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Evaluation of polymer coated attenuated total reflection (ATR) elements for the analysis of organic compounds in aqueous solution

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EVALUATION OF POLYMER COATED ATTENUATED TOTAL REFLECTION (ATR) ELEMENTS FOR THE ANALYSIS OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTION

BY

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This dissertation is dedicated to my wife Ozlem and my son Stephen.

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A significant limitation of ATR/FTIR for the analysis of aqueous solutions is the relatively high bulk concentration of analyte required. One approach to improving the detection of an analyte is to incorporate a thin polymeric phase at the surface of the ATR element. The purpose of the polymeric phase is to extract the analyte of interest and concentrate it within the depth of penetration of the evanescent wave. Utilizing a very high molecular weight poly(vinyl chloride) phase the time necessary to reach equilibrium for a 0.05% (v/v) nitrobenzene in a 1.5% (w/v) methanol/water solution was over 60 minutes. A study was undertaken to determine if incorporating a plasticizer into the polymeric phase reduces the time required to reach the maximum level of absorbance achieved for the analyte. Specifically, the ability of phases which are mixtures of PVC and chloroparaffin plasticizers to concentrate analytes from aqueous solutions has been investigated. The results indicate that incorporating chloroparaffin into a PVC phase reduces the time required to reach the maximum absorbance for the analyte in an aqueous solution containing 1.5% methanol by approximately

45%. The addition of chloroparaffin also results in an increase in the absorbance observed for the analytes investigated in this study.

Commercially available untapered and tapered chalcogenide fibers have been coated with poly(vinyl chloride) with plasticizer. These coated fibers were exposed to various analytes. All organic analytes provided readily detectable signals with the coated fibers but were not observable when the aqueous solution was sampled with the use of uncoated fibers. The results confirm the advantages of using a polymer coating to concentrate the analyte and reduced the water background for detecting non polar organic solutes in aqueous solutions.

CHAPTER I

INTRODUCTION

1.1 Introduction

Attenuated Total Reflectance (ATR)/ Fourier Transform Infrared (FTIR) Spectroscopy is a well established surface spectroscopic technique.[1-3] The basis of the technique is that infrared energy must be totally internally reflected through the ATR element in order for a measurement to be made using ATR/FTIR. As light passes from a higher refractive index material to a lower refractive index material the light is refracted at the interface of the two materials. If the angle of incidence of the light that is traversing through the more highly refractive material is increased, the angle of the refracted energy is increased as well. If the angle of incidence is greater then the critical angle the light is totally internally reflected through the material with the higher refractive index (see Figure 1.1). Some of the energy at the interface penetrates into the lower refractive media. The light that penetrates into the lower refractive media is referred to as the evanescent energy. The depth of penetration of the evanescent wave is dependent upon the wavelength of light, the refractive index of the two materials, and the angle at which the light enters the higher refractive media.[1] The depth of penetration can be calculated using Equation 1.1.

$$dp = \lambda / (2\pi[\sin^2\phi - (\eta_a/\eta_b)^2]\}^{1/2} \qquad 1.1$$

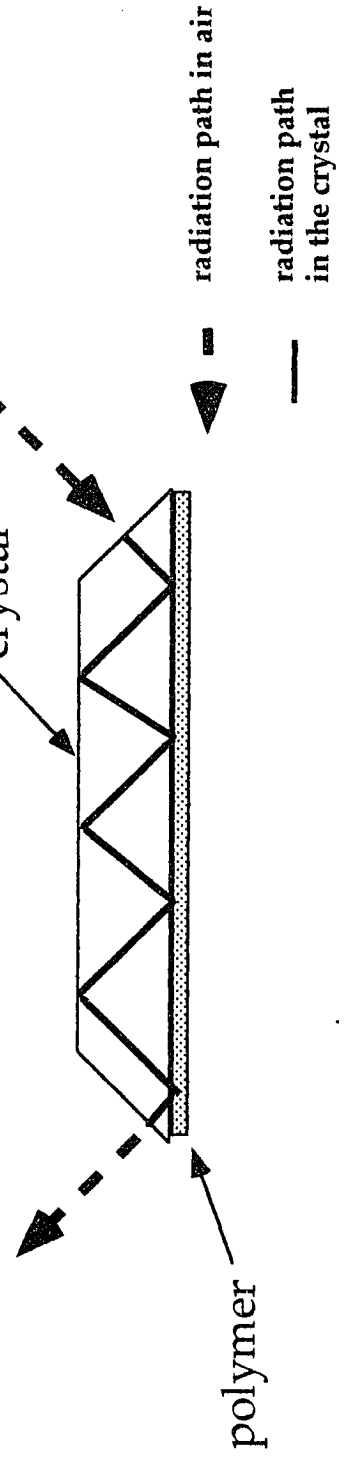

Figure 1.1 Attenuated total reflectance of infrared energy through the element

where λ is the specific wavelength in the media with the higher refractive index, ϕ is the angle of incidence of the light entering the higher refractive media, and η_a and η_b are the lower and higher refractive indices, respectively. The energy of the evanescent wave as it penetrates into the lower refractive material decreases exponentially. The exponential decrease in energy can be expressed as:

$$E = E_0 * e^{-(x/dp)} \qquad 1.2$$

where E represents the energy as a function of the distance from the crystal, E_0 represents the initial quantity of incoming energy at the interface, x is the distance from the ATR element, and dp is the depth of penetration. If the lower refractive material is an infrared absorber then some of the evanescent energy will be attenuated. By dividing the energy spectrum of the ATR element obtained with a crystal in contact with an infrared absorber by the energy spectrum obtained using an uncoated crystal produces the infrared spectrum of that material. One advantage of this analytical technique is that absorption spectra can be obtained with minimal sample preparation. Absorption spectra can be obtained of solids, such as fabrics, emulsions, and liquids using appropriate ATR devices.

The majority of ATR measurements are conducted inside the sample compartment of an FTIR using an ATR accessory. The typical path at which the infrared energy travels as it goes through a conventional ATR accessory is shown in Figure 1.2. Infrared optical fibers, which are essentially ATR elements, have become available recently. The theory of ATR as applied to fibers is essentially the same as for conventional elements. However, the infrared energy that enters into the fiber has many different launch angles

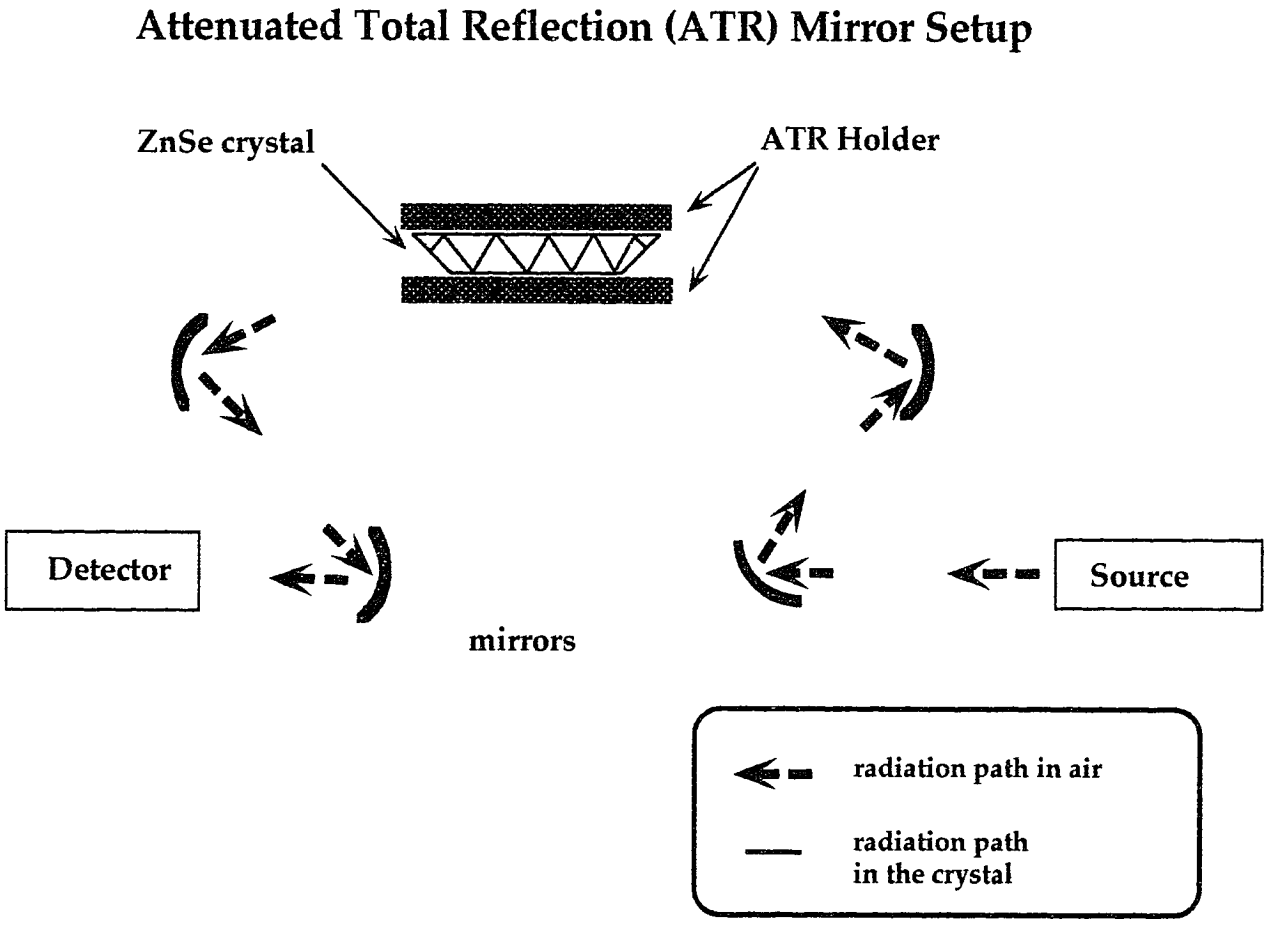

Figure 1.2 Experimental setup for Attenuated Total Reflection (ATR) using a conventional ATR element.

that are greater than the critical angle and therefore are totally internally reflected. Consequently, the depth of penetration will vary because of the many different angles of infrared energy which are entering into the fiber. The effective depth of penetration is determined by integrating over all possible launch angles entering into the fiber. The amount of energy entering into the fiber is measured by the numerical aperture (NA) which can be expressed as

$$NA = (\eta_1^2 - \eta_2^2)^{1/2} \qquad 1.3$$

where η_2 represents the lower refractive index cladding of the fiber and η_1 represents the higher refractive index core. Infrared fibers with a high NA accept more light than fibers with a low NA. Therefore, a fiber with a high NA will accept infrared radiation introduced at greater angles.

1.2 Application of infrared optical fibers for chemical analysis

There has been much interest in the use of infrared optical fibers for analytical chemical applications.[4-9] Two of the advantages of using infrared fibers over conventional ATR elements are: 1) they have more reflections per unit length, and 2) they are well suited to applications requiring remote and in situ detection. Infrared fibers are made from several materials including chalcogenide glasses,[10-13] halide glasses,[14] fluoride glasses,[15] and polycrystalline oxide glasses.[16] Each of these types of infrared fibers has some limitations.[17] For example, Karari-Barak and Katzir[18] evaluated the effects of water adsorption and desorption on infrared transmitting silver halide fibers. Their findings indicate that humidity in the air results in water being adsorbed onto silver halide fibers, which attenuates the transmission energy

through the fiber. These authors determined that the fiber was totally saturated within a few months. They also showed that this process is reversible by heating the fiber to 130°C. Artjushenko et al. studied the effect of aging on various extruded polycrystalline fibers for up to one year.[19] Barkay and Katzir investigated the mechanical resistance of silver halide fibers.[20] Experiments were performed by bending the fiber between two wheels that allowed a specified bend to be placed in the fiber. A CO_2 laser was employed as a source and a thermal detector was used to measure the magnitude of energy reaching the detector. The fiber was moved from a straight position (no bend) to a bend of 90 degrees and then back again. After this was performed several times the intensity of energy emerging from the fiber was measured. Their results indicate that the fiber tends to break more easily if small radius wheels are used to bend the fiber than if a large radius wheel is used. Moser et al. also discussed the mechanical and optical properties of unclad silver halide fibers as well as the use of these fibers as IR transmitting waveguides. These waveguides are of interest since they transmit CO_2 laser radiation for medical procedures.[21]

Bornstein et al. developed a chalcogenide bitapered optical fiber.[22] Tapering increases the number of reflections through the fiber, therefore improving sensitivity. The tapered sections were introduced into the fiber by heating a section of the fiber and then pulling the two ends apart. Tapering the fibers improves the detection of analytes in dilute solutions for weakly absorbing compounds by two orders of magnitude compared to using a typical straight fiber. Lowry et al. also discuss the signal enhancement provided by the tapered fiber method.[23] The authors demonstrate the use of a tapered fiber cell capable of containing a small sample volume of liquid that fits directly into the sample compartment of an FTIR. Spectra were obtained

using a special accessory that concentrates the energy into and out of the sampling device containing the tapered fiber with the use of gold concentrating mirrors. The sample volume required for an analysis is very small (80-100 μl). In fact, the authors suggest that the tapered area is so sensitive, data can be obtained for sample volumes as low as 10 μl. There are several disadvantages to using these tapered fibers. First, the tapered area is extremely delicate, and therefore, careless sample insertion or rough handling can damage the fiber. Second, since the body of the liquid sample holder is made out of polypropylene, measurements cannot be made if the solution will dissolve or react with the polymer holder.

Several papers in *Selected Papers on Infrared Fiber Optics,* edited by Harrington, discuss and evaluate three types of fibers, the application of fibers and infrared hollow waveguides.[24] Seitz reviewed and discussed the different types of infrared fibers that are available.[25] In his review, Seitz also addresses the specific uses of mid infrared transmitting fibers in the area of analytical chemistry. There are two ways in which infrared fibers can be used: as a means of getting the energy to a remote sensor, or as the actual sensor itself.

Remote measurements of gaseous carbon dioxide and methane have been made by Pruss et al. using fluorozirconate fibers.[26] The authors evaluated these fluorozirconate fibers for their spectral attenuation, and mechanical and environmental durability. These fibers were used to bring infrared energy to a gas cell and then to collect and return the infrared energy to the FTIR instrument. Pruss[27] also used these fibers to monitor anesthetic gases such as enflurane and N_2O and discussed achievable sensitivities using fibers coupled to FTIR systems. Another example of using a remote gas cell to improve the sensitivity of a measurement is the use of a multipass cell by

Artjushenko et al.[28] The authors utilized both chalcogenide and polycrystalline fibers to bring energy to and from the multipass gas cell. To further enhance sensitivity, a tunable diode laser was used as the infrared source. The analytes investigated using this method were gaseous ammonia, water vapor, and carbon monoxide. In a similar experiment, Sagese et al.[29] measured other gaseous analytes (methane, carbon dioxide, and carbon monoxide) using a double pass reflective gas cell.

Several authors have reported methods that have utilized one fiber to carry the infrared energy to a conventional ATR element and another fiber to return the emerging energy to the detector of an FTIR instrument. The advantage of using the conventional ATR element as the sensor is that one is not limited by the chemical, mechanical, and thermal limitations of the fiber. Burger et al. used mid-infrared fiber optic probes in high pressure reactor systems.[30] A circular internal reflectance element was embedded in the reactor system and the chalcogenide infrared fibers were used to carry the energy to and from the ATR element. The temperature and pressure of the reaction can be controlled thereby allowing the measurement of a specific reaction in situ (e.g., kinetic experiments). The cobalt catalyzed transformation of 1-hexene to heptaldehyde was monitored at a pressure of 1000 psi and 90°C for approximately two hours. Burger et al. also utilized a bifurcated chalcogenide fiber optic probe coupled to a single ended ATR element. This type of probe was used in a glass reactor or as an immersion probe. It was used to measure relatively small volumes of liquids (10-115 ml). Measurements were taken using the immersion probe of acetone/water mixtures and a spectrum of heparinized whole blood.

Another way in which these infrared transmitting fibers can be used include infrared diffuse reflectance spectroscopy. One of the fibers can be used

to carry the incident radiation to the sample and a second fiber can be used to collect the infrared radiation and bring it to the FTIR instrument. Druy et al. used this optical arrangement and an x,y translation stage to position the fibers to maximize the energy reaching the detector.[31] They studied the curing of polymer coatings on an aluminum substrate using this approach. The extent of the curing of the polymer and the presence of any residual solvents which remain in the polymer were determined. The polymer coating investigated by these authors was a substrate coated with a thermally cured melanine epoxy resin. In these experiments it was important to monitor if the epoxy cured properly. Undercured epoxy is not resistant to water and retains some of the residual solvent. Overcuring, on the other hand, causes the polymer to be brittle, hard, and inefficient in adhering to the substrate surface. Driver et al. developed a remote high pressure liquid cell that is connected to a conventional FTIR bench through the use of infrared fibers.[32] The high pressure cell has a variable pathlength and uses lenses to create a collimated optical space within the cell.

Infrared fibers have been used as the sensor for monitoring the reactions of polymers. Druy and Elandjian embedded a sapphire fiber in a polymer which was cured in an autoclave.[33] A heavy metal fluoride fiber was used to bring incident radiation to the polymer coated sapphire fiber and another heavy metal fluoride fiber was used to direct the emerging energy to an MCT detector. The sensor was then used to monitor the curing of a thermosetting epoxy. Spectra of the thermosetting epoxy were collected over a temperature range of 20°–244 °C. Compton et al. also investigated another thermosetting epoxy using a single chalcogenide infrared fiber.[34] The sensor from the fibers was constructed by removing a 3 – 6 cm section of the clad fiber and placing the thermosetting polymer onto the sensor region of the

fiber. The thermosetting polymers investigated were NARMCO 5208 epoxy/graphite and graphite/PMR-15. The polymer formulation was placed onto the sensor region and heated at a specific rate. Curing of the polymers was monitored as a function of temperature.

Böck et al. used a zirconium fluoride fiber to measure D_2O in blood.[35] The analyte, D_2O, was monitored because it assists physicians in evaluating extravascular lung water, cardiac output, and total body water. A catheter was constructed to fit directly into an arterial blood vessel. The catheter tip was constructed so that a single zirconium fluoride fiber was situated 0.1 mm from a gold reflection plate. This experimental setup sent infrared radiation down the tip of the catheter and reflected it back into the fiber. These catheters allowed for the study of D_2O kinetics in blood. Rodrigues and Sigel used a chalcogenide sensor to qualitatively and quantitatively determine ethyl alcohol content in alcoholic beverages.[36]

Infrared fiber sensors were used by Swairjo et al. to measure the concentration of urea in aqueous solution.[37] Urea is a key end product in cellular metabolism and thus an important analyte to monitor. They also measured the hydrogen/deuterium exchange of bacteriorhodopsin, a light driven proton pump from halobacterium halobium. The use of an infrared fiber optic sensor allows for continuous monitoring of the hydrogen/deuterium exchange of peptides groups. De Rochemont et al. developed an infrared fiber optic neurotoxin biosensor using a biologically active coated chalcogenide bitapered FiberCell.[38] The fibers were tapered to improve the interaction of the evanescent wave with the sample. The probe cells were initially silanized and then a phospholipid membrane containing nicotinic acetylcholine receptors was incorporated onto the silanized surface. The fiber cells were then subjected to various concentrations of toxins (d-

tubocurarine and alpha bungarotoxin). The results indicated that both toxins were able to change the conformation of the nicotinic acetylcholine receptors. These results demonstrate that coated tapered fibers can be used as a means for detecting toxins.

1.3 Detection of analytes in aqueous media by using coated ATR elements

The major disadvantage in making aqueous measurements using ATR/FTIR is that water absorbs strongly in the mid infrared region. One approach to improve the detection of analytes in aqueous solution using ATR/FTIR is to concentrate the analyte within the depth of penetration of the evanescent wave. The concentrating media which extracts the analyte of interest from the aqueous solution is a polymeric coating that is placed on a conventional ATR or a mid infrared optical fiber. The purpose of coating the ATR element is to enhance the sensitivity of the measurement. Meuse and Tomellini demonstrated that coating a ZnSe ATR element with a PVC polymeric phase resulting in the extraction of an analyte from aqueous solution.[39] They used nitrobenzene, ethylbenzoate and benzophenone as test analytes for their experiments. Heinrich et al. also demonstrated that casting a polymeric phase onto a ATR element increases the sensitivity of the measurement.[40] The primary phases that were investigated were polydimethylsiloxane (PDMS), trichloroctadecylsilane (TCOS), polyethylene, and poly-(ether-esteramide). These phases were used to detect various chlorinated organic compounds which are environmentally important (e.g., chloroform, methylene chloride). Other researchers have also used polymer coated infrared optical fibers to extract analytes from aqueous solutions. Krska et al. used silver halide fibers coated with low density polyethylene to detect chlorinated hydrocarbons in aqueous solution.[41] Glatkowski et al.

infiltrated a nylon membrane with zeolite and used it to coat a silver halide fiber badge. The fiber badge was used to detect gaseous benzene and dichloroethylene.[42] The coated fiber was placed into a polyethylene holding cell and exposed to benzene and dichloroethylene vapors for a specific amount of time. After a specified time had been reached the cell was placed into the sample compartment of an FTIR instrument and a spectrum was obtained allowing the two analytes to be qualitatively distinguished from one another. Taga et al. chemically modified unclad chalcogenide fibers by immobilizing 3-aminopropyltriethoxysilane to the fiber surface.[43] Once the fiber was silanized, glutaraldehyde was covalently attached to the surface of the fiber. Immobilization of these species on the surface of the fiber was monitored spectroscopically. Taga et al. used these modified chalcogenide fibers to produce a sensor for glucose. Once the glutaraldehyde was immobilized on the surface of the fiber an enzyme was covalently bonded to the glutaraldehyde. The enzyme used was glucose oxidase which converts β-D-glucose into gluconic acid. The enzyme immobilized fiber was washed with a bicarbonate buffer (pH=6.5) and a background spectrum was obtained. Glucose was added to the flow cell and the flow was stopped. Once the glucose was in the cell, glucose oxidase converted the glucose into gluconic acid, and the gluconic acid band at 1153 cm^{-1} was monitored over time. The concentration of glucose was determined by measuring either the rate of gluconic acid production or the maximum level of absorbance of the acid. The cell can be reused by flushing the buffer through the cell to remove the products and β-D-glucose can be reintroduced into the flow cell. Ruddy and McCabe discuss the use of Teflon clad fluoride fibers to determine the diffusion coefficient of propane as it diffuses through the coated cladding.[44] Göbel et al. evaluated the enhancement of the detection signal for low

molecular weight chlorinated compounds in aqueous solution using five different polymer phases coated onto an ATR element.[45] Their results indicate that the greatest enhancement of the analyte into the polymer phase is observed using either an ethylene/propylene copolymer or a 1, 2 polybutadiene phase. The authors also note that, for chloroform, tetrachloroethylene, and monochlorobenzene, the response times were shorter for polymers that had lower glass transition and crystallinity values.

The key to enhancing the concentration of the analyte in the polymeric phase is the diffusion of the analyte through the polymer. Thus the diffusion of the test analyte in the polymer is an important consideration. The rate of diffusion through a polymer film is dependent upon the diffusion coefficient of the analyte in the polymer, the difference in concentration between the analyte in the aqueous phase and the polymer phase, and the thickness of the polymer film. The rate of diffusion can be expressed by Fick's first law (Equation 1.4):

$$F = -D(C_1-C_2)/l \qquad 1.4$$

where F represents the flux of the analyte into the polymer film, l is the thickness of the polymer film, D is the diffusion coefficient of the analyte in the polymer film, and C_1 and C_2 represent the concentration of the analyte in the aqueous phase and the polymer phase, respectively. When an aqueous phase containing an analyte is introduced to a polymeric film, the rate of diffusion of the analyte into the phase increases initially. As the equilibration of the analyte between the aqueous and polymer phases is approached, the rate of diffusion decreases. It should be noted that the rate of diffusion

through a polymer film can be affected by many types of gradients, such as pressure, temperature, and concentration.

The flux of the analyte through a polymer also depends upon the type of polymer used since the diffusion coefficient of the analyte is polymer dependent. Polymers are often characterized by their pore sizes: macroporous, microporous, and nonporous. The diffusion coefficients of analytes through liquids is given by the Stokes-Einstein equation (Equation 1.5).

$$D = RT/6\pi nNr \qquad 1.5$$

where D is the diffusion coefficient, R is the gas law constant, n is the viscosity of the solvent, N is Avogadro's number, T is temperature (K), and r is the radius of a spherical analyte molecule. The diffusion coefficient of liquid analytes in macroporous polymer films can be estimated as long as porosity and tortuosity are taken into account. The determination of the diffusion coefficient of analytes as they traverse through a micro or nonporous polymer phase becomes more complex since both the structure of the polymer network and the solute molecules will affect diffusion.

Several approaches can be employed to improve the rate of diffusion of an analyte through a polymer film including: (1) increasing the concentration gradient between the polymer film and aqueous solution, (2) increasing the temperature at which the experiment is performed, and (3) modifying the phase to reduce the glass transition temperature. For example, a plasticizer can be incorporated into the phase making the polymer more rubbery. A plasticizer is a low molecular weight monomer that reduces the intermolecular forces in the polymer. This increase in flexibility in the

polymer is manifested as a lowering of the glass transition temperature.[46] As the fluidity of the polymer phase increases, the diffusion coefficient of the analyte will increase as well.

1.4 Goal of this research

The purpose of the research described here was to investigate ways to improve the measurement of analytes in aqueous solution by ATR/FTIR using both conventional and infrared optical fibers. The results of experiments using conventional coated (plasticizer/polymer formulations) ATR elements as a method of extracting analytes from aqueous solutions are reported in Chapter 2. The results of temperature controlled experiments using coated crystals are also evaluated in Chapter 2. Methods used to improve the sensitivity of chalcogenide fibers by bending the fiber are discussed in Chapter 3. The evaluation of untapered infrared fiber optics coated with plasticized polymer are discussed in Chapter 4. The performance of tapered infrared FiberCells coated with plasticized polymer are discussed in Chapter 5.

CHAPTER II

EVALUATION OF THE ABILITY OF POLYMER COATED (PLASTICIZER/PVC PHASES) CONVENTIONAL ATR ELEMENTS TO ENHANCE THE DETECTION OF ANALYTES IN AQUEOUS SOLUTIONS

2.1 Introduction

Coating the ATR element with a polymeric phase has been shown to improve the ability to detect an analyte assuming that analyte has an affinity for the polymeric phase. Coating the ATR element improves the detection of an analyte by increasing its concentration within the depth of penetration of the evanescent wave. Thicker coatings may also decrease spectral interferences due to the aqueous solution by excluding water from the surface of the ATR element.

An ideal polymer coating material should have the following characteristics: 1) it should not obscure the spectral region of interest for the particular analyte, 2) it should have a high extraction efficiency for the analyte, 3) the analyte should rapidly diffuse through the coating thereby resulting in short response times (i.e., the time it takes for the maximum absorbance level to be reached for the analyte) for the measurement, 4) the coating should be able to be easily removed from the expensive ATR element, and 5) the polymer should be easy to apply. Polyvinyl chloride (PVC), which has been studied

extensively,[47-48] is one coating material that meets many of these specifications. PVC was chosen as the concentrating phase primarily due to the spectral window it provides for the test analytes studied. The spectral window provided is similar to that obtained with chlorinated hydrocarbon solvents. PVC layers can be placed on solid substrates by solvent casting and are easily removed using an appropriate solution.

The results of previous work performed in our laboratory indicate that the ability to detect low concentrations of analytes using PVC coated ATR elements is hampered by the slow rate of diffusion of the analyte into the polymeric phase.[39] One approach to increasing the rate of diffusion of an analyte into a polymeric phase is to incorporate a plasticizer into the polymer.[49-56] A plasticizer is a low molecular weight compound that lowers the glass transition temperature (Tg) of the polymer. Plasticizers are commonly used to make polymers more flexible. Two different plasticizers were investigated. An ester containing plasticizer, dioctylphthalate (DOP), and a chlorinated paraffin were investigated for this application. Both of these plasticizers provide spectral windows that allow for the monitoring of the test analyte used in these experiments.

Experiments were performed to determine: 1) if incorporating a chloroparaffin plasticizer into the PVC phase reduces the time required to reach the maximum absorbance and/or increases the level of the maximum absorbance obtained for the two test analytes, nitrobenzene and benzonitrile, 2) how the physical form of the chloroparaffin (liquid or solid) affects the performance of the plasticized phase, 3) if a single application of a PVC phase containing the chloroparaffin

plasticizer can be used for several analyses, 4) how temperature affects the enrichment capabilities of chloroparaffin/PVC phases and 5) if the incorporation of DOP into PVC provides the same effects as the chloroparaffin/PVC phase. The results of these experiments are discussed.

2.2 Experimental Materials

Bulk polymerized polyvinyl chloride (Geon 143) was purchased from BF Goodrich, Geon Vinyl Division, Cleveland, OH. Chloroparaffins, 60% chlorinated (liquid) and 70% chlorinated (solid), were purchased from Scientific Polymer Products, Inc., Ontario, NY. Samples of the PVC and chloroparaffins were subjected to elemental analysis. The results show that the PVC contained 38.5% carbon and 4.8% hydrogen, the 60% chlorinated chloroparaffin had 36.2% carbon and 5.0% hydrogen, and the 70% chlorinated chloroparaffin contained 28.1% carbon and 3.0% hydrogen. Methanol (HPLC grade) and tetrahydrofuran (HPLC grade) were obtained through Fisher Scientific, Pittsburgh, PA. Nitrobenzene (reagent grade) and benzonitrile (reagent grade) were purchased from J.T. Baker, Phillipsburgh, NJ. and Velsicol Chemical Corporation, Chattanooga, TN., respectively.

2.3 Spectral Acquisition

FTIR spectra were acquired using a Nicolet G - Series 520 Bench (Nicolet Analytical Instruments, Inc., Madison, WI). Data for the nitrobenzene experiments were processed using a Nicolet 620 workstation. The spectral data for the benzonitrile experiments were processed with a 486DX2 PC using OMNIC, a Windows-based FTIR

software package developed by Nicolet. Unless otherwise stated, all spectra were obtained at a nominal 4 cm^{-1} resolution by coadding 64 scans. The ATR accessory used for this study was a Wilks Model 9 type reflectance system. The stainless steel liquid ATR holder was obtained from Wilmad Glass Company, Inc., Buena, N.J. Trapezoidal (50mm x 10mm x 3mm) zinc selenide (ZnSe) ATR elements were purchased from Spectral Systems, Irvington, N.Y. The temperature controlled experiments were performed using a computer-interfaced thermoelectric temperature controller (model # 2-060, Series TC^2 TEC controller, Alpha Omega Inc. Johnston, RI) and thermoelectric heat pump modules (Melcor Electronics Products Corporation, Trenton, NJ) that were mounted on a liquid ATR cell. The angle of incidence for all ATR experiments was 45°. Assuming a refractive index of 2.43 for the ZnSe element and 1.5 for the polymer coating, the depth of penetration at 1000 cm^{-1} is 2 μm (11). All spectral data were acquired at room temperature (except for the temperature controlled experiments).

2.4 Experimental Procedure

Polymer coatings were applied to the ATR elements by dipping one side of the trapezoidal element into a tetrahydrofuran (THF) solution containing PVC or a PVC/chloroparaffin mixture. The polymer coated element was leaned against the side of a Kimwipe after being removed from the THF solution. The Kimwipe acted as a wick allowing thinner polymer films to be obtained. The concentrations of the plasticizer in the PVC films are given based on the concentrations of the reagents in the THF solution. The actual concentration of plasticizer in the films applied to the elements was not determined.

Once the solvent evaporated, the polymer was equilibrated with a 1.5% (w/v) methanol/water solution for approximately thirty minutes. The solvent used for equilibration was removed and another solution containing the test analyte was added to the ATR cell. The cell was capped. Spectra were obtained for up to 90 minutes after loading the sample cell with the test solution. Absorbance spectra were produced using the equilibrated polymer phase in contact with the appropriate aqueous solution as the background spectrum. Nitrobenzene and benzonitrile were used as the test analytes for these studies. These analytes were chosen due to the unobscured spectral position of the cyano stretch of the benzonitrile and the strong asymmetric and symmetric nitro stretches of the nitrobenzene. Baseline corrected absorbances are reported for all measurements.

Due to the low solubility of the test analytes in water most test solutions used for these studies contained 1.5% (w/v) methanol. Experiments aimed at determining the effect which methanol has on the stability of the chloroparaffin/PVC phases were performed using lower concentration analyte solutions containing only water as the diluent.

For the temperature controlled experiments the coated crystal was equilibrated with an aqueous phase for approximately 30 minutes at a specific temperature. The equilibrating solution was removed from the cell and an aqueous solution of 0.005% v/v nitrobenzene was added to the sample cell and monitored over time. It should be noted that the analyte containing test solution was at the same temperature as the sample cell when it was added. These experiments were performed using two different phases (PVC and 47% w/w

chloroparaffin/PVC).

Spectral data acquisition was performed using a Visual Basic program that controls the FTIR instrument, the Alpha Omega temperature controller, and converted the data into a spreadsheet format. Omnic and Visual Basic programs were interfaced using Nicolet's OMNIC Macros/Pro software. Omnic Macros/Pro software drives the optical bench and acquires spectral data using Microsoft's Visual Basic. Visual Basic and the optical bench communicate through Dynamic Data Exchange (DDE) and OMTALK routines developed by Nicolet. The Visual Basic program and the spreadsheet communicate through DDE commands developed by Microsoft. Using these routines we were able to write a Visual Basic program that drives the optical bench, sends and receives voltages to and from the Alpha Omega temperature controller via a data acquisition board, monitor voltage inputs from the Alpha Omega temperature controller and the external thermocouples (which are converted to temperature values using a sub program), and finally, input pertinent data into a spreadsheet.

Figure 2.1 illustrates the input and display boxes from a Visual Basic form window used in this program. The first input box allows the operator to place a filename to distinguish between experiments. The program places a number after each filename to ensure that the spectra collected during the experiment can be distinguished. The next three input boxes allow the operator to select the number of spectra required for an experiment, the number of seconds between spectral acquisition for the first fifteen experiments, and the number of minutes between spectra after the first fifteen spectra are acquired. The next box is a display box that presents the time at which spectral data

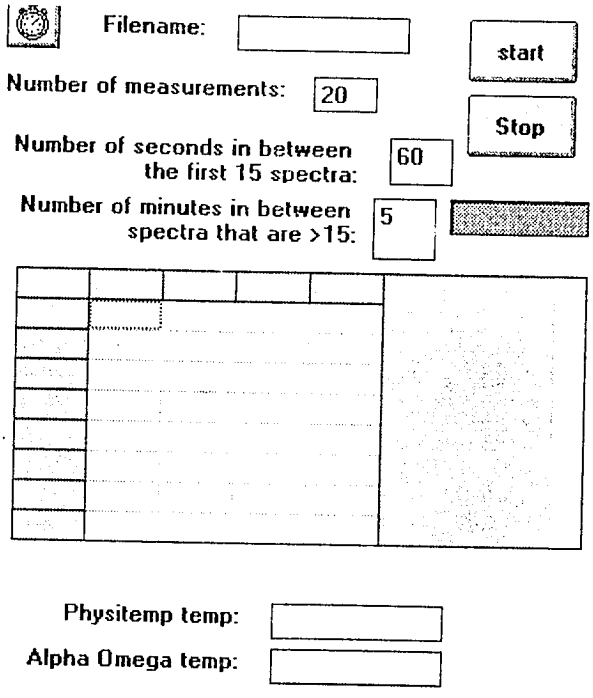

Figure 2.1 Visual Basic form window used for the temperature control experiments

acquisition was started, the peak position of the test analyte, the corrected baseline height of the analyte, the temperature of the AD590 electronic temperature probe, and an external thermocouple (Physitemp, BAT-12). The next two display boxes present the temperature of the AD590, an electronic temperature probe, and the external thermocouple (BAT-12). The temperatures were calculated using a subroutine that takes the input voltages from the thermocouples and converts them to temperature. The 'start timer' button is used to execute the program and the 'stop' button is used to abort the program at any time. The program written for the temperature controlled experiments is given in Appendix I.

2.5 Experimental Results

One of the problems which we have encountered is a difficulty in controlling the thickness of the phase applied to the ATR element when using the dip coating technique. Variations in film thickness limit the reproducibility of the results obtained for a given polymer/plasticizer composition. These variations also make it difficult to compare the effects of different polymer/plasticizer formulations. For example, the effect which the variability of coating thickness has on analyte detection can be demonstrated using two ATR elements coated with two different applications of PVC containing 23% (w/w) of the 60%-Cl chloroparaffin plasticizer. Based on the magnitude of the absorption at 2972 cm^{-1} for the unhydrated polymer films, it is estimated that one film was approximately 25 percent thicker than the other film. The results of monitoring the absorbance due to the nitro symmetric stretch (1348 cm^{-1}) for an aqueous solution

containing 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol are presented in Figure 2.2 for these two films. It is clear that a longer time is required to reach the maximum absorbance for nitrobenzene for the thicker phase. It should also be noted that the final absorbance obtained for the analyte increases as the phase thickness increases.

The thicknesses of the polymer coatings applied to the ATR elements must be similar if the data obtained using successive applications are to be compared. One method to ensure similar film thickness is to use only films which provide similar levels of absorption for one of the polymer (or polymer/plasticizer) bands. The absorbance level at 2972 cm^{-1} for the unhydrated films was used for this purpose. The absorbance level in this region for each film was determined after correcting for variations in baseline. PVC and the 60%-Cl chloroparaffin have very similar absorbances in the 2972 cm^{-1} region while the 70%-Cl chloroparaffin has a much lower absorbance in this region. Only polymer films for which the absorbance in the 2972 cm^{-1} region was 0.10 were used for these studies. Thus, based on the spectroscopic data, the film thicknesses for the PVC and 60%-Cl chloroparaffin/PVC formulations were very similar for all experiments. It should be noted, however, that the film thicknesses obtained for the experiment using 70%-Cl chloroparaffin are somewhat thicker than the other phases though the absorbance of that film in the 2972 cm^{-1} region was also 0.10.

The polymer coatings used for this study had an estimated thickness of 1 micrometer. This thickness was calculated using data obtained from a separate set of experiments. The mass of the polymer coating applied and the baseline corrected peak height at 2972 cm^{-1}

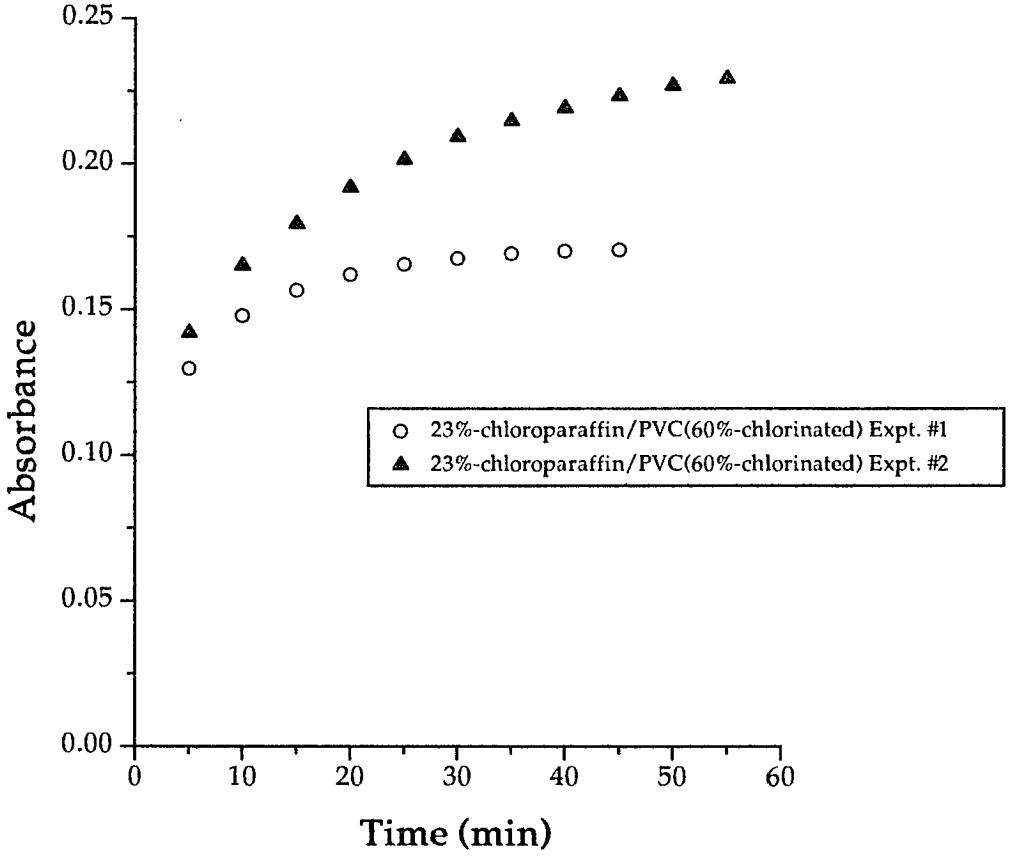

Figure 2.2 Absorbance at 1348 cm^{-1} vs. time obtained for two ATR elements coated with PVC containing 23% (w/w) of 60%-Cl chloroparaffin. The coating used for experiment 2 was approximately 25% thicker than the coating used for experiment 1.

were determined for five films prepared using various PVC and PVC/chloroparaffin formulations. The coating thickness was calculated based on the mass of the polymer layer and the area of polymer coverage exposed to the aqueous solution on the ATR element assuming a polymer density of 1.5 g/cm^3. The peak height and thickness values were averaged for the five coatings. The ratio of average height to average thickness thus obtained and the absorbance values measured for the polymer coatings were used to estimate the thickness of the polymeric phases reported here.

The spectra obtained for an aqueous solution containing 0.05% (v/v) nitrobenzene (the test analyte) and 1.5 % (w/v) methanol using both a PVC coated and an uncoated ZnSe trapezoidal ATR element are given in Figure 2.3. These spectra were obtained after allowing the analyte containing solutions to be in contact with the ATR elements for 80 minutes. The absorbance of the asymmetric (1530 cm^{-1}) and symmetric (1348 cm^{-1}) stretches of the nitro group of the test analyte are observed clearly for the PVC coated element, demonstrating that the addition of the polymer layer improves the ability to detect nitrobenzene. The spectrum shows a significant reduction in the magnitude of the OH stretching band between 3100 and 3600 cm^{-1} suggesting that the polymer is partially excluding water from the surface of the ATR element. However, because the thickness of the PVC layer is substantially less than the depth of penetration of the IR radiation, the water contribution to the spectrum remains strong. This is particularly true at the longer wavelength bending vibration where the penetration depth is larger.

It was postulated that adding a plasticizer to the PVC phase

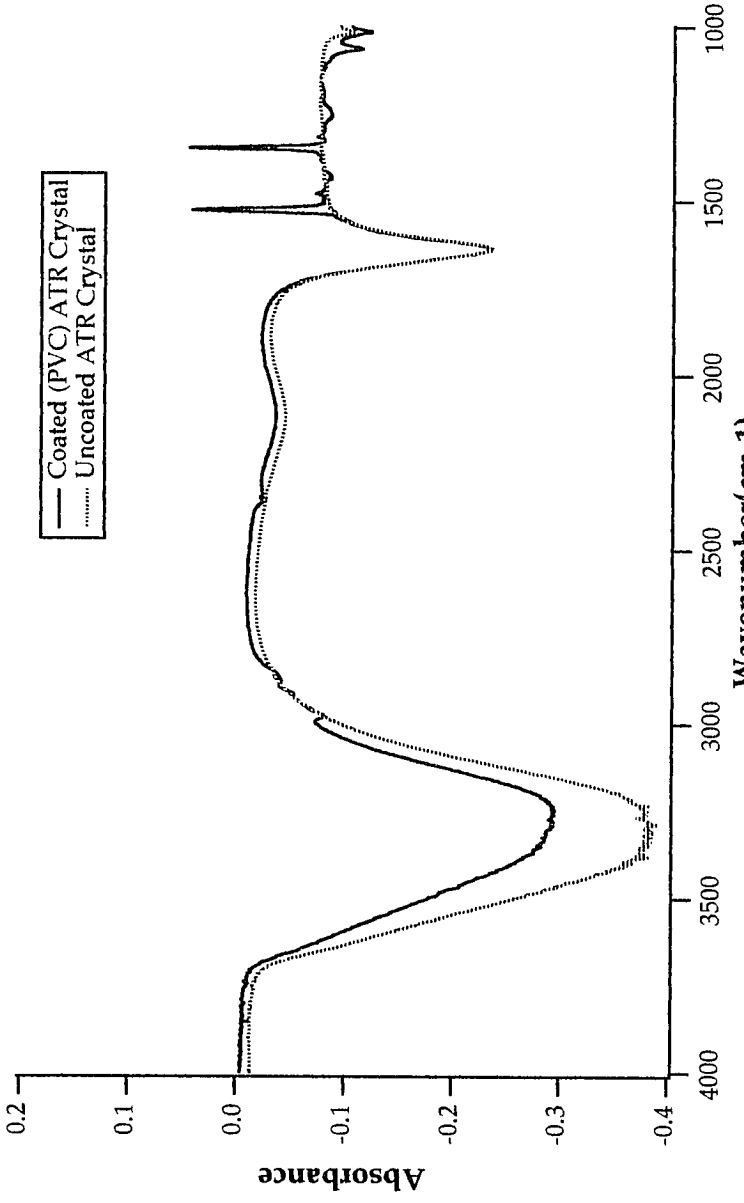

Figure 2.3 A plot of absorbance vs. wavenumber obtained for a PVC coated ATR element and an uncoated ATR element after exposure to an aqueous solution containing 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol for 80 minutes.

would result in an increase in the rate of diffusion of the analyte into the concentrating phase. An increased rate of diffusion for the analyte would result in a faster response time for the ATR/FTIR analyses. A series of experiments were performed to determine the effect of an increased percentage of chloroparaffin plasticizer in PVC on the ability of the phase to extract the test analytes from the aqueous solution. An ATR element was coated with a PVC phase which contained no plasticizer and a second element was coated with a PVC phase containing 47%-chloroparaffin (60%-Cl) by weight. The coated elements were placed in the sample holder and an aqueous solution containing 0.05% (v/v) nitrobenzene and 1.5% (v/v) methanol was added to the cell. The absorbance at 1348 cm^{-1} (nitro symmetric stretch) was monitored over time. The results of these two experiments are presented in Figure 2.4. The data clearly demonstrate that adding plasticizer to the PVC phase decreases the time required to achieve the maximum level of absorbance for the test analyte. The time required to reach the maximum absorbance for nitrobenzene using the 47%-chloroparaffin (60%-Cl)/PVC phase was approximately 25 minutes. The PVC phase containing no added plasticizer did not reach the maximum absorbance level for nitrobenzene even after being in contact with the analyte solution for 80 minutes.

The enhancement in the rate of equilibration can be attributed to an increase in fluidity (lower Tg) of the polymeric phase. It is also interesting to note the increased level of absorbance achieved for the analyte when using the plasticized PVC phase. This suggests either an increase in the molar absorptivity for the nitro band or an increase in the distribution ratio for the test analyte. It is also possible that the

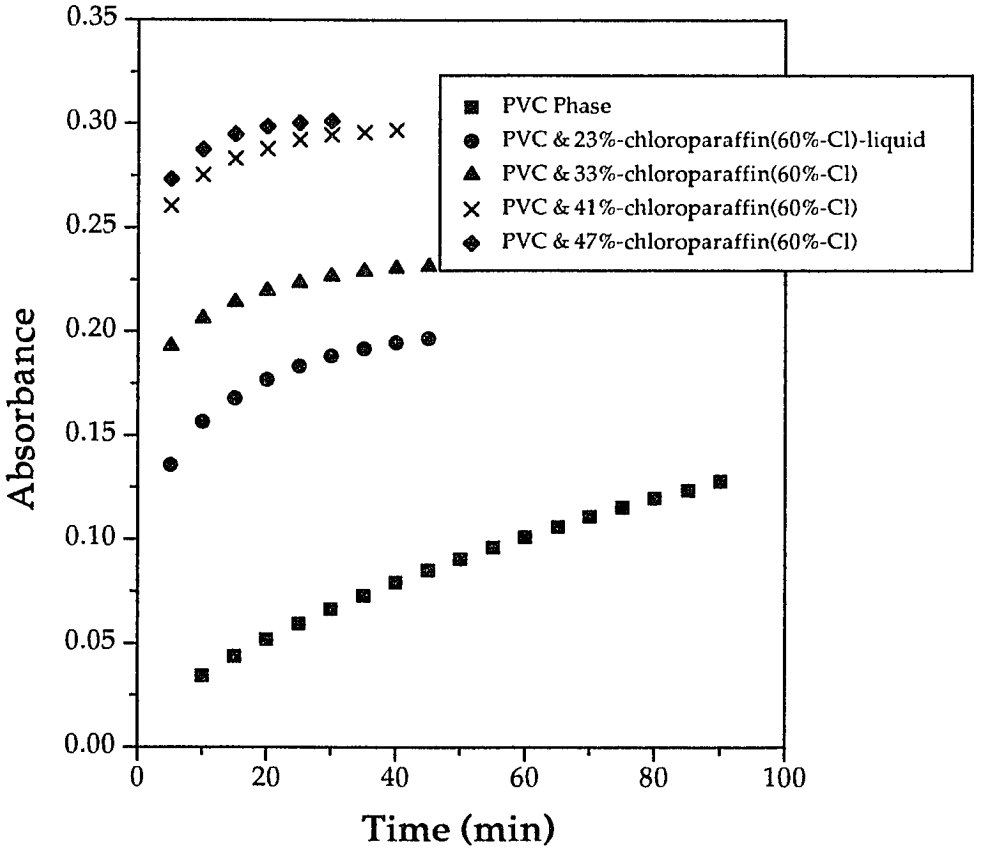

Figure 2.4 Comparison of the absorbance at 1348cm^{-1} vs. time profiles obtained for PVC coated ATR elements and a number of PVC/chloroparaffin formulations. The aqueous test solution contained 0.05% (v/v) nitrobenzene and 1.5% methanol. The data presented are the average absorbances obtained for two replicate experiments.

phases obtained using the dip coating method with our plasticized PVC phase are thicker than the unplasticized PVC phase though the spectral data obtained on the unhydrated phases suggest otherwise. The same trends are observed, including the increase in final absorbance level obtained, for the nitro asymmetric stretching band at 1530 cm^{-1}.

Additional experiments were performed to determine the effect of plasticizer concentration on the maximum absorbance achieved for the analyte and the rate at which the maximum absorbance level is reached. PVC layers containing 0, 23, 33, 41, and 47 percent by weight of the liquid chloroparaffin (60%-Cl) were evaluated using a solution containing 1.5% (w/v) methanol solution and 0.05% (v/v) nitrobenzene, the test analyte. The results of these experiments are also presented in Figure 2.4 for comparison. The data show that as the concentration of the plasticizer incorporated into the PVC increases, the maximum absorbance obtained for the nitro bands increases. The profiles also show that the rate at which the maximum absorbance is reached increases with increasing plasticizer concentration over the range studied. The results of these experiments demonstrate that the diffusion of the analyte into the polymer phase is dependent upon the polymer formulations used to coat the ATR element.

Further experiments were performed to determine if the trends observed with nitrobenzene are applicable to similar analytes having other functional groups. The test analyte chosen for these studies was benzonitrile. Experiments were performed with two polymer phases, a PVC phase with no plasticizer added and a PVC phase containing 47% by weight of the chloroparaffin (60%-Cl). An aqueous solution containing 0.1% (v/v) benzonitrile and 1.5% (w/v) methanol was

added to the ATR cell and the cyano absorbance band at 2229 cm^{-1} was monitored over time. The results of these experiments are presented in Figure 2.5. As was the case for nitrobenzene, using the plasticized phase resulted in an increase in the rate at which the maximum absorbance for the analyte is obtained and also an increase in the maximum absorbance level obtained.

Experiments were also performed to determine if the fluidity of the chloroparaffin used as a plasticizer is important for improving the response time for the PVC coated ATR experiments. The chloroparaffin plasticizers are available in both liquid and solid form at room temperature. The chloroparaffin used for the previous studies (60%-Cl) is a liquid at room temperature. Increasing the concentration of chlorine to 70 percent results in a chloroparaffin plasticizer which is a solid at room temperature. We decided to investigate if the trends observed for the PVC phases containing the 60%-chloroparaffin are observed for PVC phases containing 70%-Cl chloroparaffin when using nitrobenzene as the test analyte.

ATR elements coated with either of two PVC/plasticizer phases were prepared. The two PVC layers studied contained 23% by weight of either the 60%-Cl (liquid) or 70%-Cl (solid) chloroparaffin plasticizers. The aqueous test solution used to evaluate these phases contained 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol. Plots of absorbance at 1348 cm^{-1} vs. time for each of the polymer coated ATR elements are given in Figure 2.6. The results of these experiments clearly show that the rate at which the maximum absorbance of the nitrobenzene is achieved is slower for the solid plasticizer/polymer formulation. The maximum absorbance for the solid

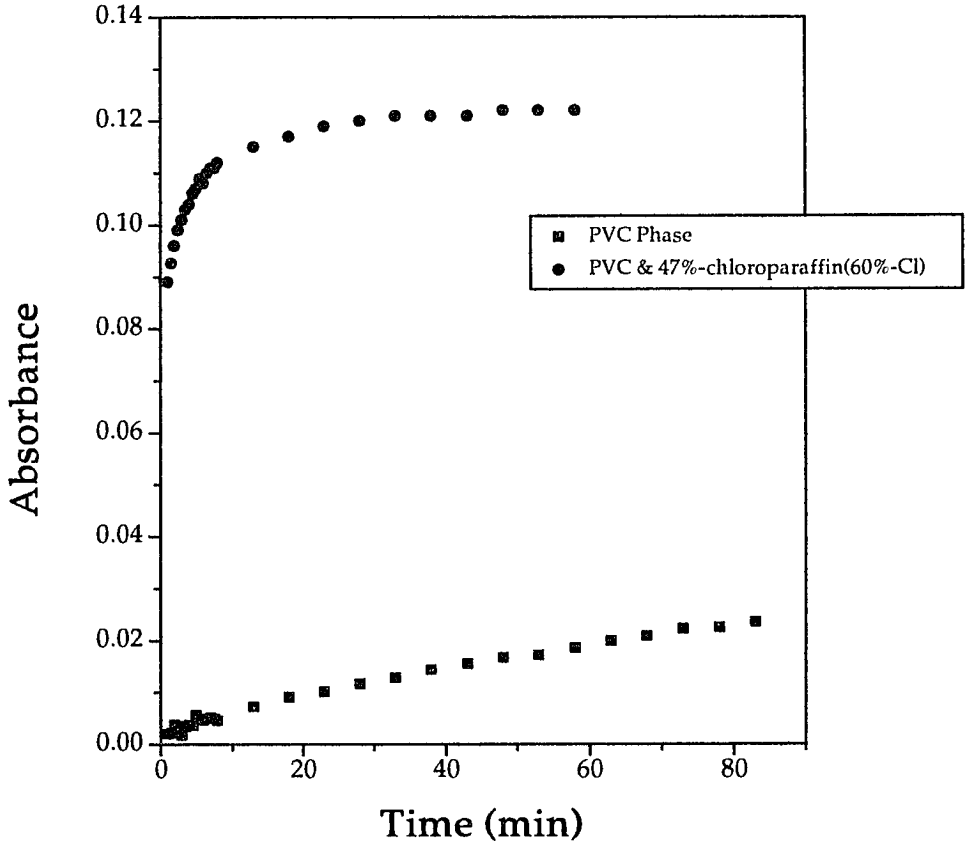

Figure 2.5 Plot of the absorbance at 2229cm^{-1} vs. time obtained using a PVC coated ATR element and an ATR element coated with PVC containing 47% (w/w) of 60%-Cl chloroparaffin. The aqueous test solution contained 0.10% (v/v) benzonitrile and 1.5% (w/v) methanol.

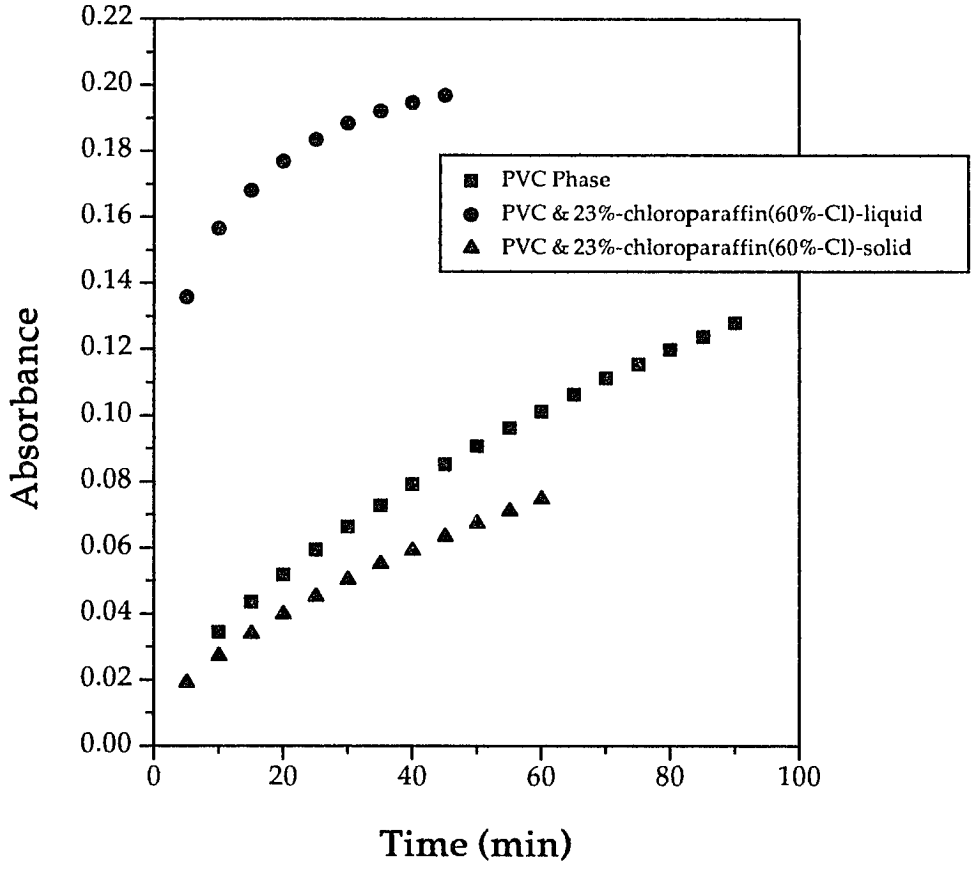

Figure 2.6 Plots comparing the absorbance at 1348 cm^{-1} vs. time for ATR elements coated with PVC, a PVC phase having 23% (w/w) of 60%-Cl chloroparaffin and another element coated with a PVC phase containing 23% (w/w) of 70%-Cl chloroparaffin. The aqueous test solution contained 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol.

plasticizer/polymer formulations had not been reached after sixty minutes whereas the experiments using the liquid plasticizer/polymer formulations reached a maximum absorbance of 0.19 at approximately 45 minutes.

Experiments were performed to determine if it is possible to use a single application of the polymer phase for several analyses. For these experiments, the method used to coat the ATR element and acquire the data were the same as given previously. These experiments were performed using an ATR element coated with a PVC phase containing 47%-chloroparaffin (60%-Cl). The phase was equilibrated with an aqueous solution containing 1.5% (w/v) methanol for approximately 30 minutes. The equilibrating solution was removed and the test solution containing 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol was added. Infrared spectra were acquired for 35 minutes after placing the test solution in contact with the ATR element. The maximum level of absorbance for the nitro symmetric stretch was reached after approximately 10 minutes. After 35 minutes, the contents of the sample cell were removed and the cell was flushed with an aqueous solution containing 1.5% (w/v) methanol until there was no indication, spectroscopically, of nitrobenzene remaining in the polymer phase. The nitrobenzene test solution was reintroduced into the sample cell and spectra were acquired for an additional 35 minutes. The procedure was repeated a third time. The results of the three experiments are presented in Figure 2.7. These results clearly indicate that the maximum absorbance for the analyte decreases with repeated use of the polymer phase. One possible explanation for the decrease in partitioning of the analyte into the polymer is that the chloroparaffin is

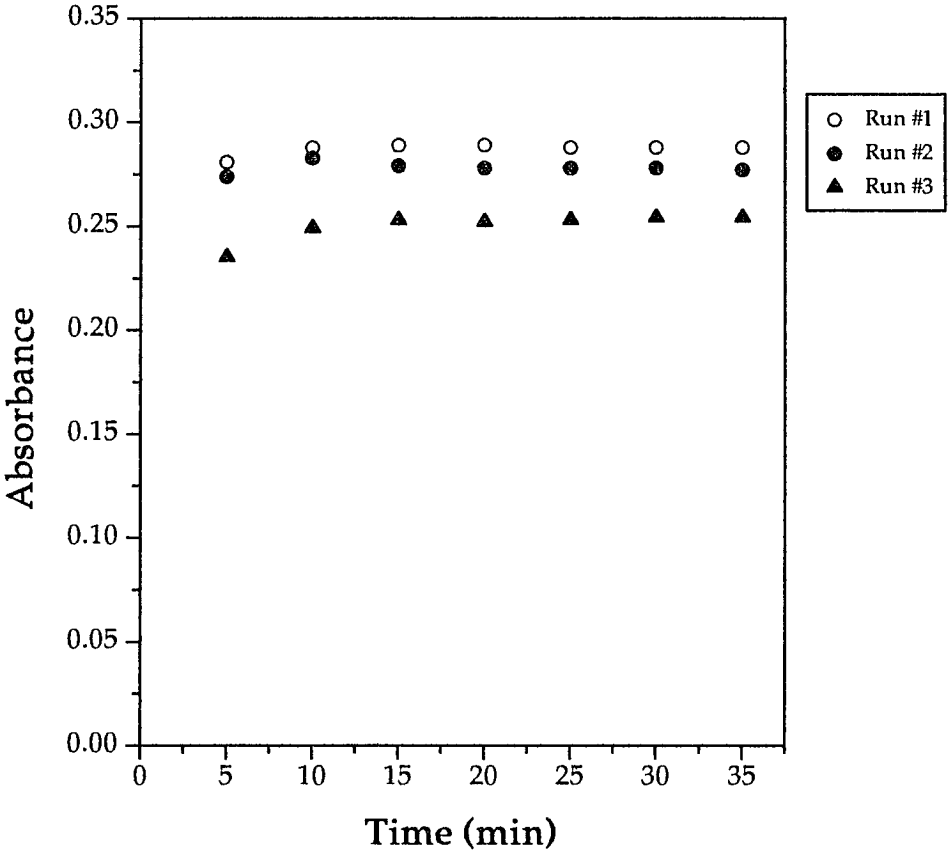

Figure 2.7 Results obtained using a single application of a PVC phase containing 47% (w/w) chloroparaffin (60%-Cl) to analyze three aqueous solutions containing 0.05% (v/v) nitrobenzene and 1.5% (w/v) methanol.

leaching out of the PVC phase. The solubility of the chloroparaffin in methanol is the reason why leaching is suspected.

Additional experiments were performed to demonstrate that the presence of methanol affects the reusability of the polymeric phase. Due to the limited solubility of nitrobenzene in water, a lower concentration of the test analyte, 0.005% (v/v) nitrobenzene, was used for these experiments. As in the previous study, the PVC phase used contained 47% (w/w)-chloroparaffin (60%-Cl). The experiments were performed as above but the cell was flushed between repeat measurements using water. The results obtained for four sequential measurements of the aqueous test solution are given in Figure 2.8. As expected, the maximum absorbance obtained for the nitro functionality is clearly lower than for the more concentrated test solution used in the previous study. Contrary to the results of the previous experiment using the test solution containing methanol, the results of this experiment showed very little change in the maximum absorbance obtained for the analyte even after four measurements. Closer inspection of the results shows the maximum absorbance level for the nitro functionality actually increases very slightly (0.001 A) on repeat exposure to the test solution. This increase may be due to the incomplete removal of the nitrobenzene from the polymer layer between measurements. Still, the results of these experiments suggest that the same polymeric phase can be reused for repeat analyses as long as the solution being analyzed does not leach the chloroparaffin from the polymer coating.

Additional experiments were performed to determine whether other types of plasticized/PVC formulations provide similar results.

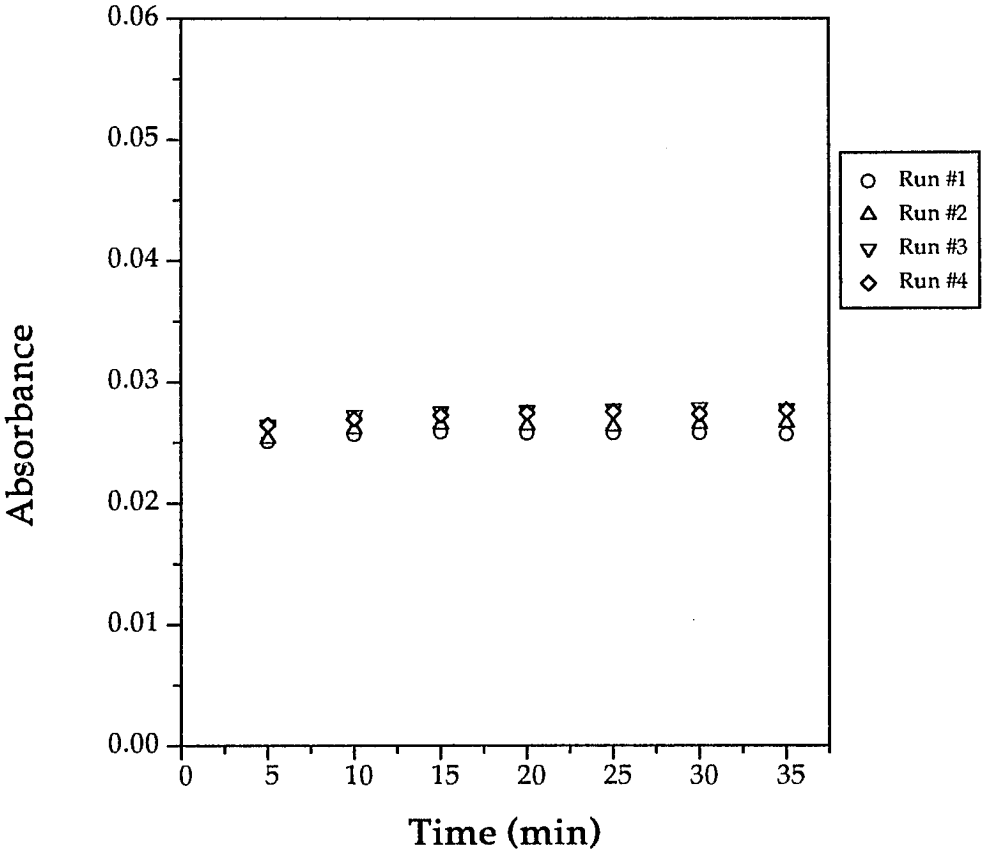

Figure 2.8 Results obtained using one application of a PVC phase containing 47% (w/w) chloroparaffin (60%-Cl) to analyze four aqueous solutions containing 0.005% (v/v) nitrobenzene with no methanol added.

The plasticizer used for these experiments was dioctylphthalate (DOP), a commonly used plasticizer for PVC. DOP was chosen as the plasticizer to see how an ester containing plasticizer affects the enrichment capabilities of analyte into a DOP/PVC phase. The test analyte was a 0.1% v/v benzonitrile in 1.5% w/v methanol/H_2O. Benzonitrile was chosen as the test analyte for these experiments because cyano stretch at 2229 cm^{-1} is unobstructed. These experiments were performed by adding a 1.5% w/v methanol/H_2O solution to a 7% v/w DOP/PVC phase. After approximately 30 minutes the solution was removed from the cell and a solution containing 0.1% v/v benzonitrile in a 1.5% methanol/H_2O solution was added to the cell. The cyano absorbance band (2229 cm^{-1}) was monitored over time. These experiments were repeated and the results are given in Figure 2.9. The data clearly illustrate that the addition of dioctylphthalate to the PVC improves both the rate at which equilibrium is achieved and the magnitude of absorption observed for the test analyte.

Several experiments were performed to determine how temperature affects the rate of enhancement of the analyte into the polymer formulation. An aqueous test solution containing 0.005% v/v nitrobenzene was used for these experiments. The test solution did not contain methanol to prevent the chloroparaffin from leaching out of the polymer layer. The polymeric phase and aqueous solution were equilibrated at a specific temperature for approximately thirty minutes. The aqueous solution was then removed from the sample cell. A 0.005% v/v nitrobenzene solution, which was at the same temperature as the ATR cell, was introduced. The nitro symmetric stretch

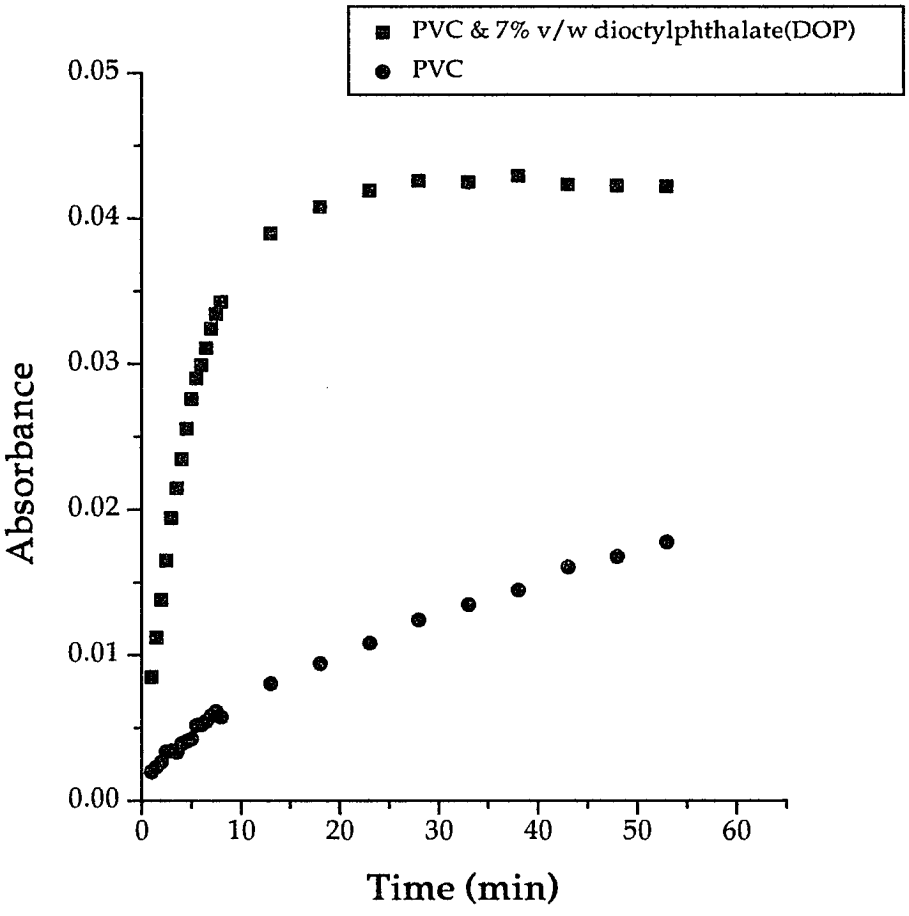

Figure 2.9 Comparison of the absorbance at 2229 cm-1 stretch vs. time profiles for PVC coated ATR elements and a PVC/7% (v/w) DOP phase. The aqueous test solution contained 0.1% (v/v) benzonitrile and 1.5% methanol.

(1348 cm^{-1}) of nitrobenzene was then monitored over time. High purity nitrogen was used to purge the ATR cell to remove the analyte from the polymeric phase. Removal of the nitrobenzene from the cell was monitored spectroscopically until the characteristic nitro band (1348 cm^{-1}) was no longer detected. The experiment was repeated at a different temperature after the nitrobenzene was removed.

Figure 2.10 presents the corrected baseline absorbance of the test analyte over time using a PVC phase at 32° and 55° C. The data clearly show that as the temperature is increased the time required to reach the maximum absorbance level for the analyte decreases. This is probably due to an increase in the fluidity of the phase, resulting in an increased rate of diffusion of the analyte into the phase. The data also show that as the temperature at which the experiment is performed increases, the magnitude of the absorption band of nitrobenzene decreases. This decrease in absorption is likely due to an increase in solubility of nitrobenzene in the aqueous phase as the temperature is increased. Similar trends, presented in Figure 2.11, were also observed for experiments performed with a 47% w/w chloroparaffin/PVC phase.

2.6 Conclusion

The results of the experiments performed clearly show that adding a liquid chloroparaffin to PVC improves both the time required to reach the maximum absorbance for an analyte and the detection capabilities for ATR/FTIR analyses using polymer coated ATR elements. The results obtained also demonstrate that a single application of the polymer phase can be used for several repeat analyses, though care must be taken not to leach the plasticizer from

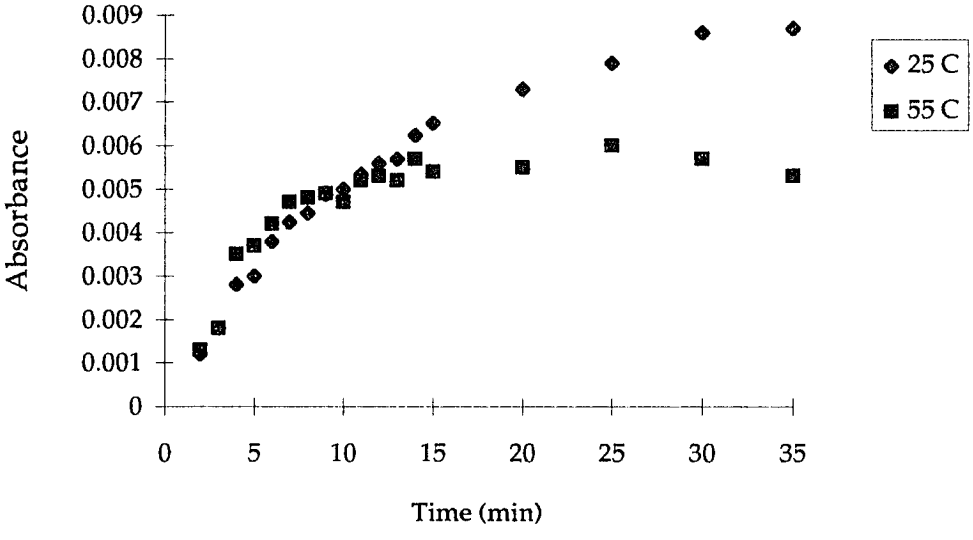

Figure 2.10 Temperature controlled experiments with a solution containing 0.005% Nitrobenzene in H20 using a PVC coated ZnSE crystal.

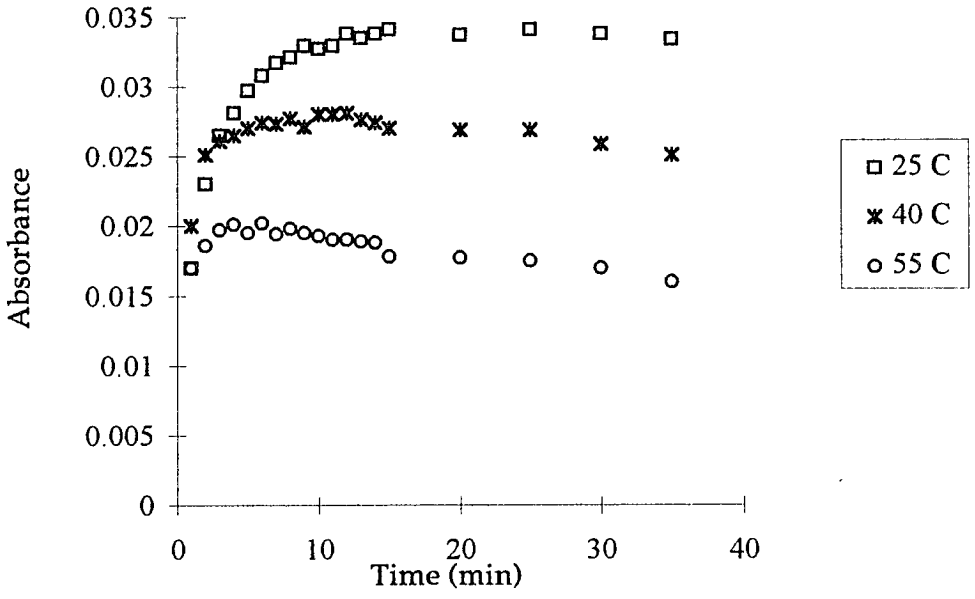

Figure 2.11 Temperature controlled experiments with a solution containing 0.005% Nitrobenzene in H_2O using a PVC/47% chloroparaffin(60%-Cl) coated ZnSe Crystal.

the phase. Experiments performed using solid chloroparaffin plasticizer/PVC formulations show very little difference from the results obtained using an unplasticized PVC phase.

A phase consisting of 47% (w/w) chloroparaffin (60%-Cl)/PVC provided the shortest time to reach the maximum absorbance level and the greatest enhancement in analyte absorption. However, the response times remain long considering that the polymer layers used for these studies are estimated to be less than one micrometer in thickness. Several factors may contribute to this observation. We have no evidence that the thickness of polymer layer is uniform. The response time would be determined by the thickest part of the polymer film. The polymer film may not be homogeneous. The concentration of chloroparaffin may vary throughout the polymer film. Diffusion in the aqueous phase may also contribute to the observed response time. Although diffusion coefficients are much higher in water than in polymers, the fact that the analyte is enriched means that the diffusion of the analyte has to occur over a longer distance in the aqueous phase than in the polymer phase. If the partition coefficient is 100 and the thickness of the polymer layer is 1 micrometer, then a 100 micrometer thick layer of aqueous phase is required to supply enough analyte to reach equilibrium. Since response times vary with the square of the layer thickness, diffusion in the aqueous phase may contribute to the observed response time. It is believed, however, that slow diffusion in the polymer phase is the primary reason for slow response. The experimental observations that the response times depend on the thickness of the polymer layer (Figure 2.1) and percent plasticizers (Figure 2.3) are consistent with this explanation.

The results of the experiments presented here suggest additional approaches to improving the response time included increasing the diffusion coefficient for the analyte in the PVC layer by increasing the temperature at which the analysis is performed and/or increasing the concentration of plasticizer. It should be noted however that the stability of the phase applied to the ATR element must be sufficient to allow the spectroscopic measurements to be performed. If a reasonable spectroscopic window can be obtained for the analyte of interest, using a plasticizer which is more effective at increasing the diffusion coefficient is also an option.

CHAPTER III

EXPERIMENTS TO DETERMINE THE MAGNITUDE OF IMPROVEMENT IN THE DETECTION OF ANALYTES USING BENT CHALCOGENIDE FIBER PROBES

3.1 Introduction

Chalcogenide mid infrared transmitting fibers are essentially attenuated total internal reflectance elements. A typical ray tracing for infrared radiation traversing through a straight fiber where the launch angle is greater than the critical angle is given in Figure 3.1. Colin et. al. have shown that bending the fiber with a mode scrambler increases the number of higher order modes of light traversing through a fiber.[57] Figure 3.2 presents an optical ray trace of a fiber optic sensor with a bend preceding the sensor region. Increase the number of higher order modes, improves the signal obtained for the analyte because more of the IR energy is sampling the sensor region. The bent section of the fiber can also be used as the sensing region. There are two advantages to using the bend as the sensor: (1) the number of higher order modes of light that are sampling the sensor region are increased, and (2) the launch angle of the light approaches the critical angle, thereby improving sensitivity as the depth of penetration of light in the lower refractive media increases.

Experiments were performed to evaluate how the angle of the bend preceding the sensor region affects the absorption spectra obtained for a liquid

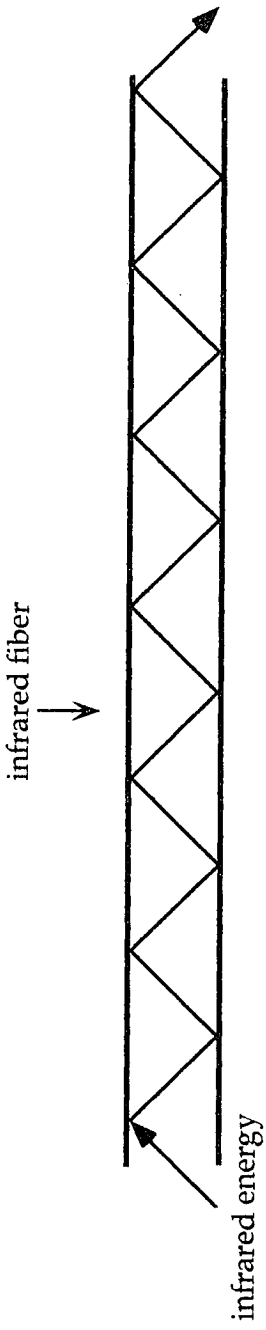

Figure 3.1 Optical ray trace of a straight chalcogenide infrared fiber

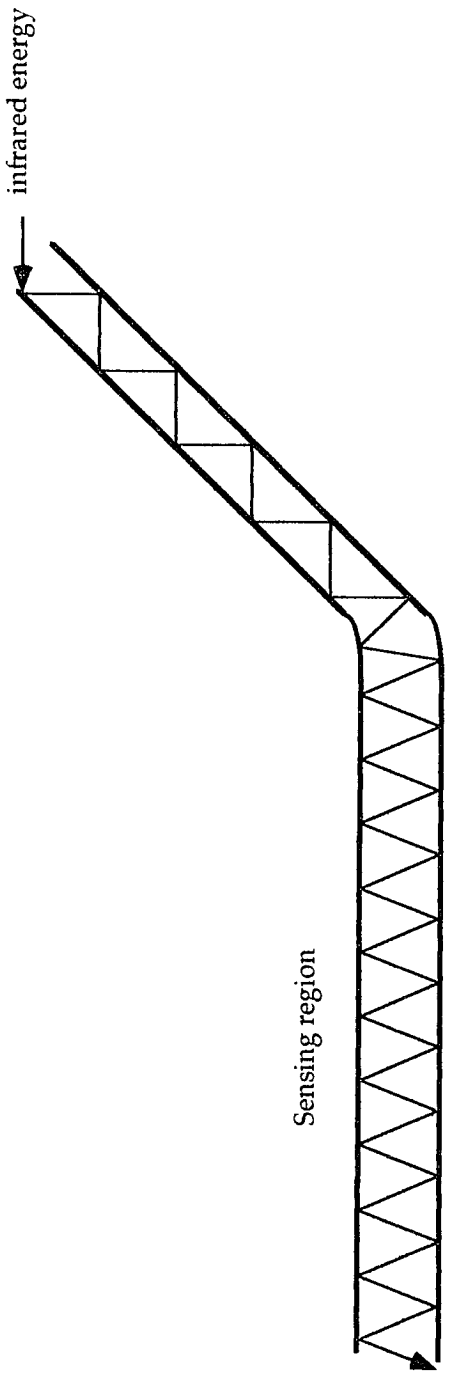

Figure 3.2 Optical ray trace through a bent infrared fiber

in contact with the sensing region. Experiments were also performed to determine if the bend portion of the mid infrared fiber can be used as the sensor. Two types of probes were developed, a "v" shaped probe and a cylindrical twisted probe.

3.2 Materials

The chalcogenide fibers (500 μm, clad and 750 μm core/glass clad) used for these experiments were acquired from Amorphous Materials, Inc. (Garland, Texas). The fiber optic interface is a commercially available accessory that fits into the sample compartment of a Nicolet FTIR spectrometer. It consists of one set of mirrors that redirect the light toward the source orifice, and another set which focus the light on the MCT-A detector. There is also an XYZ translator attached to the detector orifice that positions the light reaching the detector.

3.3 Procedure

A fiber cell was constructed by cutting a 20 cm straight piece of unclad, 500 μm chalcogenide fiber. The chalcogenide fiber was immersed in methylene chloride to remove the polyamide coating used by the manufacturer to improve the mechanical stability of the fiber. After the polyamide was removed, the fiber was placed in a glass cell. The fiber was sealed to the glass cell using epoxy to prevent leakage of the liquid samples. The glue used for this purpose was a commercially available product that can be removed easily from the cell after performing the experiment so that the cells can be reused. The epoxy was allowed to dry overnight and the sensor cell was immobilized onto a wooden platform using quick drying glue. The ends of the fiber were connected to SMA connectors and immobilized. These

SMA connectors allow the fiber to be connected to either the fiber optic interface or another fiber (usually a glass clad chalcogenide fiber). A schematic diagram of the fiber cell setup is given in Figure 3.3. The sensing region of the fiber was approximately 4 centimeters in length. Once the cell was constructed, the ends of the fiber were polished with polishing media (Buehler Fiber Optics, Inc., Lake Bluff, IL). This step was critical for maximizing the energy passing through the fiber. Using water as a lubricant, the fiber was placed onto the polishing media paper and moved in a circular motion. The fiber was first polished with 16 μm paper for the coarse polish and then with 0.5μm media for the fine polish. The fiber cell, once polished, was left overnight at room temperature to allow the water to evaporate from the SMA connectors. This step is important because of the strong absorption bands of water in the mid infrared region. The construction of a fiber cell takes approximately three to five days.

Experiments were performed to evaluate the absorbance of a test analyte using fibers with bends at various angles placed before the sensing region. The sensor was connected to a glass clad fiber that is approximately one meter long and has a diameter of 750 μm. The other end of the fiber was connected to the source orifice of the fiber optic interface as shown in Figure 3.4. Once the fiber was connected, a single beam, 100% line, and absorbance spectrum of the straight fiber were obtained. The cell was then emptied and a bend placed prior to the sensing region of the fiber. The bend was introduced using a rod type heating element with a diameter of approximately 0.5 inches to heat a small section of the fiber. An example of a fiber with a 45 degree bend is given in Figure 3.3. A Variac voltage regulator was used to obtain an optimal temperature setting for bending the fiber. The single beam spectrum, 100% line, and absorbance spectrum of ethanol were

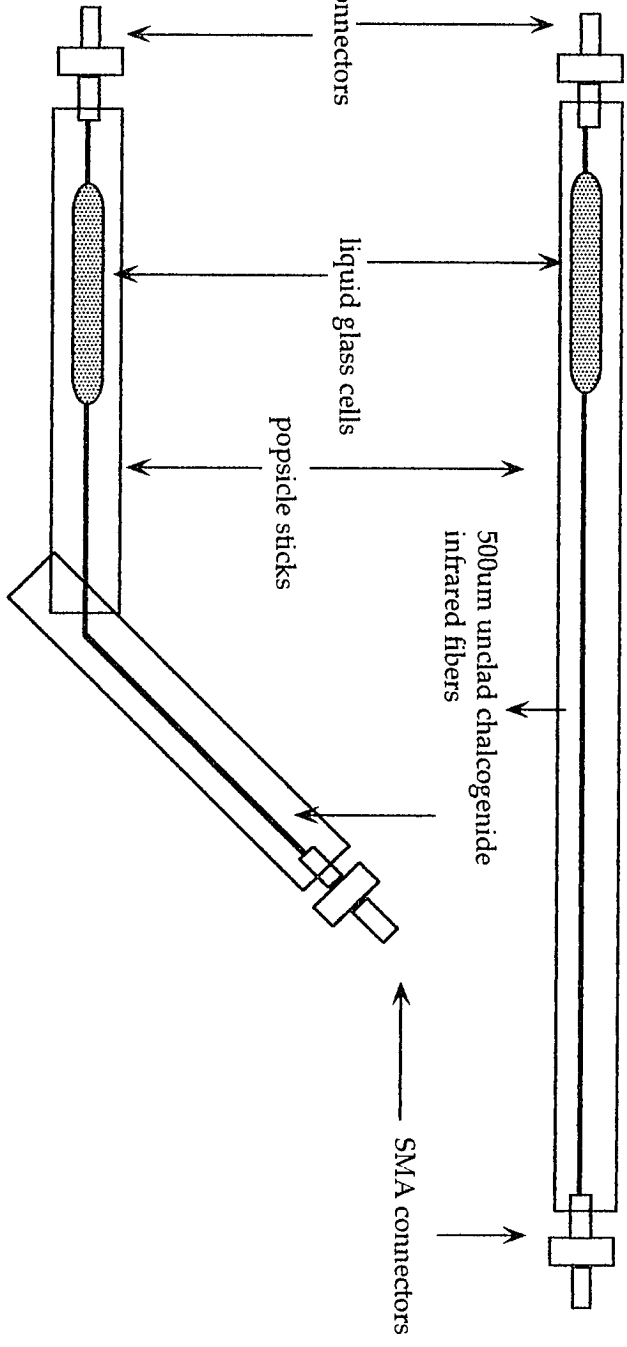

Figure 3.3 Top view of Fiber Sensor used for both the straight and bent fiber experiments

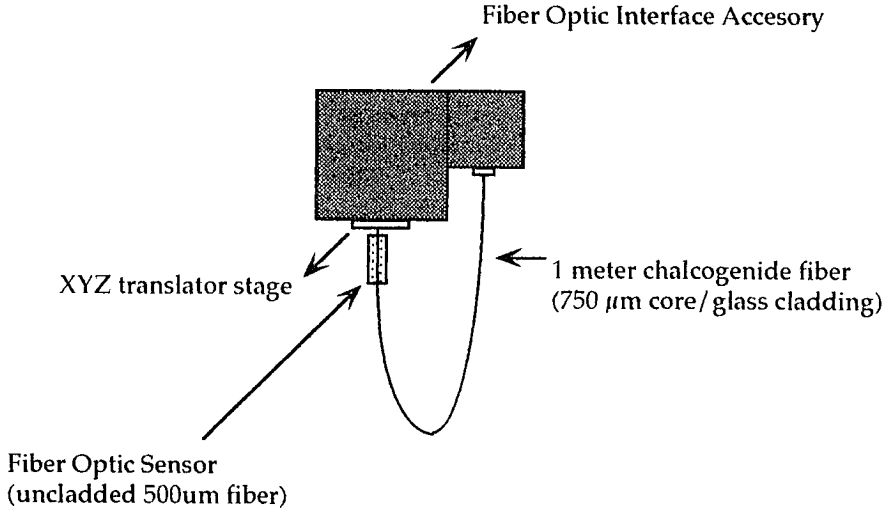

Figure 3.4 Infrared Fiberoptic Interface with Connecting Fiber and the Fiberoptic Sensor

collected using the bent probes with the bend before the sensing region. The procedure was repeated with a 90 degree bend in the fiber. Closer inspection of the fiber with the 90 degree bend, revealed a kink in the region of the bend.

A second set of experiments was conducted using the bent region of the fiber as the sensor. For this purpose, two probes (A and B) were constructed by manually inducing bends into the fiber. Diagrams of these two probes are given in Figures 3.5 and 3.6. By applying a drop of hot glue with a commercially available glue gun onto the chalcogenide fiber, the temperature was raised sufficiently to allow the fiber to be bent. As the glue cools, its viscosity increases, providing greater control over the bending procedures. The glue must be removed upon cooling and prior to use of the probes. Methylene chloride was used to remove the glue from the bend. These probes were evaluated using a series of test analytes. Ethanol and acetone were used to evaluate both probes. First, a background spectrum of the atmosphere was obtained using each probe. Spectra of the test solutions were obtained by dipping the bent probes into each of the test analytes. The spectra of the test solutions were ratioed to the background spectrum to obtain the spectra of the test analytes.

3.4 Acquiring spectral data

Spectral data for the bend experiments were acquired at a nominal resolution of 4 cm^{-1}, by coadding 200 scans for the straight fiber experiments and 500 scans for the bent fiber experiments. Spectral data for the fiber probe experiments were acquired at a nominal 4 cm^{-1} resolution coadding 64 scans. The interferograms were processed using a Nicolet 620 workstation. The fiber optic interface was placed into the sample compartment of a Nicolet G Series 520 Bench (Nicolet Analytical Instruments, Inc., Madison, WI).

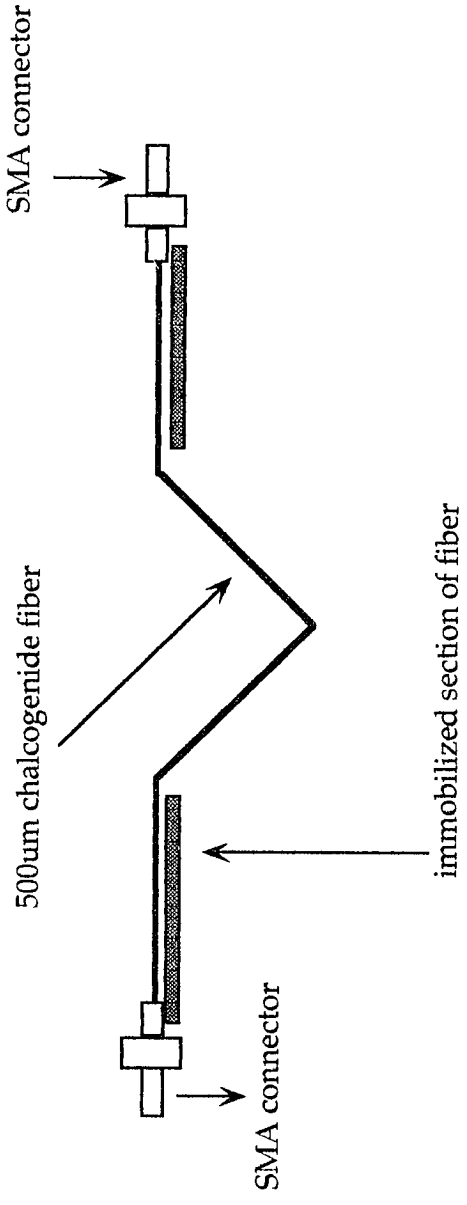

Figure 3.5 Side View of Probe A

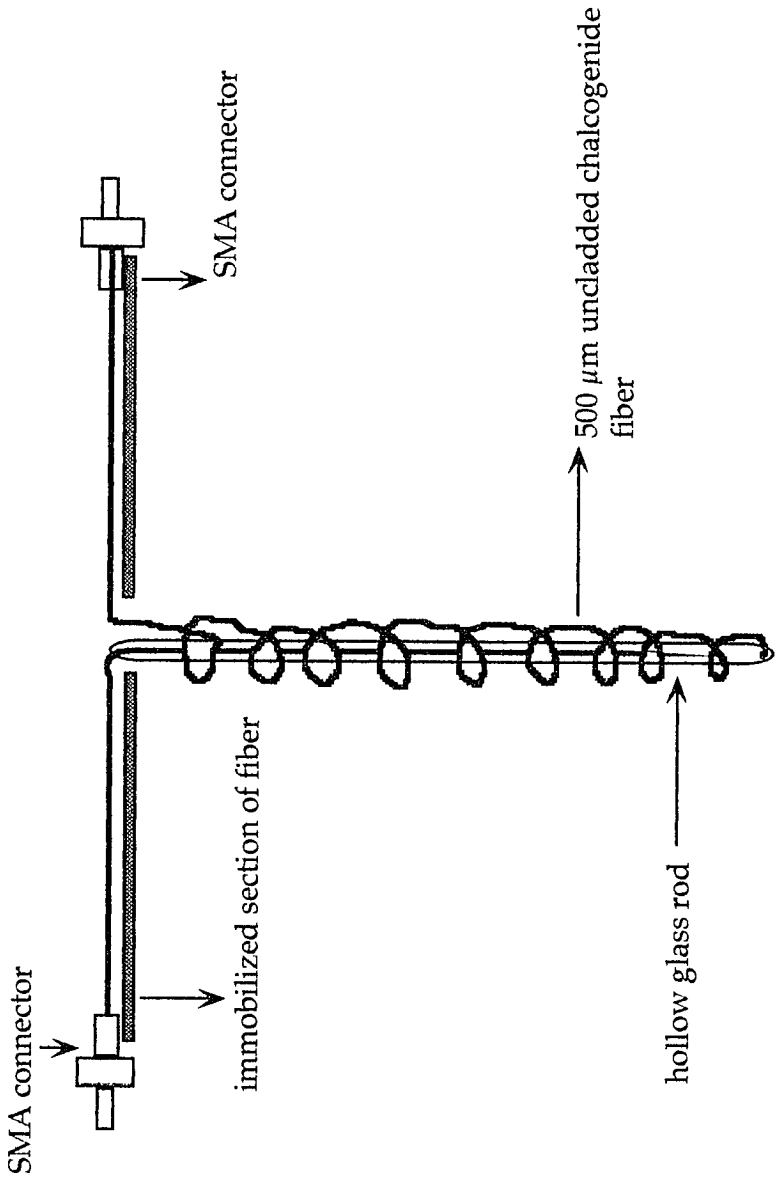

Figure 3.6 Side view of Probe B

3.5 Results and Discussion

Experiments were performed to determine if bending the fiber before the sensor increases the sensitivity of the measurement. Figures 3.7, 3.8 and 3.9 show spectra of pure ethanol (99%) which were acquired with various degrees of bending using the same infrared sensor. The baseline corrected absorbance of the C-H stretch at approximately 1050 cm^{-1} increased as the degree of bending increased. The baseline corrected absorbance values obtained for the 1050 cm^{-1} C-H stretch of ethanol were 0.086 au for the straight sensor, 0.102 au for the 45 degree sensor and 0.110 au for the 90 degree sensor. This observed increase in absorbance could be attributed to the scrambling of the lower order modes of light into higher order modes of light. This increase in the number of higher order modes of light results in more reflections through the sensor region, thereby resulting in greater levels of infrared radiation being absorbed by the solution surrounding the sensing region.

Further examination of the background spectra obtained for the bend experiments (see Figures 3.10 and 3.11 and 3.12) did show a decrease in the amount of energy transmitted in the region of the characteristic peaks of the fiber. This trend can be attributed to an increase in the number of higher order modes of light that are traversing through the fiber. This increase results in more of the fiber being sampled which leads to an increase in the absorption of the characteristic peaks.

The 100% line spectra were compared for the three bending experiments (Figures 3.13 and 3.14 and 3.15). The 100% line is obtained by dividing the spectrum of the unhydrated sensor by itself. The resulting spectrum provides an indication of the noise in each region of the spectrum. The noise level provides information about the amount of energy passing

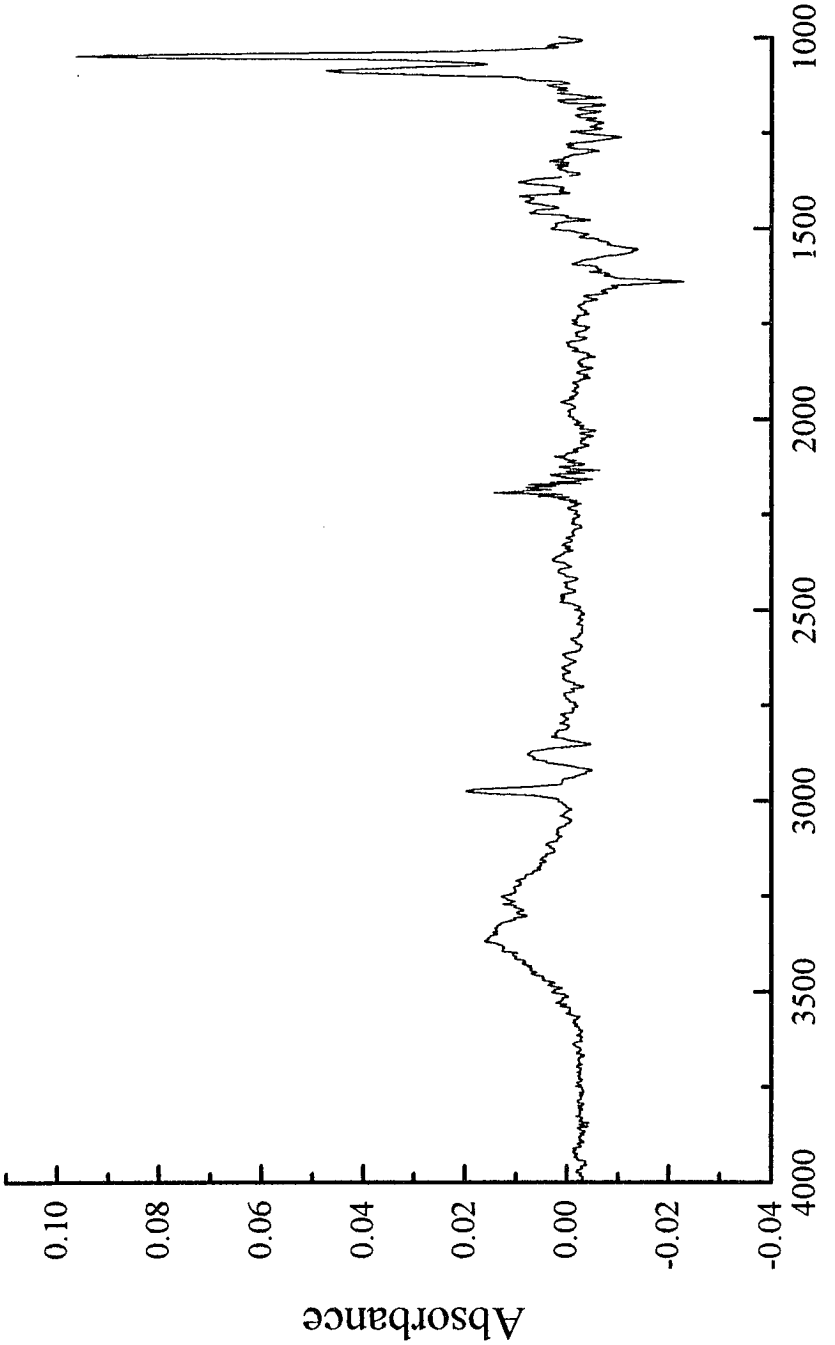

Figure 3.7 Spectrum of ethanol using a 180 degree fiber sensor

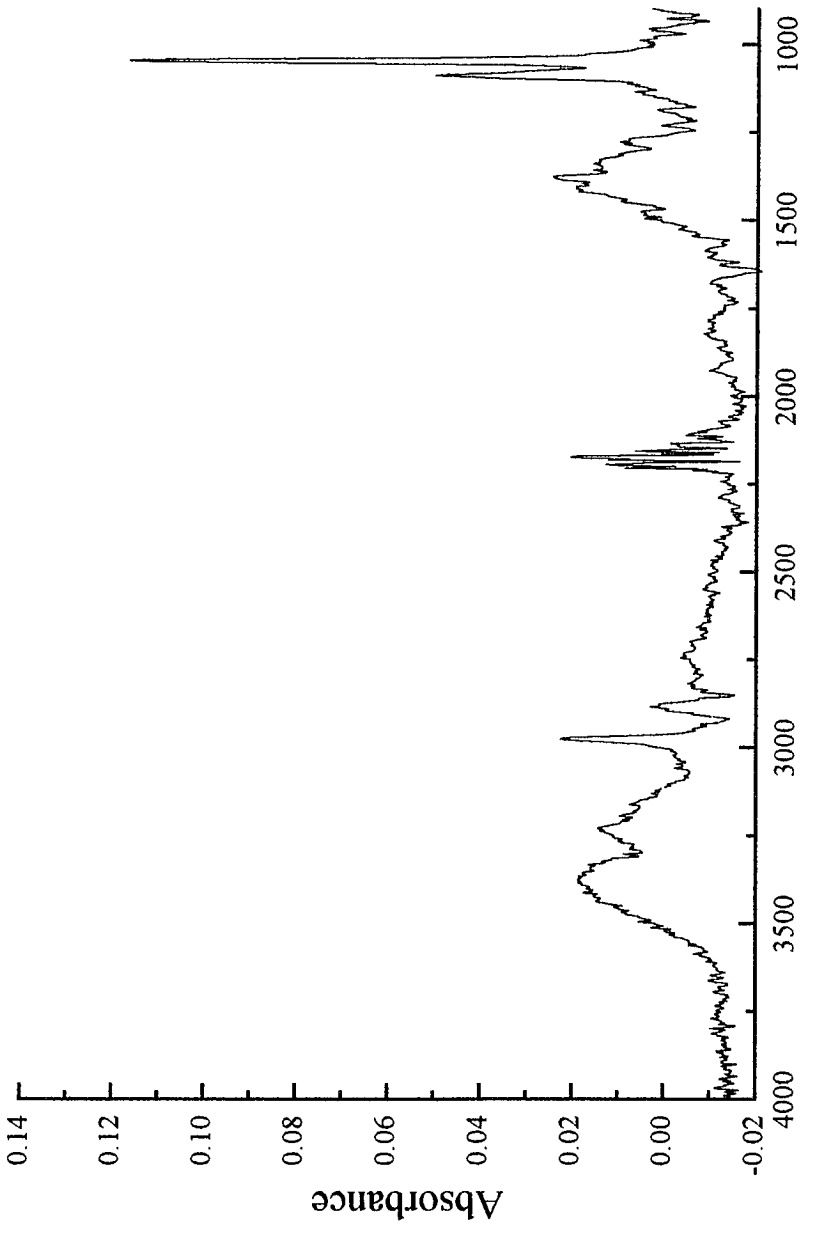

Figure 3.8 Spectrum of ethanol using a 45 degree fiber sensor

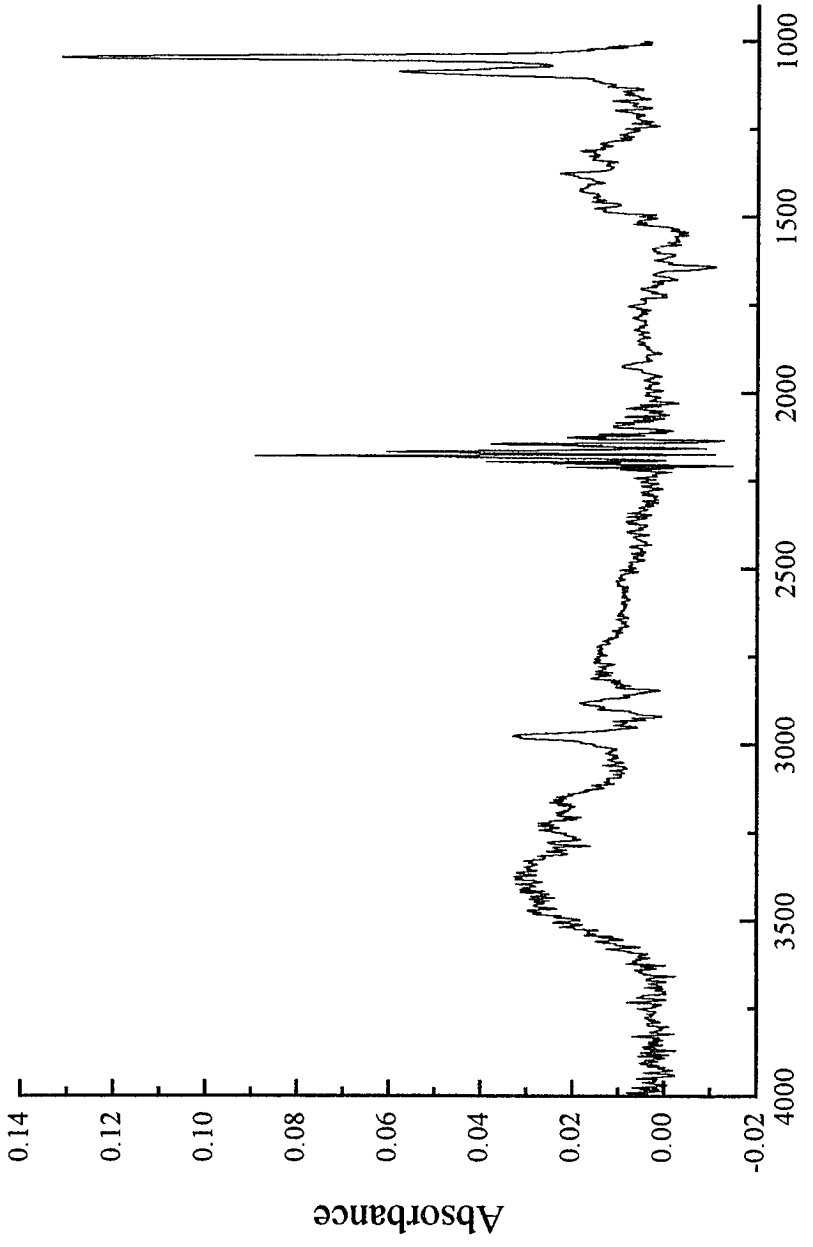

Figure 3.9 Spectrum of Ethanol using a 90 degree fiber sensor

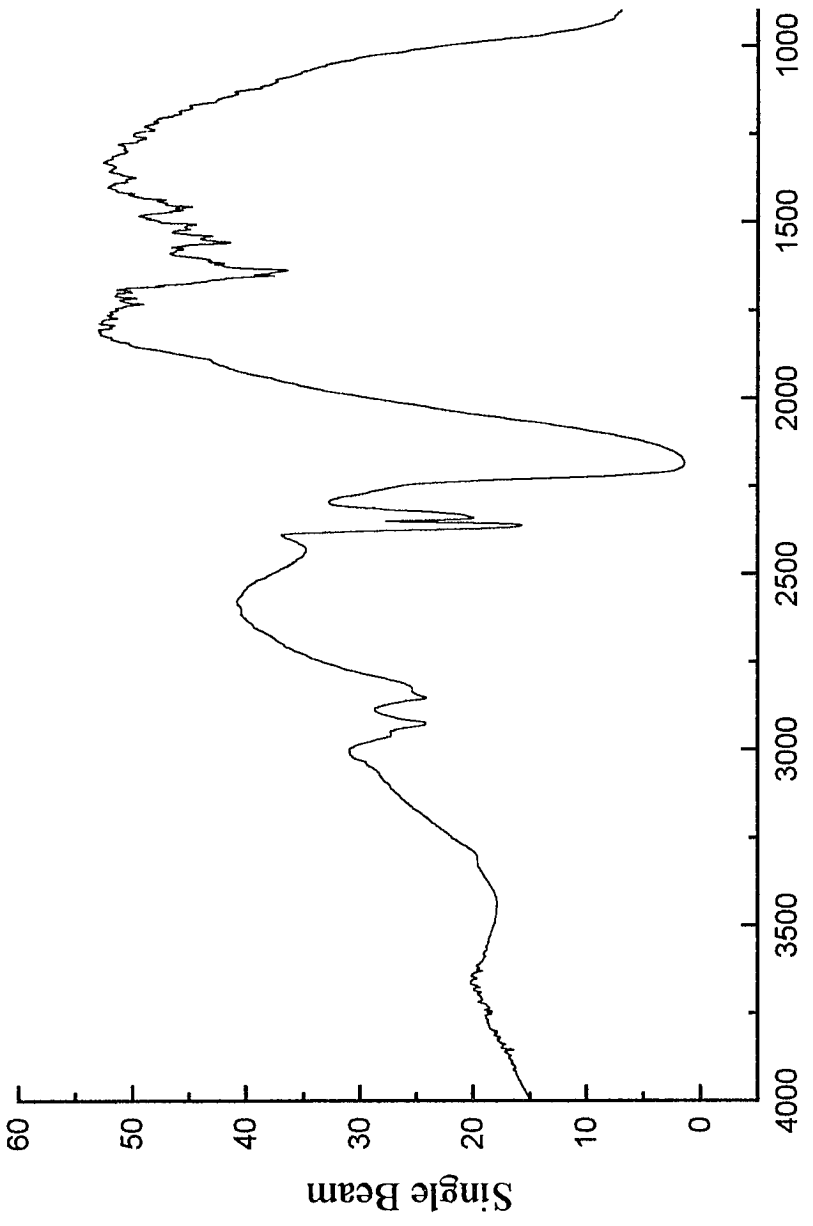

Figure 3.10 Background spectrum of a straight fiber cell

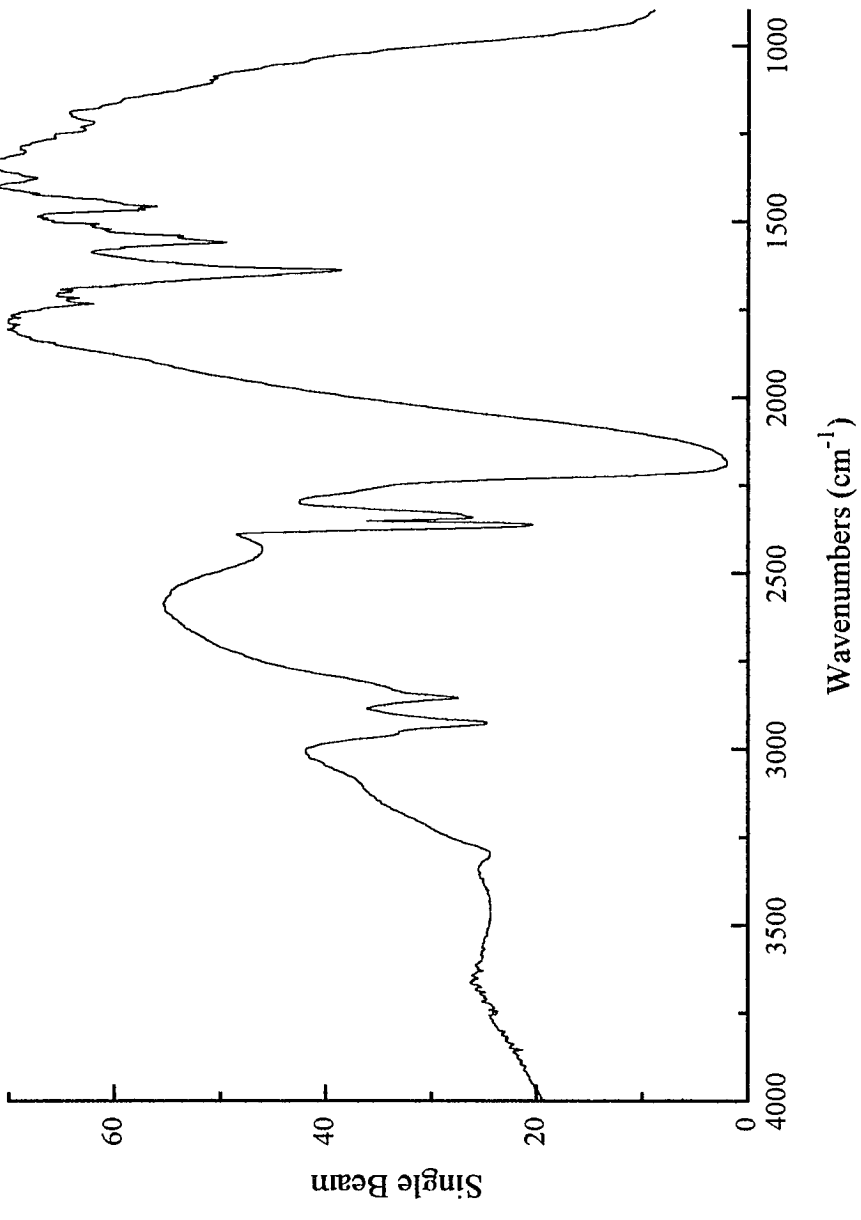

Figure 3.11 Background spectrum of a 45 degree fiber cell

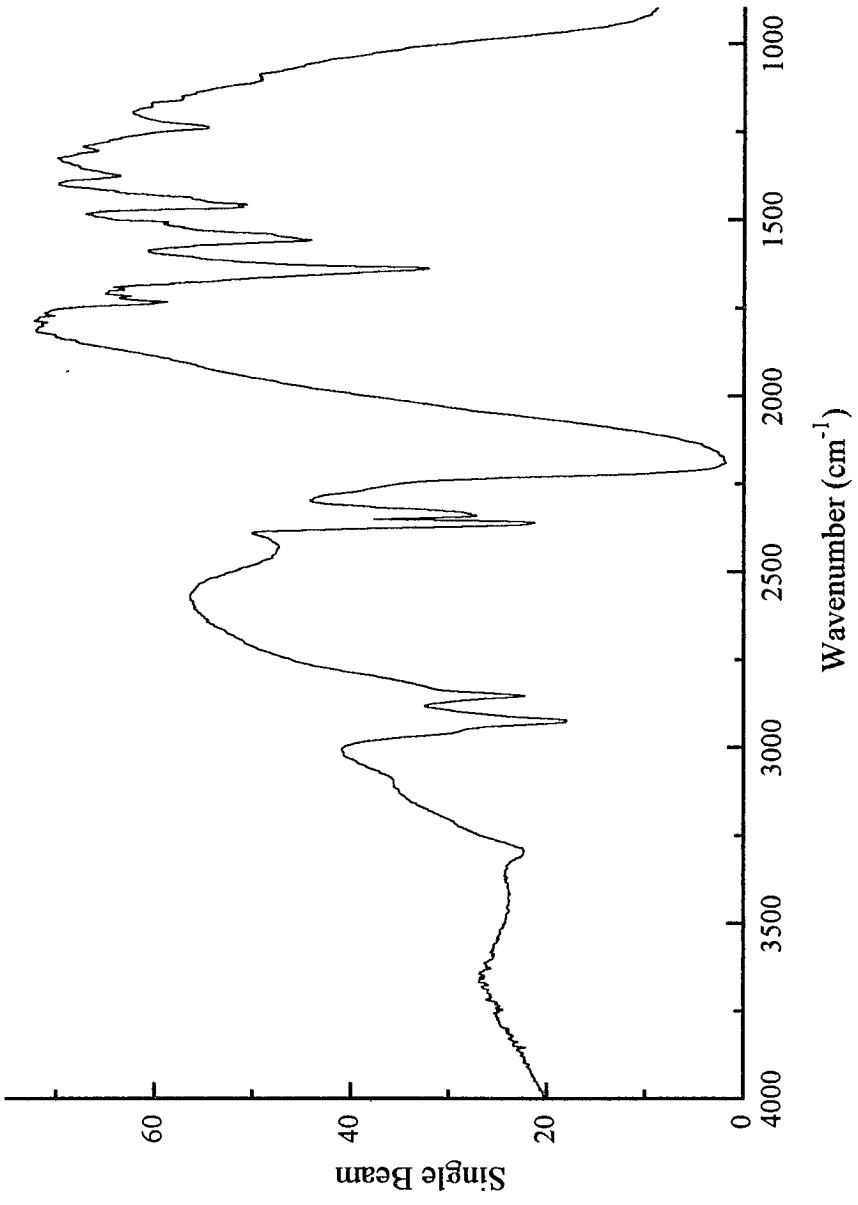

Figure 3.12 Background spectrum of a 90 degree fiber cell

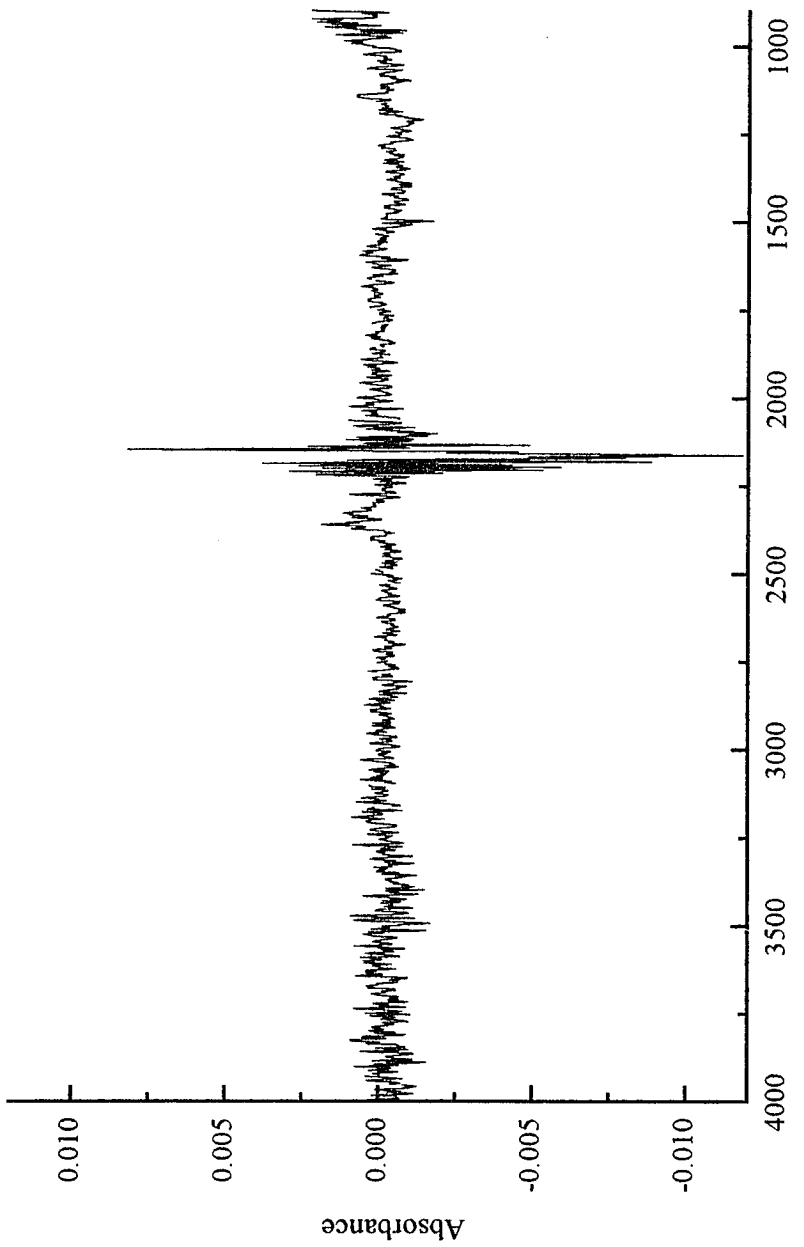

Figure 3.13 100% line of a straight fiber cell

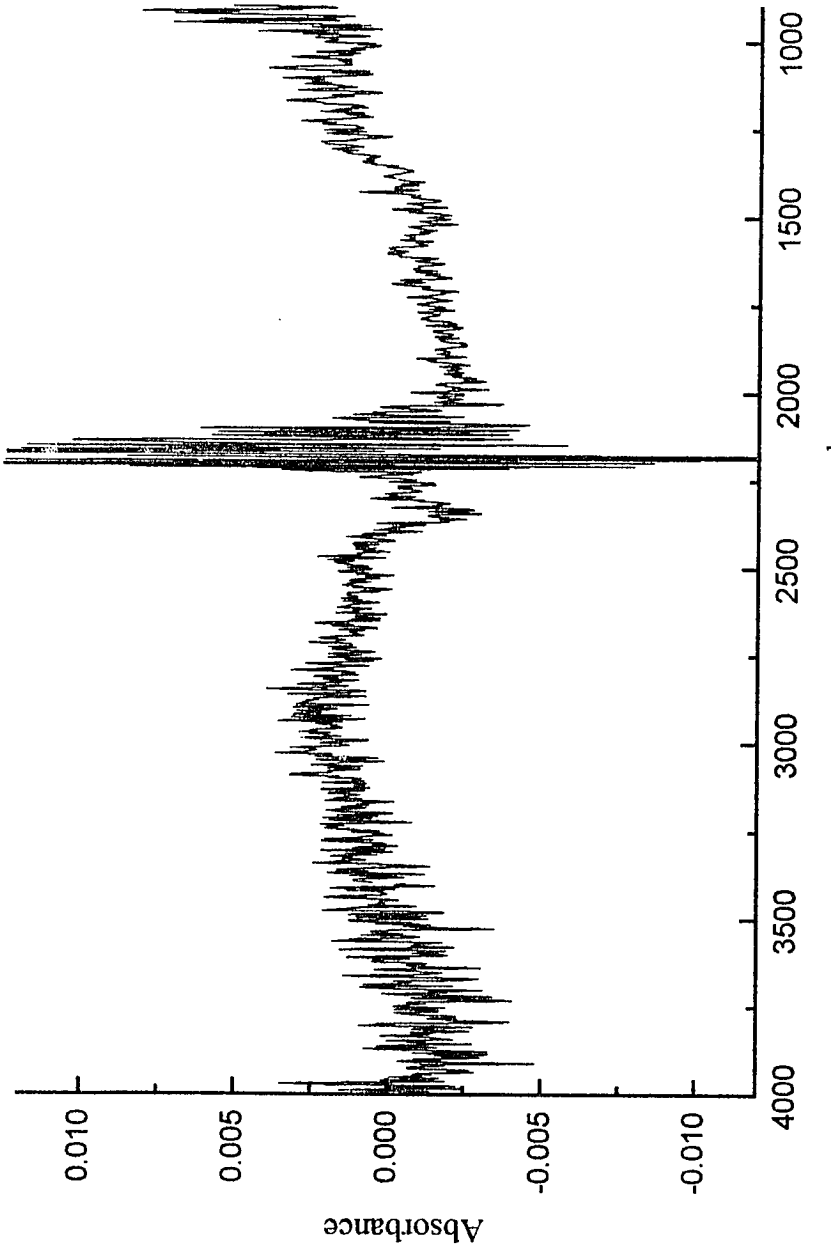

Figure 3.14 100% line of a 45 degree fiber cell

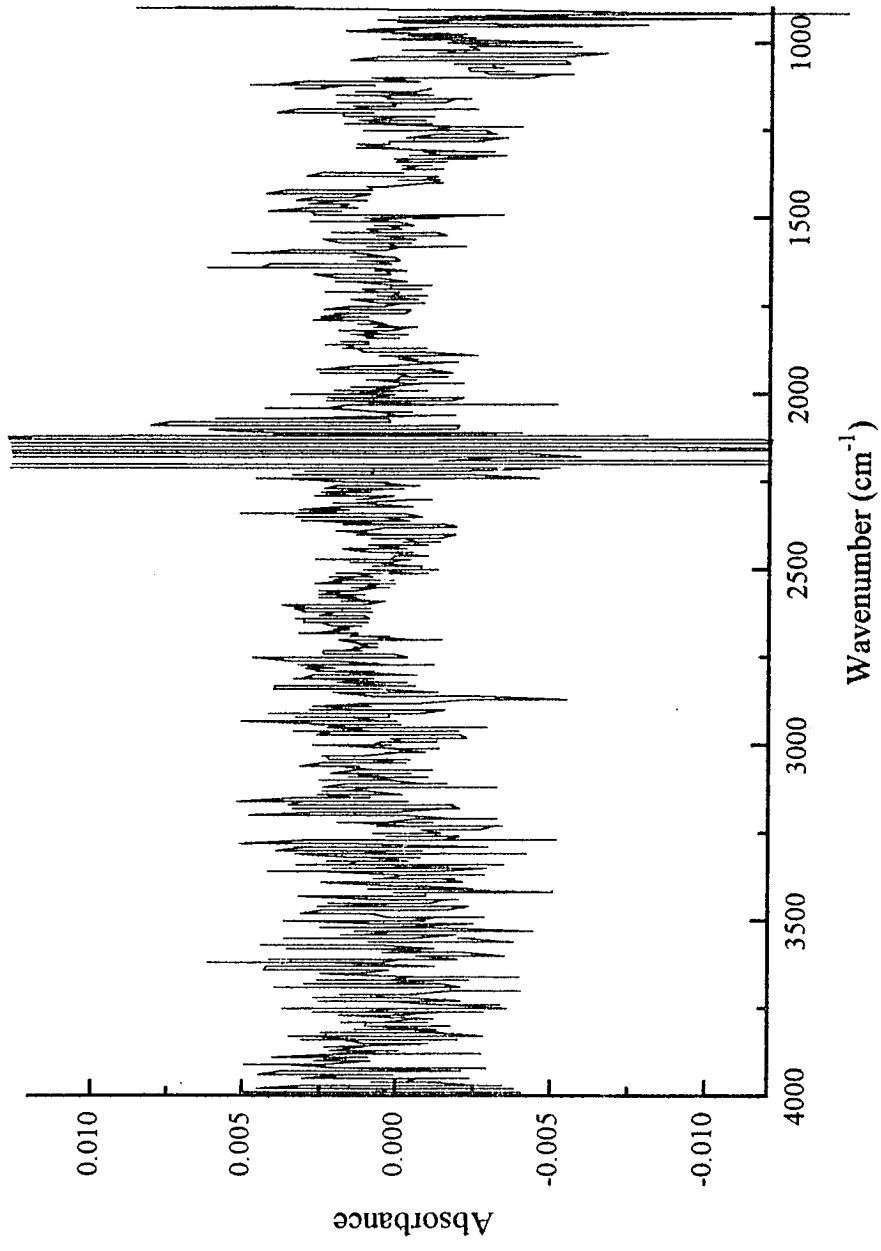

Figure 3.15 100% line of a 90 degree fiber cell

through the fiber: a greater noise level indicates that there is less energy, and vice versa. Increasing the angle of the bend resulted in an increase in the amount of noise in the spectrum. The peak to peak noise in the range from 1200 to 1000 cm^{-1} of the 0, 45, and 90 degree sensors were 0.0017 au, 0.0038 au, and 0.0096 au, respectively. One possible explanation for this increase in noise could be the existence of the bend itself. Defects (e.g., microcracks, bubbles, etc.) could also have developed when bending the fiber to the appropriate angle. Further examination of the spectra also showed some artifacts for the 0 and 90 degree sensors. The artifacts were, however, in regions that did not affect the characteristic absorbance band of ethanol, and therefore did not alter the measurements.

Additional experiments were performed to determine the performance of bent chalcogenide probes. Probe A was "v" shaped. A single beam spectrum of this probe in air was obtained. The "v" section of the probe was then immersed approximately 0.5 inches deep into several test solutions and spectra were obtained. The absorbance spectra of acetone and ethanol obtained using this probe are given in Figures 3.16 and 3.17. The absorbance spectra of ethanol are shown in Figure 3.17. The spectrum of ethanol shows an increase in the absorbance of ethanol as compared to spectra obtained using a sensor with a 90° bend before the sensing region (see Figure 3.9). It is reasonable to expect an increase in the absorbance observed due to the increase in the number of higher modes of light as the energy passes through the bends of the fiber. Further, the evanescent wave is able to sample a larger area because the launch angle of the fiber is approaching the critical angle, thereby increasing the depth of penetration of the evanescent wave.

The experiments were repeated using Probe B (schematically represented by Figure 3.7). The acetone and ethanol spectra obtained are

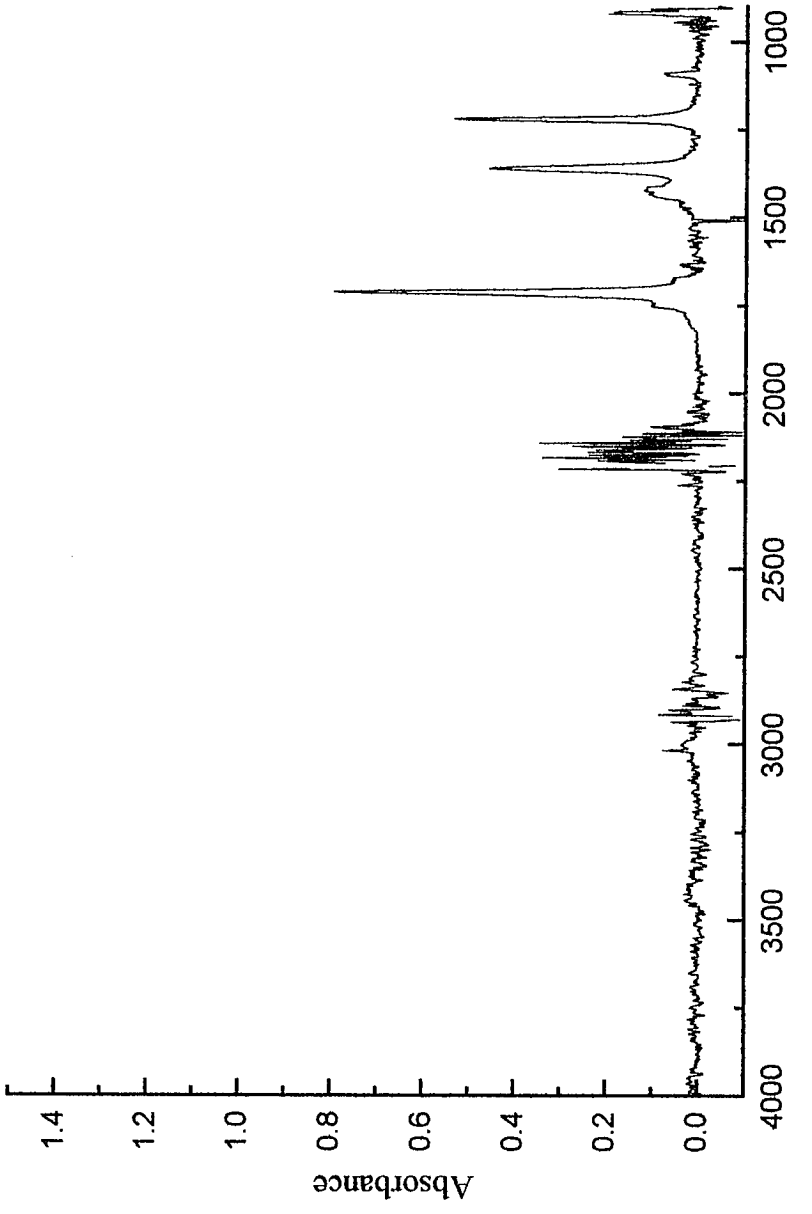

Figure 3.16 Absorbance spectrum of acetone using Probe A

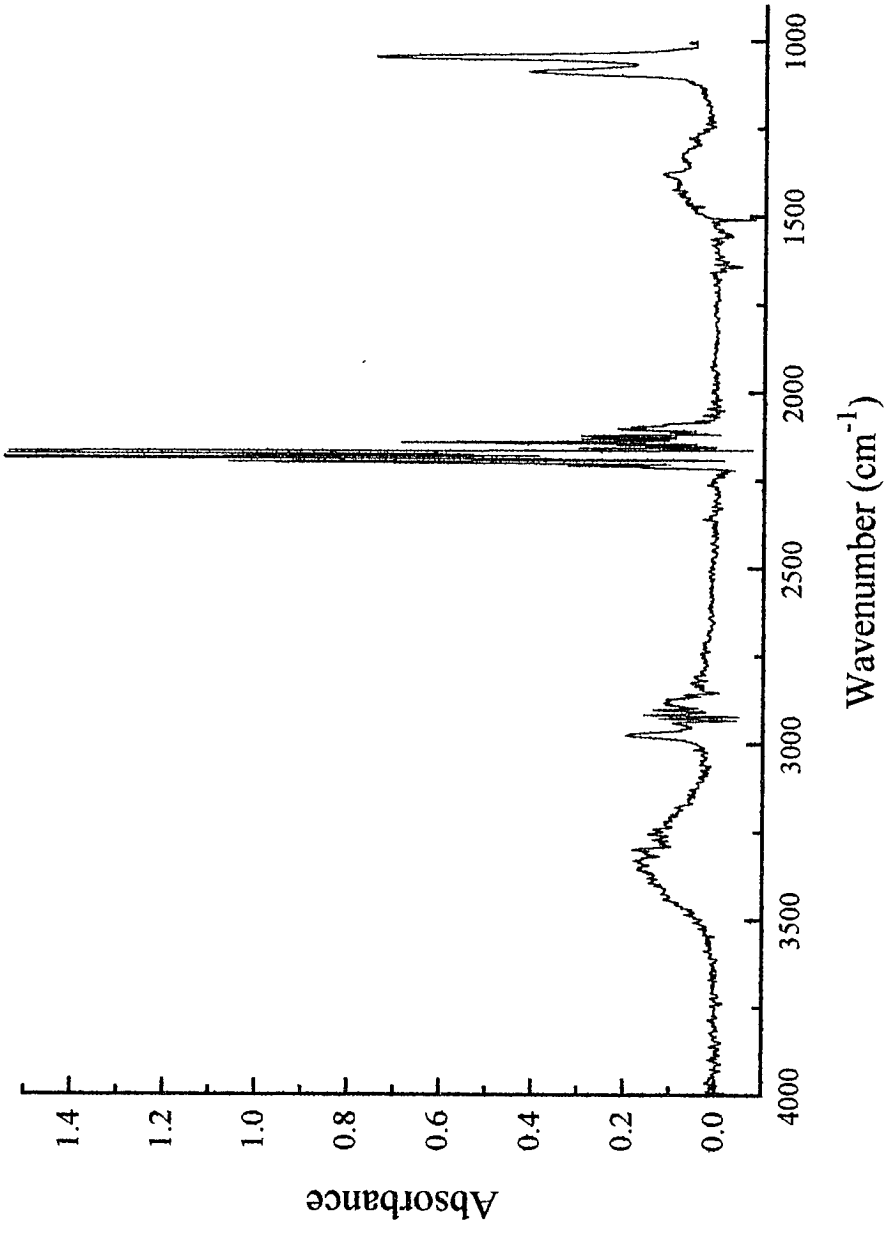

Figure 3.17 Absorbance spectrum of Ethanol using Probe A

given in Figures 3.18 and 3.19. The ethanol spectrum given in Figure 3.19 shows a large increase in the magnitude of the absorbance values of the characteristic test analyte used as compared to the ethanol spectrum obtained using a straight sensor (given in Figure 3.9). This increase in magnitude can be attributed to the same reasons mentioned earlier for Probe A. Both probes showed an improvement in the absorbance obtained for ethanol compared to the sensor with the bend preceding the sensing region. The level of absorbance for both acetone and ethanol was greater using Probe A than Probe B (see Figures 3.16 and 3.18, and Figures 3.17 and 3.19). It should be noted that some spectral artifacts did occur in the spectra but again they did not affect the characteristic peaks of interest.

3.6 Conclusion

Chalcogenide fibers can be used as ATR elements for both remote and *in situ* detection. Placing a bend before the straight sensing element improved the detection capabilities of the fiberoptic sensors developed in our lab. Several novel probes that used the bent portion as the sensor were developed. These probes also resulted in an improvement in the absorbance of analytes. There are some disadvantages in the development of these types of probes: 1) the construction of chalcogenide infrared fiber probes is very time-consuming, 2) chalcogenide fibers are extremely brittle once the polyamide coating is removed from the fiber. Care must be used during construction and handling of the probes. 3) once the coating is removed and the fiber is exposed to the environment, microcracks and breaks can develop, 4) since the procedure used to make the bends is not precise, the ability to compare two fiber probes with the same bend is limited. The main advantage of using these probes is that they lend themselves to sampling small

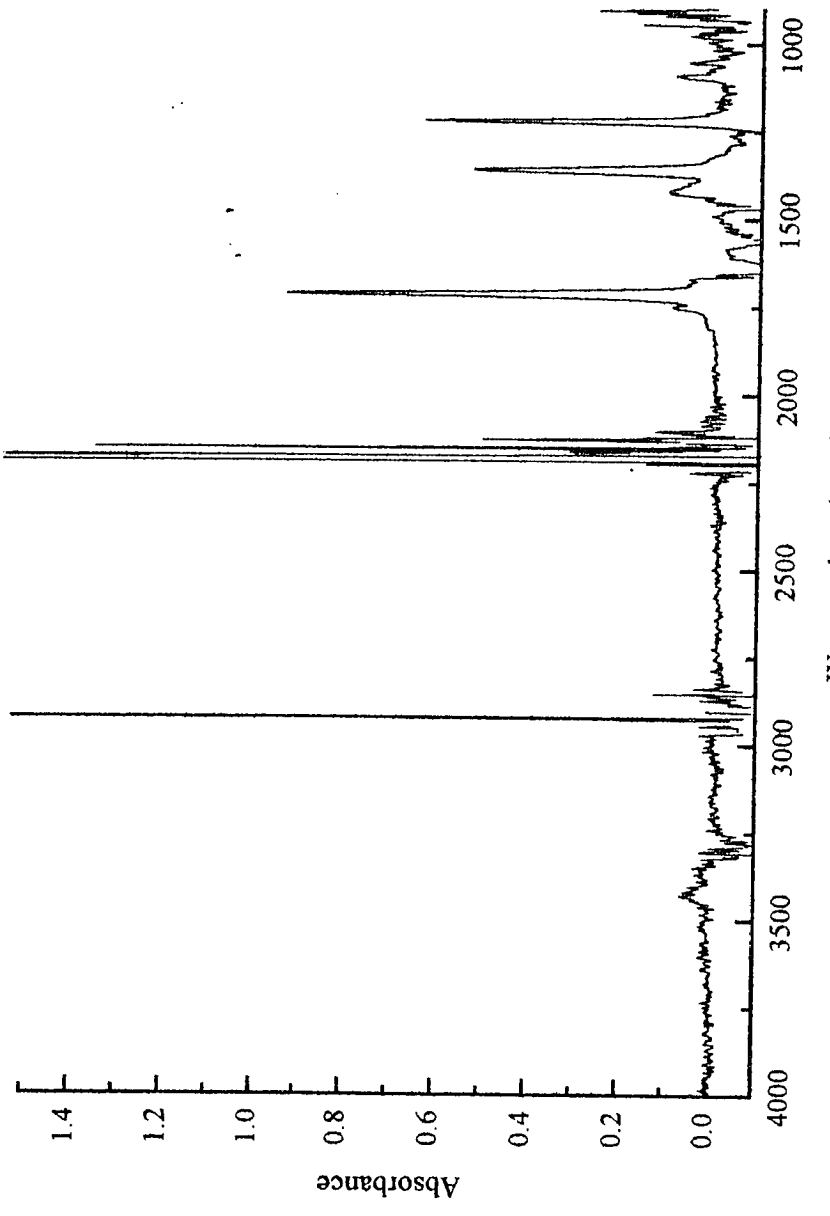

Figure 3.18 Absorbance spectrum of acetone using Probe B

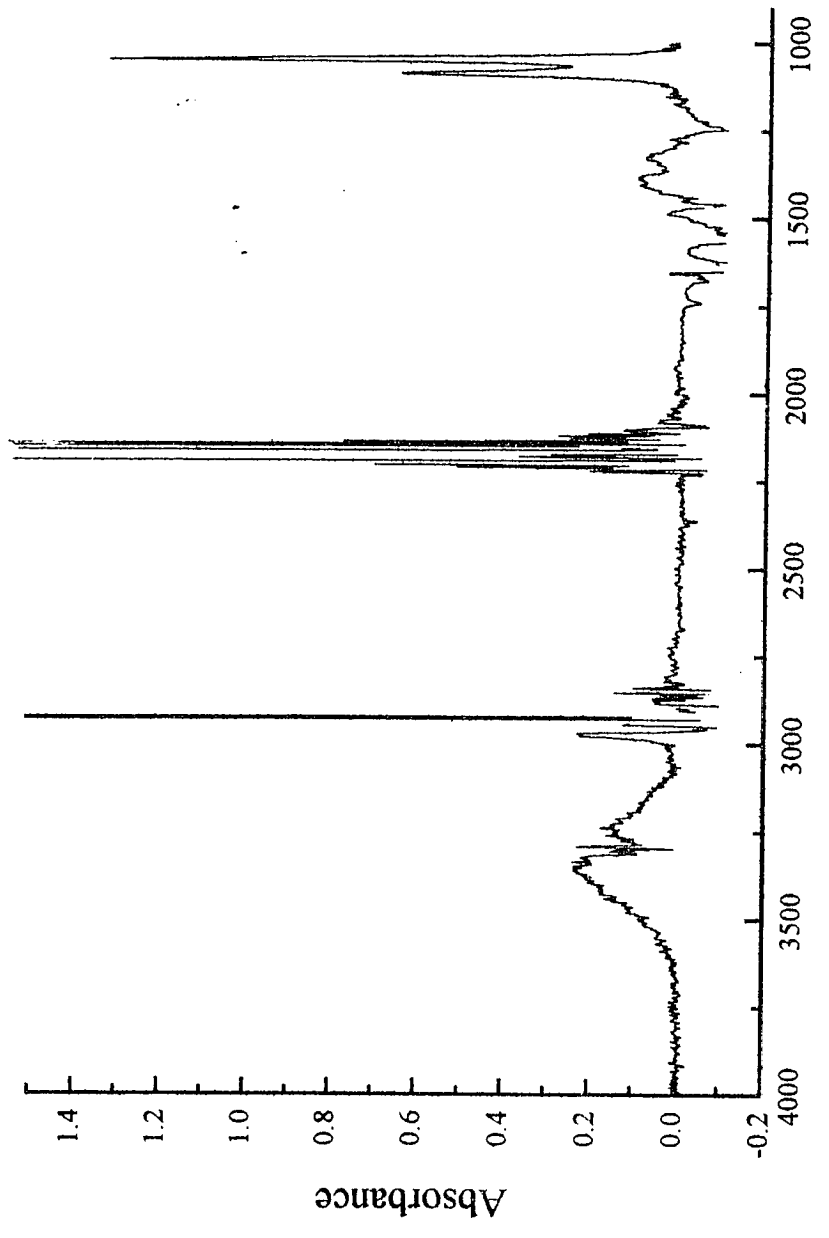

Figure 3.19 Absorbance spectrum of ethanol using Probe B

volumes. Further, as our experiments have demonstrated, the use of bent fibers (whether the sensing region used was before the bend or the bend itself) offers improved analytical sensitivity.

CHAPTER IV

EVALUATION OF POLYMER COATED UNTAPERED FIBERS FOR THE ANALYSIS OF ORGANIC COMPUNDS IN AQUEOUS SOLUTIONS

4.1 Introduction

Previous studies had indicated coating a conventional ATR element with a suitable polymeric layer can improve the detection of analytes in aqueous solution. The purpose of the polymer coating is to extract the analyte from the solution onto the fiber, assuming the analyte has a high partition coefficient. Concentrating the analyte in the polymer phase increases the amount of analyte within the depth of penetration of the evanescent wave thereby providing an enhancement in the absorbance spectrum obtained for the analyte. Experiments were performed to determine the level of enhancement in sensitivity obtained using polymer coated untapered chalcogenide fibers to detect analytes in aqueous solutions.

4.2 Experimental

4.21 Materials and Methods

For these experiments, the fiber was first coated with a polymeric phase. Both chloroparaffin and DOP plasticized PVC coated fibers were evaluated. The fibers were assembled into a liquid sample cell to obtain spectral data for aqueous solutions. The method of assembly used to construct these cells is discussed in Section 4.22. Experiments were then

performed to evaluate the ability of the coated fiber to extract the analyte from the aqueous solution. A single beam spectrum of a 750 μm glass core/glass clad chalcogenide connecting fiber was used as the background. The spectrum of the 750 μm fiber was obtained by connecting the fiber to the source and detector orifices of the fiber optic interface. Once a background of the 750 μm fiber was obtained, the 500 μm polymer coated sensor was attached between the connecting fiber and the detector orifice of the fiber optic interface. An absorbance spectrum of the polymer coated sensor was obtained by dividing the single beam spectrum of the sensor by the background spectrum of the 750 μm connecting fiber. This absorbance spectrum was used to determine the thickness of the polymer phase. This procedure will be further discussed in this section.

A background spectrum of the polymer coated sensor was acquired after hydrating the polymer for approximately 30 minutes with an aqueous solution containing 1.5% w/w methanol/H_2O. The test solution used for these experiments contained 0.1% v/v nitrobenzene in a 1.5% w/v methanol/H_2O solution. Nitrobenzene was chosen as the test analyte because of the characteristic asymmetric and symmetric stretches of the nitro group at 1530 cm^{-1} and 1350 cm^{-1}, respectively. The test solution was added to the cell and spectra were obtained by coadding twenty-five scans. Spectra were taken every minute for the first fifteen minutes, after which, spectra were acquired every five minutes.

The thickness of the polymer coatings applied to the fibers was estimated using two methods. The first method involved measuring the magnitude of the baseline corrected height of the C-H stretch of the polymer coating. The second method entailed measuring the actual thickness of the fiber using scanning electron microscopy. The sensing region of the fiber was

cleaved and an electron micrograph of the cross section of the unclad fiber was obtained. This method obviously destroys the sensor so the micrographs were acquired after the spectroscopic experiments had been completed.

The data were collected using a Nicolet FTIR 520 bench and processed with Nicolet's PC driven software, OMNIC. These measurements were obtained with a special program that was written in Visual Basic (given in Appendix II). As mentioned earlier, OMNIC and Visual Basic were interfaced using Nicolet's OMNIC Macros/Pro. The program was written to collect data at one minute intervals for the first fifteen minutes after which time a spectrum was acquired every five minutes. The program used for these studies is a modified version of the program described in Chapter 2. The only change made to this program was the removal of the temperature control subroutines that were previously developed. An illustration of the Visual Basic Form window used for these experiments is shown in Figure 4.1. The form window shows the input boxes that can be set as well as the display boxes that allow the operator to monitor the experiment. The first input box allows the experimenter to differentiate between experiments by adding a filename. The next three boxes allow the operator to input the number of spectra obtained for this experiment, the number of seconds between the first fifteen spectra and the number of minutes between spectra after fifteen spectra are acquired. Finally, a display box that shows the time at which spectra were obtained, the peak position of the test analyte, and the baseline corrected height of the analyte is presented. The peak position under study is written directly into the program. The last two buttons are the 'start' button which allows the operator to initiate the program and the 'exit' button that allows the operator to terminate the program at any time.

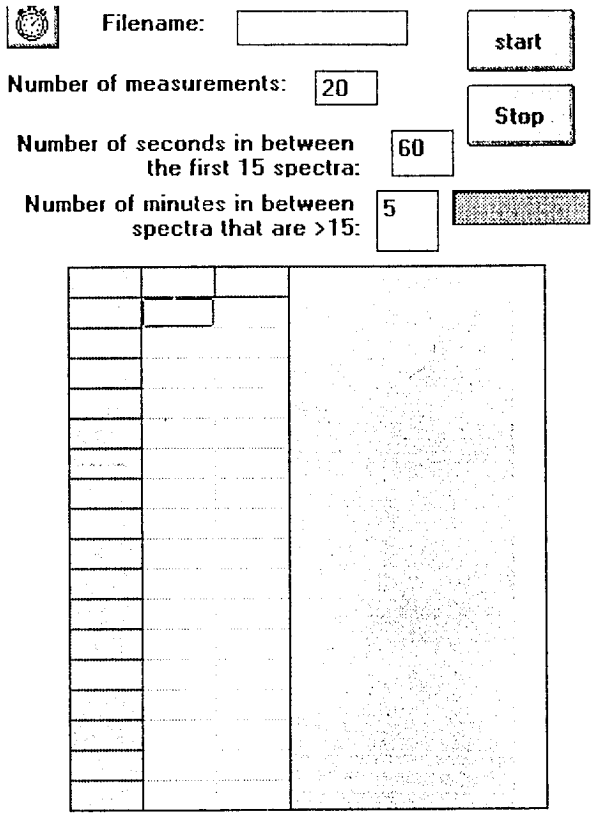

Figure 4.1 Visual Basic form window used for the monitoring of test analytes in aqueous solutions

4.22 Coating the Fiber and Construction of the Fiber Cell

The 500 μm fibers used for these experiments were obtained from Amorphous Materials, Inc. (Garland, Texas). These fibers are an amorphous mixture of selenium, tellurium and arsenic and tend to be very brittle. Fibers were cut into 13 cm sections. The fibers were then immersed in tetrahydrofuran (THF) to remove the polyamide coating placed on the fiber by the manufacturer for mechanical stability. Once the polyamide coating was removed, the polymer phase used to concentrate the analyte was applied to the sensing region of the fiber by dipping the fiber into a solution containing the polymer formulation. The sensing region was approximately 4 cm in length and located in the center of the 13 cm section of fiber. The polymer formulations used for these experiments were 47% w/w chloroparaffin (60%-Cl)/PVC and a 12.8% w/w dioctylphthalate/PVC. Both plasticizer/polymer formulations were applied from the THF solutions. These phases were used because their ability to extract the test analyte had previously been verified (Chapter 2).

The coatings were applied to the fiber using the following procedure. The fiber was dipped into the polymer solution for approximately one second and removed from the solution. The THF was allowed to evaporate resulting in a polymer coating being left on the fiber. The fiber was dipped into the solution several times to ensure complete coverage of the sensing area. The fiber was then placed into a glass cell designed to hold liquids. The fiber was sealed to the glass cell using an epoxy glue to prevent leakage of the aqueous solutions. The glass cell was further immobilized onto a flat platform and SMA connectors were attached to the ends of the fiber. The ends of the fiber were polished using the method described in Chapter 3. The top of the cell has two openings to allow the addition of aqueous solution. Teflon caps were

placed into the openings to prevent sample evaporation. Figure 4.2 is a schematic diagram of the cell used for these experiments.

4.3 Results of the Untapered Chalcogenide Fiber Experiments

An experiment was performed to determine the level of absorbance obtained for an aqueous solution containing 0.1% v/v of the test analyte nitrobenzene and 1.5% methanol/H_2O, using an uncoated chalcogenide fiber as the ATR element. First, a background spectrum of the 750μm fiber, sensor, and aqueous solution of 1.5% methanol were acquired. The water was removed from the cell and the test solution containing the analyte (nitrobenzene) was added to the same cell. Spectra were acquired up to 90 minutes. Figure 4.3 is a plot of the absorbance at 1348 cm^{-1} vs. time. The data obtained clearly indicate that the symmetric stretch of the nitro group is detected using an uncoated chalcogenide fiber when using this test solution.

Similar experiments were performed to determine if coating the infrared fibers with an appropriate polymeric layer provided sufficient sensitivity for monitoring analytes in aqueous solutions. The polymer coating used for these experiments was polyvinyl chloride. Figure 4.4 is an absorbance spectrum obtained for the nitrobenzene solution collected after 90 minutes using a PVC coated sensor. The lack of an absorbance band at 1348 cm^{-1} in Figure 4.4 clearly illustrates that the presence of nitrobenzene in an aqueous solution containing 0.1% v/v nitrobenzene and 1.5% w/v methanol cannot be detected after 90 minutes.

Experiments were performed to determine if incorporating a plasticizer into the PVC phase improves the sensitivity of the measurement. A 47% w/w chloroparaffin(60%-Cl)/PVC phase was coated onto the 500 μm unclad chalcogenide fiber. The characteristic spectral absorption bands for

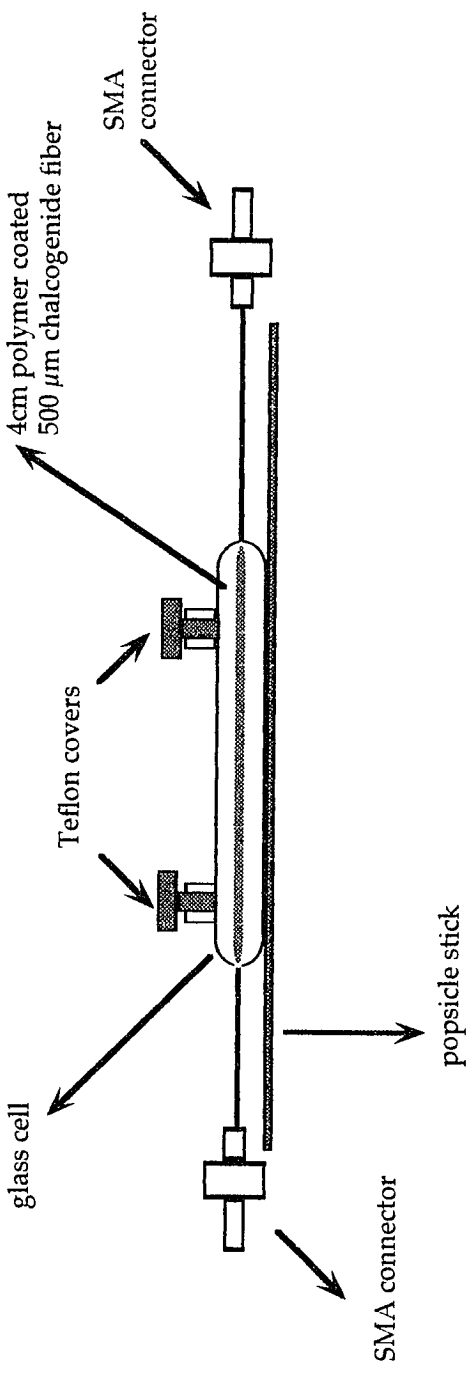

Figure 4.2 Schematic diagram of a liquid fiber cell

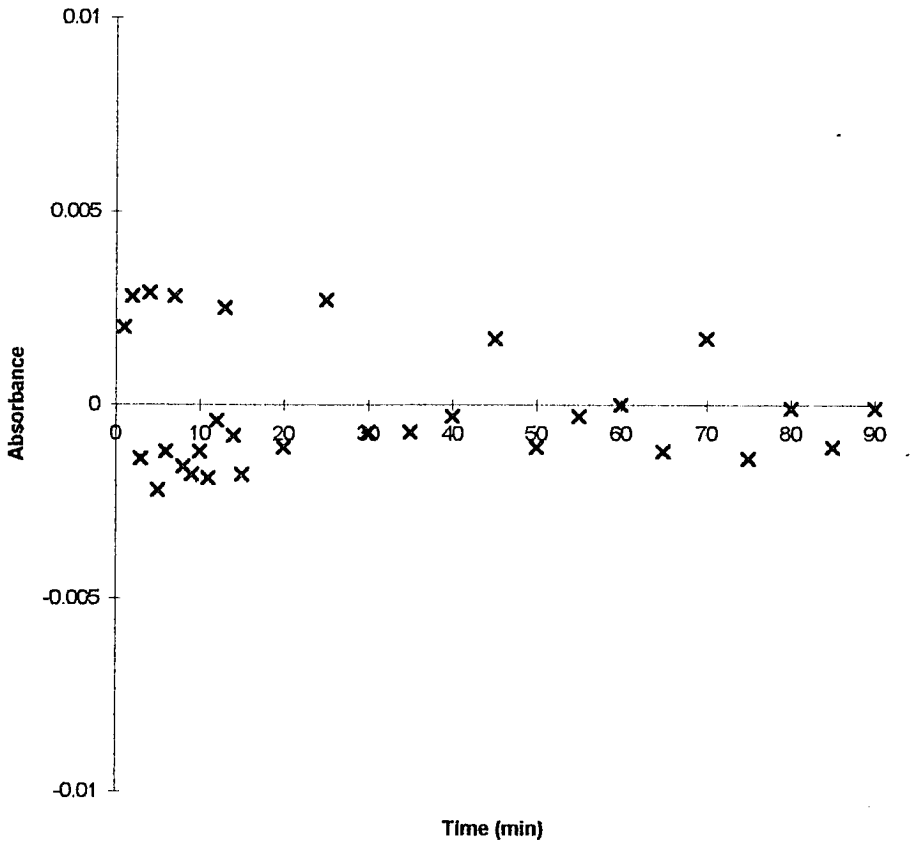

Figure 4.3 Absorbance at 1348 cm-1 vs. time profile for an uncoated chalcogenide fiber

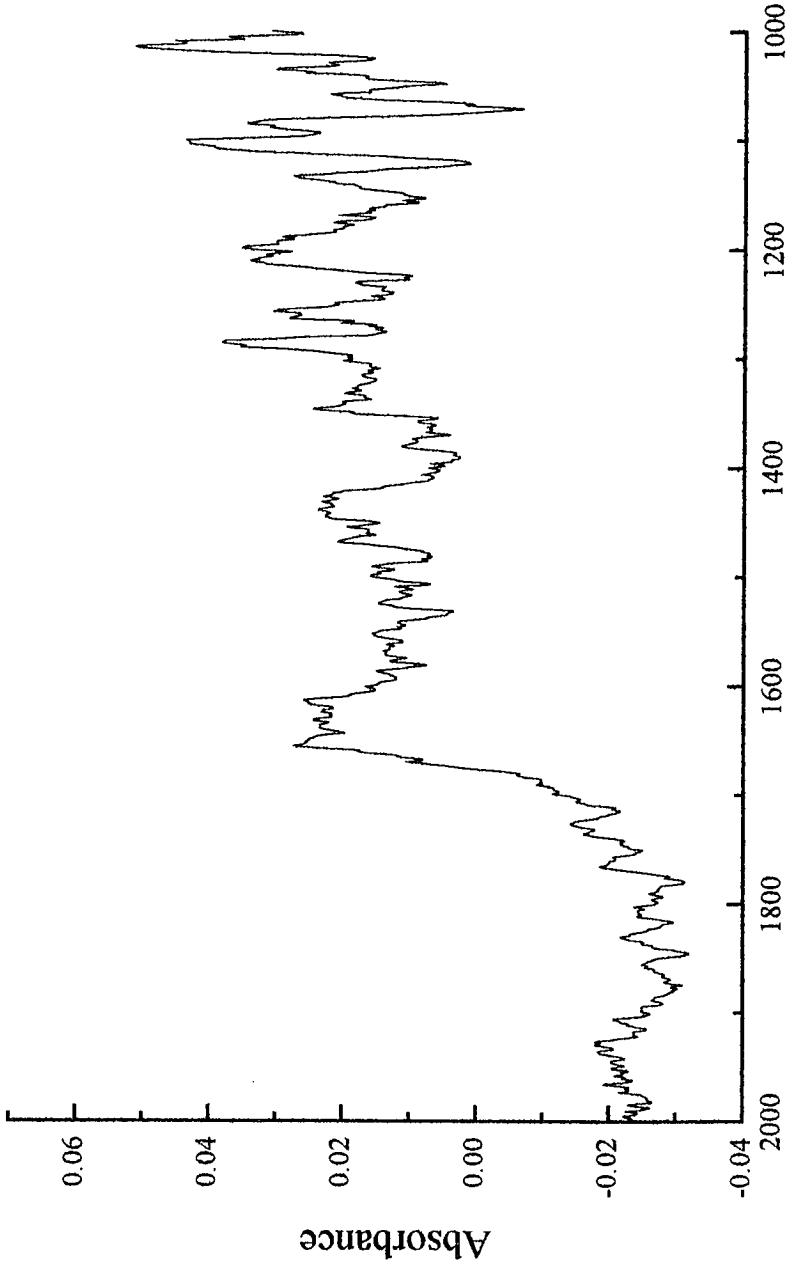

Figure 4.4 Spectrum of nitrobenzene using a PVC coated untapered 500um fiber

nitrobenzene were monitored over time after adding the test solution. The absorbance spectrum obtained after exposing the fiber to the solution for 90 minutes (Figure 4.5) clearly show the symmetric and asymmetric stretch of the nitro group. Similar results were obtained using a 7% w/w DOP/PVC phase as the coating material (Figure 4.6).

Once the polymer coated infrared fiber experiments were performed, the fibers were cleaved in the sensing region and the thickness of the unhydrated polymer coating was determined using scanning electron microscopy. The scanning electron micrographs obtained are presented in Figures 4.7, 4.8, 4.9, 4.10 and 4.11. The scanning electron micrographs show the unclad 500 μm chalcogenide fibers coated with an unhydrated polymer coating. These electron micrographs demonstrate the limits of the procedure used to apply the coating on the fiber. Table 1 gives the average thickness of the polymer phase that was coated on each of the fibers based on the EM data. These average values were determined by measuring the thickness in four different areas around the fiber. Table 2 also gives the thickness of the unhydrated polymer determined by measuring the baseline corrected absorbance of the C-H stretch at 2920 cm^{-1}. These data reconfirm the limitations of coating fibers reproducibly in this way. Figure 4.12 gives the baseline corrected absorbance at 1348 cm^{-1} for a 0.1% v/v nitrobenzene in a 1.5% methanol/H_2O solution as it is preconcentrated into a 47% w/w chloroparaffin (60%-Cl)/ PVC phase over time. These data indicate that response times obtained using the chloroparaffin/PVC coated fibers were much slower than the response times obtained for ATR crystals coated with a similar phase (Chapter 2). This difference can probably be attributed to thicker coatings placed onto the fibers as indicated by the electron micrographs.

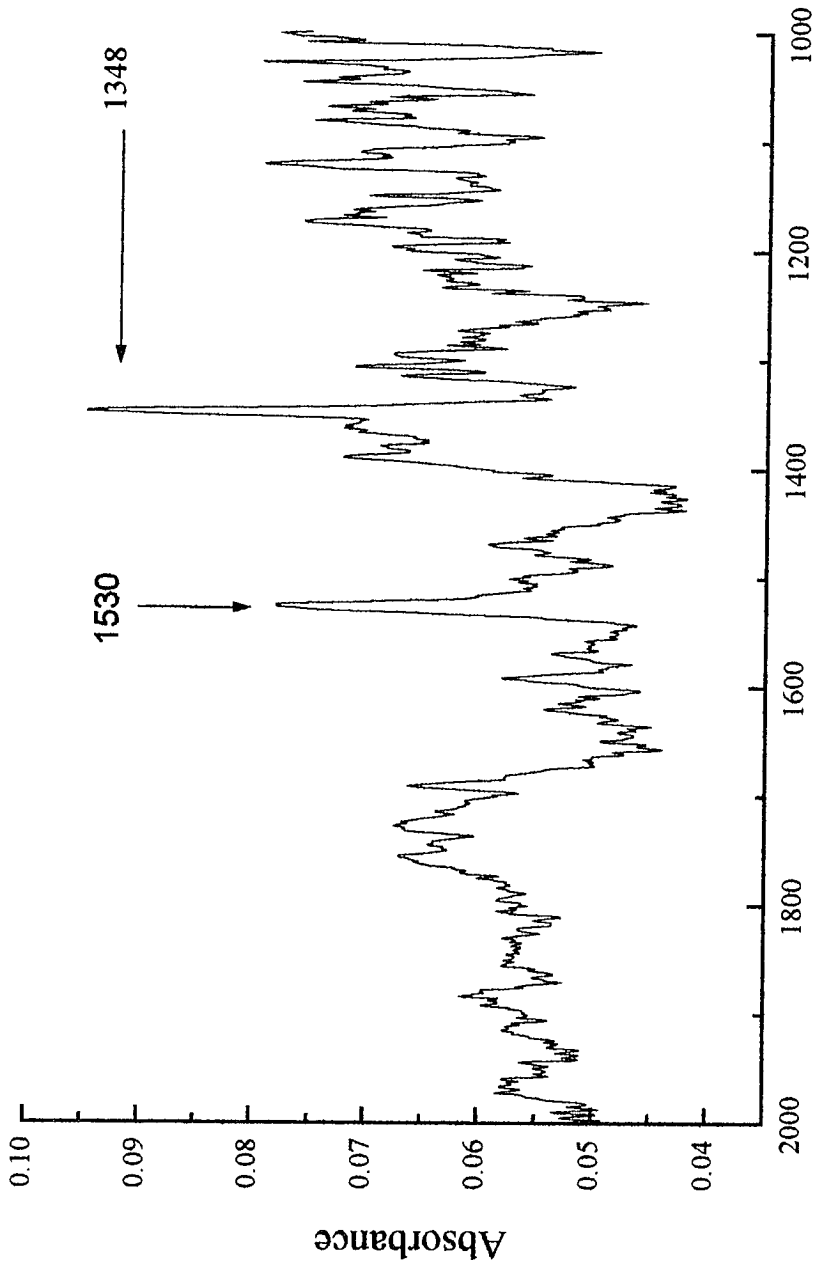

Figure 4.5 Absorbance spectrum of nitrobenzene using a chloroparaffin/PVC coated untapered fiber

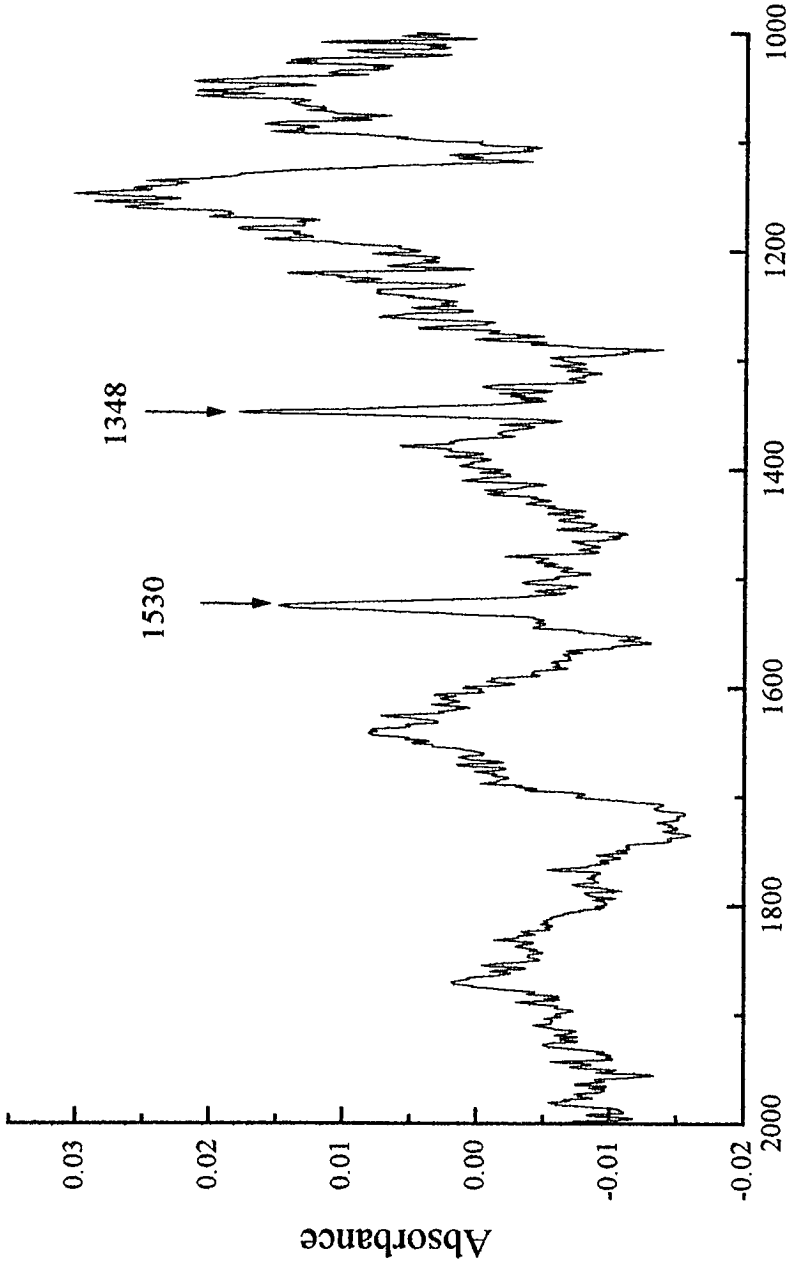

Figure 4.6 Absorbance spectrum of nitrobenzene using a DOP/PVC coated untapered fiber

Figure 4.7 Scanning electron micrograph of a PVC coated 500 μm chalcogenide fiber

Figure 4.8 Scanning electron micrograph of a chloroparaffin/PVC coated 500 μm chalcogenide fiber

Figure 4.9 Scanning electron micrograph of a chloroparaffin/PVC coated 500 μm chalcogenide fiber

Figure 4.10 Scanning electron micrograph of a DOP/PVC coated 500 μm chalcogenide fiber

Figure 4.11 Scanning electron micrograph of a DOP/PVC coated 500 μm chalcogenide fiber

Table 1

Scanning Electron Microscopy Measurements

Run Number	Polymer Coating	Average thickness of the polymer phase on the chalcogenide fiber (μm)
1	Polyvinylchloride (PVC)	31.8
2	Polyvinylchloride (PVC)	11.0
1	47% w/w chloroparaffin/PVC	13.0
2	47% w/w chloroparaffin/PVC	54.0
1	12.8% w/w dioctylphthalate/PVC	20.0
2	12.8% w/w dioctylphthalate/PVC	13.5

Table 2

Baseline Corrected Absorbance with Different Polymer Formulations

Run Number	Polymer Coating	Baseline Corrected Absorbance (2920 cm^{-1})
1	Polyvinylchloride (PVC)	0.097
2	Polyvinylchloride (PVC)	0.153
1	47% w/w chloroparaffin/PVC	0.059
2	47% w/w chloroparaffin/PVC	0.013
1	12.8% w/w dioctylphthalate/PVC	0.056
2	12.8% w/w dioctylphthalate/PVC	0.020

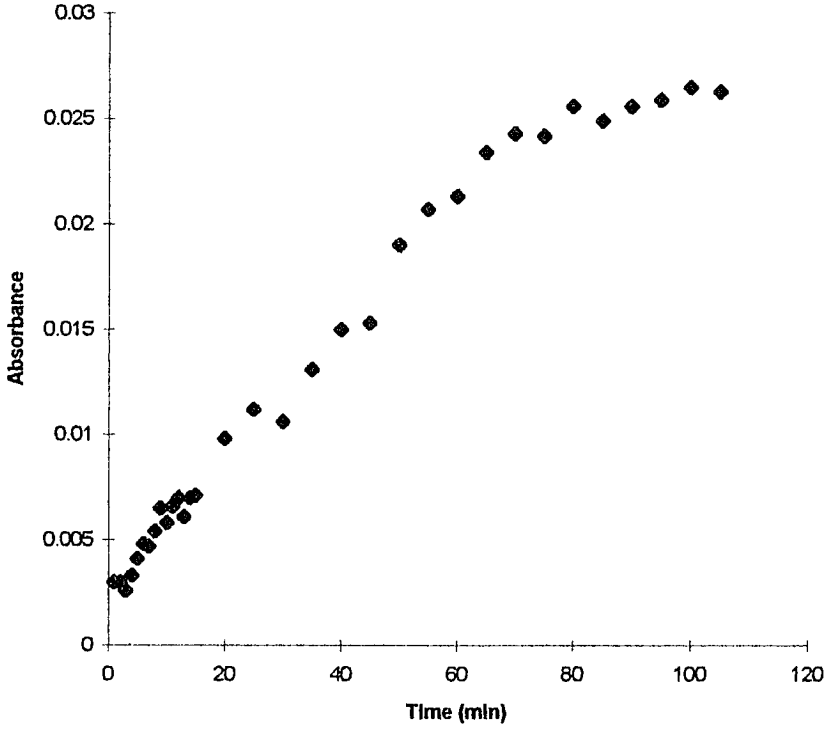

Figure 4.12 The absorbance of 1348cm-1 vs. time profile of nitrobenzene using a 47% w/w chloroparaffin(60%-Cl)/PVC coated chalcogenide fiber

4.4 Conclusion

Experiments with polymer coated chalcogenide infrared fibers showed that the use of a plasticizer polymer formulation improves the detection of an analyte in aqueous solutions. The use of "pure" polyvinylchloride, did not show any detectable level of absorbance for the test analyte after 90 minutes. One method of improving the sensitivity would be to increase the pathlength by making the sensor longer. A longer sensor would allow for a greater sampling of the infrared energy thereby improving the detection capabilities for the test analyte in aqueous solution. The results also indicate that care must be taken to ensure that a homogeneous coating is applied to the chalcogenide fiber. Nevertheless, these plasticizer/PVC phases did show an improvement in the sensitivity of an analyte in aqueous solution, as was expected based on the polymer coated conventional ATR experiments performed in Chapter 2.

CHAPTER V

IMPROVING THE SENSITIVITY OF TAPERED CYLINDRICAL ATR ELEMENTS FOR DETECTING ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS

5.1 Introduction

Recent advances in the manufacture of mid-IR transmitting chalcogenide optical fibers have resulted in the availability of these fibers for use as cylindrical ATR elements. The low cost of short sections of fiber allows them to be incorporated as the sensing element in disposable or limited use sampling devices. One significant limitation to using a short section of fiber as the ATR element is the small effective pathlength obtained for the measurement. It has been demonstrated that one way to increase the effective pathlength is to taper the fiber in the sensing region. A commercially available sampling device employing a short section of tapered chalcogenide fiber contained in a cell having an internal volume of 80-100 ul has been developed. The device is called a FiberCell and using appropriate optics fits directly into the sample compartment of a standard FTIR instrument.

Studies have shown that the effective depth of penetration for the evanescent wave into the surrounding solution when using the FiberCell depends upon two factors. First, the tapered fiber changes the number of higher order modes of light that traverse through the fiber. As the light

traverses through the tapered section of the fiber the number of modes of light increases. This increase improves the detection of the analyte by allowing more of the sample to be measured. Second, the launch angle of the light increases as it is traversing through the tapered fiber, resulting in a greater depth of penetration. The average pathlength for a FiberCell varies between 7 μm at 3000 cm^{-1} and 25 μm at 750 cm^{-1} (21).

Experiments were performed to determine if coating the tapered sensing region of the FiberCell using 47% w/w chloroparaffin(60%-Cl)/PVC results in an increase in the infrared absorbance obtained for the analytes in aqueous solution. The results for measurements made using polymer coated elements and uncoated elements are compared for the three test analytes: benzene, chloroform and nitrobenzene.

5.2 Materials and Methods

The FiberCell used for these studies was developed by Isorad Ltd, Yavne, Israel and is marketed by Nicolet Analytical Instruments. The sampling device consists of two molded pieces of polypropylene with the tapered chalcogenide fiber located in the middle of the plastic pieces. Th two halves of the cell are sealed together with epoxy. The ends of the fiber which protrude through the cell are polished to improve optical throughput. The internal volume of the cell, as provided, is approximately 80 ul, though lower volume cells could be easily produced. A sealable cap is also provided with the cell which is important when analyzing aqueous solutions containing volatile species. The Fiber Cell fits into an accessory that is placed in the sample compartment of a conventional FTIR instrument. The optical components of the accessory include two gold-coated beam condensers. One

condenser focuses the incident radiation onto one end of the fiber while the second collects the attenuated radiation and directs it toward the detector.

Chloroparaffin (60% - chlorinated) was purchased from Scientific Polymer Products, Inc., Ontario, NY. The bulk polymerized polyvinyl chloride was purchased from BF Goodrich, Geon Vinyl Division, Cleveland, OH. Chloroform (reagent grade), benzene (reagent grade), tetrahydrofuran (HPLC grade) and methanol (HPLC grade) were obtained from Fisher Scientific, Pittsburgh PA. Nitrobenzene was purchased from J.T. Baker, Phillipsburgh, NJ.

All spectroscopic data were obtained with a Nicolet 520, G-Series optical bench (Nicolet Analytical Instruments, Inc. Madison, WI) using an MCT-B detector. A 486DX2, 66 MHz microcomputer was used for instrument control and data processing. The Windows-based program, OMNIC, was used for data acquisition and spectral processing. The spectral data were collected at a nominal 2 cm^{-1} resolution. Twenty five scans were coadded to obtain each spectrum.

The polymer layer was applied to the tapered sensing region of the fiber using a solution containing 1.35 g chloroparaffin (60% Cl) and 1.50 g PVC dissolved in 100 mLs of tetrahydrofuran (THF). The polymer formulation was placed onto the fiber using a syringe with a needle. A drop of the polymer solution was pushed out so that it hung from the end of the needle. After allowing some of the solvent to evaporate in air, to increase the viscosity of the solution, the drop was pushed carefully from side to side along the fiber using the needle until the solvent evaporated leaving a thin film of polymer. A second drop of the solution was applied if the first drop did not appear to coat the fiber completely. In some cases, part of the drop fell off the fiber onto the bottom of the cell leaving behind a thin polymer layer. Visual inspection of

the fiber under a stereomicroscope showed that the thickness of the polymer coating varied considerably along the fiber. The maximum thickness was approximately 125 micrometers. The polymer layer was considerably thinner along most of the fiber.

To demonstrate the enhancement obtained with the use of the polymer coating, the following procedure was employed. Test solutions were prepared containing onre of three analytes. The test analytes used were benzene, chloroform and nitrobenzene. These analytes were chosen because their characteristic spectroscopic absorption bands were not obscured by the absorption bands of the chloroparaffin or the PVC. Benzene and chloroform were dissolved in aqueous solution while nitrobenzene was dissolved in 1.5% w/v methanol/water. All data are plotted as the baseline corrected absorbance to diminish the effect of baseline variations.

The experiments for the test analyte benzene were performed using a single FiberCell to obtained both the uncoated and polymercoated data. Two different FiberCells, one containing an uncoated fiber and the other with a polymer coated fiber, were used to obtain the data for the chloroform and nitrobenzene test solutions. The light throughput, and the signal to noise level of the spectral data, for these cells depends greatly on the characteristics of the tapered region. It is for this region that FiberCells having similar throughputs were chosen for the chloroform and nitrobenznen experiments.

Spectra were acquired for the benzene containg test solution before applying the coating to the fiber. The coating was then applied as described above, and the fibers were equilibrated with solvent, aqueous solution, for approximately 30 minutes. After thirty minutes the equilibrating solvent was removed and the benzene containing test solution was added to the FiberCell. Absorbance spectra were obtained by ratioing the single beam spectra to a

background spectrum obtained for the cell when filled with the solvent used for equilibration. The same procedure was employed for the chloroform and nitrobenzene containg solutions, except one FiberCell was used to acquire the uncoated fiber data and a second FiberCell was used to acquire the coated fiber data. The baseline corrected height of the characteristic absorbance band of the test analyte was plotted vs. time after introducing the sample solution. The data presented in the figures begins three minutes after introducing the sample. This time delay was provided to allow the sample compartment of the instrument to purge.

After the measurement was complete, the solution was removed from the Fibercell and air was blown over the polymer to remove the test solute by volatilization.

5.3 Results and Discussion

Experiments were performed to compare the ability of FiberCells containing polymer coated and uncoated chalcogenide fibers to detect common organic test analytes in aqueous solutions. The test analytes benzene, nitrobenzene and chloroform were chosen due to their distinctive infrared absorption bands. Three aqueous test solutions were prepared, each containing one of the test analytes. The initial experiments were performed using the FiberCells as received from the manufacturer. The FiberCells containing the uncoated chalcogenide fibers were filled with the test solutions and spectra were acquired for several minutes. Upon completion of data acquisition, the test solution was removed from the cell and the cell was dried by purging with high purity nitrogen to remove any remaining analyte. The FiberCells were then coated with a polymeric layer in the sensing region (using the same FiberCell for benzene and using two different FiberCells for

the acquisition of the chloroform and nitrobenzene data) procedure previously described. The polymeric formulation used for all of these studies was 47% w/w chloroparaffin(60%-Cl)/PVC. The polymeric layer was allowed to dry overnight at room temperature to ensure the removal of the solvent used to cast the polymer onto the fiber. Prior to acquiring spectra for the FiberCells containing the polymerically clad sensing region, the cell was equilibrated with the same solution used to prepare the test analytes for approximately thirty minutes. The equilibrating solution was removed and the cell was filled with the analyte containing test solutions. The procedure was repeated for each of the test solutions used for this study.

An example of the spectra obtained using a FiberCell containing a polymer coated sensing region when filled with an aqueous solution containing 0.15% v/v benzene is given in Figure 5.1. The absorbance of the characteristic aromatic C=C stretch of the benzene molecule which occurs at approximately 1479 cm^{-1} is clearly evident. The absorbance at 1479 cm^{-1} was monitored over time for FiberCells having both coated and uncoated fibers after filling with the same benzene containing aqueous solution. Plots of the baseline corrected absorbance at 1479 cm^{-1} vs. time for these experiments are presented in Figure 5.2. The results clearly illustrate that no spectral signature is observed for benzene at 1479 cm^{-1} for the FiberCell containing the uncoated, tapered chalcogenide fiber. The absorbance level of the 1479 cm^{-1} band for the FiberCell containing the polymer coated sensing region quickly increased to and remained reasonably constant at this level for approximately thirty minutes.

Additional experiments were performed to determine if analytes with other functional groups would provide similar results. Two aqueous test solutions, one containing 0.4% chloroform and another containing 0.1%

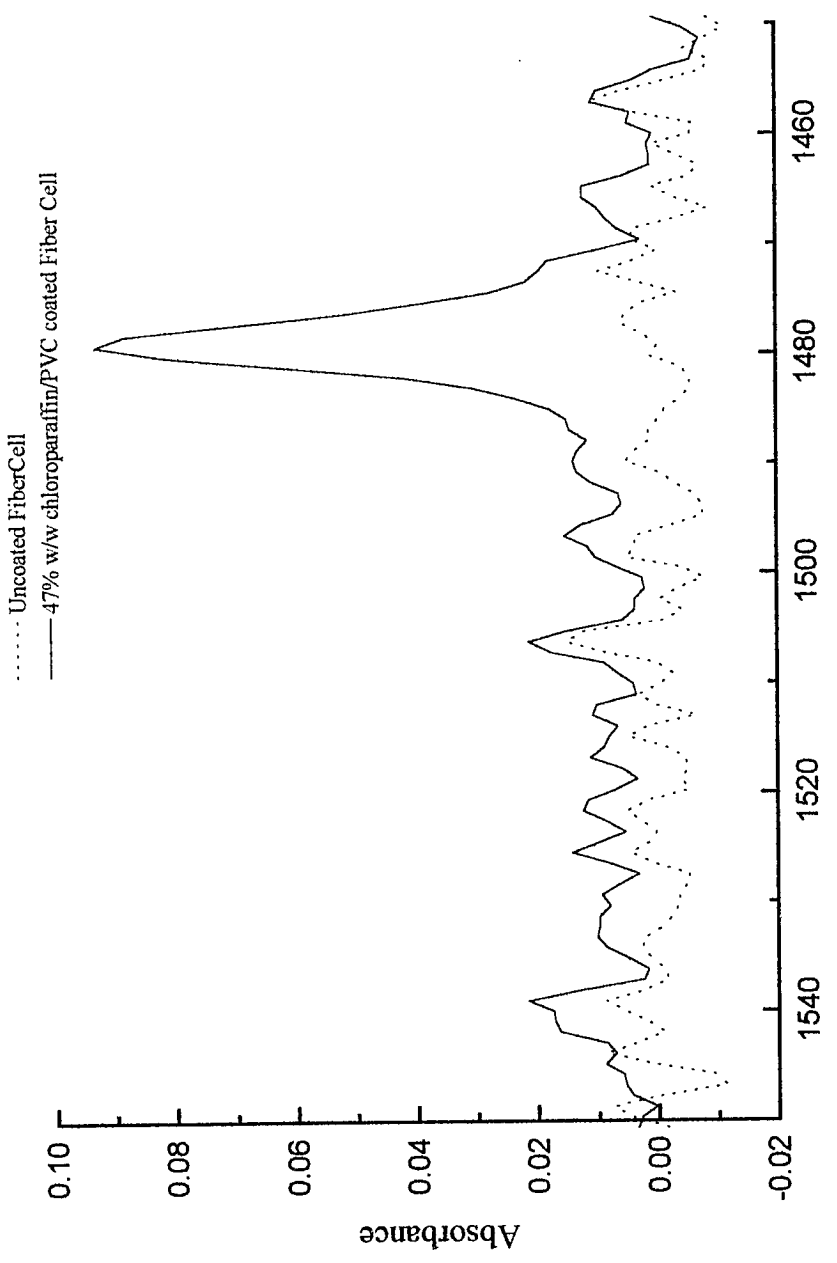

Figure 5.1 Absorbance spectra of 0.15% v/v benzene (1479 cm^{-1}) in aqueous solution using uncoated and 47% (w/w) chloroparaffin/PVC coated FiberCells

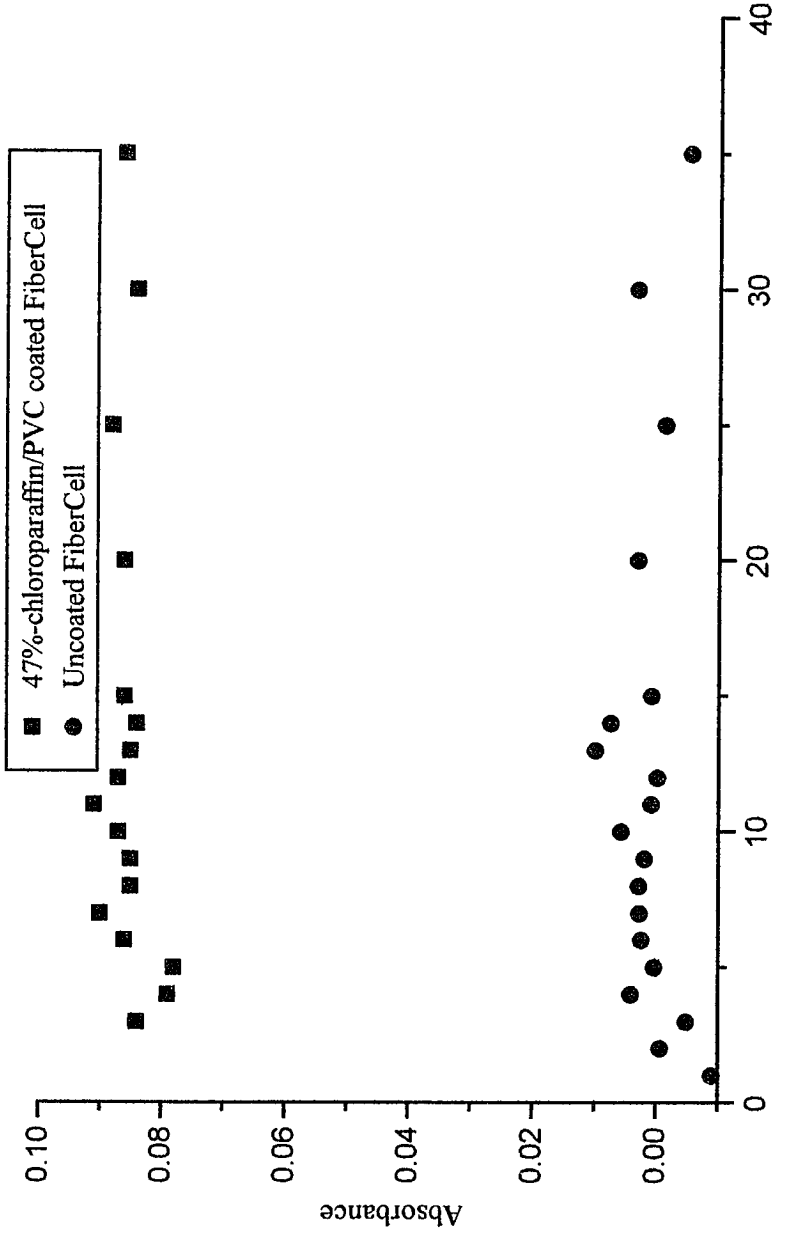

Figure 5.2 Plots comparing the absorbance vs. time for FiberCells coated with PVC and a 47% (w/w) chloroparaffin/PVC phase. The test analyte used was a 0.15% (v/v) benzene in aqueous solution

nitrobenzene and 1.5% v/v methanol were used for these experiments. The absorbance at the nitro symmetric stretch at 1348 cm^{-1} was monitored for the nitrobenzene containing solution and the C-H bend at 1216 cm^{-1} was monitored for the solution containing chloroform. Plots of the baseline corrected absorbance at 1348 cm^{-1} vs. time for experiments using uncoated and polymer coated sensing elements exposed to the nitrobenzene containing test solution are presented in Figure 5.3. The experimental data obtained using the test solution containing chloroform is presented in Figure 5.4. As was the case for the benzene containing test solution, the polymer coated elements clearly provided enhanced detectability for nitrobenzene.

5.4 Conclusion

The results of the experiments performed clearly demonstrate that applying a thin polymeric layer to the tapered sensing element of the FiberCell greatly enhances the detectability of organic analytes in aqueous solution. Previous studies using conventional ATR elements coated with the same plasticizer/polymer formulation demonstrated that a single application of the coating could be used for multiple analyses if proper care is taken not to degrade the coating material. These experiments indicate that FiberCells containing a polymer coated sensing region should have at least limited reusability. Polymer coating the fragile tapered region also serves to add mechanical strength to the sensing element making the FiberCell more robust.

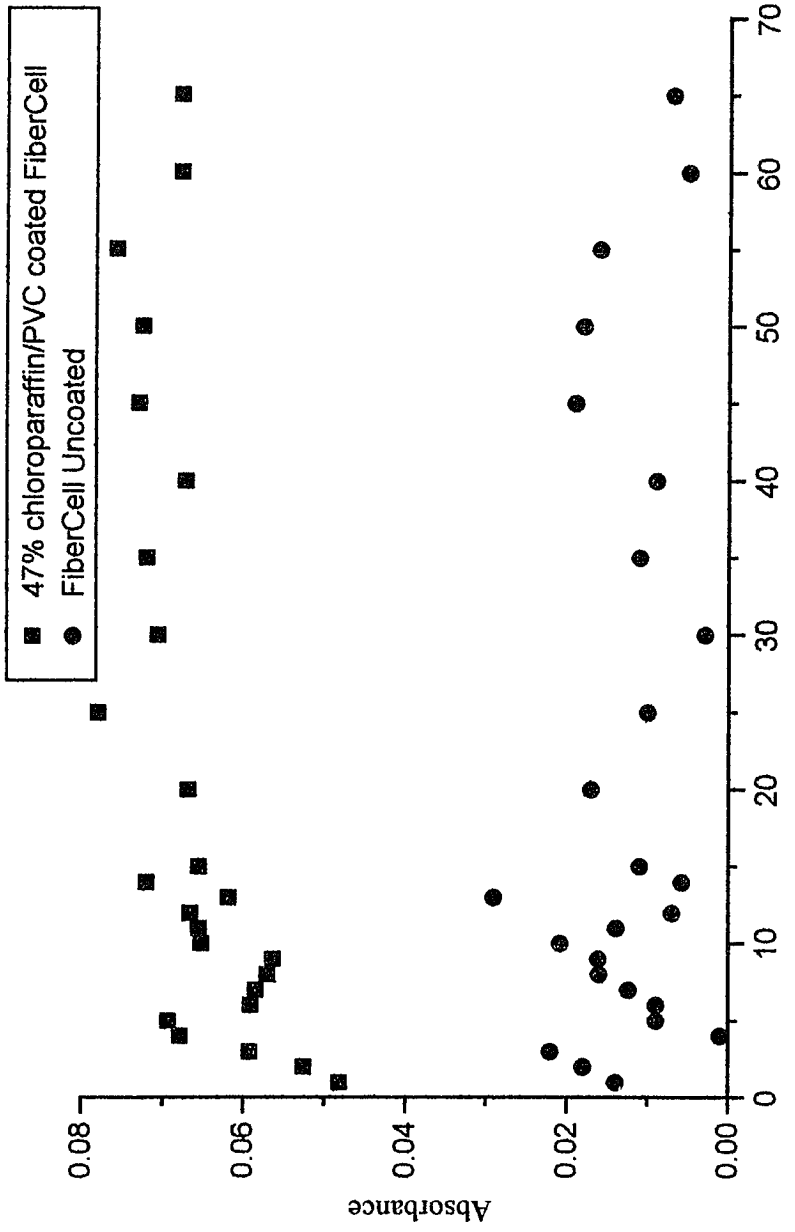

Figure 5.3 Plots comparing the absorbance vs. time for FiberCells coated with PVC and a 47% (w/w) chloroparaffin/PVC phase. The test analyte used was a 0.4% (v/v) chloroform in 1.5% MeOH/H_2O

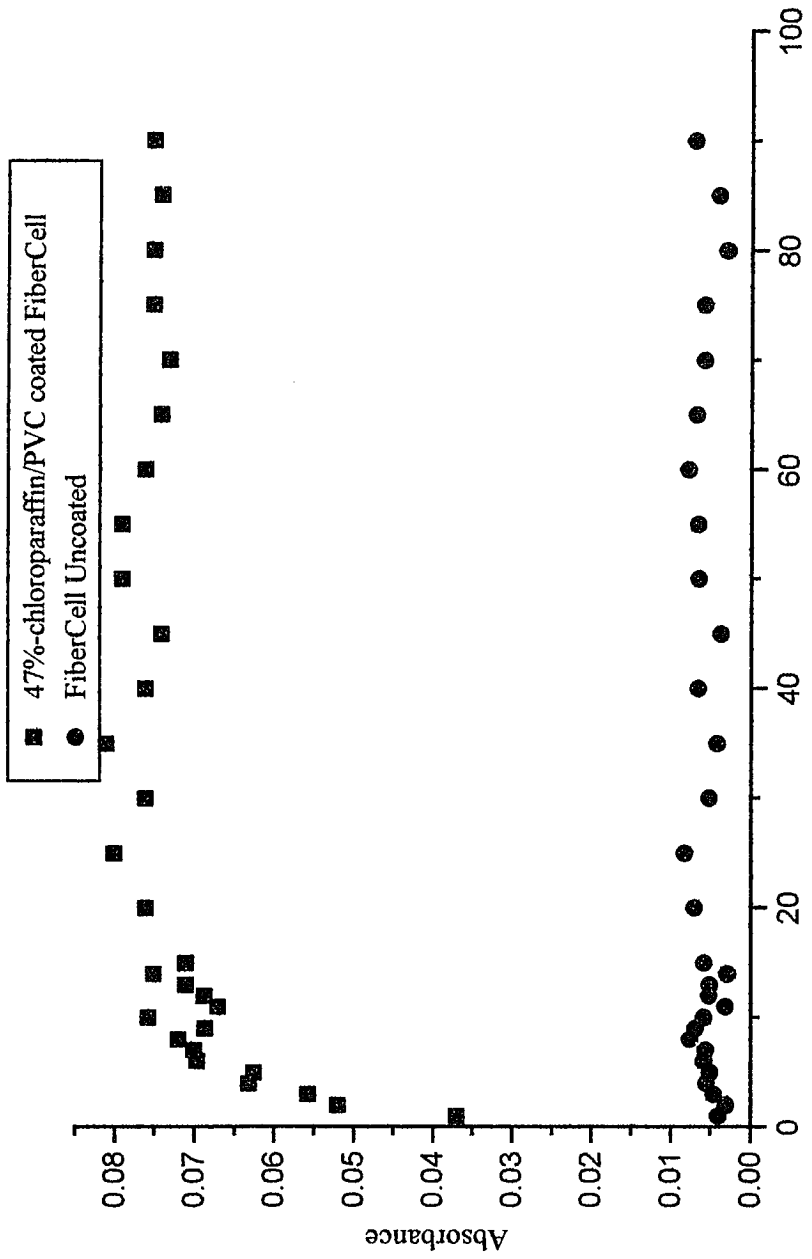

Figure 5.4 Plots comparing the absorbance vs. time for FiberCells coated with PVC and a 47% (w/w) chloroparaffin/PVC phase. The test analyte used was a 0.1% (v/v) nitrobenzene in 1.5% MeOH/H_2O

LIST OF REFERENCES

(1). F. M. Mirabella, Jr., Ed., *Internal Reflection Spectroscopy, Theory and Applications.* Marcel Dekker, Inc., New York (1993).

(2). N. J. Harrick, *Internal Reflection Spectroscopy.* John Wiley, New York (1967).

(3). F. M. Mirabella, Jr. and N.J. Harrick, Eds, *Internal Reflection Spectroscopy: Review and Supplement.* Harrick Scientific Corp., New York (1985).

(4). N. A. Wright, R. Curbelo, D. C. Compton and S. L. Hill, *Proc. SPIE* **1048**, 153 (1989).

(5). S. R. Nagel, *IEEE Circuits and Devices Magazine,* 36 (March, 1989).

(6). M. G. Drexhage, *Proc. SPIE* **1228**, 2 (1990).

(7). M. G. Drexhage and C. T. Moynihan, *Scient. Am.* 110 (November, 1988).

(8). W. A. Stevenson, U.S. Patent 4,798,954 (1989).

(9). W. D. Vidrine, Jr. and M. S. Roth, U.S. Patent 4,827,121 (1989).

(10). A. R. Hilton, Sr., *Proc. SPIE* **1591**, 34 (1991).

(11). J. Heo, J. S. Sanghera and J. D. Mackenzie, *Opt. Eng.* **30**, 470 (1991).

(12). T. Kanamori, Y. Terunuma and T. Miyashita, *Review of the Electrical Communication Laboratories* **32**, 469 (1984).

(13). N. J. Pitt, *Proc. SPIE* **799**, 25 (1987).

(14). J. A. Harrington, *Appl. Opt.* **27**, 3097 (1988).

(15). S. J. Saggese, M. R. Shahriari and G. H. Sigel Jr., *Proc. SPIE* **929**, 106 (1988).

(16). P. W. France, M. G. Drexhage, J. M. Parker, M.W. Moore, S. F. Carter and J. V. Wright, *Fluoride Glass Optical Fibers.* Blackie, Glasgow (1990).

(17). J. A. Harrington, *Proc. SPIE* **1591**, 2 (1991).

(18). Y. Karari-Barak and A. Katzir, *Proc. SPIE* **1591**, 90 (1991).

(19). V. G. Artjushenko, A. A. Lerman, E. G. Litvinenko, A. O. Nabatov, V. I. Konov, R. I. Kuznetsov, V. G. Plotnichenko, I. L. Pylnov, V. A. Shtein-Margolina, A. A. Urusovskaja, V. V. Vojtsekhovsky, N. D. Zaharov, W. Neuberger and K. Moran, *Proc. SPIE* **1591**, 83 (1991).

(20). N. Barkay and A. Katzir, *Proc. SPIE* **1591**, 50 (1991).

(21). F. Moser, N. Barkay, A. Levite, E. Margalit, I. Praiss, A. Sa'ar, I. Schnitzer, A. Zur and A. Katzir, *Proc. SPIE* **1228**, 128 (1990).

(22). A. Bornstein, M. Katz, A. Baram and D. Wolfman, *Proc. SPIE* **1591**, 256 (1991).

(23). S. R. Lowry, T. E. May and A. Bornstein, *Appl. Spec.* **47**, 30 (1993).

(24). J. A. Harrington, Ed., *Selected Papers on Infrared Fiber Optics.* SPIE, Bellingham, WA.

(25). W. R. Seitz, *Spectrochemica Acta Rev.* **15**, 477 (1993).

(26). D. Pruss, P. Dreyer and E. Koch, *Proc. SPIE* **799**, 117 (1987).

(27). D. Pruss, *Sci. Forum* **32-33**, 321 (1988).

(28). V. G. Artjushenko, V. G. Plotnichenko, E. V. Stepanov, A. I. Nadezchdinskii, A. I. Kuznetsov and K. L. Moskalenko, *Proc. SPIE* **1591**, 206 (1991).

(29). S. J. Saggese, M. R. Shahriari and G. H. Sigel Jr., *Proc. SPIE* **1172**, 2 (1989).

(30). R J. Burger and P. J. Melling, *Proc. SPIE* **1591**, 246 (1991).

(31). M. A. Druy, P. J. Glatkowski and W. A. Stevenson, *Proc. SPIE* **1591**, 218 (1991).

(32). R. D. Driver, G. M. Leskowitz and L. E. Curtiss, *Proc. SPIE* **1172**, 60 (1989).

(33). M. A. Druy and L. Elandjian, *Proc. SPIE* **986**, 130 (1988).

(34). D. A. C. Compton, S. L. Hill, N. A. Wright, M. A. Druy, J. Piche, W. A. Stevenson and D. W. Vidrine, *Appl. Spec.* **42**, 972 (1988).

(35). J. Böck, E. Gersing, F. Sundmacher and G. Hellige, *Proc. SPIE* **906**, 169 (1988).

(36). M. Rodrigues and G. H. Sigel, Jr., *Proc. SPIE* **1591**, 225 (1991).

(37). M. Swairjo, K. J. Rothschild, B. Nappi, A. Lane and H. Gold, *Proc. SPIE* **1437**, 60 (1991).

(38). L. P. de Rochemont, N. W. Downer, T. E. May, H. G. Smith, C. E. Oakes and M. Ertan-Lamontagne, *Proc. SPIE* **1796**, 349 (1992).

(39). C. W. Meuse and S. A. Tomellini, *Anal. Lett.* **22**, 2065 (1989).

(40). P. Heinrich, R. Wyzgol, B. Schrader, A. Hatzilazaru and D. W. Lübbers, *Appl. Spec.* **44**, 1641 (1990).

(41). R. Krska, E. Rosenberg, K. Taga, R. Kellner, A. Messica and A. Katzir, *Appl. Phys. Lett.* **61**, 1778 (1992).

(42). P. J. Glatkowski, M. A. Druy and W. A. Stevenson, *Proc. SPIE* **1796**, 243 (1992).

(43). K. Taga, Ch. Weigel and R. Kellner, *Vib. Spec.* **1**, 125 (1990).

(44). V. Ruddy and S. McCabe, *Appl. Spec.* **44**, 1461 (1990).

(45). R. Göbel, R. Krska, R. Kellner, R. W. Seitz and S. A. Tomellini, *Appl. Spec.* **48**, 678 (1994).

(46). F. Bueche, *Jr. Chem. Phys.* **21**, 1850 (1953).

(47). *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, 388.

(48). C. A. Kumins and J. Roteman, *Jr. Polymer Sci.* **55**, 699 (1961).

(49). J. Crank and G. S. Park, *Diffusion In Polymers.* Academic Press, London (1968).

(50). W. R. Vieth, *Diffusion In and Through Polymers.* Hanser Publishing, New York (1991).

(51). D. Messadi and J. M. Vergnaud, *Jr. Appl. Polym. Sci.* **26**, 2315 (1981).

(52). J. L. Taverdet and J. M. Vergnaud, *Jr. Appl. Polym. Sci.* **29**, 3391 (1984).

(53). D. C. H. Bigg, *Jr. Appl. Polym. Sci.* **19**, 3119 (1975).

(54). C. S. Su, D. Patterson and H. P. Schreiber, *Jr. Appl. Polym. Sci.* **20**, 1025 (1976).

(55). S. V. Patel and M. Gilbert, *Plast. Rub. Process. Appl.* **6**, 321 (1986).

(56). C. S. Miser, K. L. McNesby, R. A. Pesce-Rodriguez and R. A. Fifer, *Proc. SPIE* **1575**, 356 (1991).

(57). T. B. Colin, K.-H. Yang and W. C. Stwalley, *Appl. Spec.* **45**, 1291 (1991).

APPENDICES

APPENDIX A

This Visual Basic program was created to drive the Nicolet 520 FTIR bench, control the temperature of the ATR device, and to transform the data into a Microsoft Excel spreadsheet format for further processing. The development of this program was essential for spectral data acquisition at a specified time and temperature.

Kinetic/Temperature Program

```
VERSION 2.00
Begin Form Form1
  BackColor      = &H00C0C000&
  Height         = 6945
  Left           = 4695
  LinkMode       = 1 'Source
  LinkTopic      = "Form1"
  ScaleHeight    = 6540
  ScaleWidth     = 4680
  Top            = 180
  Width          = 4800
  Begin TextBox Text6
    Height       = 285
    Left         = 2160
    TabIndex     = 15
    Top          = 5160
    Width        = 1335
  End
  Begin TextBox Text5
    Height       = 285
    Left         = 2160
    TabIndex     = 14
    Top          = 4800
    Width        = 1335
  End
  Begin TextBox DDEText
    BackColor    = &H00FF8080&
    ForeColor    = &H008080FF&
    Height       = 285
    Left         = 3480
    MultiLine    = -1 'True
    TabIndex     = 9
    Top          = 1560
    Width        = 1095
  End
  Begin Grid Grid1
    BackColor    = &H00FFFF80&
    Cols         = 5
    Height       = 2175
    Left         = 120
    Rows         = 30
    TabIndex     = 8
    Top          = 2160
```

```
  Width          = 4455
End
Begin TextBox Text4
  Height         = 495
  Left           = 2880
  TabIndex       = 7
  Text           = "5"
  Top            = 1560
  Width          = 495
End
Begin TextBox Text3
  Height         = 375
  Left           = 3000
  TabIndex       = 6
  Text           = "60"
  Top            = 1080
  Width          = 495
End
Begin CommandButton Command2
  Caption        = "Stop"
  Height         = 495
  Left           = 3600
  TabIndex       = 5
  Top            = 720
  Width          = 855
End
Begin CommandButton command1
  Caption        = "start"
  Height         = 495
  Left           = 3600
  TabIndex       = 4
  Top            = 120
  Width          = 855
End
Begin Timer Timer1
  Enabled        = 0  'False
  Interval       = 60000
  Left           = 0
  Top            = 0
End
Begin TextBox Text2
  Height         = 285
  Left           = 2400
  TabIndex       = 3
  Text           = "20"
  Top            = 600
```

```
    Width          = 495
  End
  Begin TextBox Text1
    Height         = 285
    Left           = 1800
    TabIndex       = 2
    Top            = 120
    Width          = 1335
  End
  Begin Label Label6
    Alignment      = 1  'Right Justify
    Caption        = "Alpha Omega temp:"
    Height         = 255
    Left           = 240
    TabIndex       = 13
    Top            = 5160
    Width          = 1695
  End
  Begin Label Label4
    Alignment      = 1  'Right Justify
    Caption        = "Physitemp temp:"
    Height         = 255
    Left           = 240
    TabIndex       = 12
    Top            = 4800
    Width          = 1695
  End
  Begin Label Label3
    Alignment      = 1  'Right Justify
    Caption        = "Number of minutes in between spectra that are >15:"
    Height         = 495
    Left           = 0
    TabIndex       = 11
    Top            = 1560
    Width          = 2775
  End
  Begin Label Label5
    Alignment      = 1  'Right Justify
    Caption        = "Number of seconds in between the first 15 spectra:"
    Height         = 375
    Left           = 0
    TabIndex       = 10
    Top            = 1080
    Width          = 2775
  End
  Begin Label Label2
```

```
    Caption        =  "Number of measurements:"
    Height         =  255
    Left           =  0
    TabIndex       =  1
    Top            =  600
    Width          =  2295
  End
  Begin Label Label1
    Alignment      =  1  'Right Justify
    Caption        =  "Filename:"
    Height         =  255
    Left           =  720
    TabIndex       =  0
    Top            =  120
    Width          =  855
  End
End
Declare Function INBYTE Lib "port_io.dll" (ByVal port%) As Integer
Declare Function INWORD Lib "port_io.dll" (ByVal port%) As Integer
Declare Sub OUTBYTE Lib "port_io.dll" (ByVal port As Integer, ByVal
databyte As Integer)
Declare Sub OUTWORD Lib "port_io.dll" (ByVal port As Integer, ByVal
databyte As Integer)
Dim RowCount As Integer
Dim Parameter As String
Dim Wavenum As String



Sub command1_Click ()
'Grid1.Col = 0
'w% = 1
'nn% = text4
'For i% = 1 To text2
'Grid1.Row = w%
'Grid1.Text = Format$(nn%, "####.00")
'nn% = nn% + text4
'w% = w% + 1
'Next
  timer1.Interval = 60000
  nn% = 60
   timer1.Enabled = True
Grid1.Row = 0

End Sub
```

```
Sub Command2_Click ()
 executeOMNIC "exit"
Beep
MsgBox "program terminated"
End
End Sub

Sub ExcelDDEAction ()

'This subroutine determines the correct row and column for the the
'next piece of information and pokes the info into the calculated Excel cell.
        DDEText.LinkMode = 2
        DDEText.LinkMode = 0
        DDEText.LinkTopic = "EXCEL|SHEET1"

          StuffIt$ = "R" + Format$(RowCount, "0") + "C2"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
       DDEText.LinkMode = 2
       DDEText.Text = Parameter$
       DDEText.LinkPoke
       DDEText.LinkMode = 0

          StuffIt$ = "R" + Format$(RowCount, "0") + "C1"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
       DDEText.LinkMode = 2
       DDEText.Text = Timsec$
       DDEText.LinkPoke
       DDEText.LinkMode = 0

          StuffIt$ = "R" + Format$(RowCount, "0") + "C3"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
       DDEText.LinkMode = 2
        DDEText.Text = Wavenum$
       DDEText.LinkPoke
       DDEText.LinkMode = 0

          StuffIt$ = "R" + Format$(RowCount, "0") + "C4"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
      DDEText.LinkMode = 2
      DDEText.Text = ptemp$
      DDEText.LinkPoke
```

```
        DDEText.LinkMode = 0

          StuffIt$ = "R" + Format$(RowCount, "0") + "C5"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.Text = atemp$
        DDEText.LinkPoke
        DDEText.LinkMode = 0

        'RowCount = RowCount + 1

End Sub

Sub ExcelDDEAction1 ()

'This subroutine determines the correct row and column for the the
'next piece of information and pokes the info into the calculated Excel cell.
        DDEText.LinkMode = 2
        DDEText.LinkMode = 0

        DDEText.Text = Parameter$
        DDEText.LinkTopic = "EXCEL|SHEET1"
          StuffIt$ = "R" + Format$(RowCount, "0") + "C1"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1

        DDEText.LinkMode = 2
        DDEText.LinkMode = 0
        RowCount = RowCount + 1

End Sub

Sub Form_Load ()
    Rem here are the port variables
   Cls
   ba% = 768
    STRTCONV% = ba% + 0
    UPDAT% = ba% + 1
    Clr% = ba% + 2
    stat% = ba% + 0
    dat% = ba% + 1
    PA% = ba% + 4
    PB% = ba% + 5
    PC% = ba% + 6
    CW% = ba% + 7
```

```
    TA% = ba% + 8
    TB% = ba% + 9
    TC% = ba% + 10
    TCW% = ba% + 11
    DA1LSB% = ba% + 12
    DA1MSB% = ba% + 13
    DA2LSB% = ba% + 14
    DA2MSB% = ba% + 15
      OUTBYTE CW%, 153
      OUTBYTE STRTCONV%, 0
     For yy = 1 To 300
     Next
     done% = INBYTE(stat%) And 1
     Do
       If done% = 1 Then
          Exit Do
       End If
     Loop
     OUTBYTE Clr%, 0
     OUTBYTE PB%, 0


  Rem set start temperature
     volts! = (28 * 10)
     voltage! = volts! / 1000
     Value! = voltage! * (4096 / 5)
     MSB% = Value! \ 256
     LSB% = Value! Mod 256
     OUTBYTE DA1LSB%, LSB%
     OUTBYTE DA1MSB%, MSB%
     OUTBYTE DA2LSB%, LSB%
     OUTBYTE DA2MSB%, MSB%
     OUTBYTE UPDAT%, 0
   'text1.Text = Format$(temp!, "###.0")
Rem calls up sub routine for Physitemp thermocouple
  physitemp

Rem calls up sub routine for external thermocouple
   'thermocouple
 'voltT

Load OMTALK

    setOMNIC "Correlation", "simple"
  CorrErr = 25
Grid1.ColWidth(4) = 1000
```

```
Grid1.ColWidth(3) = 1000
Grid1.ColWidth(2) = 1600
Grid1.ColWidth(1) = 1600
Grid1.ColWidth(0) = 1000
Grid1.Rows = 60
Grid1.Cols = 5
'setup column titles for the spreadsheet
z% = 1
Grid1.Row = 0
Grid1.Col = 0
Grid1.Text = "Time(sec)"
Grid1.Col = 1
Grid1.Text = "Wavenumber"
Grid1.Col = 2
Grid1.Text = "Absorbance"
Grid1.Col = 3
Grid1.Text = "atemp"
Grid1.Col = 4
Grid1.Text = "ptemp"

executeOMNIC "BenchSetup"
executeOMNIC "Invoke Collectsetup"
executeOMNIC "Invoke PrintSetup"
executeOMNIC "Invoke displaysetup"
'setOMNIC "Collect NumScans", 32
'setOMNIC "Collect Resolution", 2

timer1.Enabled = False
y% = 1
qq% = 1
specnumber! = 1

nn% = 0
'This procedure opens a DDE link to Excel.  If Excel is not open an
'error is generated and the program jumps to the "Open Excel"
'code section.  After this code is executed the program returns to
'the "Startup" section. For more information on using DDE please refer
'to the Visual Basic users manual.

Startup:
    On Error GoTo OpenExcel
      DDEText.LinkTopic = "Excel|Sheet1"
      DDEText.LinkItem = "R12C12"
      DDEText.LinkTimeout = -1
     DDEText.LinkMode = 2
      DDEText.LinkPoke
```

```
        DDEText.LinkMode = 0
        Exit Sub

OpenExcel:
        If Err = 282 Then
           X = Shell("c:\Excel\Excel.exe", 3)
             Resume Startup
        Else
             Error Err
        End If

End Sub

Sub kinetics_timer ()

 start = Timer

timer1.Enabled = False


  Rem MsgBox "before if"



   executeOMNIC "SizeWindow 285 450"
   executeOMNIC "MoveWindow 0 0"

Rem this statement tells omnic to scan a sample

        executeOMNIC "Invoke Collectsample Auto "

 Rem these statements stores the binary data
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Export" + " " + filename1$
      executeOMNIC cmdtxt$

'-------------------------------------------------
Rem This portion of the program allows you to store the
Rem data into ascii format

'filename$ = Format$(text2) + Format$(specnumber!, "0") + ".csv"
        'filename1$ = "b:" + filename$
        Rem filename3$ = "a:" + filename$
        'cmdtxt$ = "Export" + " " + filename1$
      'executeOMNIC cmdtxt$
```

```
Rem these statements displays the data in a particular region of the x-axis
    executeOMNIC "set display Xstart 1600"
    executeOMNIC "set display Xend 1300"
    'SetOMNIC "display xcrossHairLoc", 2925
Rem This part allows us to determine the highest point of
Rem the peak
   executeOMNIC "PeakHeight 1348 shift"
    area$ = GetOMNIC("result Current")
Rem This portion of the program allows us to get specific info
Rem of the position of the peak
    OnlyX# = GetVal(area$, "X:")
    OnlyY# = GetVal(area$, "Y:")
    'Print OnlyY#
Rem This part determines the corrected height using a baseline
    peak$ = "CorrectedPeakHeight 1355" + " " + Str(OnlyX#) + " " + "1340"
    executeOMNIC peak$

    area1$ = GetOMNIC("result current")

    OnlyY1# = GetVal(area1$, "Height:")
    'physitemp
    'voltT

    Grid1.Row = Grid1.Row + 1
   Grid1.Col = 1
    Grid1.Text = Str(OnlyX#)
   Grid1.Col = 2
    Grid1.Text = Str(OnlyY1#)
   Grid1.Col = 3
    Grid1.Text = Str(temp2!)
   Grid1.Col = 4
    Grid1.Text = Str(temp8!)

      'Parameter$ = filename$
     'ExcelDDEAction
    ExcelDDEAction1

'text5.Text = text5.Text + "time" + Str$(OnlyX#) + Str$(OnlyY#) + NewLine$
'-------------------------------------------------------
  Grid1.Col = 0
   'Print (ppp%)
   pppp% = nn%
    'Grid1.Text = Format$(pppp%, "####.##")
  Rem Puts the time onto the grid sheet
  Grid1.Text = pppp%
```

```
Rem This puts the data onto the spread sheet
        Parameter$ = Str(OnlyY1#)
        Timsec$ = Str(pppp%)
         Wavenum$ = Str(OnlyX#)
        atemp$ = Str(temp2!)
        ptemp$ = Str(temp8!)
        ExcelDDEAction

'timer1.Interval = (Val(text3.Text - ppp%) * 1000)

      timer1.Enabled = False

specnumber! = specnumber! + 1
y% = y% + 1
 nn% = Val(text3.Text) + pppp%
   Rem t%=0 resets the timer interval
    finish = Timer
   ppp% = (finish - start)

'Print ppp%

timer1.Interval = (text3.Text - ppp%) * 1000

If y% = 16 Then
nn% = nn% - Val(text3.Text)
timer1.Interval = 60000
End If
 timer1.Enabled = True

End Sub

Sub longtime ()
Print text2.Text
timer1.Enabled = False
nn% = nn% + 60

If qq% = Val(text4.Text) Then
  If (text2.Text) + 1 <> y% Then
start = Timer
 timer1.Enabled = False
 'Print text4.Text

    executeOMNIC "SizeWindow 285 450"
    executeOMNIC "MoveWindow 0 0"

Rem this statement tells omnic to scan a sample
```

```
        executeOMNIC "Invoke Collectsample Auto "

 Rem these statements stores the binary data
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "d:\kinetic\" + filename$
        cmdtxt$ = "Export" + " " + filename1$
       executeOMNIC cmdtxt$


'-------------------------------------------------
Rem This portion of the program allows you to store the
Rem data into ascii format

'filename$ = Format$(text2) + Format$(specnumber!, "0") + ".csv"
        'filename1$ = "b:" + filename$
        Rem filename3$ = "a:" + filename$
        'cmdtxt$ = "Export" + " " + filename1$
       'executeOMNIC cmdtxt$
 Rem these statements displays the data in a particular region of the x-axis
      executeOMNIC "set display Xstart 1600"
      executeOMNIC "set display Xend 1300"
      'SetOMNIC "display xcrossHairLoc", 2925
 Rem This part allows us to determine the highest point of
 Rem the peak
     executeOMNIC "PeakHeight 1348 shift"
      area$ = GetOMNIC("result Current")
 Rem This portion of the program allows us to get specific info
 Rem of the position of the peak
       OnlyX# = GetVal(area$, "X:")
       OnlyY# = GetVal(area$, "Y:")
       'Print OnlyY#
Rem This part determines the corrected height using a baseline
        peak$ = "CorrectedPeakHeight 1355" + " " + Str(OnlyX#) + " " + "1340"
       executeOMNIC peak$

       area1$ = GetOMNIC("result current")

       OnlyY1# = GetVal(area1$, "Height:")


      Grid1.Row = Grid1.Row + 1
     Grid1.Col = 1
      Grid1.Text = Str(OnlyX#)
     Grid1.Col = 2
      Grid1.Text = Str(OnlyY1#)
```

```
        Grid1.Col = 3
        Grid1.Text = Str(temp2!)
        Grid1.Col = 4
        Grid1.Text = Str(temp8!)

          'Parameter$ = filename$
         'ExcelDDEAction
        ExcelDDEAction1
 'text5.Text = text5.Text + "time" + Str$(OnlyX#) + Str$(OnlyY#) + NewLine$
'-----------------------------------------------------

   Grid1.Col = 0


   pppp% = nn%
   'Grid1.Text = Format$(pppp%, "####.##")
   Rem Puts the time onto the grid sheet
  Grid1.Text = pppp%

Rem This puts the data onto the spread sheet
        Parameter$ = Str(OnlyY1#)
        Timsec$ = Str(pppp%)
         Wavenum$ = Str(OnlyX#)
        atemp$ = Str(temp2!)
        ptemp$ = Str(temp8!)
       ExcelDDEAction
      timer1.Enabled = False
     specnumber! = specnumber! + 1
    y% = y% + 1
    qq% = 0
  Else
        executeOMNIC "Select All"
      executeOMNIC "set display Xstart 4000"
      executeOMNIC "set display Xend 1000"

         executeOMNIC "CutSelectedSpectra"
       specnumber! = 5
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "d:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
       executeOMNIC cmdtxt$

       executeOMNIC "Print"
       executeOMNIC "Select All"
       executeOMNIC "CutSelectedSpectra"
      specnumber! = 10
```

```
    filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
    filename1$ = "d:\kinetic\" + filename$
    cmdtxt$ = "Import" + " " + filename1$

   executeOMNIC cmdtxt$
    executeOMNIC "Print"
     executeOMNIC "Select All"
      executeOMNIC "CutSelectedSpectra"
    specnumber! = 15
     filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
     filename1$ = "d:\kinetic\" + filename$
     cmdtxt$ = "Import" + " " + filename1$
    executeOMNIC cmdtxt$
     executeOMNIC "Print"
     executeOMNIC "Select All"
     executeOMNIC "CutSelectedSpectra"
   specnumber! = 20
    filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
    filename1$ = "d:\kinetic\" + filename$
    cmdtxt$ = "Import" + " " + filename1$

   executeOMNIC cmdtxt$

    executeOMNIC "Print"
     executeOMNIC "Select All"
     executeOMNIC "CutSelectedSpectra"
   specnumber! = 25
    filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
    filename1$ = "d:\kinetic\" + filename$
    cmdtxt$ = "Import" + " " + filename1$
   executeOMNIC cmdtxt$
    executeOMNIC "Print"
     executeOMNIC "Select All"
     executeOMNIC "CutSelectedSpectra"

   specnumber! = 30
    filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
    filename1$ = "d:\kinetic\" + filename$
    cmdtxt$ = "Import" + " " + filename1$

   executeOMNIC cmdtxt$

    executeOMNIC "Print"
executeOMNIC "EXIT"
Beep
```

```
    MsgBox "Program Terminated"
   End
  End If
   Rem t%=0 resets the timer interval

  'nn% = Val(text3.Text) + pppp%
    finish = Timer
   ppp% = (finish - start)

 'Print ppp%
 End If
 If qq% = 0 Then
 timer1.Interval = (60 - ppp%) * 1000
 Else
 timer1.Interval = 60000
 End If

  qq% = qq% + 1
 timer1.Enabled = True

End Sub

Sub physitemp ()
      OUTBYTE PB%, 0
       Rem for statement is to delay so switches can settle
      For i = 1 To 300
      Next
       'OUTBYTE CW%, Hex(99)
       OUTBYTE STRTCONV%, 0
       OUTBYTE STRTCONV%, 0
       OUTBYTE STRTCONV%, 0
       OUTBYTE STRTCONV%, 0
       OUTBYTE STRTCONV%, 0
       done% = INBYTE(stat%) And 1
      Do
        If done% = 1 Then
           Exit Do
        End If
      Loop


LSB2% = INBYTE(dat%)
'Print LSB2%

MSB2% = INBYTE(dat%) And 15
'Print MSB2%
```

```
MSB2% = MSB2% * 256
'Print Tab(60); MSB2%

result1% = MSB2% + LSB2%

If result1% > 2047 Then
result1% = result1% - 4096
End If

voltage2! = result1% * (10 / 4096)
'Print voltage2!
volts2! = voltage2! * 1000
'Print volts2!

temp2! = volts2! / 10

    text6.Text = Format$(temp2!, "###.0")


'Print temp2!
'Print volts2!

End Sub

Sub Timer1_Timer ()
'tt% = tt% + 1
'If tt% = text4 \ text3 Then
If y% < 15 + 1 Then

    kinetics_timer
Else

  setOMNIC "Collect NumScans", 25
  longtime
End If

End Sub

Sub voltT ()

      'OUTBYTE PB%, 0 'connect to channel one

      'OUTBYTE PB%, 2 'connect to channel three

      'OUTBYTE PB%, 3 'connect to channel four
```

```
 OUTBYTE PB%, 1 'connect to channel two
For i = 1 To 300
Next
 'OUTBYTE CW%, Hex(99)
 OUTBYTE STRTCONV%, 0

 done% = INBYTE(stat%) And 1
Do
   If done% = 1 Then
      Exit Do
  End If
Loop


LSB1% = INBYTE(dat%)
'Print LSB1%

MSB1% = INBYTE(dat%) And 15
'Print MSB1%
MSB1% = MSB1% * 256
'Print Tab(60); MSB1%

result% = MSB1% + LSB1%

If result% > 2047 Then
result% = result% - 4096
End If


voltage2! = result% * (10 / 4096)
'voltage2! = voltage2! * -1
If (voltage2! >= .069) And (voltage2! < .071) Then
x1! = .069
y1! = 13.5
x2! = .071
y2! = 13.8
End If
If (voltage2! >= .071) And (voltage2! < .076) Then
x1! = .071
y1! = 13.8
x2! = .076
y2! = 14.2
End If
If (voltage2! >= .076) And (voltage2! < .081) Then
x1! = .076
y1! = 14.2
```

```
x2! = .081
y2! = 14.8
End If
If (voltage2! >= .081) And (voltage2! < .089) Then
x1! = .081
y1! = 14.8
x2! = .089
y2! = 15.6
End If
If (voltage2! >= .089) And (voltage2! < .097) Then
x1! = .089
y1! = 15.6
x2! = .097
y2! = 16.4
End If
If (voltage2! >= .097) And (voltage2! < .105) Then
x1! = .097
y1! = 16.4
x2! = .105
y2! = 17.3
End If
If (voltage2! >= .105) And (voltage2! < .115) Then
x1! = .105
y1! = 17.3
x2! = .115
y2! = 18.2
End If
If (voltage2! >= .115) And (voltage2! < .126) Then
x1! = .115
y1! = 18.2
x2! = .126
y2! = 19.4
End If
If (voltage2! >= .126) And (voltage2! < .14) Then
x1! = .126
y1! = 19.4
x2! = .14
y2! = 20.9
End If
If (voltage2! >= .14) And (voltage2! < .161) Then
x1! = .14
y1! = 20.9
x2! = .161
y2! = 23.1
End If
If (voltage2! >= .161) And (voltage2! < .175) Then
```

```
x1! = .161
y1! = 23.1
x2! = .175
y2! = 24.6
End If
If (voltage2! >= .175) And (voltage2! < .184) Then
x1! = .175
y1! = 24.6
x2! = .184
y2! = 25.4
End If
If (voltage2! >= .184) And (voltage2! < .188) Then
x1! = .184
y1! = 25.4
x2! = .188
y2! = 25.8
End If
If (voltage2! >= .188) And (voltage2! < .19) Then
x1! = .188
y1! = 25.8
x2! = .19
y2! = 26.1
End If
If (voltage2! >= .19) And (voltage2! < .194) Then
x1! = .19
y1! = 26.1
x2! = .194
y2! = 26.4
End If
If (voltage2! >= .194) And (voltage2! < .198) Then
x1! = .194
y1! = 26.4
x2! = .198
y2! = 26.9
End If
If (voltage2! >= .198) And (voltage2! < .203) Then
x1! = .198
y1! = 26.9
x2! = .203
y2! = 27.3
End If
If (voltage2! >= .203) And (voltage2! < .207) Then
x1! = .203
y1! = 27.3
x2! = .207
y2! = 27.7
```

```
End If
If (voltage2! >= .207) And (voltage2! < .212) Then
x1! = .207
y1! = 27.7
x2! = .212
y2! = 28.2
End If
If (voltage2! >= .212) And (voltage2! < .215) Then
x1! = .212
y1! = 28.2
x2! = .215
y2! = 28.6
End If
If (voltage2! >= .215) And (voltage2! < .219) Then
x1! = .215
y1! = 28.6
x2! = .219
y2! = 28.9
End If
If (voltage2! >= .219) And (voltage2! < .222) Then
x1! = .219
y1! = 28.9
x2! = .222
y2! = 29.2
End If
If (voltage2! >= .222) And (voltage2! < .226) Then
x1! = .222
y1! = 29.2
x2! = .226
y2! = 29.6
End If
If (voltage2! >= .226) And (voltage2! < .229) Then
x1! = .226
y1! = 29.6
x2! = .229
y2! = 30!
End If
If (voltage2! >= .229) And (voltage2! < .234) Then
x1! = .229
y1! = 30!
x2! = .234
y2! = 30.4
End If
If (voltage2! >= .234) And (voltage2! < .238) Then
x1! = .234
y1! = 30.4
```

```
x2! = .238
y2! = 30.8
End If
If (voltage2! >= .238) And (voltage2! < .242) Then
x1! = .238
y1! = 30.8
x2! = .242
y2! = 31.2
End If
If (voltage2! >= .242) And (voltage2! < .247) Then
x1! = .242
y1! = 31.2
x2! = .247
y2! = 31.6
End If
If (voltage2! >= .247) And (voltage2! < .251) Then
x1! = .247
y1! = 31.6
x2! = .251
y2! = 32!
End If
If (voltage2! >= .251) And (voltage2! < .254) Then
x1! = .251
y1! = 32!
x2! = .254
y2! = 32.3
End If
If (voltage2! >= .254) And (voltage2! < .257) Then
x1! = .254
y1! = 32.3
x2! = .257
y2! = 32.7
End If
If (voltage2! >= .257) And (voltage2! < .261) Then
x1! = .257
y1! = 32.7
x2! = .261
y2! = 33.1
End If
If (voltage2! >= .261) And (voltage2! < .265) Then
x1! = .261
y1! = 33.1
x2! = .265
y2! = 33.4
End If
If (voltage2! >= .265) And (voltage2! < .27) Then
```

```
x1! = .265
y1! = 33.4
x2! = .27
y2! = 33.9
End If
If (voltage2! >= .27) And (voltage2! < .273) Then
x1! = .27
y1! = 33.9
x2! = .273
y2! = 34.2
End If
If (voltage2! >= .273) And (voltage2! < .277) Then
x1! = .273
y1! = 34.2
x2! = .277
y2! = 34.6
End If
If (voltage2! >= .277) And (voltage2! < .281) Then
x1! = .277
y1! = 34.6
x2! = .281
y2! = 35!
End If
If (voltage2! >= .281) And (voltage2! < .285) Then
x1! = .281
y1! = 35!
x2! = .285
y2! = 35.4
End If
If (voltage2! >= .285) And (voltage2! < .288) Then
x1! = .285
y1! = 35.4
x2! = .288
y2! = 35.7
End If
If (voltage2! >= .288) And (voltage2! < .291) Then
x1! = .288
y1! = 35.7
x2! = .291
y2! = 36!
End If
If (voltage2! >= .291) And (voltage2! < .296) Then
x1! = .291
y1! = 36!
x2! = .296
y2! = 36.4
```

```
End If
If (voltage2! >= .296) And (voltage2! < .298) Then
x1! = .296
y1! = 36.4
x2! = .298
y2! = 36.8
End If
If (voltage2! >= .298) And (voltage2! < .303) Then
x1! = .298
y1! = 36.8
x2! = .303
y2! = 37.2
End If
If (voltage2! >= .303) And (voltage2! < .308) Then
x1! = .303
y1! = 37.2
x2! = .308
y2! = 37.7
End If
If (voltage2! >= .308) And (voltage2! < .314) Then
x1! = .308
y1! = 37.7
x2! = .314
y2! = 38.2
End If
If (voltage2! >= .314) And (voltage2! < .318) Then
x1! = .314
y1! = 38.2
x2! = .318
y2! = 38.6
End If
If (voltage2! >= .318) And (voltage2! < .322) Then
x1! = .318
y1! = 38.6
x2! = .322
y2! = 39!
End If
If (voltage2! >= .322) And (voltage2! < .326) Then
x1! = .322
y1! = 39!
x2! = .326
y2! = 39.4
End If
If (voltage2! >= .326) And (voltage2! < .331) Then
x1! = .326
y1! = 39.4
```

```
x2! = .331
y2! = 39.9
End If
If (voltage2! >= .331) And (voltage2! < .334) Then
x1! = .331
y1! = 39.9
x2! = .334
y2! = 40.2
End If
If (voltage2! >= .334) And (voltage2! < .338) Then
x1! = .334
y1! = 40.2
x2! = .338
y2! = 40.6
End If
If (voltage2! >= .338) And (voltage2! < .342) Then
x1! = .338
y1! = 40.6
x2! = .342
y2! = 41!
End If
If (voltage2! >= .342) And (voltage2! < .346) Then
x1! = .342
y1! = 41!
x2! = .346
y2! = 41.4
End If
If (voltage2! >= .346) And (voltage2! < .352) Then
x1! = .346
y1! = 41.4
x2! = .352
y2! = 42!
End If
If (voltage2! >= .352) And (voltage2! < .356) Then
x1! = .352
y1! = 42!
x2! = .356
y2! = 42.4
End If
If (voltage2! >= .356) And (voltage2! < .361) Then
x1! = .356
y1! = 42.4
x2! = .361
y2! = 42.8
End If
If (voltage2! >= .361) And (voltage2! < .366) Then
```

```
x1! = .361
y1! = 42.8
x2! = .366
y2! = 43.4
End If
If (voltage2! >= .366) And (voltage2! < .371) Then
x1! = .366
y1! = 43.4
x2! = .371
y2! = 43.8
End If
If (voltage2! >= .371) And (voltage2! < .377) Then
x1! = .371
y1! = 43.8
x2! = .377
y2! = 44.4
End If
If (voltage2! >= .377) And (voltage2! < .383) Then
x1! = .377
y1! = 44.4
x2! = .383
y2! = 45!
End If
If (voltage2! >= .383) And (voltage2! < .388) Then
x1! = .383
y1! = 45!
x2! = .388
y2! = 45.5
End If
If (voltage2! >= .388) And (voltage2! < .393) Then
x1! = .388
y1! = 45.5
x2! = .303
y2! = 46!
End If
If (voltage2! >= .393) And (voltage2! < .397) Then
x1! = .393
y1! = 46!
x2! = .397
y2! = 46.5
End If
If (voltage2! >= .397) And (voltage2! < .403) Then
x1! = .397
y1! = 46.5
x2! = .403
y2! = 47!
```

```
End If
If (voltage2! >= .403) And (voltage2! < .408) Then
x1! = .403
y1! = 47!
x2! = .408
y2! = 47.5
End If
If (voltage2! >= .408) And (voltage2! < .413) Then
x1! = .408
y1! = 47.5
x2! = .413
y2! = 48!
End If
If (voltage2! >= .413) And (voltage2! < .418) Then
x1! = .413
y1! = 48!
x2! = .418
y2! = 48.5
End If
If (voltage2! >= .418) And (voltage2! < .423) Then
x1! = .418
y1! = 48.5
x2! = .423
y2! = 49!
End If
If (voltage2! >= .423) And (voltage2! < .428) Then
x1! = .423
y1! = 49!
x2! = .428
y2! = 49.5
End If
If (voltage2! >= .428) And (voltage2! < .433) Then
x1! = .428
y1! = 49.5
x2! = .433
y2! = 50!
End If
If (voltage2! >= .433) And (voltage2! < .443) Then
x1! = .433
y1! = 50!
x2! = .443
y2! = 51!
End If
If (voltage2! >= .443) And (voltage2! < .479) Then
x1! = .443
y1! = 51!
```

```
x2! = .479
y2! = 54.3
End If

' Calc slope
m! = (y2! - y1!) / (x2! - x1!)
' calc intercept
b! = y1! - (m!) * (x1!)
'Equation of line
temp8! = (m!) * voltage2! + b!

    text5.Text = Format$(temp8!, "###.0")
     'text5.Text = Format$(voltage2!, "####.##0")

End Sub
```

APPENDIX B

This Visual Basic program was created to drive the Nicolet 520 FTIR bench, control the temperature of the ATR device, and to transform the data into a Microsoft Excel spreadsheet format for further processing. The development of this program was essential for spectral data acquisition at a specified time.

Kinetic Program

```
VERSION 2.00
Begin Form Form1
        BackColor      = &H00C0C000&
        Caption        = "j"
        Height         = 6945
        Left           = 4725
        LinkMode       = 1 'Source
        LinkTopic      = "Form1"
        ScaleHeight    = 6540
        ScaleWidth     = 4650
        Top            = 180
        Width          = 4770
Begin TextBox DDEText
        BackColor      = &H00FF8080&
        ForeColor      = &H008080FF&
        Height         = 285
        Left           = 3480
        MultiLine      = -1 'True
        TabIndex       = 9
        Top            = 1560
        Width          = 1095
End
Begin Grid Grid1
        BackColor      = &H00FFFF80&
        Cols           = 3
        Height         = 4335
        Left           = 120
        Rows           = 30
        TabIndex       = 8
        Top            = 2160
        Width          = 4335
End
Begin TextBox Text4
        Height         = 495
        Left           = 2880
        TabIndex       = 7
        Text           = "5"
        Top            = 1560
        Width          = 495
End
Begin TextBox Text3
        Height         = 375
        Left           = 3000
        TabIndex       = 6
```

```
        Text        = "60"
        Top         = 1080
        Width       = 495
End
Begin CommandButton Command2
        Caption     = "Stop"
        Height      = 495
        Left        = 3600
        TabIndex    = 5
        Top         = 720
        Width       = 855
End
Begin CommandButton command1
        Caption     = "start"
        Height      = 495
        Left        = 3600
        TabIndex    = 4
        Top         = 120
        Width       = 855
End
Begin Timer Timer1
        Enabled     = 0  'False
        Interval    = 60000
        Left        = 0
        Top         = 0
End
Begin TextBox Text2
        Height      = 285
        Left        = 2400
        TabIndex    = 3
        Text        = "20"
        Top         = 600
        Width       = 495
End
Begin TextBox Text1
        Height      = 285
        Left        = 1800
        TabIndex    = 2
        Top         = 120
        Width       = 1335
End
Begin Label Label3
        Alignment   = 1  'Right Justify
        Caption     = "Number of minutes in between spectra that are >15:"
        Height      = 495
        Left        = 0
```

```
        TabIndex      = 11
        Top           = 1560
        Width         = 2775
End
Begin Label Label5
        Alignment     = 1  'Right Justify
        Caption       = "Number of seconds in between the first 15 spectra:"
        Height        = 375
        Left          = 0
        TabIndex      = 10
        Top           = 1080
        Width         = 2775
End
Begin Label Label2
        Caption       = "Number of measurements:"
        Height        = 255
        Left          = 0
        TabIndex      = 1
        Top           = 600
        Width         = 2295
End
Begin Label Label1
        Alignment     = 1  'Right Justify
        Caption       = "Filename:"
        Height        = 255
        Left          = 720
        TabIndex      = 0
        Top           = 120
        Width         = 855
End
End
Dim RowCount As Integer
Dim Parameter As String
Dim Wavenum As String

Sub command1_Click ()
'Grid1.Col = 0
'w% = 1
'nn% = text4
'For i% = 1 To text2
'Grid1.Row = w%
'Grid1.Text = Format$(nn%, "####.00")
'nn% = nn% + text4
'w% = w% + 1
'Next
        timer1.Interval = 60000
```

```
        nn% = 60
        timer1.Enabled = True
Grid1.Row = 0
End Sub

Sub Command2_Click ()
 executeOMNIC "exit"
Beep
MsgBox "program terminated"
End
End Sub
Sub ExcelDDEAction ()

'This subroutine determines the correct row and column for the the
'next piece of information and pokes the info into the calculated Excel cell.
        DDEText.LinkMode = 2
        DDEText.LinkMode = 0
        DDEText.LinkTopic = "EXCEL|SHEET1"
         StuffIt$ = "R" + Format$(RowCount, "0") + "C2"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.Text = Parameter$
        DDEText.LinkPoke
        DDEText.LinkMode = 0
        StuffIt$ = "R" + Format$(RowCount, "0") + "C1"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.Text = Timsec$
        DDEText.LinkPoke
        DDEText.LinkMode = 0
        StuffIt$ = "R" + Format$(RowCount, "0") + "C3"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.Text = Wavenum$
        DDEText.LinkPoke
        DDEText.LinkMode = 0
        'RowCount = RowCount + 1
End Sub

Sub ExcelDDEAction1 ()
'This subroutine determines the correct row and column for the the
'next piece of information and pokes the info into the calculated Excel cell.
        DDEText.LinkMode = 2
```

```
        DDEText.LinkMode = 0
        DDEText.Text = Parameter$
        DDEText.LinkTopic = "EXCEL|SHEET1"
        StuffIt$ = "R" + Format$(RowCount, "0") + "C1"
        DDEText.LinkItem = StuffIt$
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.LinkMode = 0
        RowCount = RowCount + 1
End Sub

Sub Form_Load ()

Load OMTALK

        setOMNIC "Correlation", "simple"
        CorrErr = 25
Grid1.ColWidth(2) = 1600
Grid1.ColWidth(1) = 1600
Grid1.ColWidth(0) = 1000
Grid1.Rows = 60
Grid1.Cols = 3
'setup column titles for the spreadsheet
z% = 1
Grid1.Row = 0
Grid1.Col = 0
Grid1.Text = "Time(sec)"
Grid1.Col = 1
Grid1.Text = "Wavenumber"
Grid1.Col = 2
Grid1.Text = "Absorbance"
executeOMNIC "BenchSetup"
executeOMNIC "Invoke Collectsetup"
executeOMNIC "Invoke PrintSetup"
executeOMNIC "Invoke displaysetup"
'setOMNIC "Collect NumScans", 32
'setOMNIC "Collect Resolution", 2
timer1.Enabled = False
 y% = 1
 qq% = 1
 specnumber! = 1
nn% = 0
'This procedure opens a DDE link to Excel.  If Excel is not open an
'error is generated and the program jumps to the "Open Excel"
'code section.  After this code is executed the program returns to
'the "Startup" section. For more information on using DDE please refer
```

```
'to the Visual Basic users manual.

Startup:
        On Error GoTo OpenExcel
        DDEText.LinkTopic = "Excel|Sheet1"
        DDEText.LinkItem = "R12C12"
        DDEText.LinkTimeout = -1
        DDEText.LinkMode = 2
        DDEText.LinkPoke
        DDEText.LinkMode = 0
        Exit Sub

OpenExcel:
        If Err = 282 Then
        X = Shell("c:\Excel\Excel.exe", 3)
        Resume Startup
        Else
        Error Err
        End If
End Sub

Sub kinetics_timer ()
        start = Timer
        timer1.Enabled = False
        Rem MsgBox "before if"
        executeOMNIC "SizeWindow 285 450"
        executeOMNIC "MoveWindow 0 0"
Rem this statement tells omnic to scan a sample
        executeOMNIC "Invoke Collectsample Auto "
 Rem these statements stores the binary data
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Export" + " " + filename1$
        executeOMNIC cmdtxt$
'-------------------------------------------------
Rem This portion of the program allows you to store the
Rem data into ascii format
'filename$ = Format$(text2) + Format$(specnumber!, "0") + ".csv"
        'filename1$ = "b:" + filename$
        Rem filename3$ = "a:" + filename$
        'cmdtxt$ = "Export" + " " + filename1$
        'executeOMNIC cmdtxt$
 Rem these statements displays the data in a particular region of the x-axis
        executeOMNIC "set display Xstart 2300"
        executeOMNIC "set display Xend 2200"
        'SetOMNIC "display xcrossHairLoc", 2925
```

```
Rem This part allows us to determine the highest point of
Rem the peak
        executeOMNIC "PeakHeight 2250 shift"
        area$ = GetOMNIC("result Current")
Rem This portion of the program allows us to get specific info
Rem of the position of the peak
        OnlyX# = GetVal(area$, "X:")
        OnlyY# = GetVal(area$, "Y:")
        'Print OnlyY#
Rem This part determines the corrected height using a baseline
        peak$ = "CorrectedPeakHeight 2280" + " " + Str(OnlyX#) + " " + "2175"
        executeOMNIC peak$
        area1$ = GetOMNIC("result current")
        OnlyY1# = GetVal(area1$, "Height:")
         Grid1.Row = Grid1.Row + 1
        Grid1.Col = 1
        Grid1.Text = Str(OnlyX#)
        Grid1.Col = 2
        Grid1.Text = Str(OnlyY1#)
        'Parameter$ = filename$
        'ExcelDDEAction
        ExcelDDEAction1
'text5.Text = text5.Text + "time" + Str$(OnlyX#) + Str$(OnlyY#) + NewLine$
'-------------------------------------------------------
        Grid1.Col = 0
        'Print (ppp%)
        pppp% = nn%
        'Grid1.Text = Format$(pppp%, "####.##")
        Rem Puts the time onto the grid sheet
        Grid1.Text = pppp%

Rem This puts the data onto the spread sheet
        Parameter$ = Str(OnlyY1#)
        Timsec$ = Str(pppp%)
        Wavenum$ = Str(OnlyX#)
        ExcelDDEAction
        timer1.Enabled = False
        specnumber! = specnumber! + 1
        y% = y% + 1
        nn% = Val(text3.Text) + pppp%
        Rem t%=0 resets the timer interval
        finish = Timer
        ppp% = (finish - start)

'Print ppp%
```

```
timer1.Interval = (text3.Text - ppp%) * 1000
If y% = 16 Then
nn% = nn% - Val(text3.Text)
timer1.Interval = 60000
End If
 timer1.Enabled = True
End Sub

Sub longtime ()
Print text2.Text
timer1.Enabled = False
nn% = nn% + 60
        If qq% = Val(text4.Text) Then
        If (text2.Text) + 1 <> y% Then
        start = Timer
        timer1.Enabled = False
 'Print text4.Text
        executeOMNIC "SizeWindow 285 450"
        executeOMNIC "MoveWindow 0 0"
Rem this statement tells omnic to scan a sample
        executeOMNIC "Invoke Collectsample Auto "
        Rem these statements stores the binary data
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Export" + " " + filename1$
        executeOMNIC cmdtxt$
'-------------------------------------------------
Rem This portion of the program allows you to store the
Rem data into ascii format
'filename$ = Format$(text2) + Format$(specnumber!, "0") + ".csv"
        'filename1$ = "b:" + filename$
        Rem filename3$ = "a:" + filename$
        'cmdtxt$ = "Export" + " " + filename1$
        'executeOMNIC cmdtxt$
Rem these statements displays the data in a particular region of the x-axis
        executeOMNIC "set display Xstart 2300"
        executeOMNIC "set display Xend 2200"
        'SetOMNIC "display xcrossHairLoc", 2925
Rem This part allows us to determine the highest point of
Rem the peak
        executeOMNIC "PeakHeight 2250 shift"
        area$ = GetOMNIC("result Current")
Rem This portion of the program allows us to get specific info
Rem of the position of the peak
        OnlyX# = GetVal(area$, "X:")
        OnlyY# = GetVal(area$, "Y:")
```

```
        'Print OnlyY#
Rem This part determines the corrected height using a baseline
        peak$ = "CorrectedPeakHeight 2280" + " " + Str(OnlyX#) + " " + "2175"
        executeOMNIC peak$
        area1$ = GetOMNIC("result current")
        OnlyY1# = GetVal(area1$, "Height:")
        Grid1.Row = Grid1.Row + 1
        Grid1.Col = 1
        Grid1.Text = Str(OnlyX#)
        Grid1.Col = 2
        Grid1.Text = Str(OnlyY1#)
        'Parameter$ = filename$
        'ExcelDDEAction
        ExcelDDEAction1
'text5.Text = text5.Text + "time" + Str$(OnlyX#) + Str$(OnlyY#) + NewLine$
'-----------------------------------------------------
        Grid1.Col = 0
        pppp% = nn%
        'Grid1.Text = Format$(pppp%, "####.##")
        Rem Puts the time onto the grid sheet
        Grid1.Text = pppp%
Rem This puts the data onto the spread sheet
        Parameter$ = Str(OnlyY1#)
        Timsec$ = Str(pppp%)
        Wavenum$ = Str(OnlyX#)
        ExcelDDEAction
        timer1.Enabled = False
        specnumber! = specnumber! + 1
        y% = y% + 1
        qq% = 0
 Else
        executeOMNIC "Select All"
        executeOMNIC "set display Xstart 4000"
        executeOMNIC "set display Xend 1000"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 5
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "Select All"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 10
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
```

```
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "Select All"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 15
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "Select All"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 20
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "Select All"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 25
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "Select All"
        executeOMNIC "CutSelectedSpectra"
        specnumber! = 30
        filename$ = Format$(text1) + Format$(specnumber!, "0") + ".spa"
        filename1$ = "c:\kinetic\" + filename$
        cmdtxt$ = "Import" + " " + filename1$
        executeOMNIC cmdtxt$
        executeOMNIC "Print"
        executeOMNIC "EXIT"
        Beep

MsgBox "Program Terminated"
        End
        End If
Rem t%=0 resets the timer interval
'nn% = Val(text3.Text) + pppp%
        finish = Timer
        ppp% = (finish - start)
 'Print ppp%
```

```
 End If
 If qq% = 0 Then
 timer1.Interval = (60 - ppp%) * 1000
 Else
 timer1.Interval = 60000
 End If
        qq% = qq% + 1
        timer1.Enabled = True
End Sub
Sub Timer1_Timer ()
'tt% = tt% + 1
'If tt% = text4 \ text3 Then
If y% < 15 + 1 Then
        kinetics_timer
Else
        setOMNIC "Collect NumScans", 25
        longtime
End If
End Sub
```