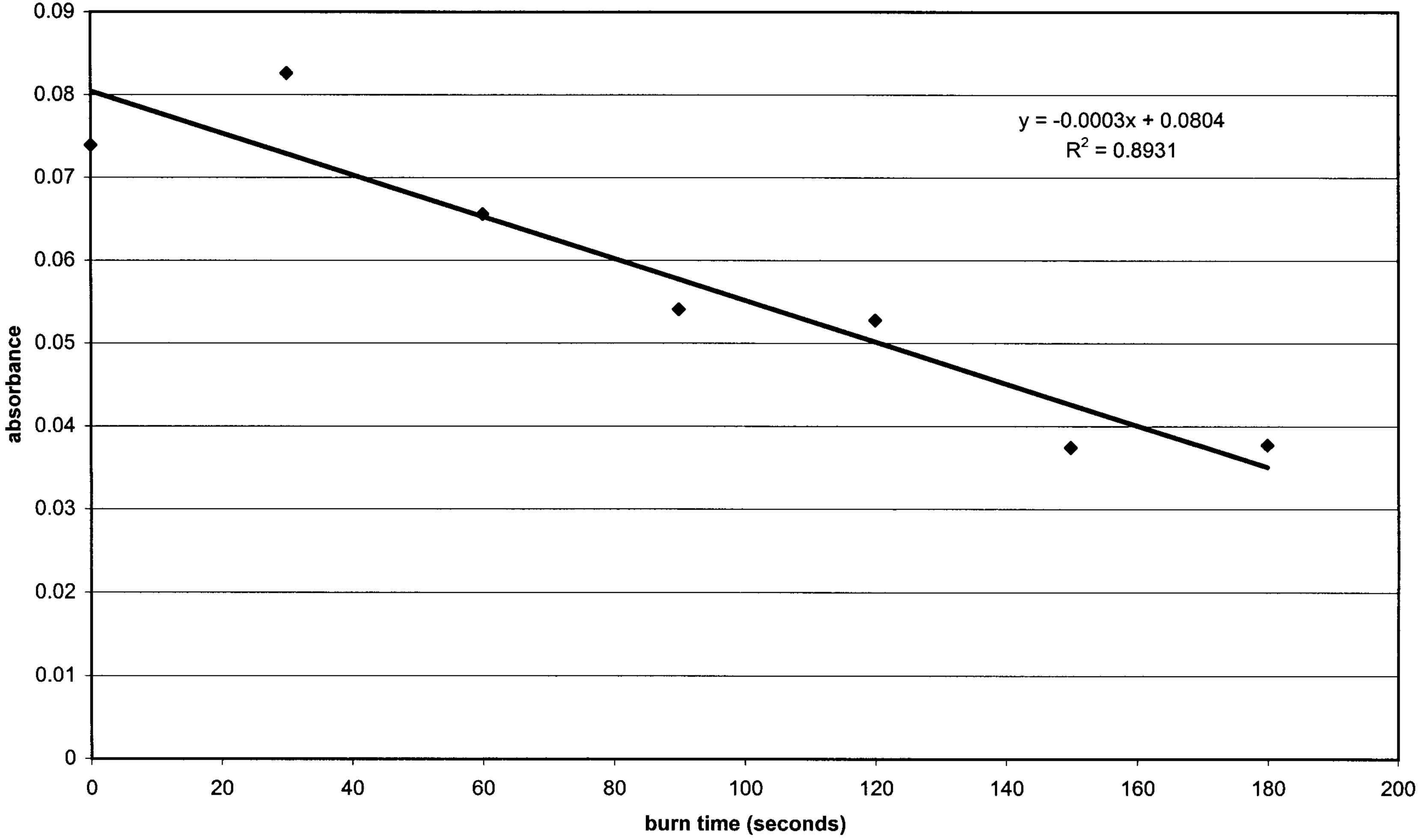


Figure 4.42: Isopropanol Burn 2/19 1164 cm-1

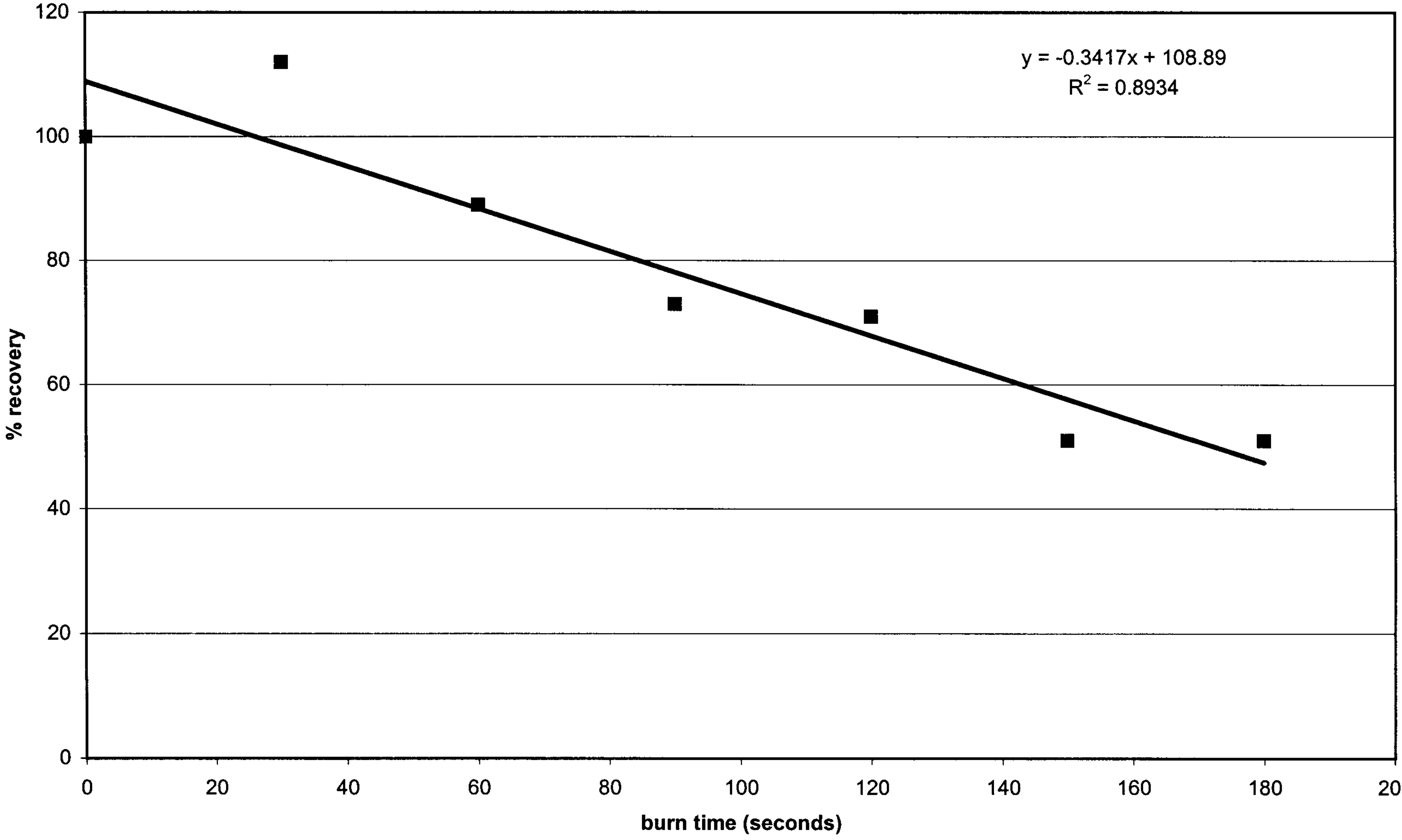


Figure 4.43: **15mL water added to 30sec. burn sample from 3-2-98**

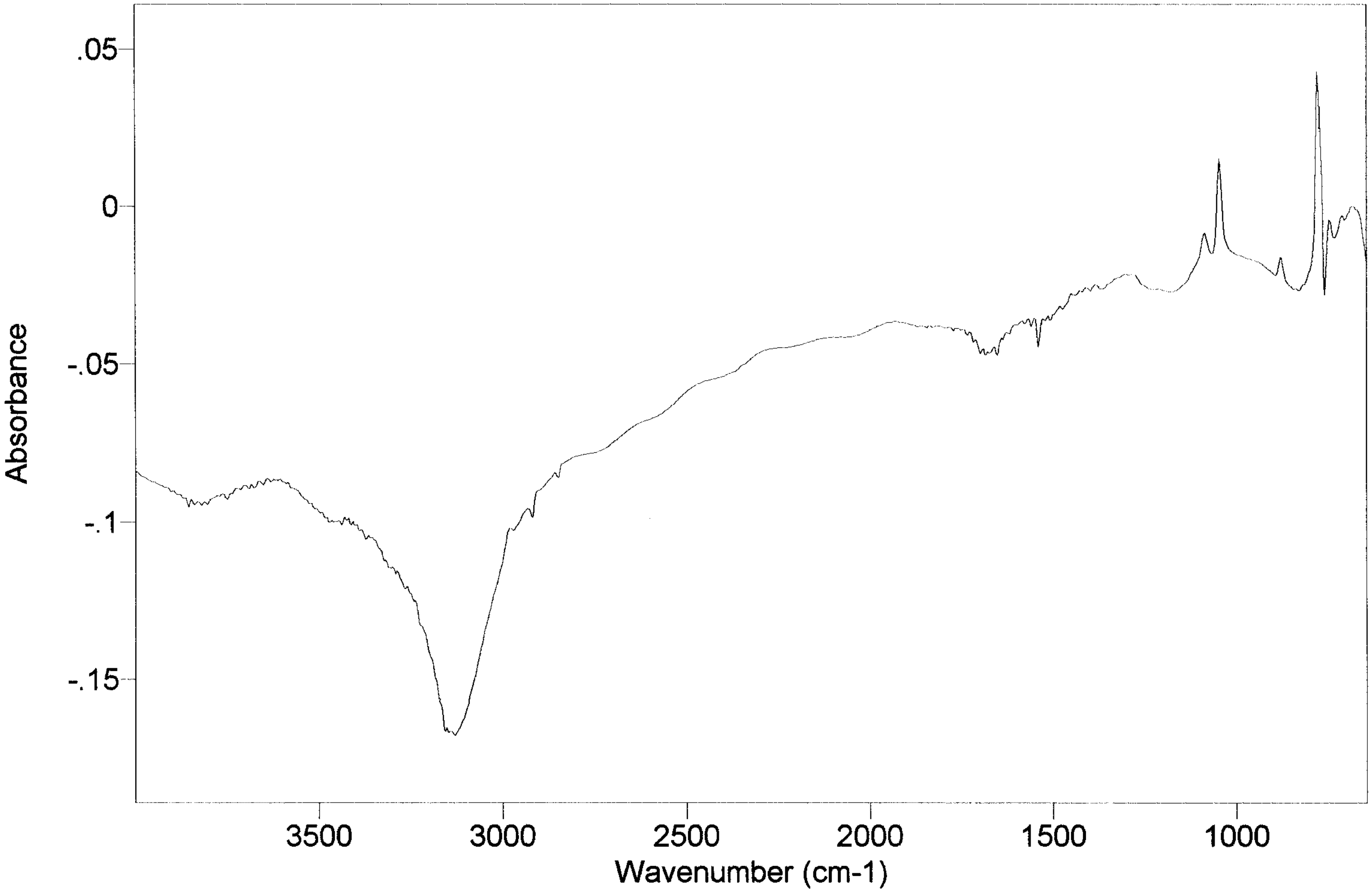


Figure 4.44: **15mL water added to 90sec. burn sample from 3-2-98**

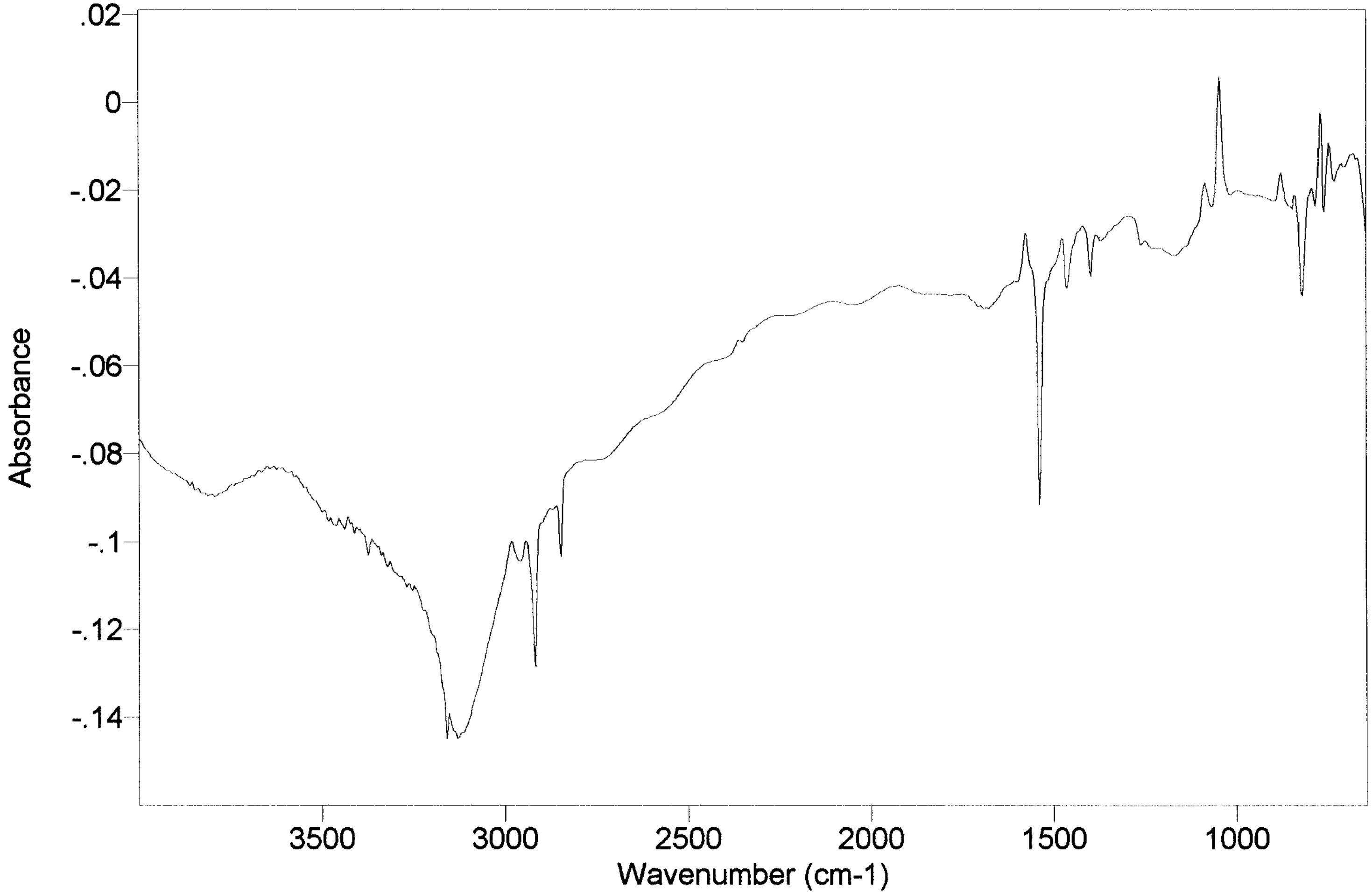


Figure 4.45: **15mL water added to 240sec. burn sample from 3-2-98**

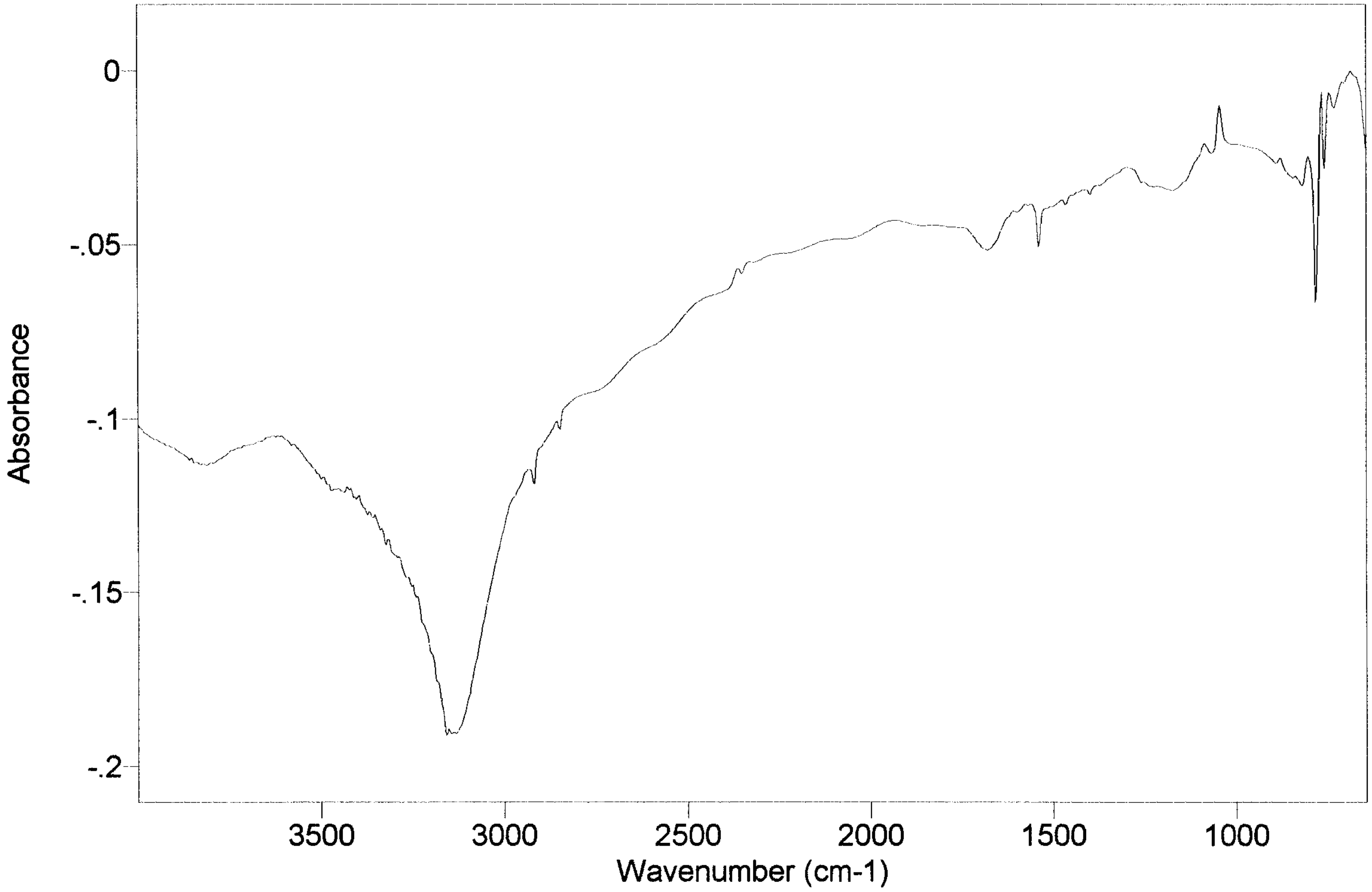


Table 4.4: Ethanol Burns - Second Stage

Ethanol 3/2/98

Burn Time	1045 cm-1 absorbance	1045 cm-1 % recovery
0	0.3312	
30	0.0153	
60	0.0115	
90	0.0059	
120	0.0078	
150		
180		
210	-0.0062	
240	-0.0099	

Figure 4.46: Ethanol Burn - second Stage 3/2/98 1045 cm-1

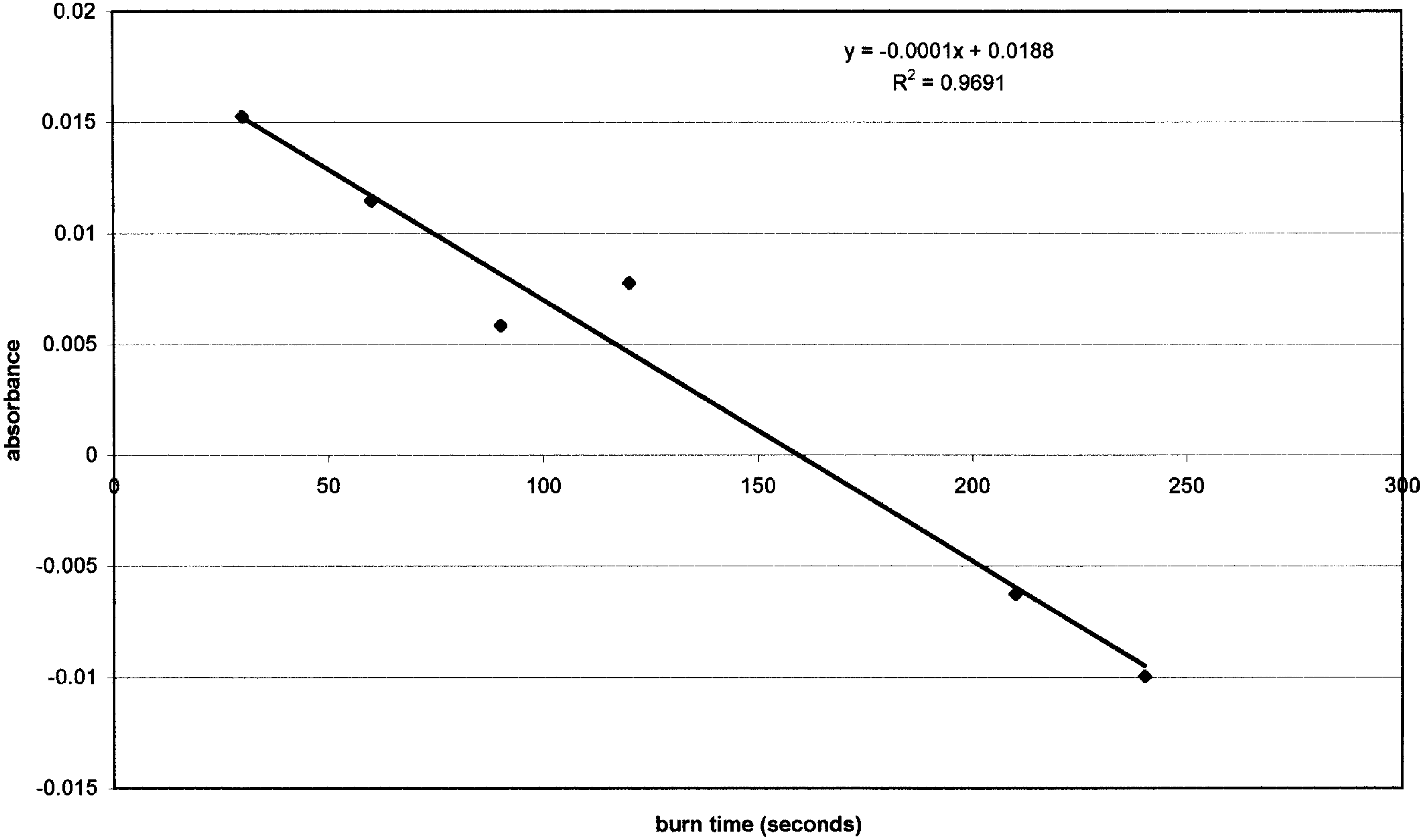


Figure 4.47: **sample 2 fron4/29 - water that was in can**

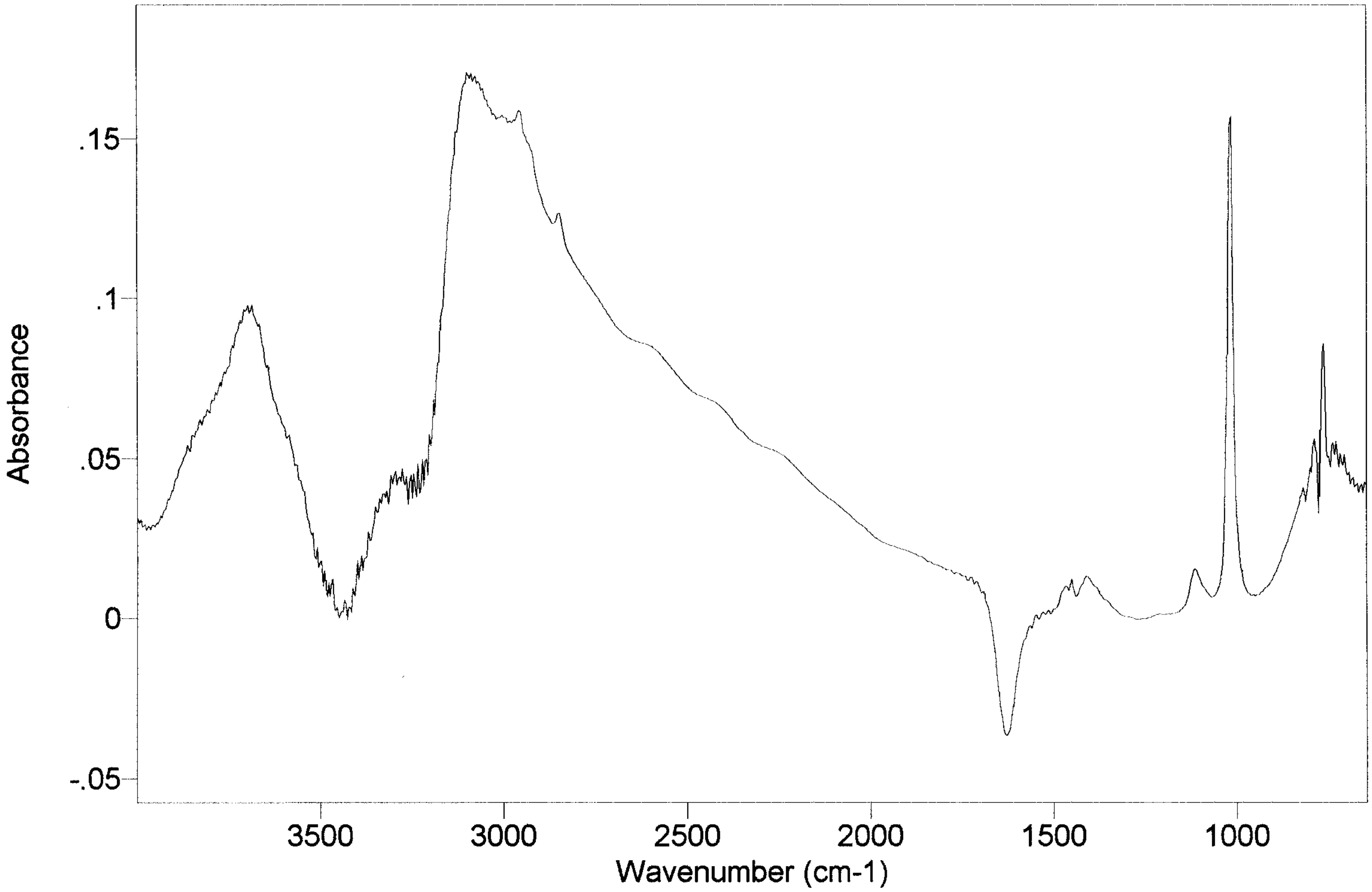


Figure 4.48: **sample 3 fron4/29 - water that was in can - carpet**

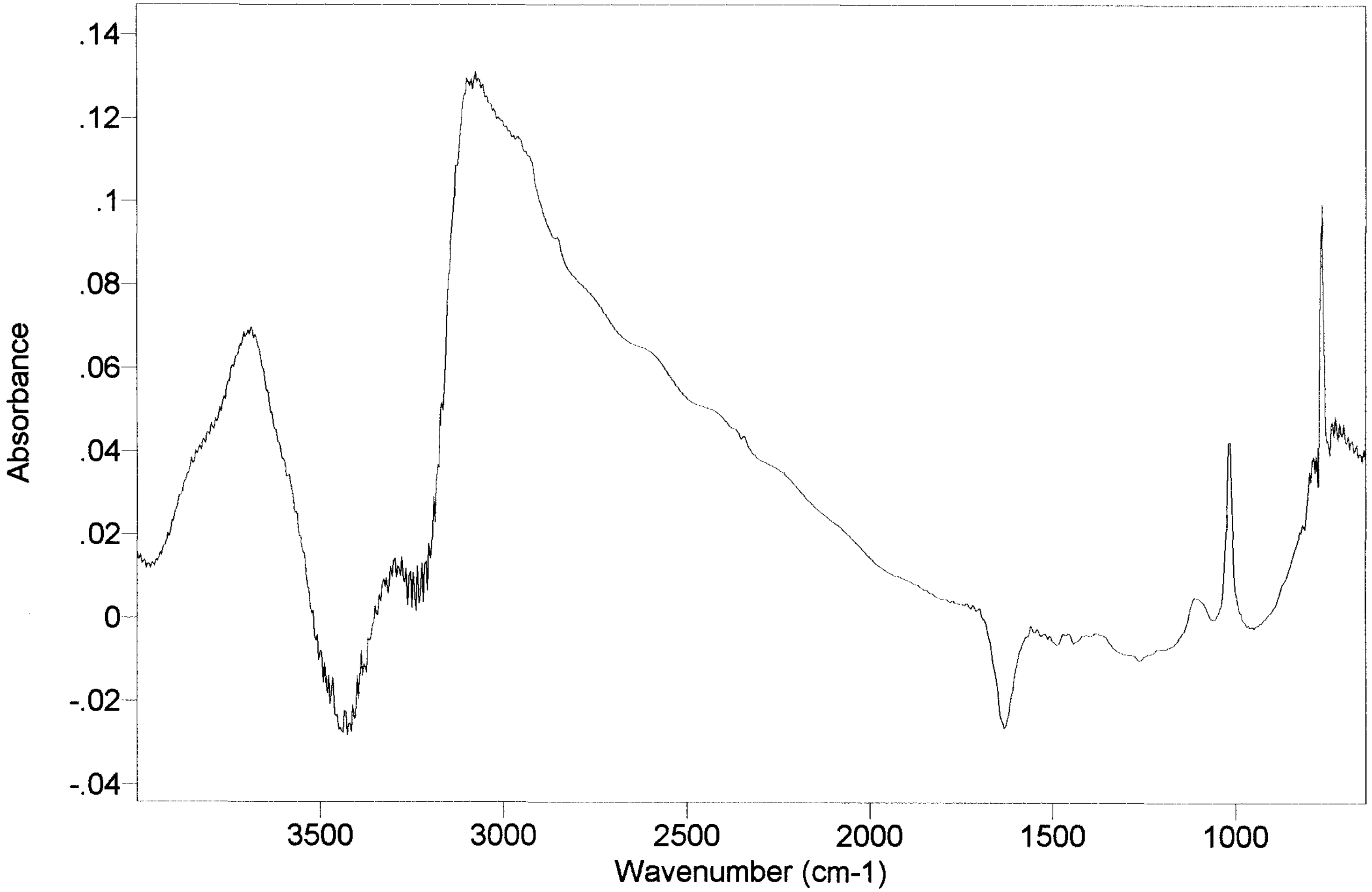


Figure 4.49: **sample 4 fron4/29 - water that was in can - carpet**

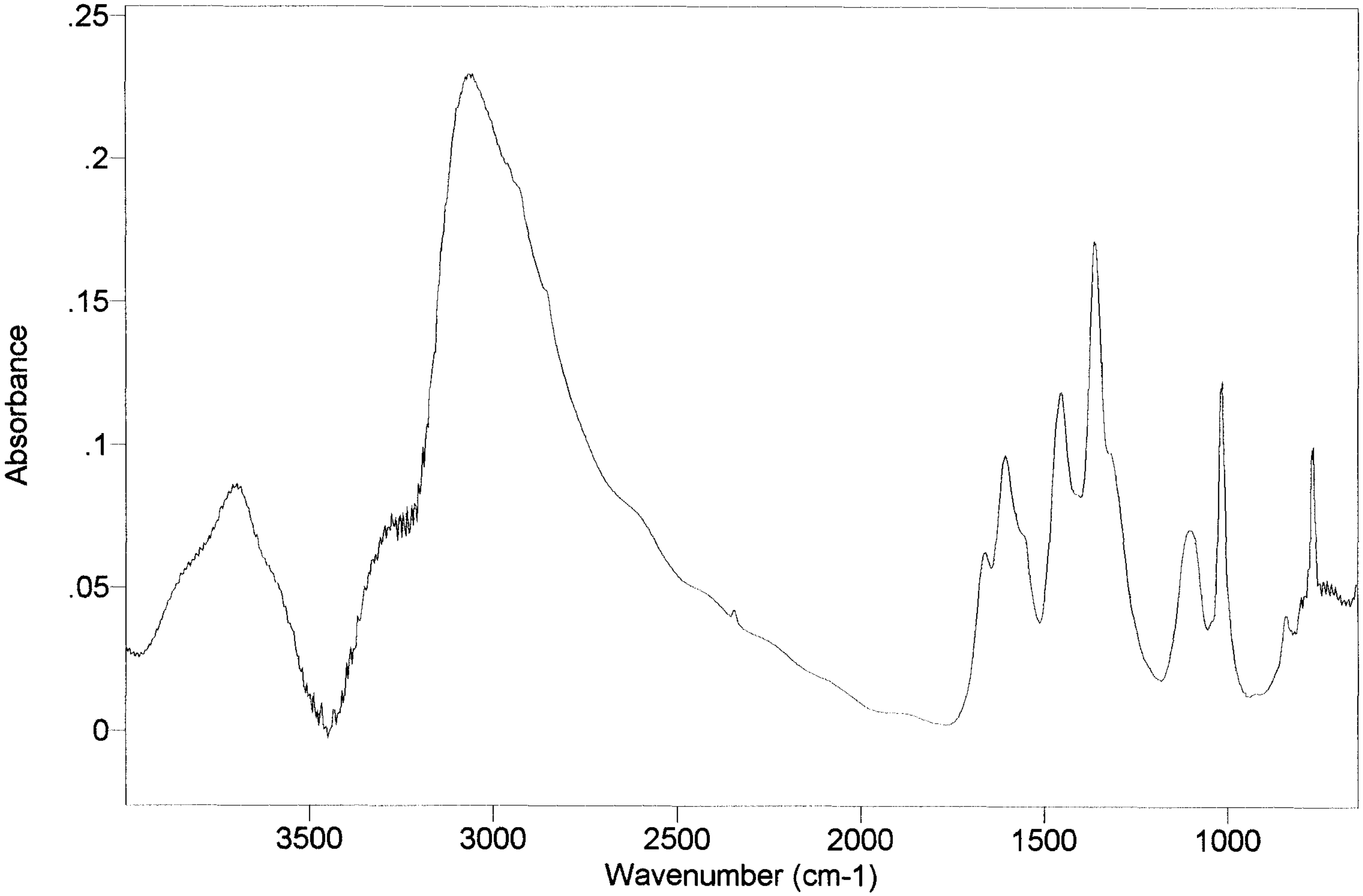


Figure 4.50: **sample 5 from 4/29 - free standing water - unknown A**

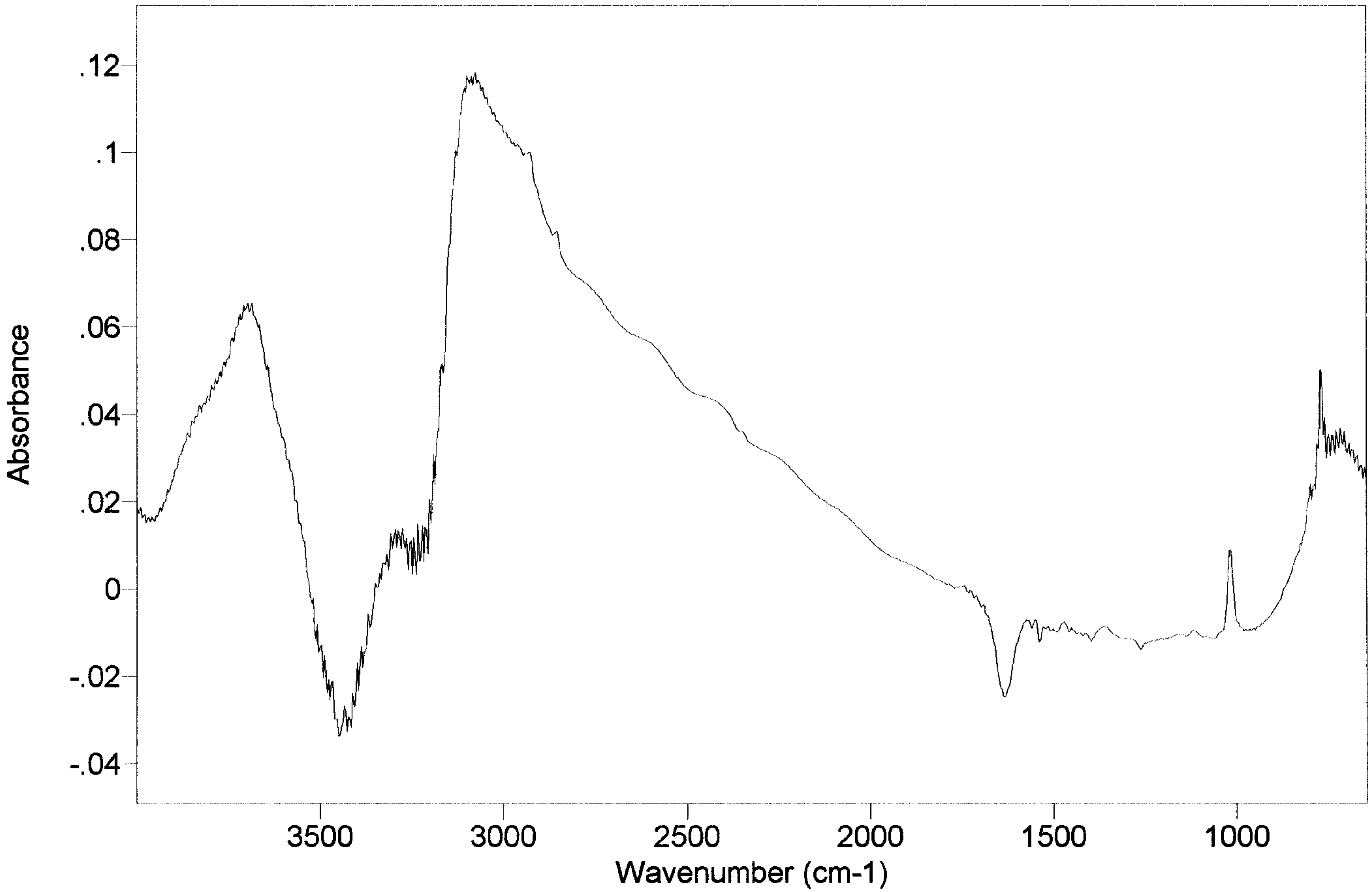


Figure 4.51: **sample 8 from 4/29 - carpet - unknown A**

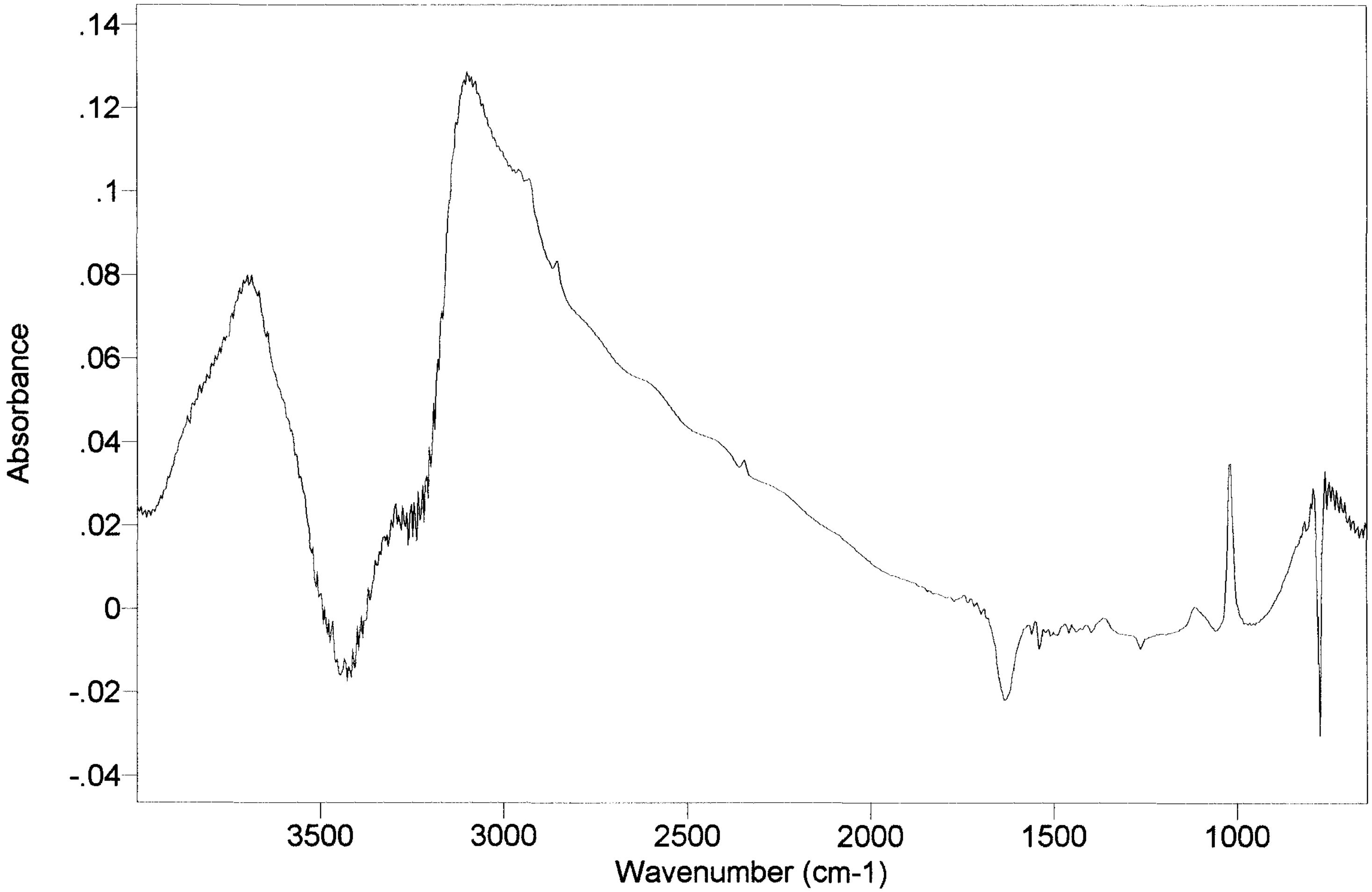


Figure 4.52: **sample 10 from 4/29 - water extracted - part a of cloth**

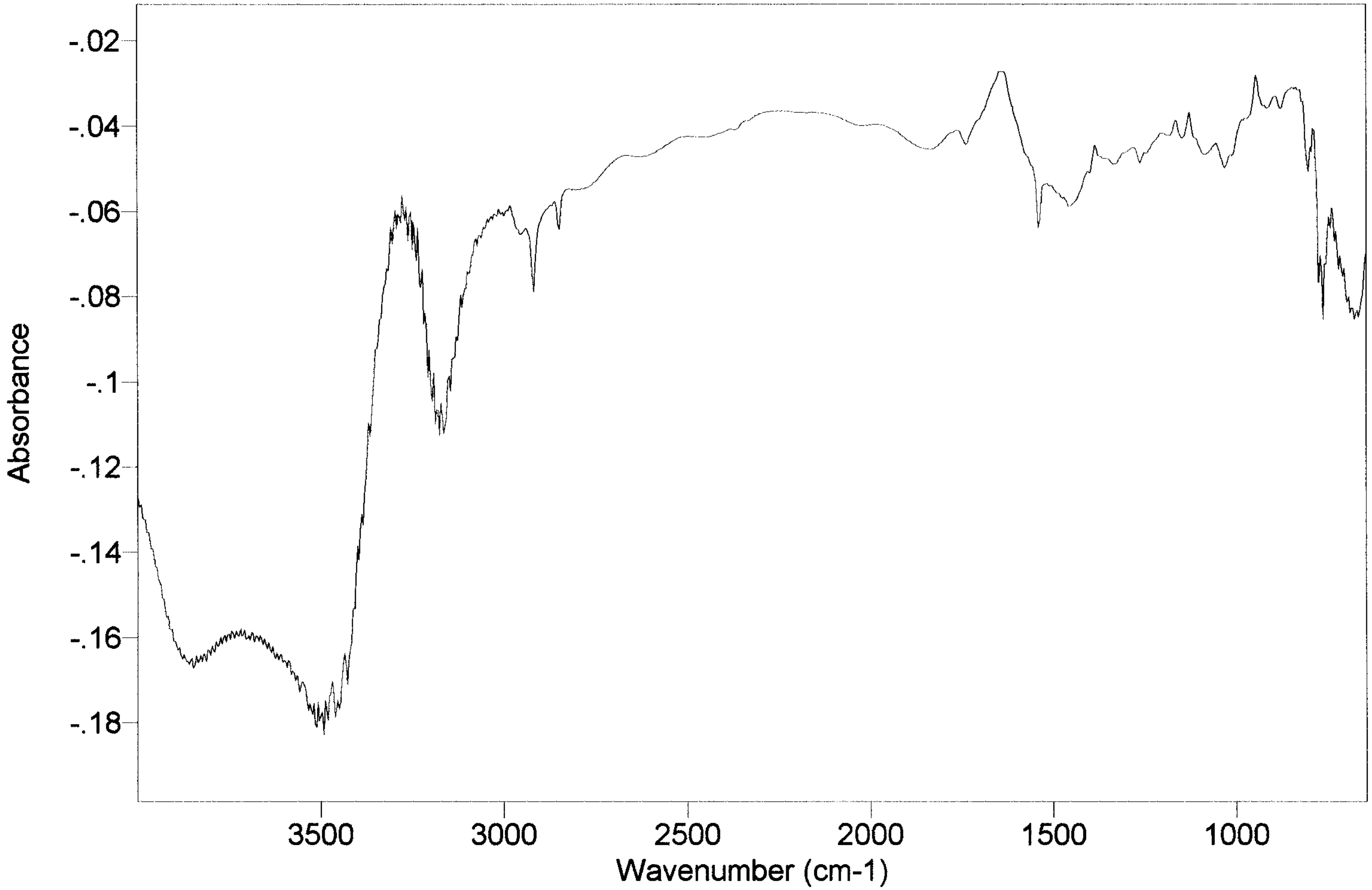


Figure 4.53: sample 11 from 4/29 - water in can - curtains

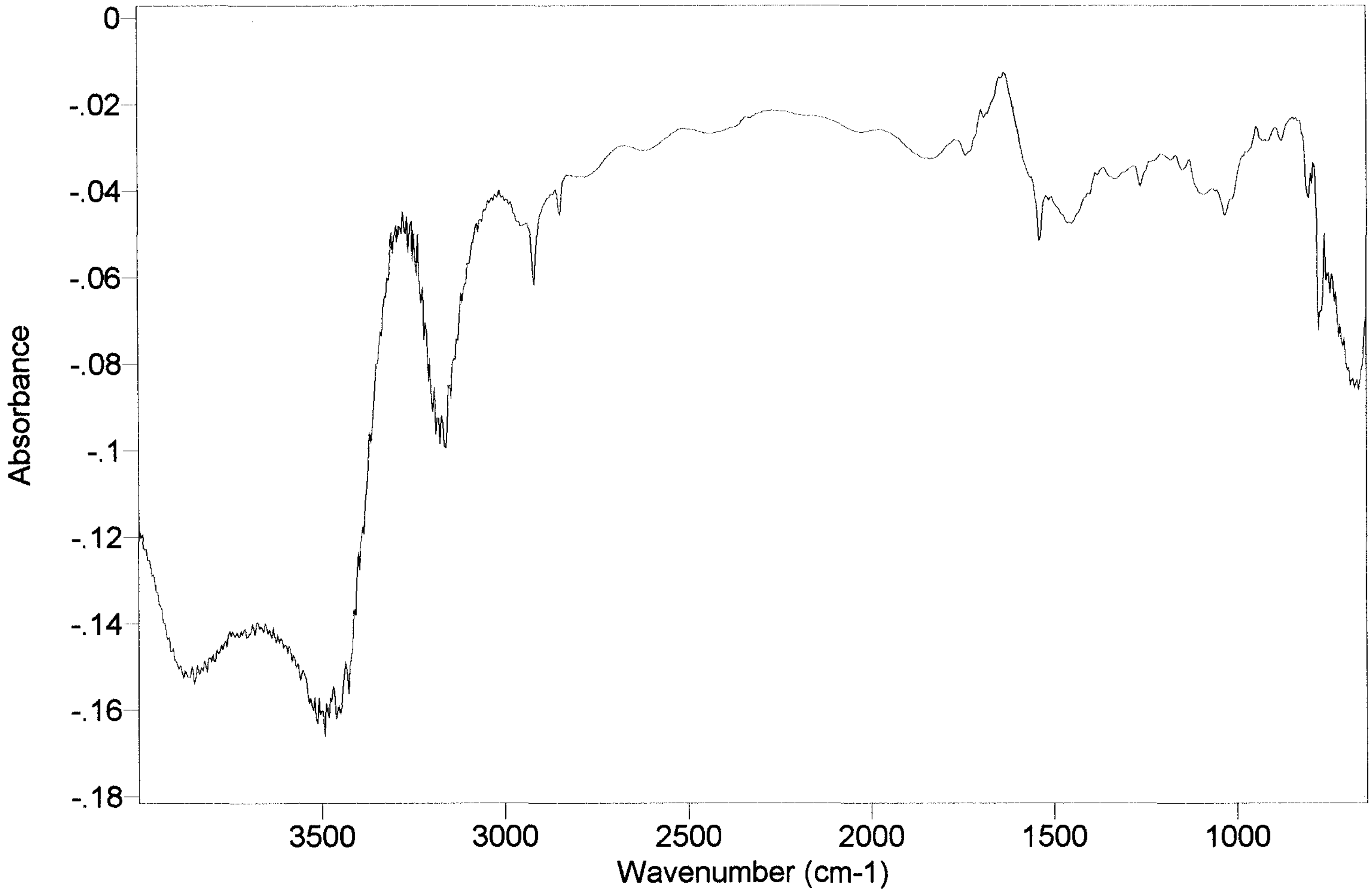


Figure 4.54: **sample 12 from 4/29 - water that was in can - carpet**

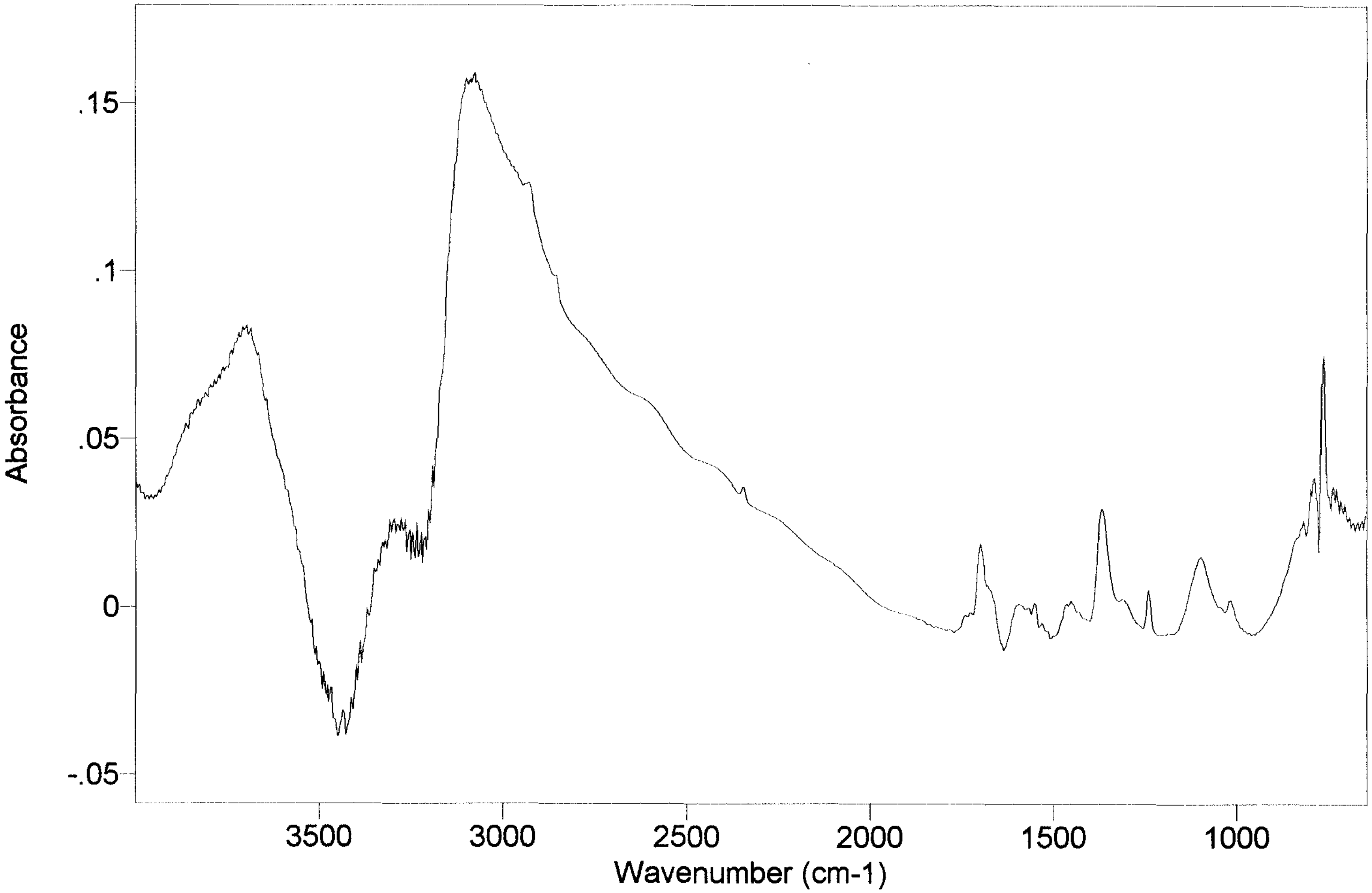


Figure 4.55: **sample 15 from 4/29 - water extracted - foam of cushion**

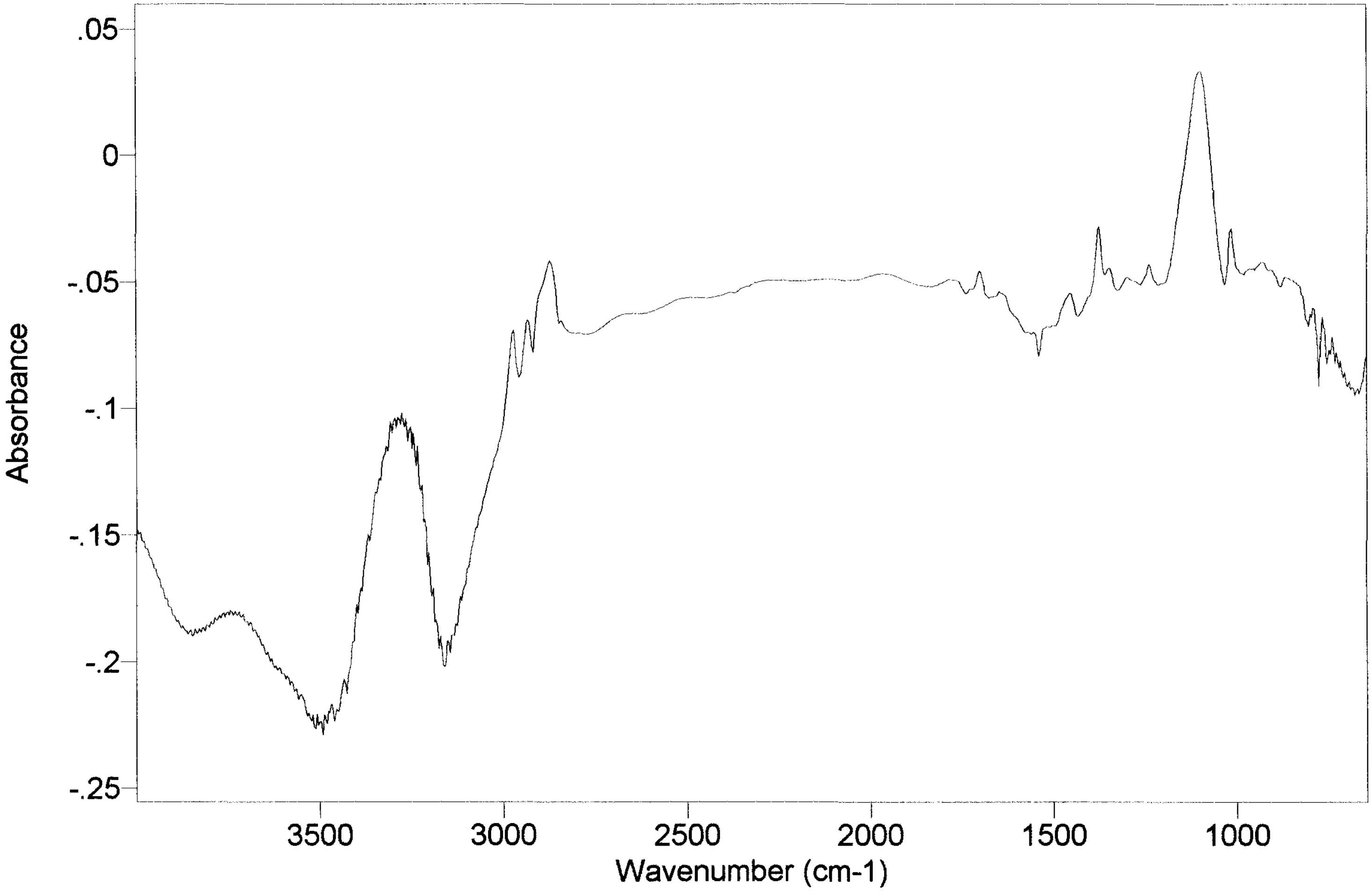


Figure 4.56: **sample 16 from 4/29 - water extracted - foam of cushion**

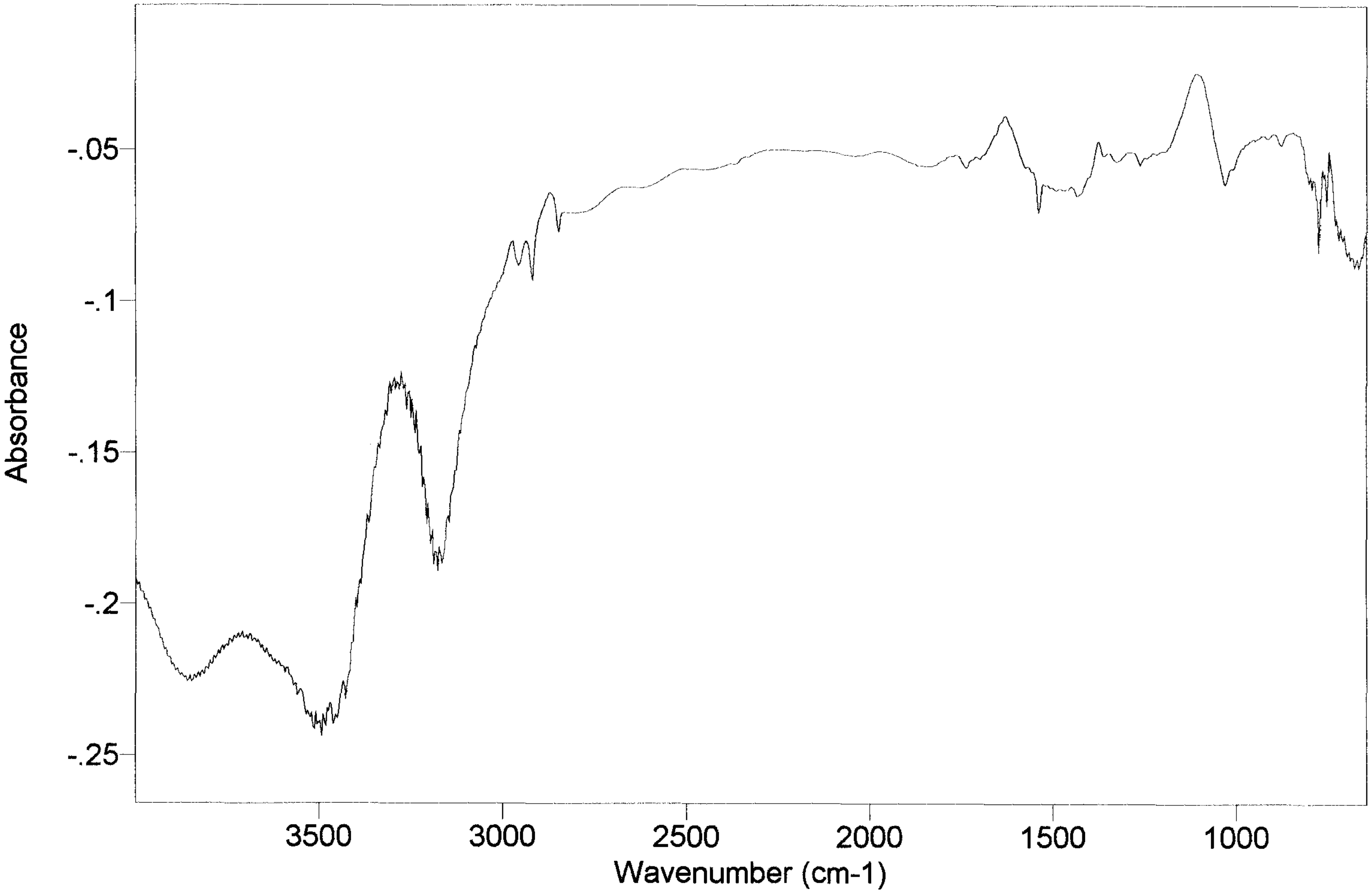


Figure 4.57: **sample 17 from 4/29 - water extracted - fabric of cushion**

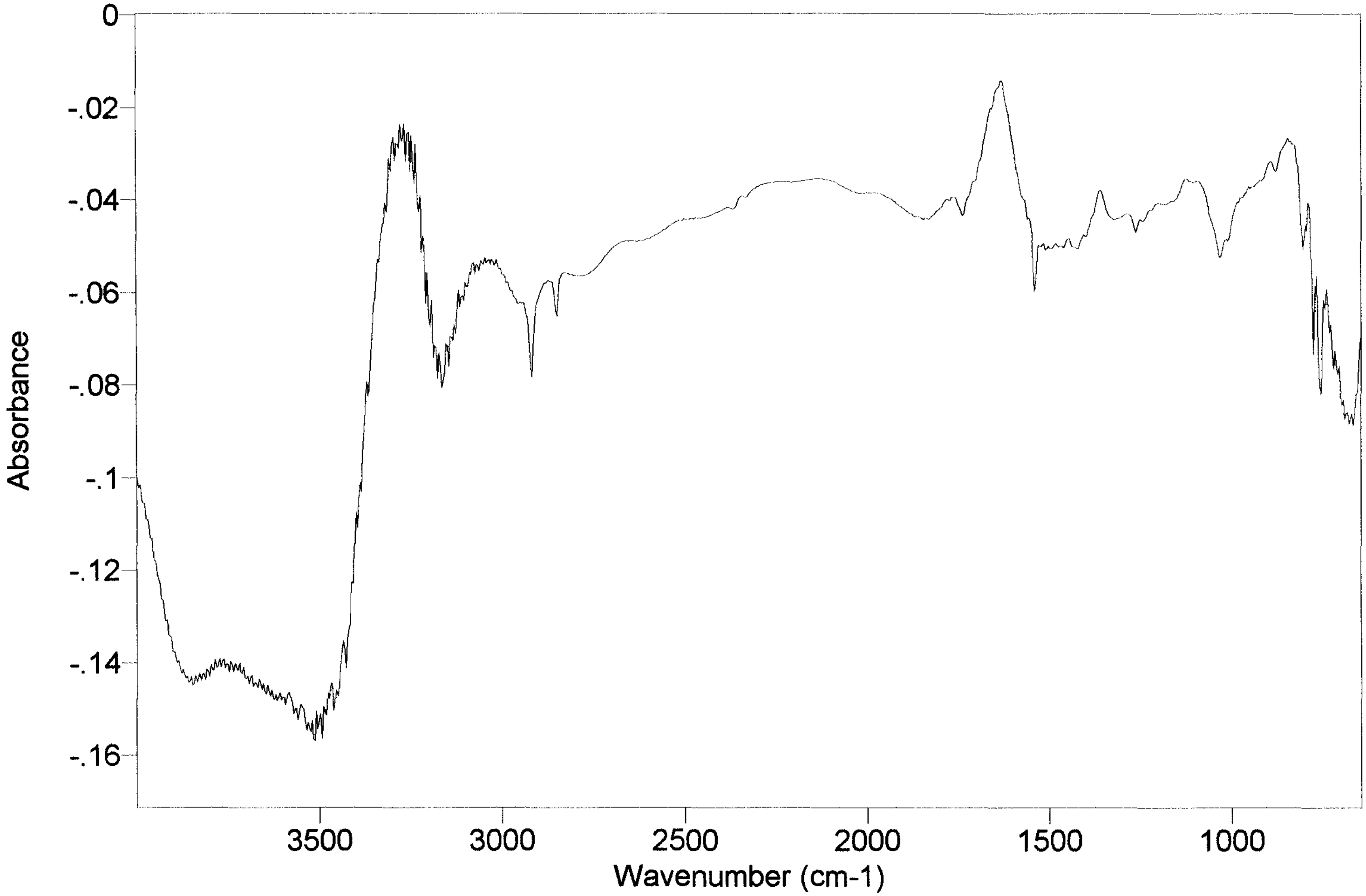


Figure 4.58: sample 18 from 4/29-water that was in can-free standing H_2O

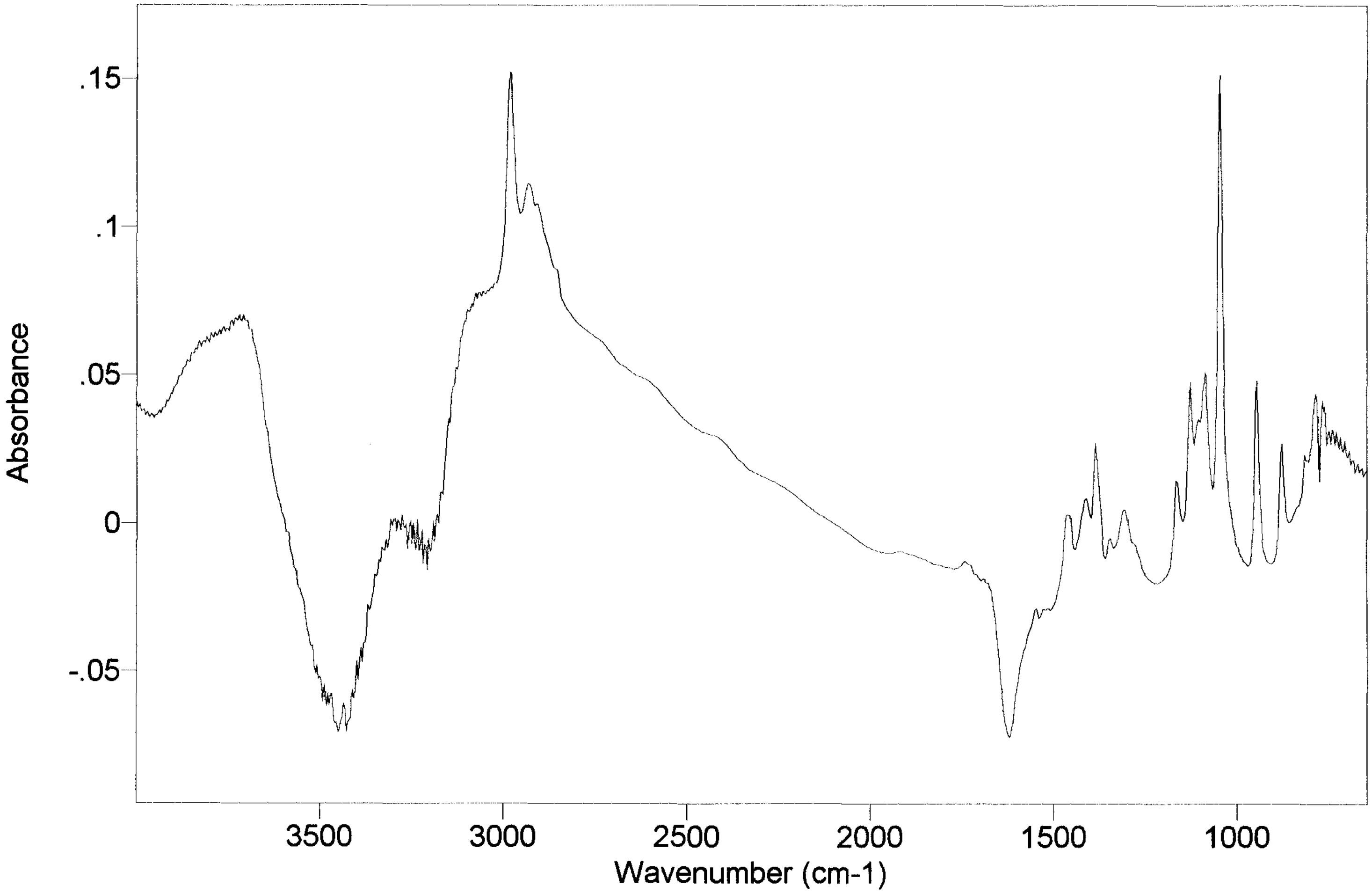


Figure 4.59: **sample 19 from 4/29-water that was in can-carpet**

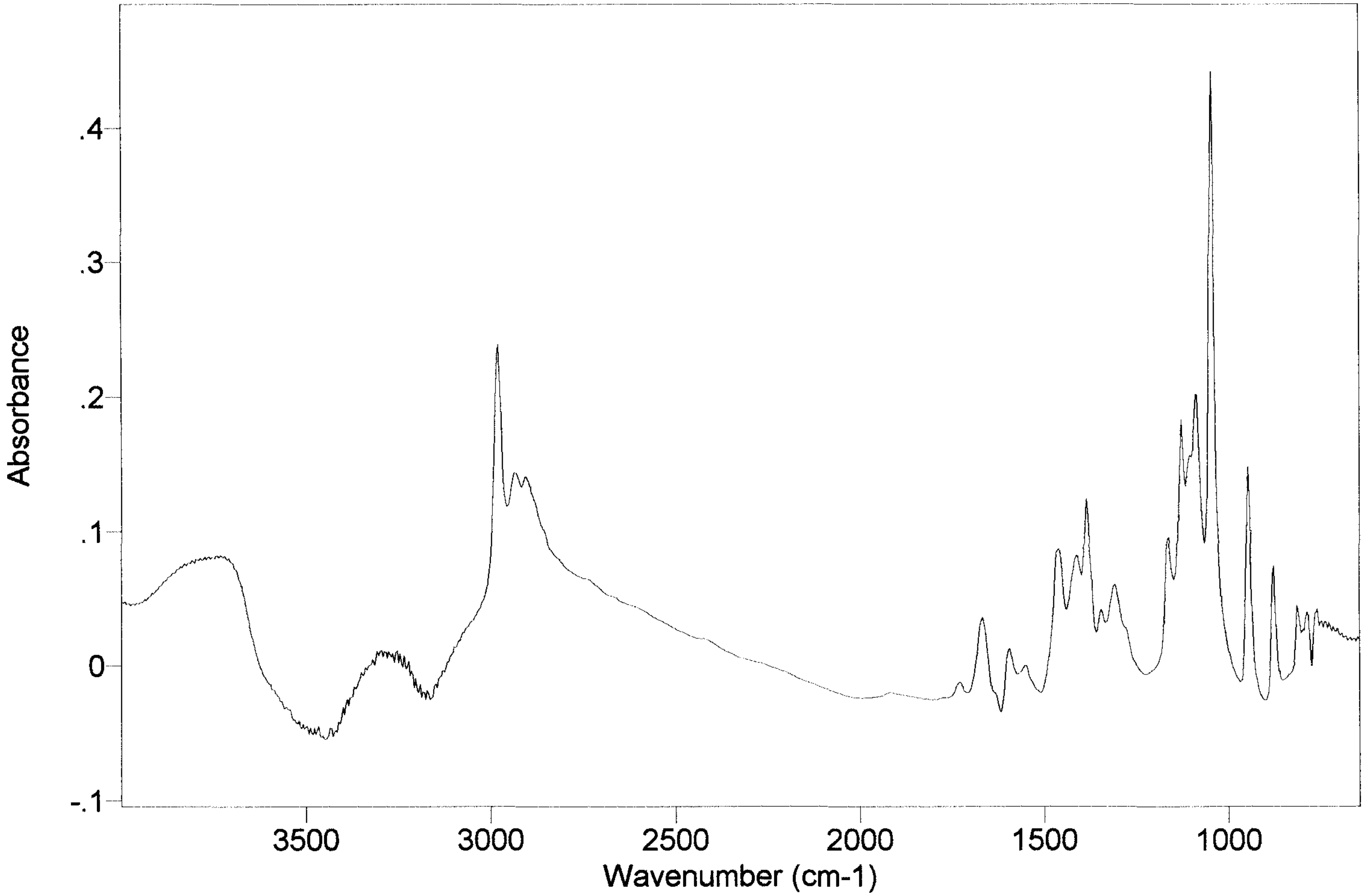


Figure 4.60: **sample 20 from 4/29-water that was in can-carpet**

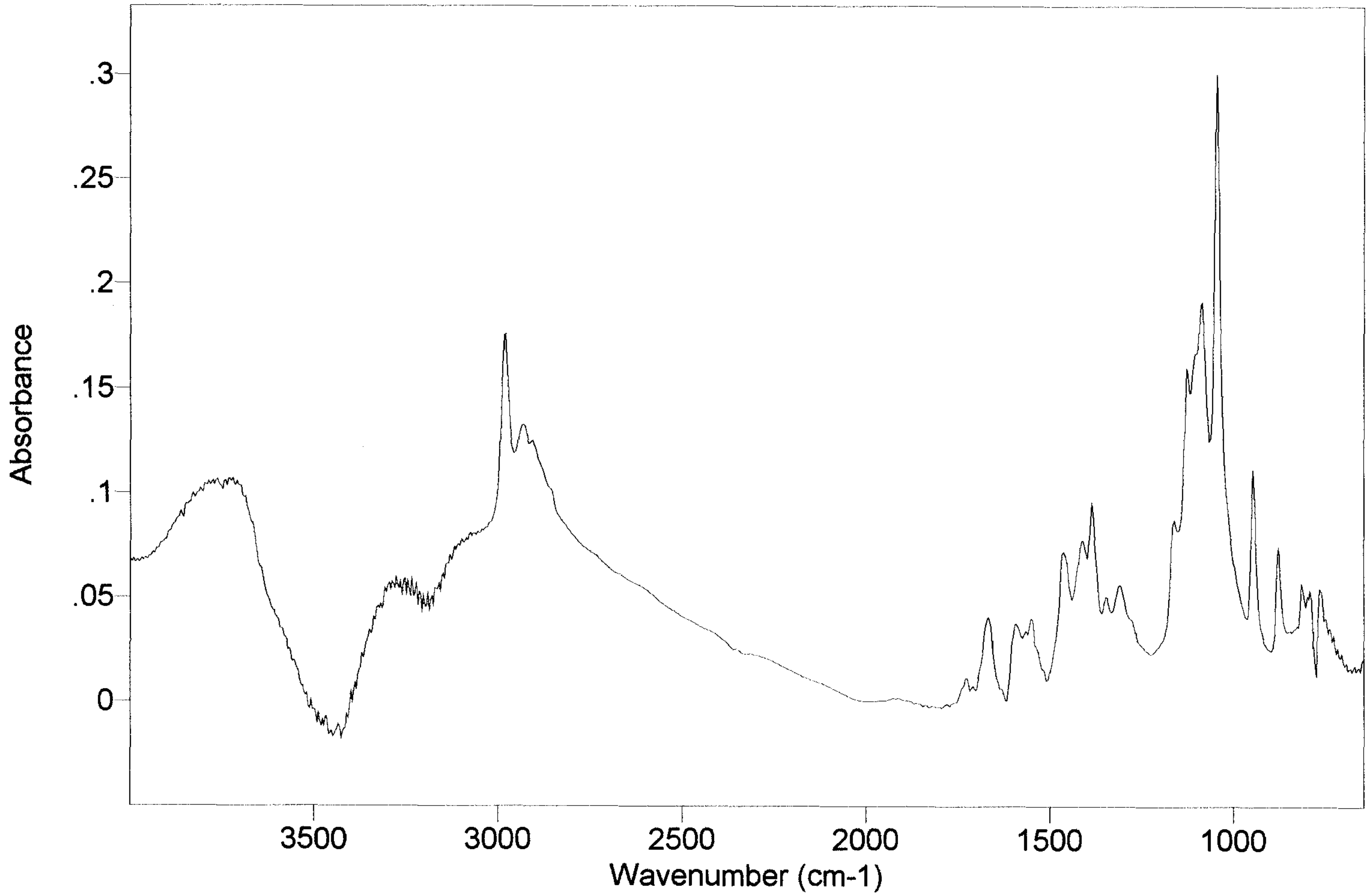
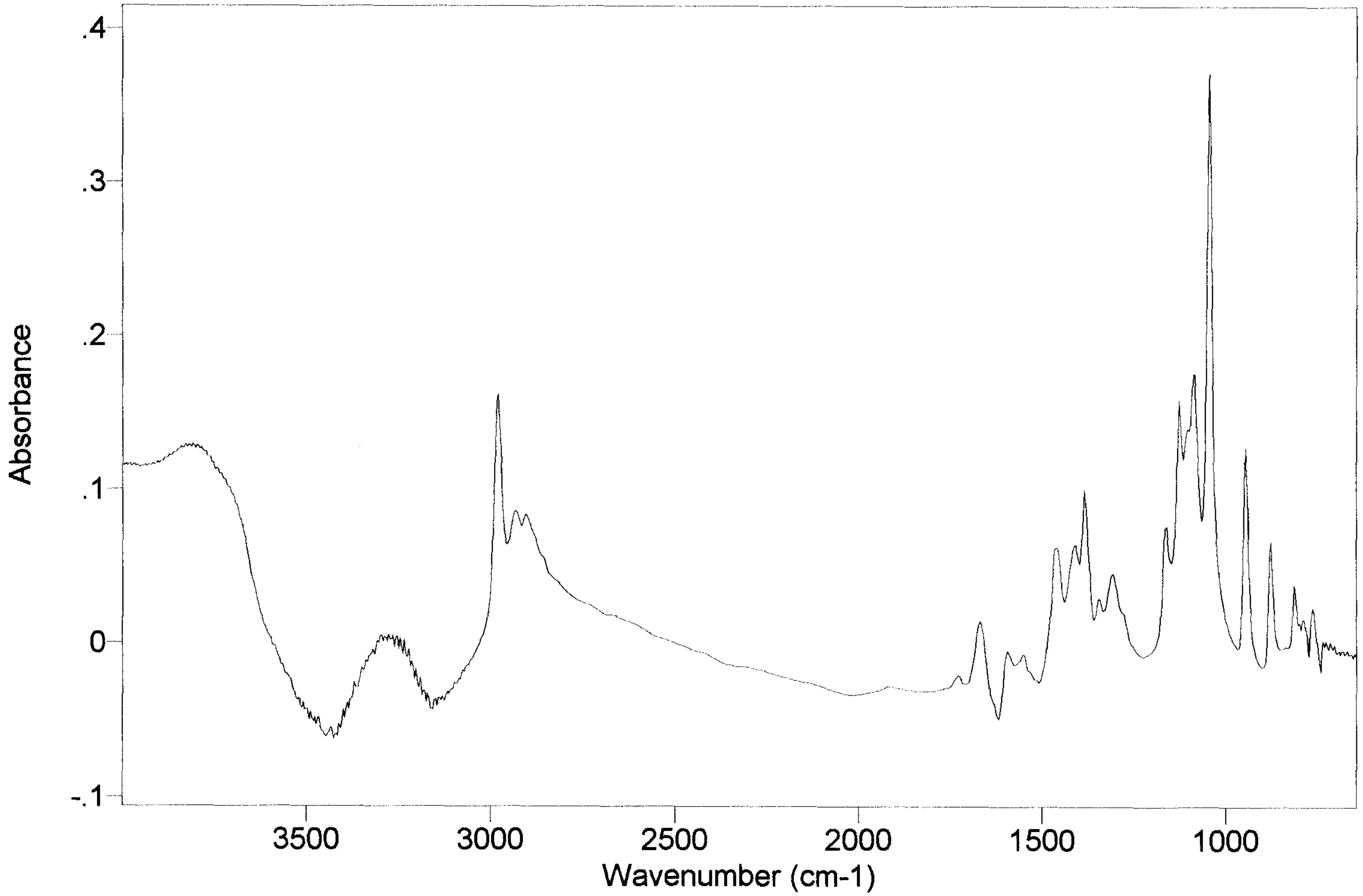


Figure 4.61: **sample 21 from 4/29-water that was in can-carpet**



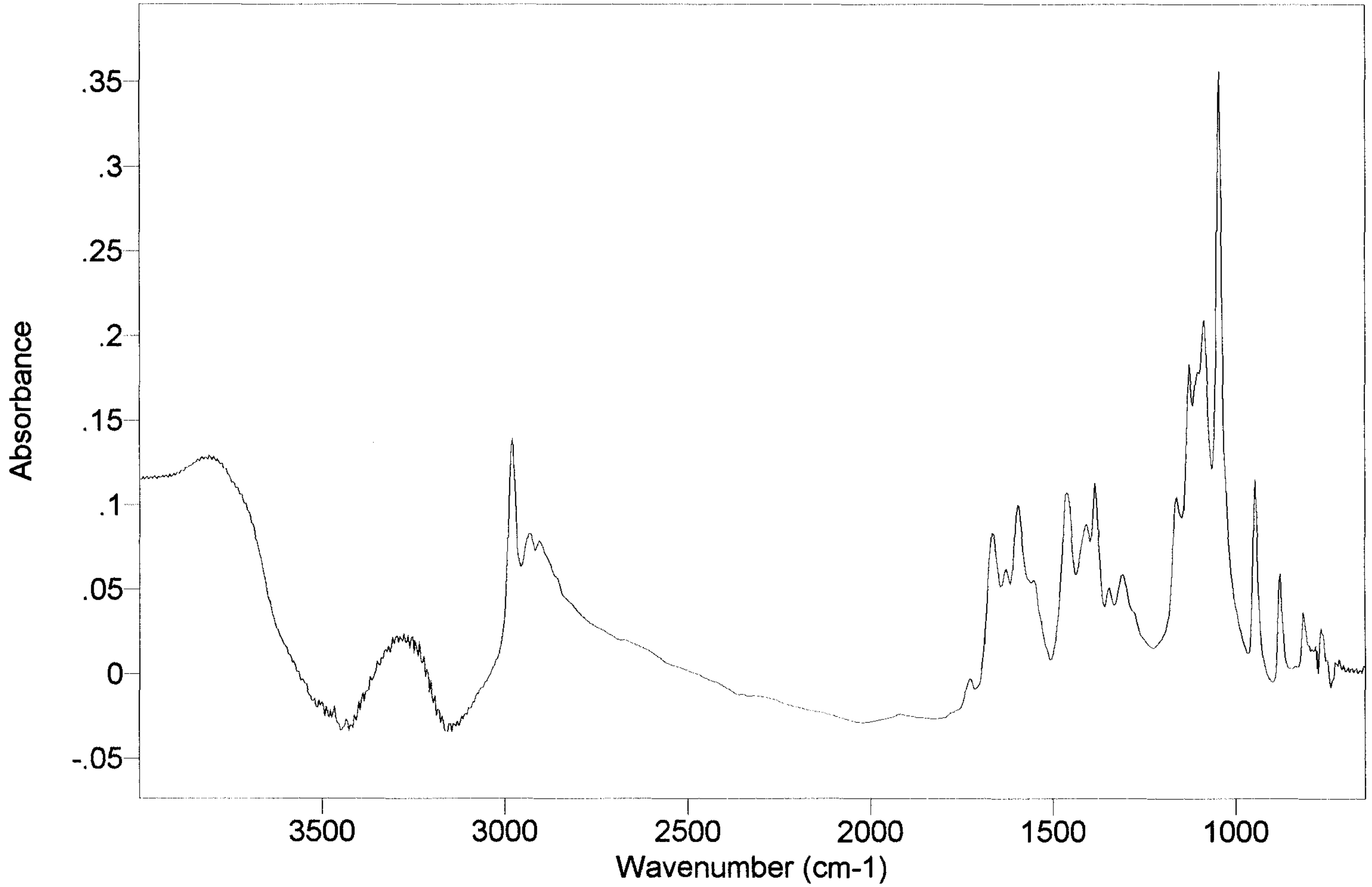


Figure 4.62: **sample 22 from 4/29-water that was in can-carpet**

Chapter Five

Discussion and Conclusions

The concentration gradient curve was done so that an estimate of detection limits could be made and an approximate concentration of unknown alcohols could be determined. The determination of the presence of accelerant were based on those. The percent recoveries were calculated based on the 9 % v:v solution which gives the maximum recoverable since 10 mL of accelerant and 100 mL of water were used.

On the concentration gradient graphs, a linear regression line is shown with the line equation and the R^2 value. The R^2 values range from 0.9676 for ethanol at 1086 cm^{-1} to 0.9996 for methanol. The graphs also show that the strength of absorption is directly related to the concentration.

As can be seen in Table 4.3, the accelerant is still able to be detected after as long as 240 sec. of burning. For each of these burns, the percent recovery was calculated. For the graphs corresponding to Table 4.3, a linear regression line is shown with the line equation and the R^2 value. The R^2 values range from 0.8931 for isopropanol at 1164 cm^{-1} to 0.9569 for methanol. The R^2 values were not expected to be linear. There are several factors, such as intense heat, that have an effect on the accelerant. The R^2 value is given only to show that burn time is not the only factor acting upon the accelerant while burning. From the line equation, the detection limit can be calculated. For each accelerant, the limit would be around 240 seconds. Further inquiry in this project should look at extending burn times past this time to determine the exact limit. In Table 4.3, a second list of values was included for methanol. After examining the 120 second point, it was determined to be an erroneous value and therefore dropped. The graph that is shown reflects this point not being included. It changed the R^2 value from .6497 to .9569.

In these burns, only a few milliliters of accelerant were used. The typical arsonist will use a considerable amount of accelerant which would only make it easier to detect.

Third Stage Burns

The results of these burns were qualitative. The purpose behind these burns was to determine if the accelerant could be detected.

The peaks found in samples 2-4, 1017 cm^{-1} and 1112 cm^{-1}, correspond to those of the 5.0% v:v methanol spectrum.

The peaks that were found in samples 5 and 8, 1017 cm^{-1} and 1112 cm^{-1}, corresponded to those of methanol. Therefore, unknown A was concluded to be methanol. However, when a 5.0% v:v solution of unknown A was run, it shows the presence of both methanol and ethanol. Unknown A was 4:1 methanol:ethanol. There is the loss of the ethanol peaks in the samples. Although the exact composition of the unknown accelerant was unable to be determined, the presence of an accelerant was still detected. Further inquiry into this project might look at the interaction of methanol and ethanol, both before and after being used as an accelerant.

Samples 10 has two peaks, 1165 cm^{-1} and 1128 cm^{-1}, that correspond to isopropanol. Sample 11 has one peak, 1129 cm^{-1}, that corresponds to isopropanol.

Samples 15 had peaks at 1016 cm^{-1}, 1375 cm^{-1}, and 1453 cm^{-1} that best corresponded to both methanol and acetone. Samples 16 and 17 did not have peaks that corresponded to any of the accelerants. Therefore, unknown B was concluded to be made up of acetone and methanol. Further analysis proved this conclusion correct. The fact that only one sample had peaks that corresponded shows the importance of taking several samples from each area.

Samples 18-22 each showed four peaks, 1045 cm^{-1}, 1086 cm^{-1}, 1126 cm^{-1}, and 1164 cm^{-1} that correspond to ethanol and isopropanol. There did not appear to be any effects of interaction between these accelerants which were encountered analyzing unknown A.

The results of the vacant house burns are very promising. However, further inquiry into this project should deal with a larger scale burn. When the fires were extinguished, a minimal amount of water was used. Because of this, the detection limits were not tested. The Youngstown Arson Bureau is willing to help with any further burns that need to be done in this project. Time limitations could not allow for a full scale burn to be done in time to be included in this project.

For the samples that were too bulky to be analyzed, a distillation method should be looked at. The evidence cans are sealed air tight. The cans could be heated to the boiling point of these low molecular weight alcohols and puncturing the lid of the can with the distillation apparatus to allow for the collection of the fraction coming off. This can be diluted with water to give the desired volume to use in the cell reservoir.

In this study, Attenuated Total Reflectance Spectroscopy was used as a way of analyzing arson accelerants that are water soluble. According to Bertsch in his article, few laboratories routinely test for accelerants that are not petroleum based and there is little evidence that current analytical methods are capable of dealing with water-soluble accelerants. ATR has proven to be a method that is well suitable for the detection of water-soluble accelerants. There is little time needed for sample preparation. The concentration gradient curve for each accelerant show that the detection limit is lower than this study has tried. Further inquiry into this project should look at finding the lowest concentration still detectable not only by the concentration gradient method but also by burning.

The area of arson investigation is constantly changing with the introduction of new technology. Most new methods still require a lot of human time whether in sample preparation or analysis. Further inquiry into this project should look at expanding the methods proven here in to other materials, such as cloth or cushions. As technology makes it easier to detect petroleum based accelerants, the arsonist will find new ways to beat the system. Attenuated Total Reflectance Spectroscopy is a relatively cheap, easy method that is capable of dealing with accelerants that most new methods are unable to deal with.

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