Research Technical Completion Report

GROUNDWATER CONTAMINATION FROM AGRICULTURALLY APPLIED PESTICIDES

by

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ABSTRACT

Approximately 90 % of the public water supply in Idaho originates
from groundwater, thus making potential pesticide contamination a key
issue. A small, but significant portion of the applied pesticide is
transported through the soil column more quickly than predicted by
currently available models. It has been proposed that increased
pesticide mobility occurs as a result of pesticide complexation with a
water soluble soil organic fraction, in which the pesticide-organic
complex moves faster than the pesticide alone. The present research
project is being conducted to 1) develop the methodologies for
qualitatively and quantitatively studying pesticide complexation with
water soluble soil materials, 2) define the key variables controlling
complexation, 3) compare predicted complexation and pesticide mobility
alteration with actual results obtained in simulated field situations,
and 4) propose a model input variable to produce more accurate estimates
of pesticide transport in soil. Fourier Transform Infrared spectroscopy
(FT-IR) was combined with a Cylindrical Internal Reflectance (CIR)
sample cell to determine the infrared spectra of commercially available
humic acid and soil extracts. This technique, which makes it possible
to determine the infrared spectra of dissolved solutes in aqueous
solution, has not previously been used with soil extracts. Instead
previous investigators have resorted to nonaqueous sampling techniques.
In this research, solution phase parameters were altered to illustrate
that the spectra of humic acid in water varied with humic acid
concentration, ionic strength, and pH as explained by humic acid
conformational changes and functional group protonation. These factors
have been proposed by other investigators to control pesticide

interactions with soil organic materials. Spectral scans from 670 to 4000 cm^{-1} indicate that the region of greatest resolution for observing characteristic humic acid absorbance bands occurs from 1000 to 2000 cm^{-1}. Absorbance bands reflecting ester-bonded polysaccharides (1050, 1088, and 1164 cm^{-1}), aliphatic C-H groups (1450, 2860, and 2920 cm^{-1}), and carboxyl groups (1380, 1565, and 1713 cm^{-1}) were detected. CIR was also used to obtain the spectra of soil extracts in the form of dissolved humic and fulvic acids as well as water soluble materials. Comparison of CIR spectra with a traditional nonaqueous sampling procedure (Nujol mull) demonstrated increased C-H peak intensities and near total elimination of ester absorbance peaks in the mull preparations. The ability to determine the infrared spectra of soil extracts in their native wet state will prove advantageous in determining humic material interaction with pesticides. Studies in this area are currently in progress.

INTRODUCTION

United States agriculture relies heavily on the use of pesticides for weed and insect control. As a result of past use, a total of 12 different pesticides have contaminated groundwater supplies of 18 states (Cohen et al., 1984). Significant national, regional, and local concern has been expressed, because 118 million Americans depend upon groundwater for their drinking water. In Idaho, groundwater represents the source of 90% of the public water supply.

Groundwater contamination has occurred in various locations around the country from application of pesticides at levels necessary for agricultural production. Studies in Nebraska (Spalding et al., 1980) and South Carolina (Achari et al., 1975) showed that groundwater below agricultural lands was contaminated by atrazine and DDT, respectively. More recent work in Iowa showed that groundwater was contaminated by atrazine, alachlor, cyanazine, metolachlor, metribuzin, 2,4-D, chloramben, dicamba, trifluralin, and fonofos (Hallberg, 1986). Groundwater supplies in Ontario, Oregon, near the Idaho border, are contaminated by the hydrolyzed form of the herbicide DCPA (dimethyl tetrachloroterephthalate) (Bruck, 1986). The relationship between aquifer NO_3^- levels and agricultural practices has been the topic of research in Idaho and levels of inorganic chemical species in groundwater have been quantified (Yee and Souza, 1984). Little else is known about present or potential contamination of groundwater in Idaho. This represents a critically important situation in the Rathdrum Prairie area of northern Idaho and eastern Washington, because the underlying aquifer is one of three sole-source aquifers in the U.S. as designated by the EPA. Protection of the aquifer is thus critical because of the

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lack of alternate drinking water sources. Regular monitoring of pesticide concentrations present in groundwater is not feasible because of the large number of different pesticides used and the lack of a sufficient quantity and distribution of monitoring wells. Groundwater reclamation is costly and difficult, thus necessitating the recognition of potential contamination problems.

Models have been developed for other regions of the country in order to overcome the site-specific problems associated with assessing pesticide movement in soils. Unfortunately such models have not yet proven accurate enough to serve as a predictive tool for making management decisions.

The greatest current limitation concerning the prediction of pesticide behavior in the environment lies not in the development of additional models, but rather in the accurate description of complex interactions occurring between the pesticide and soil system components. Without the development of an adequate understanding of the fundamental concepts any modeling attempt will be severely limited. It will therefore be impossible to adequately regulate pesticide use and prevent future groundwater contamination.

Prevention of future groundwater contamination is hindered because a small, but significant portion of the applied pesticide is transported through the soil column more quickly than predicted by currently available models. Recently, a mathematical relationship between dissolved organic carbon (water soluble soil organic materials) and relatively immobile chemicals such as pesticides has been proposed for inclusion into pesticide transport models (Enfield, 1985; Enfield and Bengtsson, 1986). Computer simulation demonstrated that measurable

increases in mobility of pesticides may occur through an interaction with water soluble soil organic materials (Enfield, 1985). Although the addition of this parameter into a model describing pesticide transport thus appears to be critical, the proponents acknowledge that the approach is currently limited by a lack of data describing the physical and chemical processes occurring during complexation and pesticide movement. In other words, pesticide complexation with a water soluble soil organic material can cause increased pesticide mobility, but an inadequate understanding of the interaction itself prohibits the development of an accurate model input parameter.

The objectives of the research in progress are to 1) develop the methodologies for qualitatively and quantitatively studying pesticide complexation with water soluble soil materials, 2) define the key variables controlling complexation, 3) compare predicted complexation and pesticide mobility alteration with actual results obtained in simulated field situations, and 4) propose a model input variable to produce more accurate estimates of pesticide transport in soil.

This report presents the first year results of the three-year study. An attempt was made to develop the methodologies for qualitatively and quantitatively studying pesticide complexation with water soluble soil materials.

FOURIER TRANSFORM INFRARED ANALYSIS OF HUMIC MATERIALS

Introduction

Humic and fulvic acids have been operationally defined as NaOH
extractable soil organic fractions insoluble and soluble in acid,
respectively. The fractions therefore necessarily represent
heterogeneous mixtures of organic materials possessing a range in
chemical characteristics. Previous studies involving infrared analyses
of humic or water soluble soil materials have been conducted with dried
material pressed into KBr disks (MacCarthy and Rice, 1985; Stevenson,
1982; Madhun et al., 1986), Nujol mulls (Orlov et al., 1962; Wagner and
Stevenson, 1965), or solid films (Schaumberg et al., 1980; Baham and
Sposito, 1983). Such drastic procedures may not only alter the
extracted materials (Stevenson and Goh, 1974; Theng et al., 1966), but
do not allow for spectral observation of the materials in their native
wet state. Analysis in the presence of water has been conducted, but in
both reported instances a humic acid slurry was used rather than an
aqueous solution (MacCarthy et al., 1975; MacCarthy and Mark, 1975).
The lack of infrared studies using aqueous solutions of humic materials
has occurred because of the formidable problems associated with
measuring infrared solution spectra in a highly infrared-absorbing
solvent such as water.

The use of cylindrical internal reflectance (CIR) in Fourier
Transform Infrared spectroscopy (FT-IR) represents a recently developed
approach to obtain the infrared spectra of dissolved materials in
aqueous solution. The theory and practical applications of CIR have
previously been described (Bartick and Messerschmidt, 1984), but will be

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summarized here because no studies with soil extracts have been reported in the literature.

Infrared radiation passes through a rod-shaped crystal possessing a high refractive index and cone-shaped ends (Fig. 1). The cone-shaped ends cause input infrared radiation to be directed at the angle of incidence necessary for reflection off crystal walls and transmission to the output end of the crystal. Infrared radiation penetrates the liquid surrounding the rod-shaped crystal to a fixed distance sufficiently small so as to prevent highly absorbing solvents from obscuring spectral observation of contained solutes. When working with aqueous solutions, computer subtraction can be used to eliminate water absorbance bands from the spectra of water plus dissolved material. This technique has been used for both qualitative and quantitative analysis of biological and nonbiological liquids (Braue and Pannella, 1987).

Commercially available Aldrich humic acid is used to demonstrate the advantages of CIR for the infrared analysis of humic materials. This material was chosen because characterization by spectroscopic and other means has been reported in the literature and is available for comparison purposes, and because relatively large quantities of a single material were required. Techniques developed with Aldrich humic acid were then applied to soil extracts to determine the usefulness of CIR in studies concerning pesticide complexation with water soluble materials.

Materials and Methods

A Digilab FTS-80 FT-IR spectrometer with a computer data system, 0.25 cm^{-1} resolution, and a spectral range of 5000 to 10 cm^{-1} was used
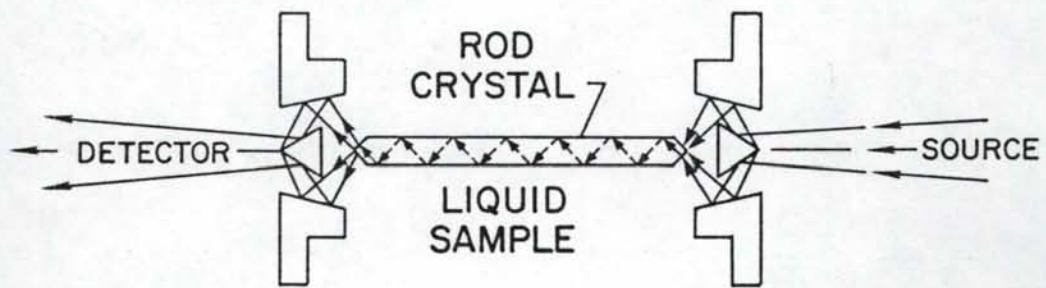
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Fig. 1. Optical configuration of the cylindrical internal reflectance

sample cell.

in the analyses. A cylindrical internal reflectance sampling cell (CIRCLE CELL, Spectra Tech, Inc., Stamford, CT) with a ZnSe rod crystal in the open boat configuration was fitted into the Digilab instrument.

Humic acid in the form of a sodium salt was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. All solutions were prepared 5.0 g L^{-1} in humic acid and adjusted to pH 7.0 using 2.0 M HCl (unless otherwise noted). Solutions were stored no longer than 24 h prior to FT-IR analysis. The sample cell chamber was in most instances purged for 1 h with moisture free air prior to spectral data collection. All spectra were recorded in the absorbance mode from 670 to 4000 cm^{-1} and signal averaged for 1024 scans. Background spectra consisted of the CIRCLE CELL filled with water or the appropriate sample matrix. The reported spectra were obtained by referencing the background spectra to the sample spectra. The presented spectra represent those having the highest signal to noise ratio of three replications performed with different solutions. Nujol mull preparations were prepared using paraffin oil. A Digilab Qualimatic FT-IR spectrometer with a 7 mm aperature was used to determine the spectra.

Six soils were selected to obtain a range in organic matter, pH, and texture (Table 1). Surface (0-15 cm) samples were collected, air-dried, and crushed to pass a 2-mm sieve. Analyses were conducted using the following methods: pH by glass electrode (1:1 soil to water ratio), organic C by the Walkley-Black method (Allison, 1965), total nitrogen by Dumas combustion (LECO 600-CHN Determinator), and particle-size distribution by the hydrometer method (Day, 1956).

Table 1. Soil characteristics.

Soil			Organic carbon	Total nitrogen	Clay	Sand
Series	Subgroup	pH	------------(g kg^{-1})--------------			
Nyssaton	Xerollic Calciorthid	6.9	8.5	0.83	32	301
Feltham	Xeric Torriorthent	6.3	6.3	0.83	46	828
Palouse	Pachic Ultic Haploxeroll	5.7	19.2	1.60	166	328
Melton	Humic Cryaquept	5.8	29.0	2.30	209	435
Sudduth	Argic Pachic Cryoborolls	5.6	44.2	3.23	317	306
Fenn	Chromic Pelloxerert	5.9	27.8	2.00	417	216

Humic and fulvic acids were extracted and purified from the six Idaho soils characterized as above. Standard methods involving differential solubility in acid and base were followed (Schnitzer, 1982). Extracted humic and fulvic acids were first filtered using a 50 mL Amicon stirred ultrafiltration cell (Amicon, Danvers MA) and a PM10 ultrafiltration membrane having a MW cutoff of 10,000. Humic acid was retained by the membrane and washed with a 200 mL aliquot of distilled water. Fulvic acid in the filtrate where then concentrated to a volume of approximately 20 mL using a YCO5 membrane having a 500 MW cutoff. Infrared spectra of the concentrated humic and fulvic acid samples were obtained using CIR after adjustment of solution pH to 7.0. Humic and fulvic acids were freeze-dried, dissolved in distilled water, and again analyzed using FT-IR and the CIR sample cell.

Water extracts were also obtained from the same soils by shaking 2,
100 g samples of air-dried soil with 200 mL of water for a 4 h time
period. The water extract was filtered through Whatman No. 42 filter
paper and then through a 0.45 μm membrane filter. Concentration of the
extract for FT-IR analysis was performed using ultrafiltration and a 500
MW cutoff membrane (YC05). Final volume of the water extract was
approximately 20 mL. Spectral scans from 670 to 4000 cm^{-1} were
conducted using FT-IR and CIR.

Results and Discussion

Characteristic Absorbance Bands of Aldrich Humic Acid

A spectral scan from 670 to 4000 cm^{-1} indicates that the region of
greatest absorbance for humic acid occurs between 1000 and 2000 cm^{-1}
(Fig. 2). The spectrum presented depicts a 200 g L^{-1} humic acid
solution, thus indicating that work at more realistic natural
concentrations approaching the limits of detection would best be
achieved using the 1000 to 2000 cm^{-1} region. Spectra from a variety of
humic acids in the form of KBr pellets (MacCarthy and Rice, 1985;
Stevenson, 1982) or sodium humate slurries (MacCarthy and Mark, 1975)
usually depict an absorbance peak at 3400 cm^{-1} and sometimes peaks at
2920 and 2860 cm^{-1} which equal those of lower frequencies in peak
height. Figure 2 shows peaks at 2920 and 2860 cm^{-1}, but at a much lower
absorbance intensity than the peaks between 1000 and 2000 cm^{-1}. This
distinction between previously reported spectra and those shown here may
represent a difference in the humic materials used or an effect of the
humic acid being in solution as opposed to a solid or slurry form. The
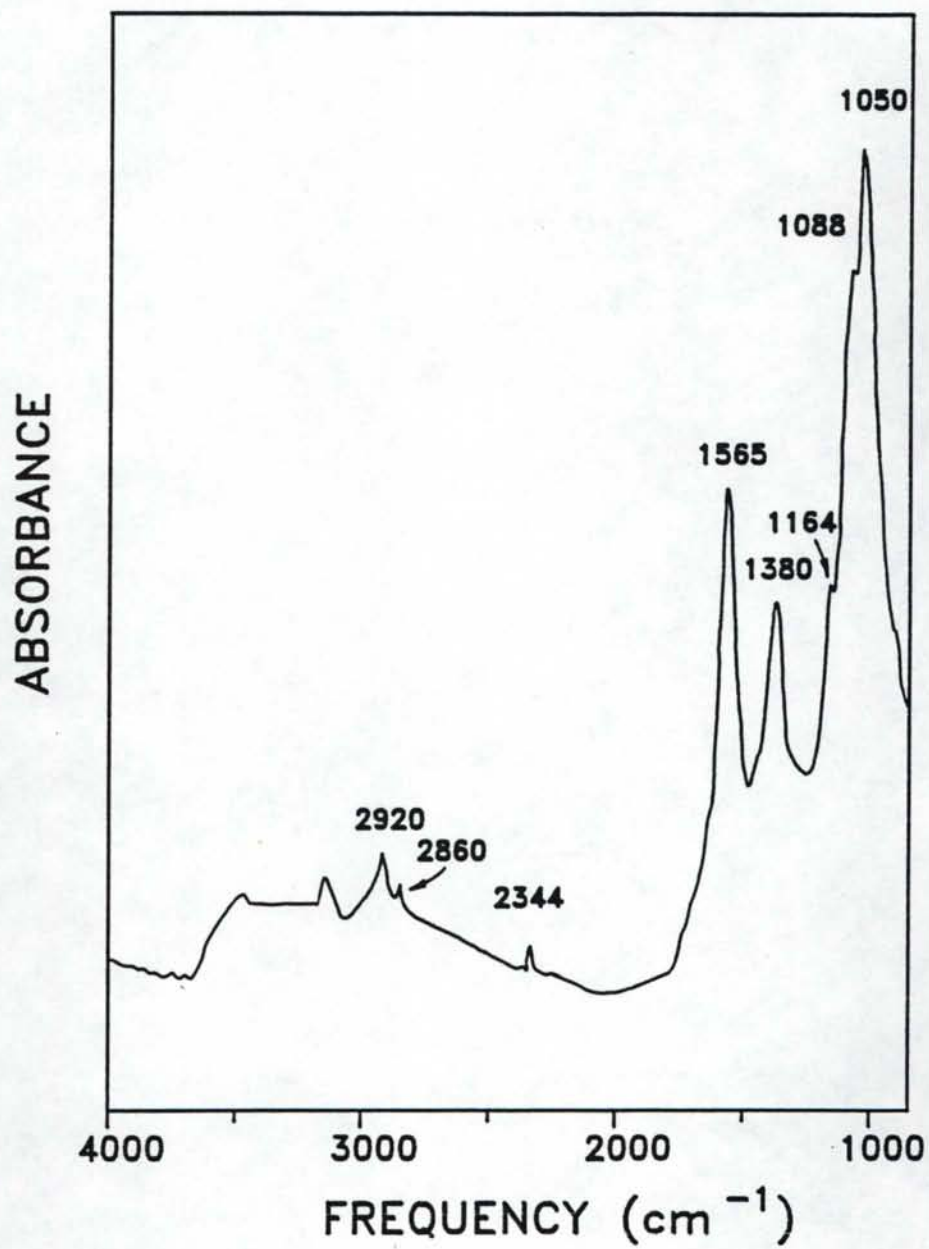latter hypothesis was tested and will be discussed below.

Fig. 2.   FT-IR spectral scan of Aldrich humic acid (200 g L^{-1}) using cylindrical internal reflectance.

Absorbance peaks at frequencies greater than 3000 cm^{-1} reflect the inability to overcome, through background subtraction, the strong water absorbance centered at 3400 cm^{-1} (Fig. 2). A similar difficulty occurred in previous work with humic acid slurries in which no spectra at frequencies higher than 3100 cm^{-1} were reported (MacCarthy and Mark, 1975). Absorbance peaks at 2920 and 2860 cm^{-1} represent characteristic features displayed by most humic and fulvic acids and are attributed to asymmetric and symmetric stretching vibrations, respectively, of aliphatic C-H bonds in methyl or methylene units (Theng et al., 1966). The absorbance band located at 2344 cm^{-1} is present in a region usually devoid of any peaks from infrared active functional groups in humic acids and represents CO_2. Carbon dioxide most likely existed in the humic acid solution as a dissolved gas, because increased interferometer chamber purge times failed to remove this absorbance band. Buffering capacity, solution pH, and exposure time to ambient air differed between the water reference and humic acid solutions leading to unequal dissolved CO_2 levels in the two samples.

Major absorbance bands occur at 1050 and 1088 cm^{-1} with increased humic acid concentration increasing the relative intensity of the 1050 cm^{-1} band to a greater extent than the adjacent 1088 cm^{-1} band (Figs. 2,3). In contrast, below humic acid concentrations of 10 g L^{-1}, the 1088 cm^{-1} band becomes dominant of the two (Fig. 4). Infrared activity in the 1000 to 1100 cm^{-1} region has been attributed to C-O stretching of polysaccharides or Si-O stretching of silicate impurities (Stevenson, 1982). The 1050 cm^{-1} band has been most often considered to represent the presence of polysaccharides (Stevenson and Goh, 1971; Clark and Tan, 1969). Silicate contamination is also possible in that Aldrich humic
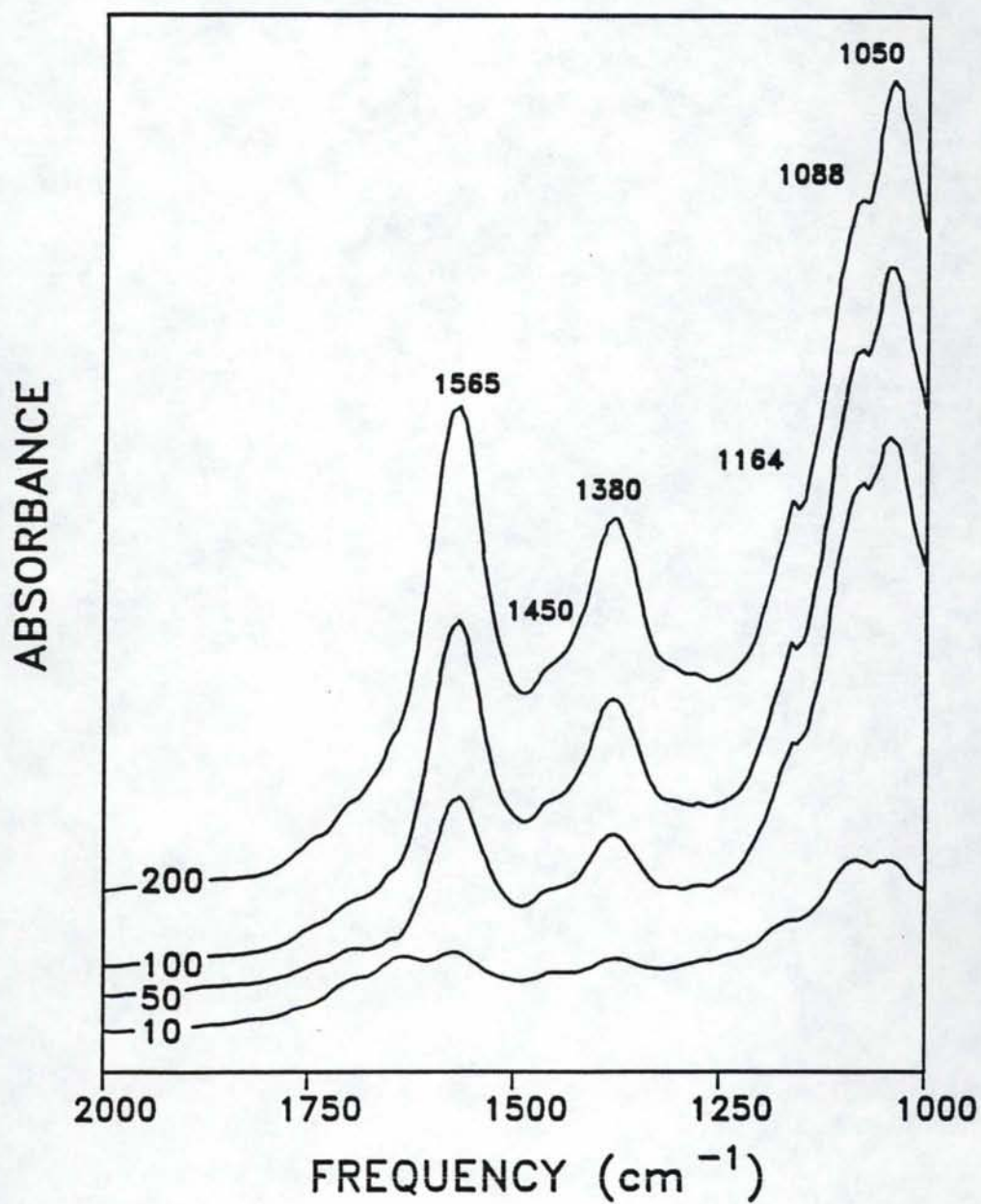
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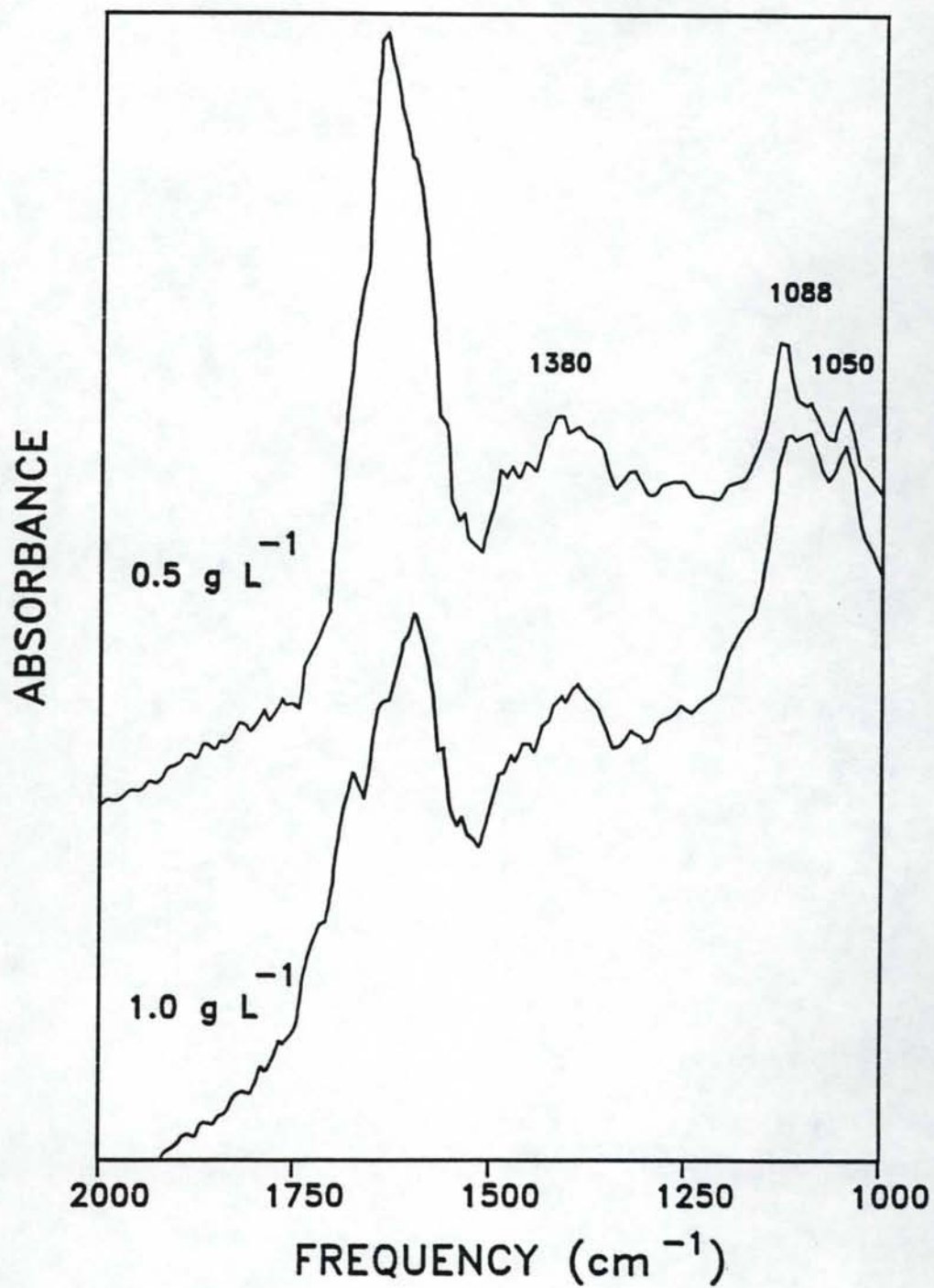Fig. 3. FT-IR spectra of Aldrich humic acid in water at concentrations from 10 to 200 g L^{-1}.

Fig. 4. FT-IR spectra of Aldrich humic acid in water at concentrations of 0.5 and 1.0 g L^{-1}.

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acid has been reported to have an ash content of 60% (Carter and Suffet, 1982).

An increase in humic acid concentration would decrease the absorbance intensity of functional groups involved in intra- or intermolecular bonding as compared to the absorbance intensity of those groups not involved. Previous work has shown that humic acids behave as rigid, uncharged colloids at concentrations greater than 3.5 to 5.0 g L^{-1}, while at concentrations less than 3.5 g L^{-1} they behave as flexible, linear polyelectrolytes (Gosh and Schnitzer, 1980). Although a definite functional group assignment cannot be made to either of the two peaks, it is proposed that the interaction of each group differs when humic acid changes from a colloid to a polyelectrolyte. A functional group participating in intra- or intermolecular interaction and colloid formation would increase in intensity with decreased humic acid concentration (1088 cm^{-1} band) relative to a functional group participating to a lesser extent (1050 cm^{-1} band).

The absorbance band at 1164 cm^{-1} has been found in derivatized humic acids and was proposed to represent C-O stretching of mixed anhydrides or acetate esters (Wagner and Stevenson, 1965) (Figs. 2,3). Most studies using underivatized humic acids have not shown an absorbance peak in this region (Stevenson, 1982). However, polysaccharides are attached to humic acids through an ester linkage (Clark and Tan, 1969) which would provide an absorbance band at approximately 1170 cm^{-1} as a result of C - O stretching (Streitwieser and Heathcock, 1976). The reported peak at 1164 cm^{-1} thus supports the presence of polysaccharides indicated by the peaks at 1050 and 1088 cm^{-1}. A second absorbance band for C = O stretching in the ester linkage

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would be expected at approximately 1735 cm^{-1} (Streitwieser and Heathcock, 1976). A peak occurs at 1713 cm^{-1}, but this absorbance has been most often recognized to represent C = O stretching vibration occurring mainly to carboxyl groups (MacCarthy and Rice, 1985; Stevenson, 1982; Stevenson and Goh, 1971). It is possible that a portion of this absorbance represents C = O stretching vibration occurring in ester linkages as proposed by Clark and Tan (1969). Absorbance peaks at 1380 and 1565 cm^{-1} have been attributed to the COO$^-$ ion present when a humic acid is in the salt form (Stevenson and Goh, 1971), the form used in the present case. Aliphatic C-H groups produce the shoulder peak at 1450 cm^{-1} (MacCarthy and Rice, 1985; Stevenson, 1982; Juo and Barber, 1969) (Fig. 3).

Comparison of CIR spectra to a spectrum produced using a Nujol mull of the Aldrich humic acid provides distinct differences in peak absorbance intensity. Peak intensities in the mull spectrum are increased in the 2800 to 3000 cm^{-1} region and almost eliminated in the 1000 to 1200 cm^{-1} region as compared to CIR results (Fig. 5). As a result of these changes, the mull spectrum more closely resembles previously recorded spectra in which nonaqueous preparations of humic acids were used (Stevenson, 1982). This comparison demonstrates that aqueous interactions cause dramatic spectral changes particularly with respect to relative peak heights. Large increases in absorbance at 2920, 2860, and 1450 cm^{-1} in the mull spectrum as compared to CIR spectra indicate increased C-H character of the humic acid even though the same material was used in both instances. Spectral differences in the 1000 to 1200 cm^{-1} range already noted, most likely reflect hydrogen
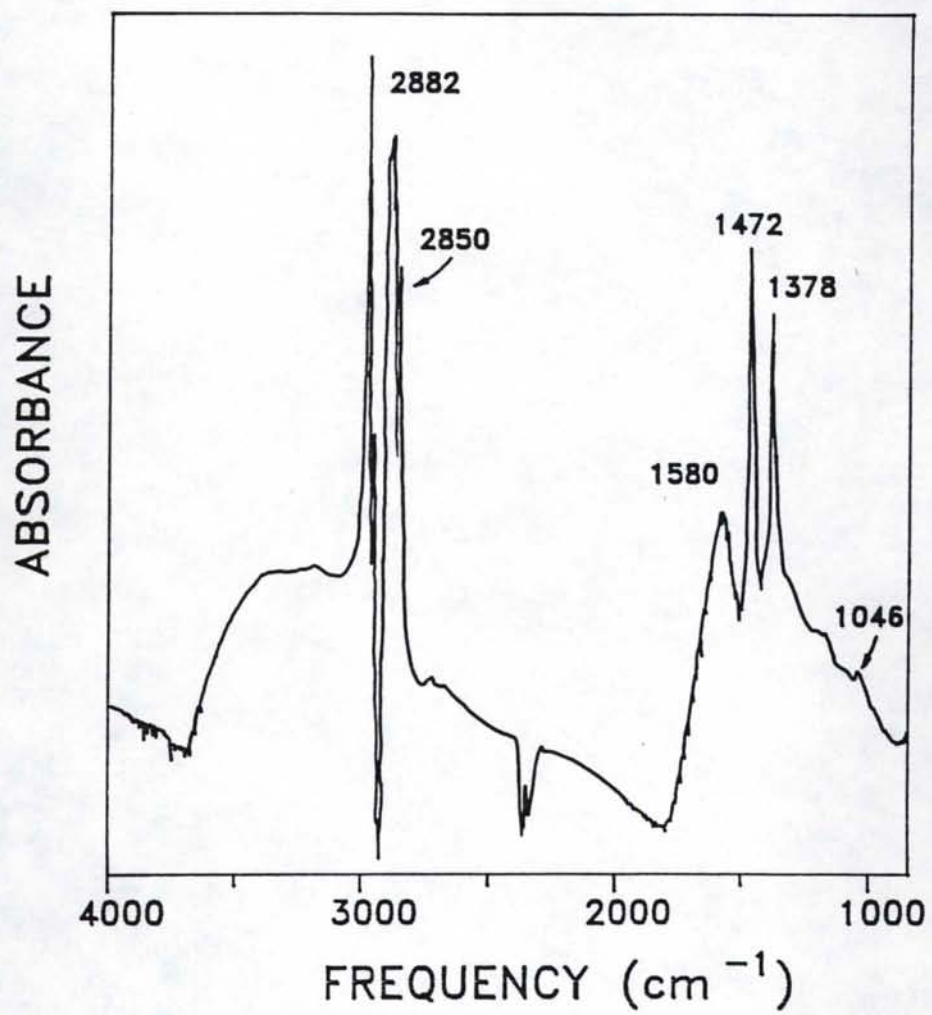
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Fig. 5. Infrared spectrum of Aldrich humic acid using a Nujol mull.

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bonding effects occurring to the oxygen in the ester bond of the polysaccharide linkage.

Detection Limits

Precipitation was visually evident at concentrations of 100 and 200 g L^{-1} humic acid, an observation which has been explained based on the formation of a spherocolloid (Ghosh and Schnitzer, 1980). This did not affect the characteristic absorbance bands previously noted except to decrease visibility of the 1450 and 1713 cm^{-1} peaks (Fig. 3). Humic acid could be detected at concentrations as low as 0.5 g L^{-1} (Fig. 4). Humic materials exist as linear polyelectrolytes at concentrations below 3.5 g L^{-1} (Ghosh and Schnitzer, 1980), thus indicating that CIR FT-IR is possible on sufficiently low concentrations of humic acid to observe this linear form. This is important when considering practical applications of the CIR technique in that pesticide interactions with humic materials have been shown to depend upon humic material concentration (Tramonti et al., 1986; Carter and Suffet, 1982).

Ionic Strength and pH Effects on Aldrich Humic Acid

Ionic strength was adjusted with both divalent and monovalent cation salts because of the vastly different interaction occurring between each cation and humic acid. Divalent cations such as Ca^{2+} function to electrostatically link negatively charged functional groups on the humic acid molecules causing coagulation (Hayes and Himes, 1986). This was visually observed in the 6.67 x 10^{-2} M $CaCl_2$ treatment and is evident in the recorded spectrum (Fig. 6). A decrease in band strength or complete elimination is shown for most of the characteristic
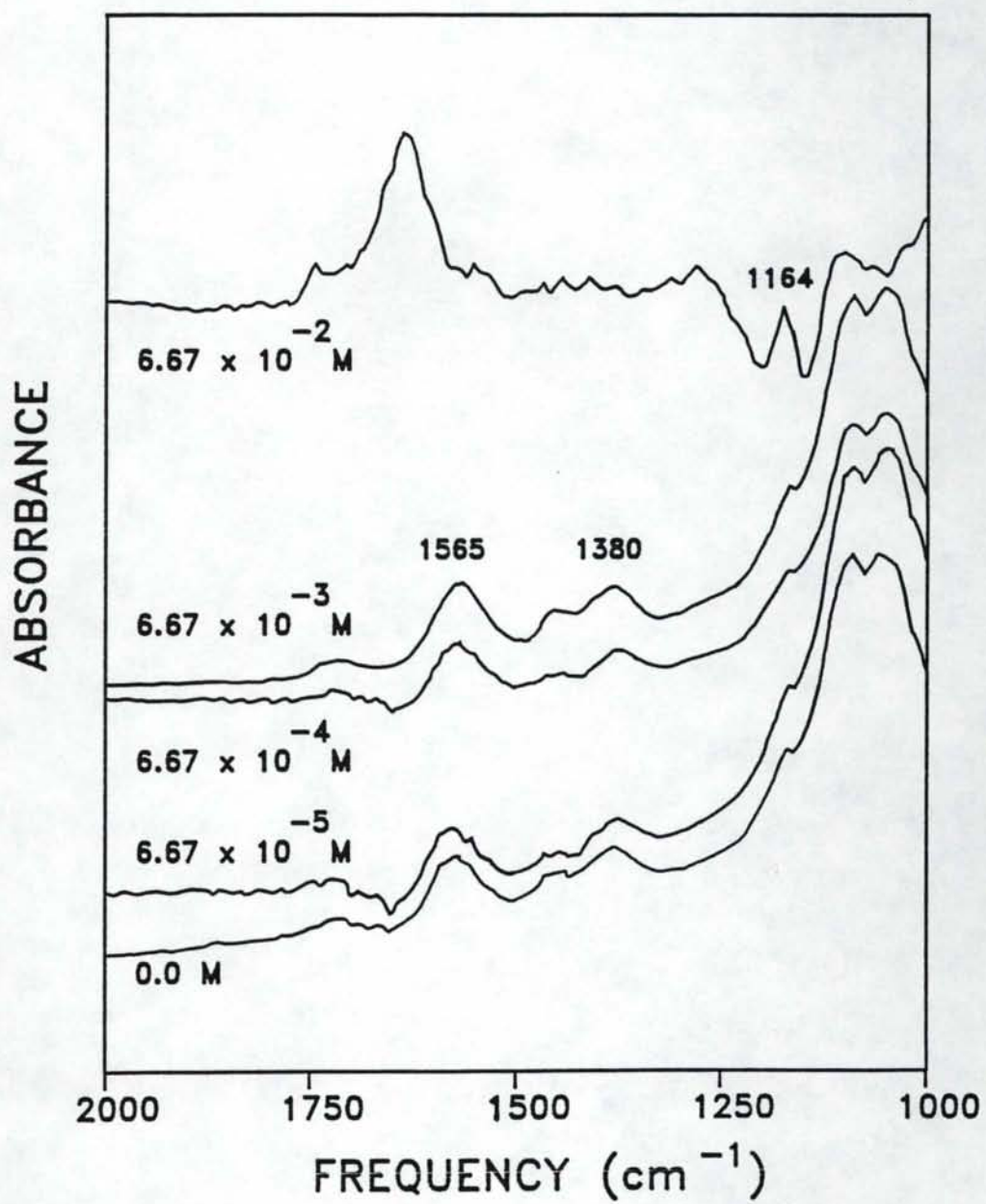
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Fig. 6. FT-IR spectra of Aldrich humic acid in $CaCl_2$ solution at levels from 0 to 6.67 x 10^{-2} M.

absorbance bands except for the enhancement of the band at 1164 cm^{-1}. This would be anticipated for the bands at 1380 and 1565 cm^{-1} because of their association with COO^- groups of the humic acid, also the major location for Ca^{2+} interaction. Increased signal strength of the 1164 cm^{-1} band may represent an exterior physical location for the responsible functional groups of the colloid as opposed to an internal location, or lack of involvement of the responsible functional groups in Ca^{2+} interaction and coagulation. The latter is probable if the absorbance band indicates an ester linkage of polysaccharides to humic acid, as previously postulated.

It has been suggested that upon drying, the polar groups of humic materials orient towards the interior of humic colloids exposing the hydrophobic portions of the material on the exterior of the colloid (Hayes and Himes, 1986). Increased ionic strength may have a similar effect on colloid conformational changes. This behavior has been used to explain increased pyrene binding to estuarine organic matter with increased ionic strength of the solution (Ostazeski and Means, 1984). Conformational changes of humic materials, as dictated by ionic strength, would thus promote similar changes with respect to pesticide interaction with soil constituents.

Ionic strength adjustment with KCl would not be expected to show the same alteration of the humic acid spectra as $CaCl_2$ (Hayes and Himes, 1986). Figure 7 demonstrates that K^+ at a concentration of 1.0×10^{-1} M does not interact with the humic acid in the same manner as does Ca^{2+} and as a result, only small changes in the spectra are observed with all levels of KCl ionic strength adjustment.
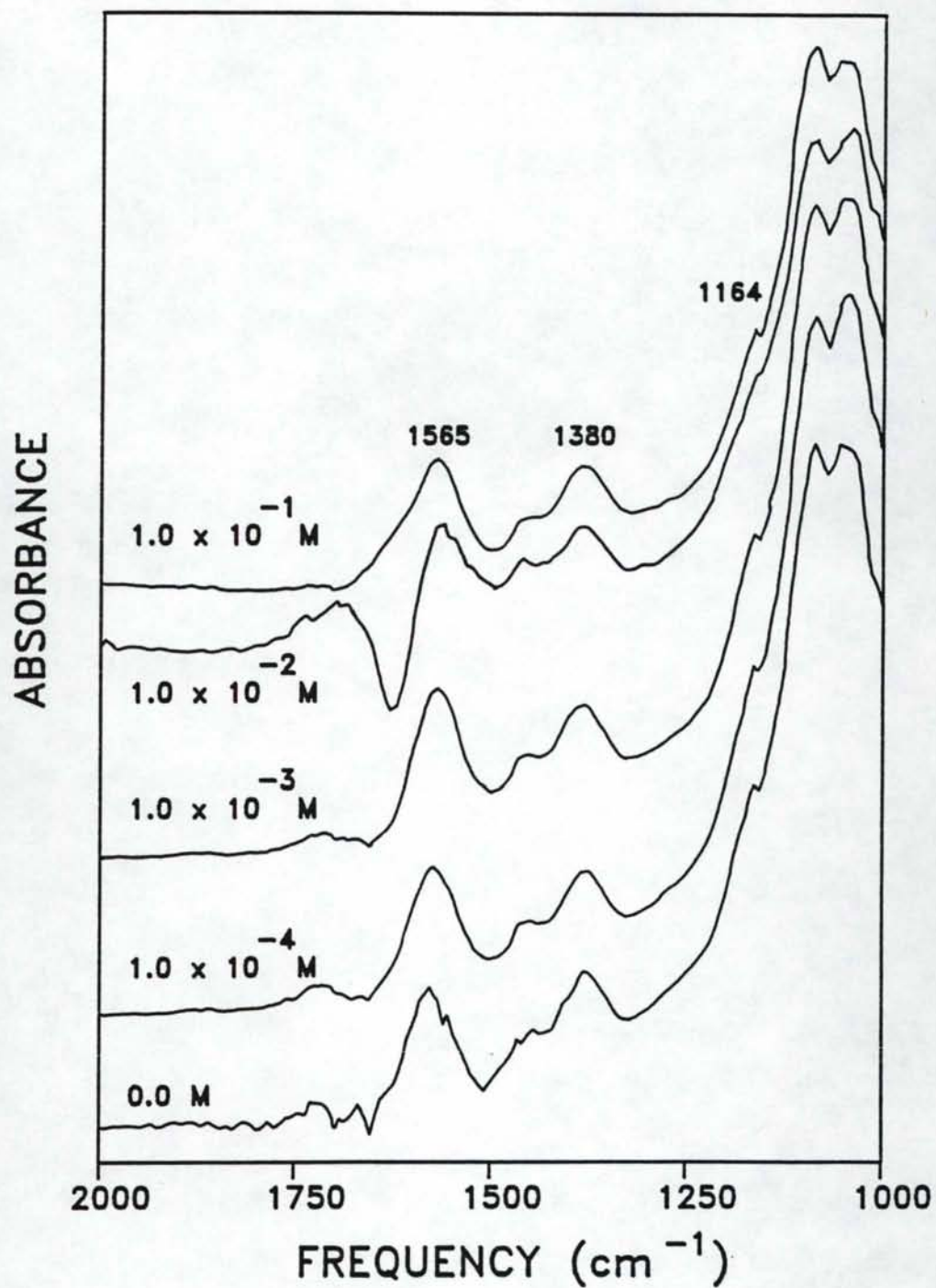
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Fig. 7.   FT-IR spectra of Aldrich humic acid in KCl solution at levels
from 0 to 1.0×10^{-1} M.

Through protonation, titration of the salt form of humic acid to a lower pH would decrease the absorbance bands associated with COO⁻ groups (1380 and 1565 cm^{-1}) and increase the intensity of the $C = O$ absorbance (1713 cm^{-1}) in those groups (Stevenson and Goh, 1971). A slight decrease in the 1380 and 1565 cm^{-1} peaks is recorded, while a relatively noticeable increase in the 1713 cm^{-1} band is also shown (Fig. 8). A shoulder appears at 1600 cm^{-1} when the humic acid is titrated to pH values of 5 and 6, indicating behavior similar to that expressed by simple carboxylic acids (MacCarthy and Rice, 1985).

The ability to control solution ionic strength and pH is an additional advantage of CIR when considering application of this technique to organic pollutant or trace element interaction studies. For example, the extent of lindane interaction with fulvic acid is highly dependent upon pH and ionic strength (Tramonti et al., 1986). DDT binding to humic acid was also shown to be dependent upon pH, ionic strength, and calcium concentration. Metal binding to humic materials also responds to pH changes (Ghosh and Schnitzer, 1981; Perdue and Lytle, 1983; Reuter and Perdue, 1977).

Water Absorbance Band

Referencing the sample cell for purposes of background subtraction resulted in variable results with respect to water absorbance at 1640 cm^{-1}. Fluctuation ranging from a negative to a positive absorbance was recorded (Figs. 6-8). No consistent trend was observed with repeated spectra showing the range of possible water absorbance values. It is not known if this is an artifact of the preparation, analysis procedure, or a yet undetermined phenomenon. Recent evidence indicates that water
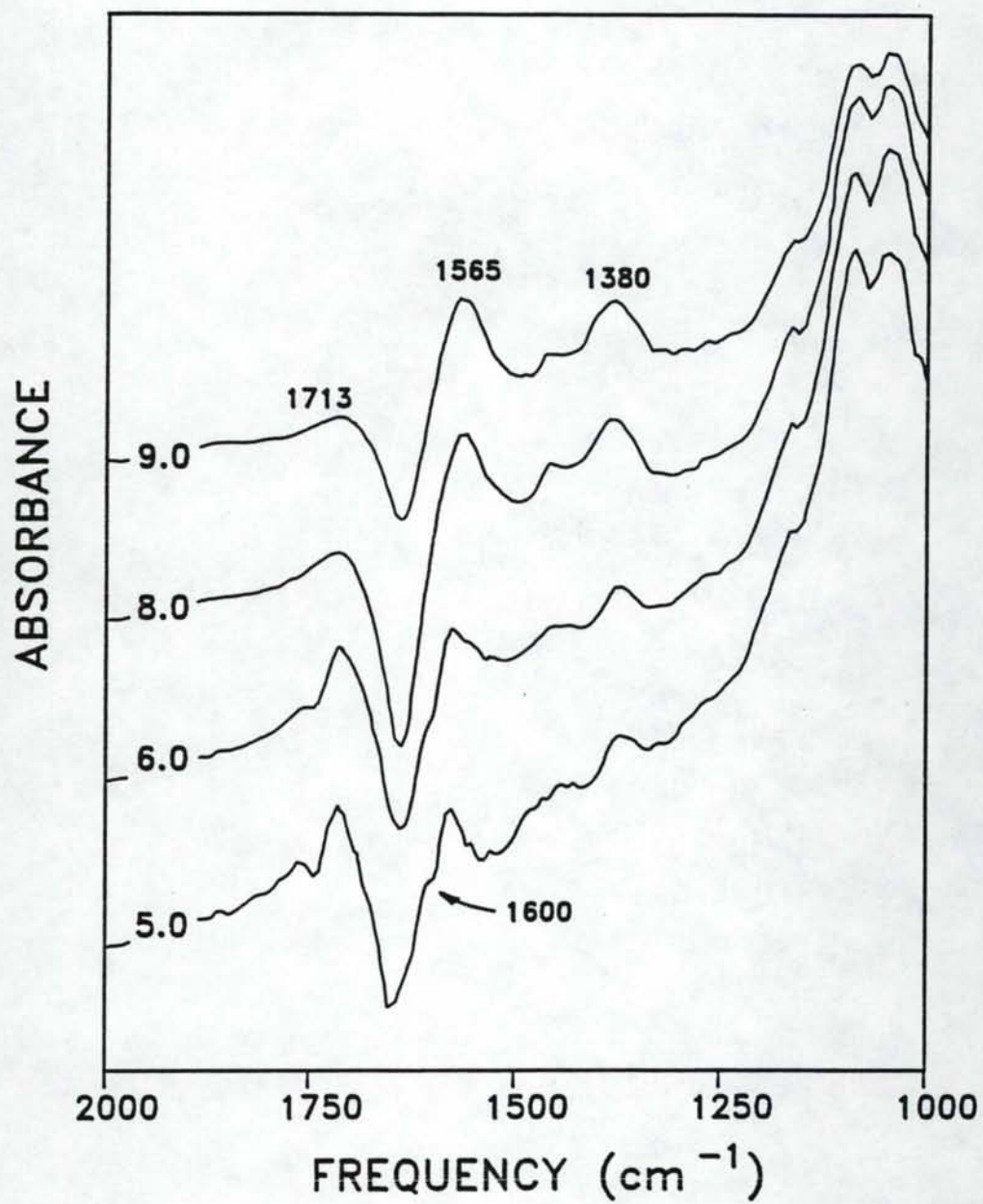
Fig. 8. FT-IR spectra of Aldrich humic acid titrated to pH values ranging from 5.0 to 9.0.

subtraction in the 1640 cm^{-1} region may result in spectral artifacts when using a CIRCLE CELL with a micro-boat sample configuration (Braue and Pannella, 1987). The possibility also exists that two distinct pools of water occur in humic acid solutions. One pool represents free water not associated with the humic material and therefore subtracted in background referencing. A second pool of trapped water interacting through hydrogen bonding to the functional groups of the humic acid might also exist and result in unpredictable absorbance in the 1640 cm^{-1} region.

FT-IR Analysis of Soil Extracts

Fulvic acid extracts from Fenn soil displayed absorbance peaks indicating polysaccharides (1081 cm^{-1}), carboxyl groups (1394 and 1557 cm^{-1}), and aliphatic C-H groups (1460 cm^{-1}) (Fig. 9). Freeze drying the extract altered the material and resulted in spectral changes especially in the 1000 to 1100 cm^{-1} region (Fig. 10). The spectrum of freeze dried fulvic acid possesses multiple absorbance peaks (1042, 1079, and 1125 cm^{-1}) in this area, as compared to the non-freeze dried material spectrum in which one peak predominated. Freeze drying created similar artifacts with fulvic acids extracted from Sudduth soil, again resulting in multiple peaks in the 1000 to 1100 cm^{-1} region (Figs. 11, 12).

Freeze drying fulvic acids after extraction from soils is a standard procedure (Schnitzer, 1982). Present FT-IR data indicate that freeze drying alters fulvic acids chemically, thus also altering their potential interaction with pesticides. The exact nature of the change cannot be determined from present information. However as discussed previously, the drying of humic materials causes polar groups
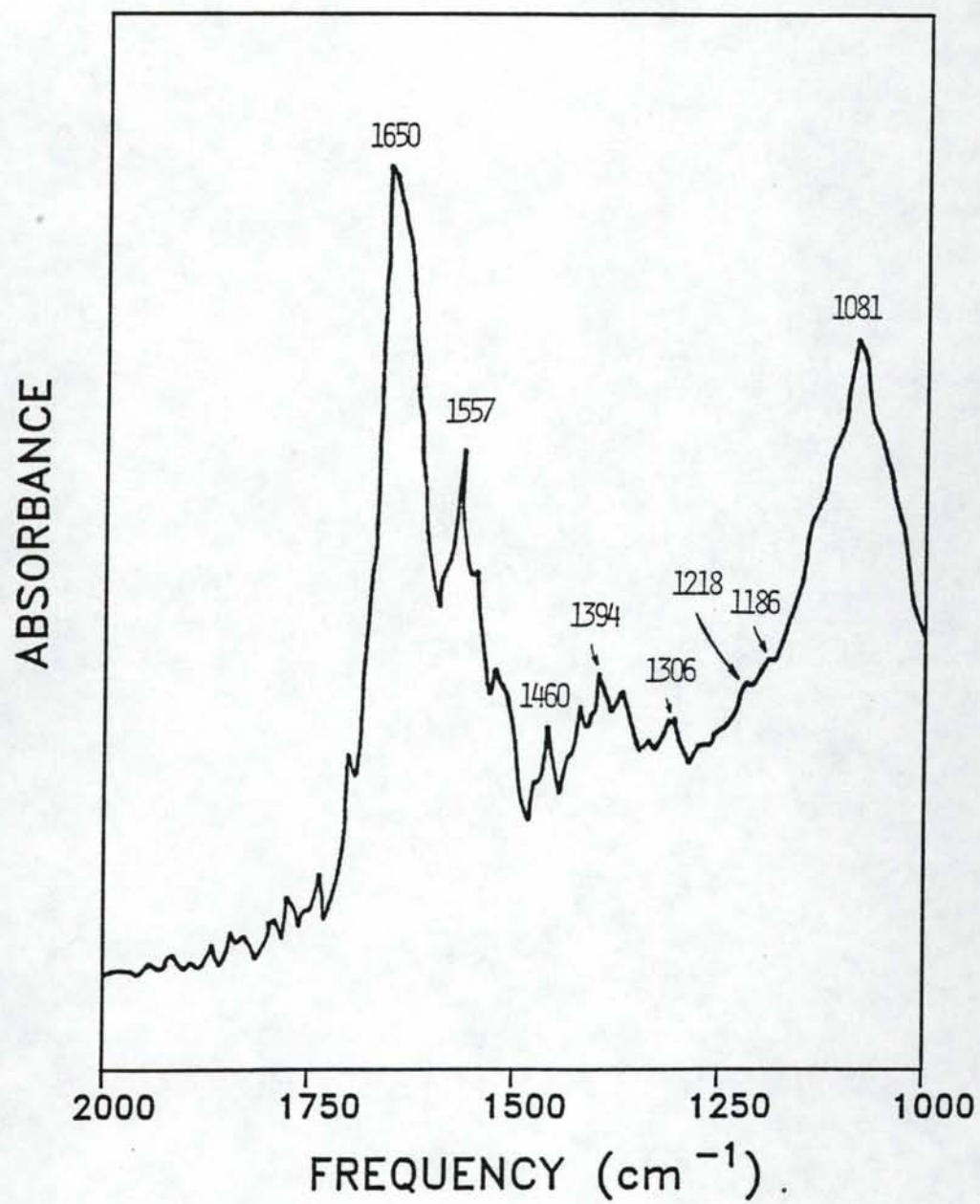
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Fig. 9. CIR spectrum of Fenn fulvic acid extract prior to freeze drying.
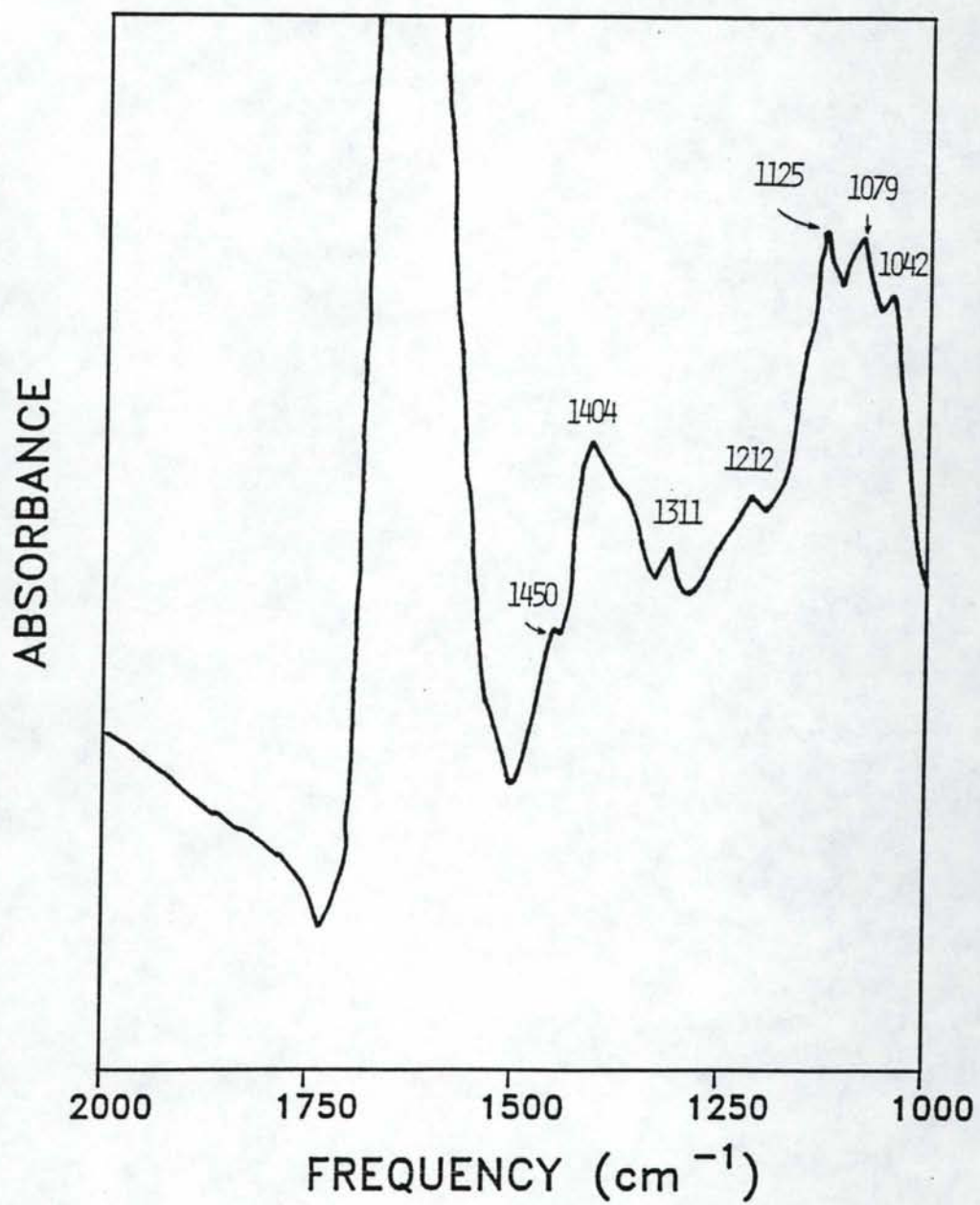
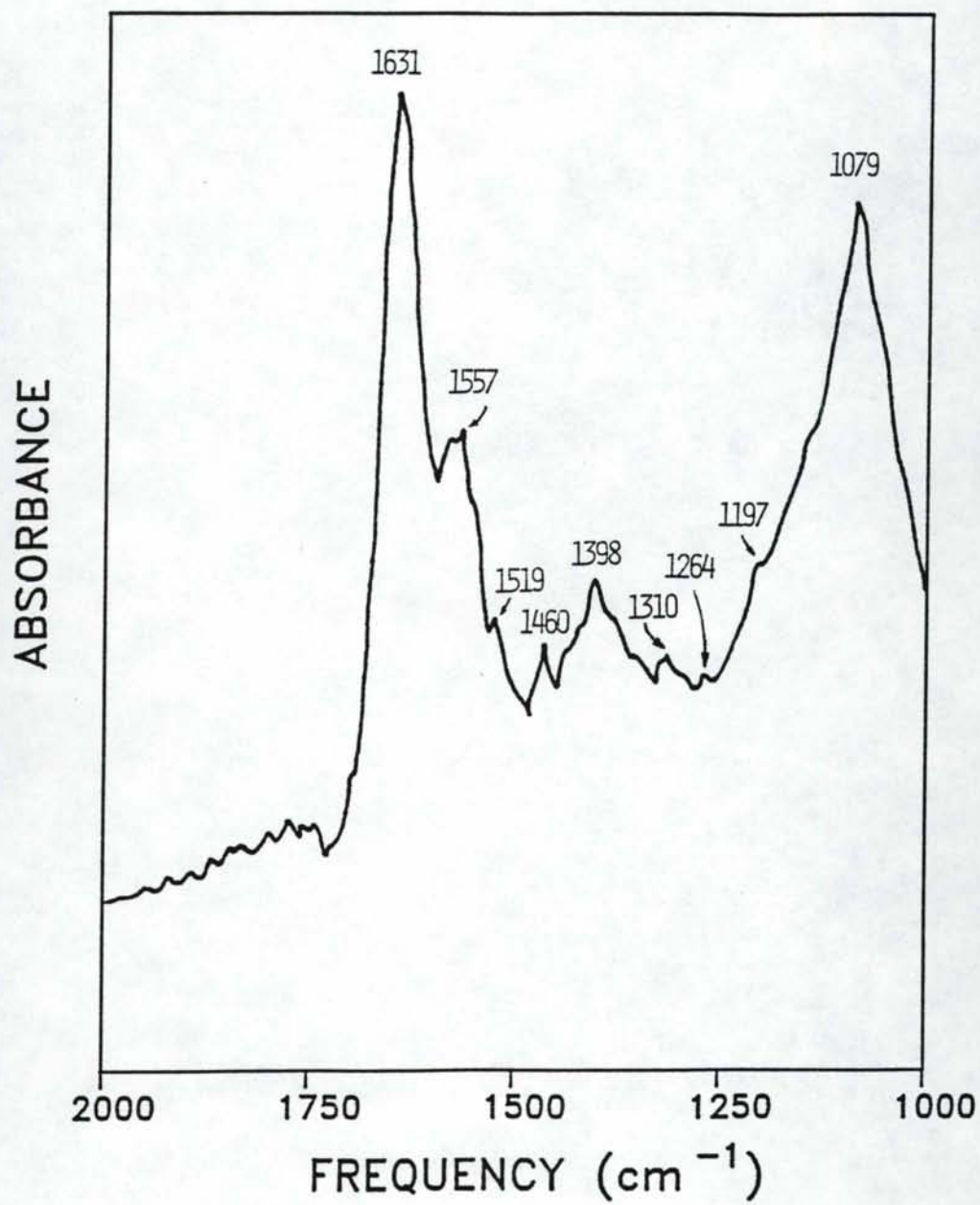Fig. 10. CIR spectrum of Fenn fulvic acid extract after freeze drying.

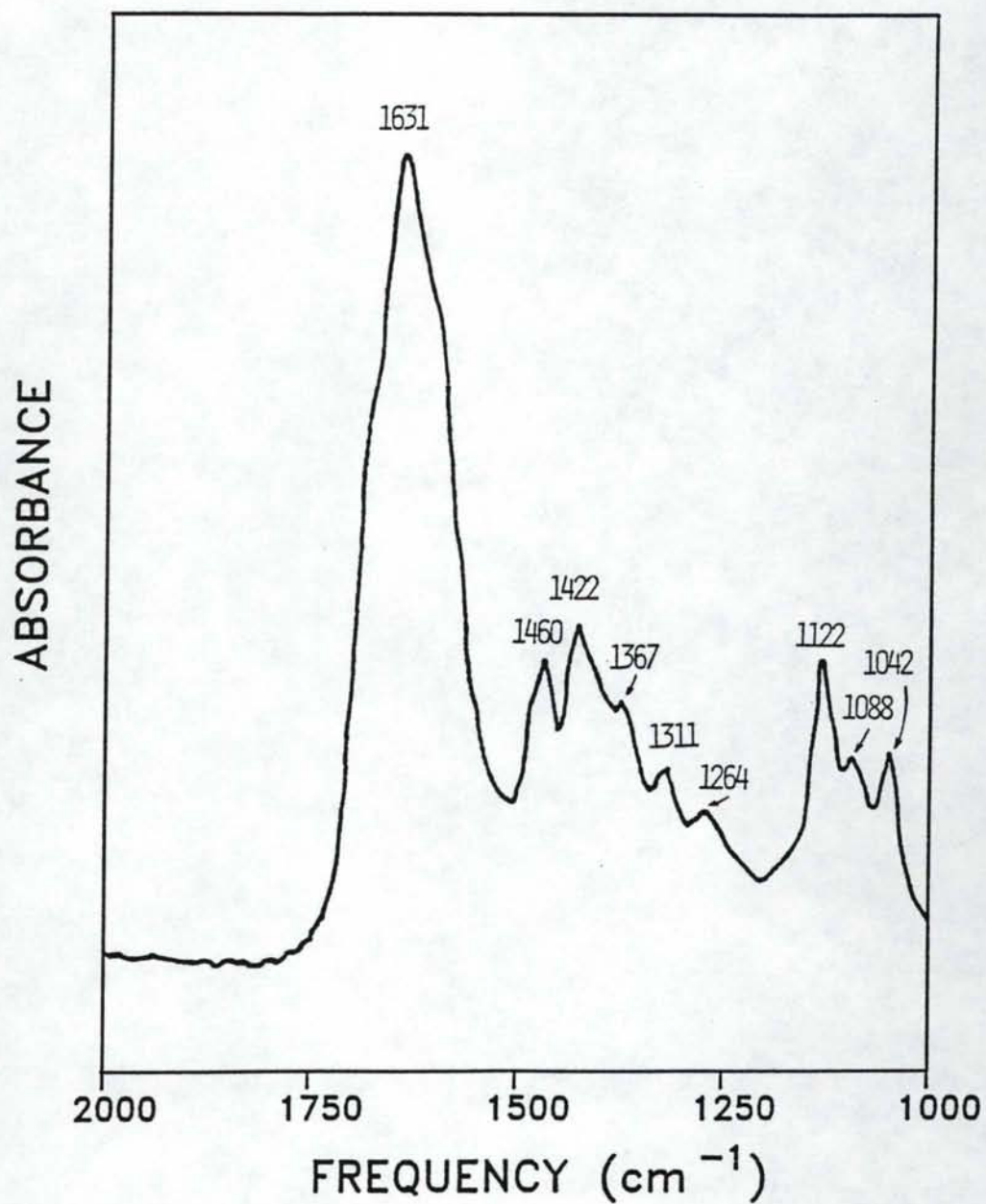Fig. 11. CIR spectrum of Sudduth fulvic acid extract prior to freeze drying.

Fig. 12. CIR spectrum of Sudduth fulvic acid extract after freeze drying.

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to orient towards the interior of the colloid exposing hydrophobic portions of the material on the colloid exterior (Hayes and Himes, 1986).

A Nujol mull spectrum for fulvic acid extracted from Fenn soil (Fig. 13) showed much less absorbance intensity in the 1000 to 1100 cm^{-1} region as compared to aqueous spectra obtained using CIR (Figs. 9,10). The Nujol mull spectrum also displayed increased absorbance intensity for aliphatic C-H groups (1460 cm^{-1}) and carboxyl groups (1380 cm^{-1}), similar to the spectral differences noted when using Aldrich humic acid in comparing the same two sampling techniques.

Humic acids extracted from Fenn and Sudduth soils yielded similar spectra when using CIR on aqueous solutions analyzed before and after freeze drying. Absorbance peaks for humic acid extracts from Fenn soil were 1042, 1081, and 1125 cm^{-1} before freeze drying and 1043, 1079, and 1125 cm^{-1} after freeze drying, thus illustrating no effect as a result of the procedure (Figs. 14, 15). Freeze drying Sudduth soil altered the spectra less than Fenn soil across the 1000 to 2000 cm^{-1} region (Figs. 16, 17). Freeze drying humic acids does not create obvious chemical alteration of extracted humic acid as reflected in the aqueous infrared spectra.

Aqueous interactions with Fenn humic acid create differences between spectra obtained using CIR as compared to the Nujol mull technique. Nujol mull preparations resulted in only one major absorbance peak in the 1000 to 2000 cm^{-1} region (Fig. 18) as compared to three separate peaks for aqueous preparations (Figs. 16, 17). Aliphatic C-H character of the humic acid appears more predominant in the Nujol mull preparation similar to fulvic acid extracted from Fenn soil. Use
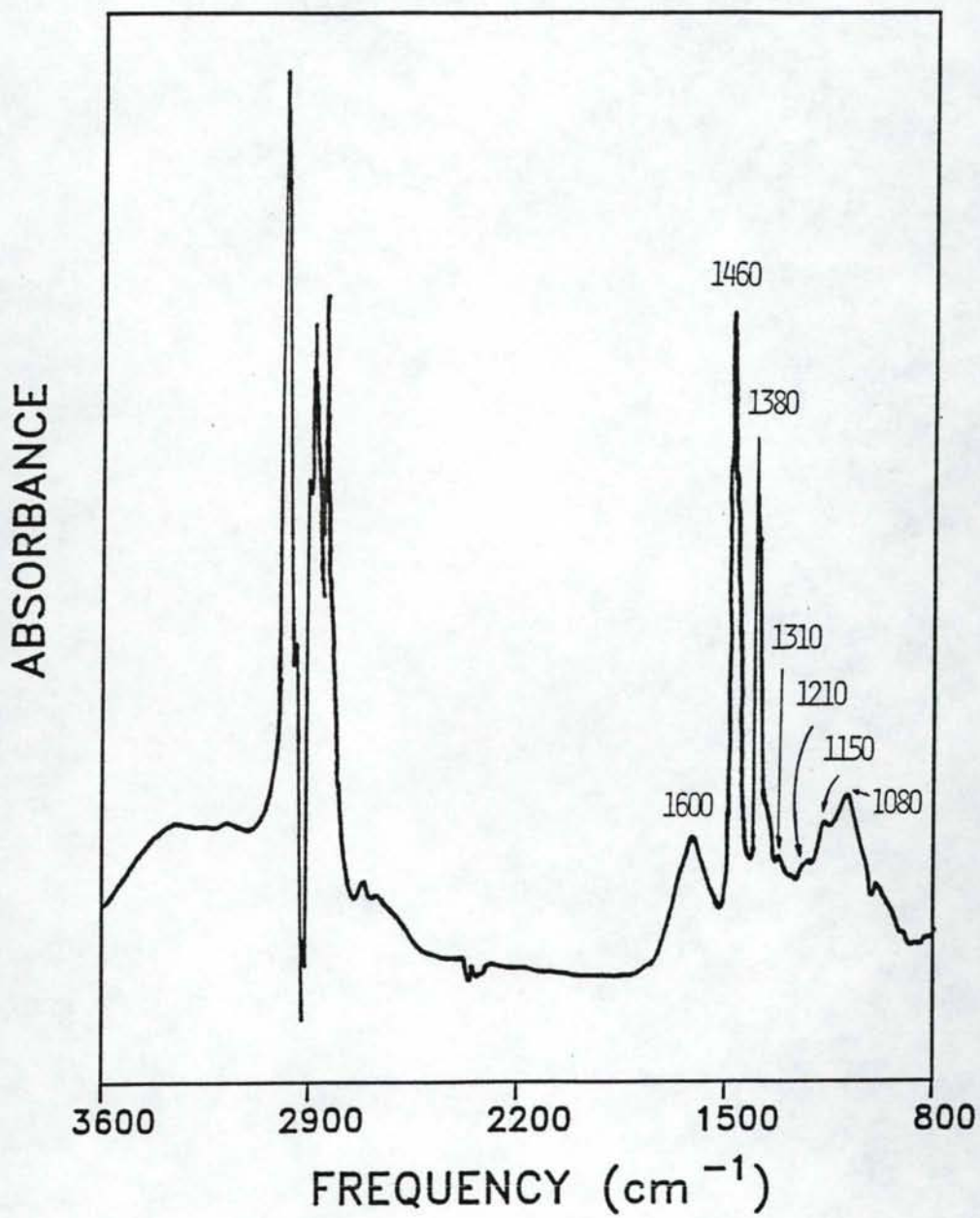
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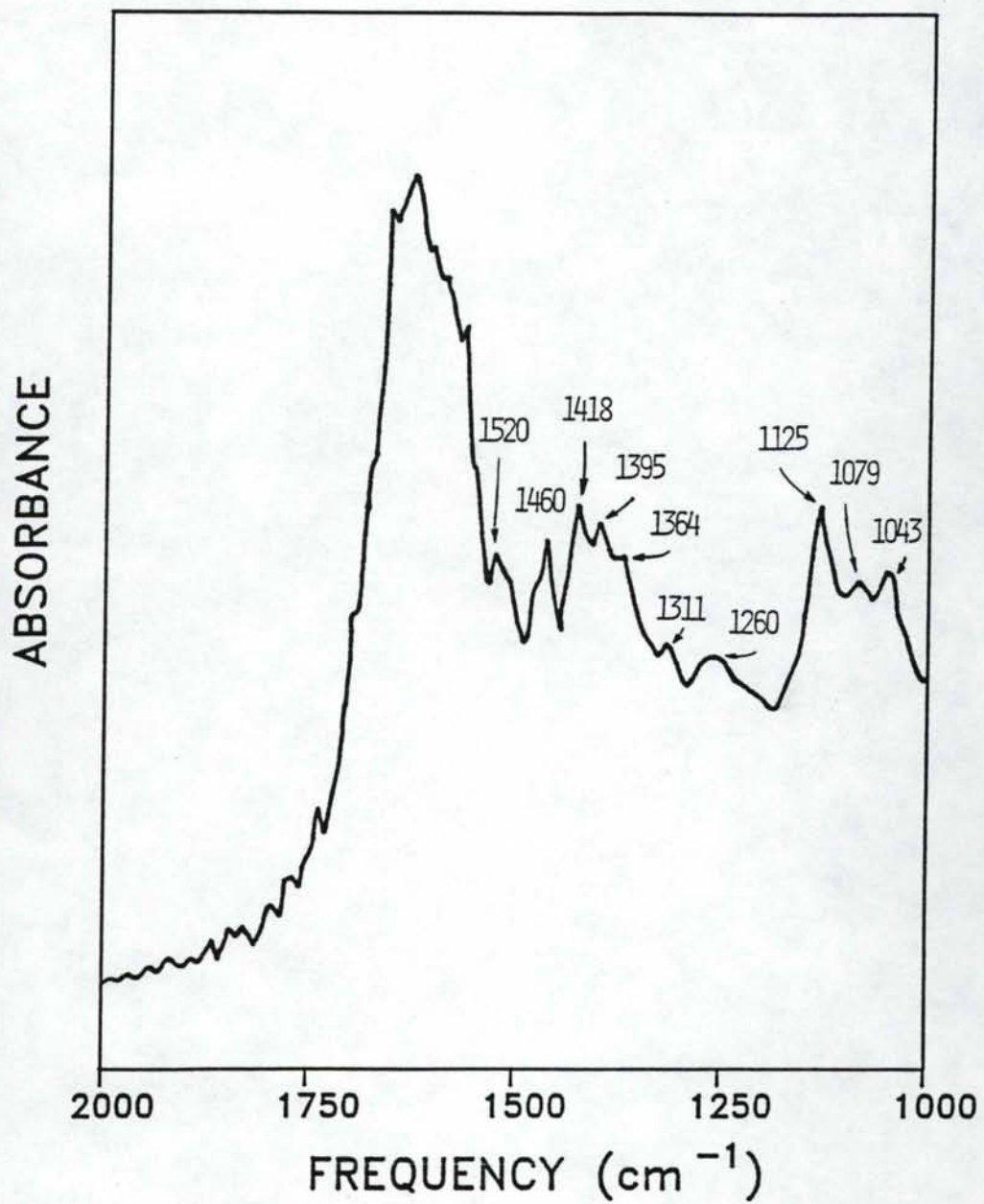Fig. 13. Nujol mull spectrum of Fenn fulvic acid.

Fig. 14.   CIR spectrum of Fenn humic acid extract prior to freeze
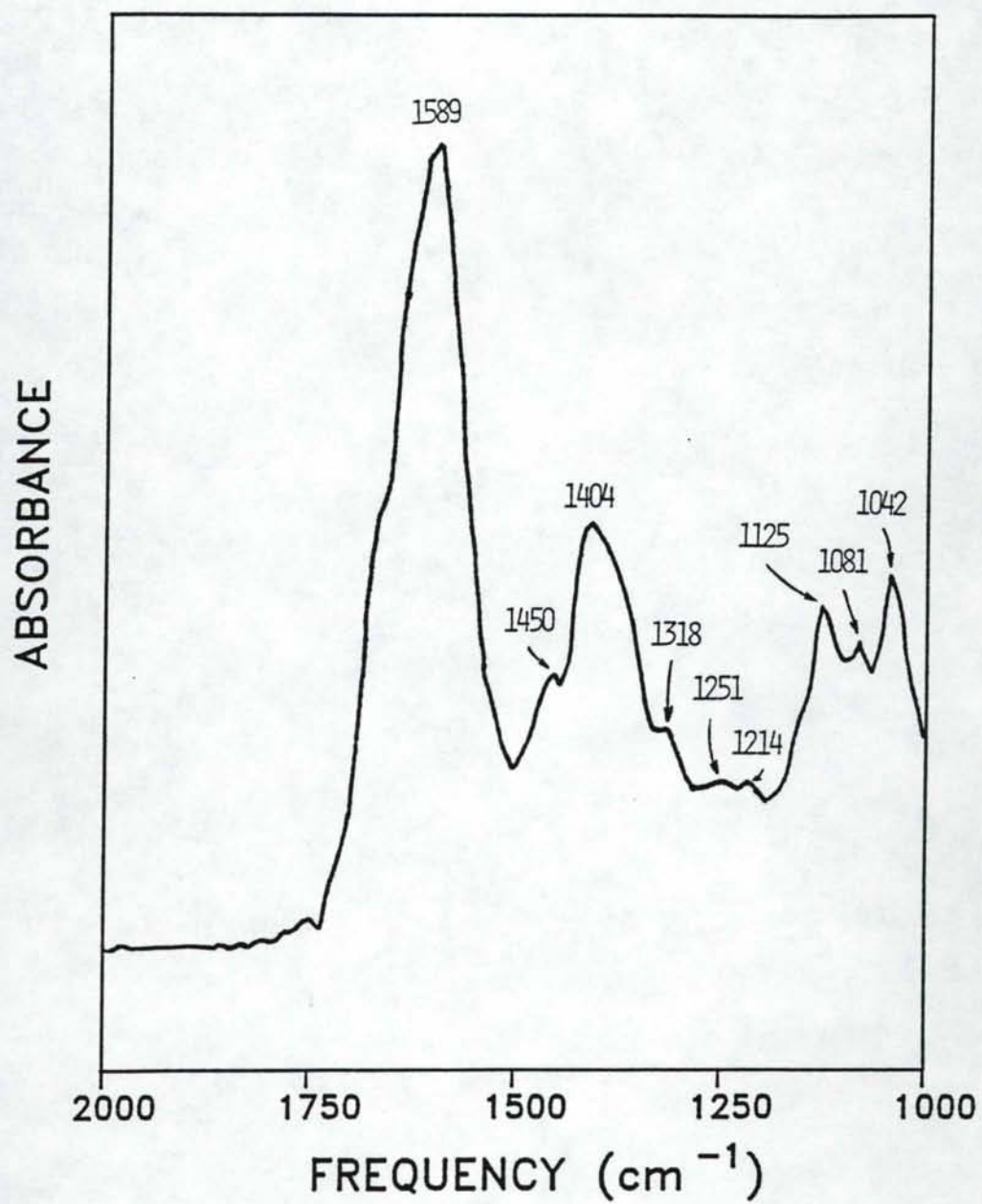drying.

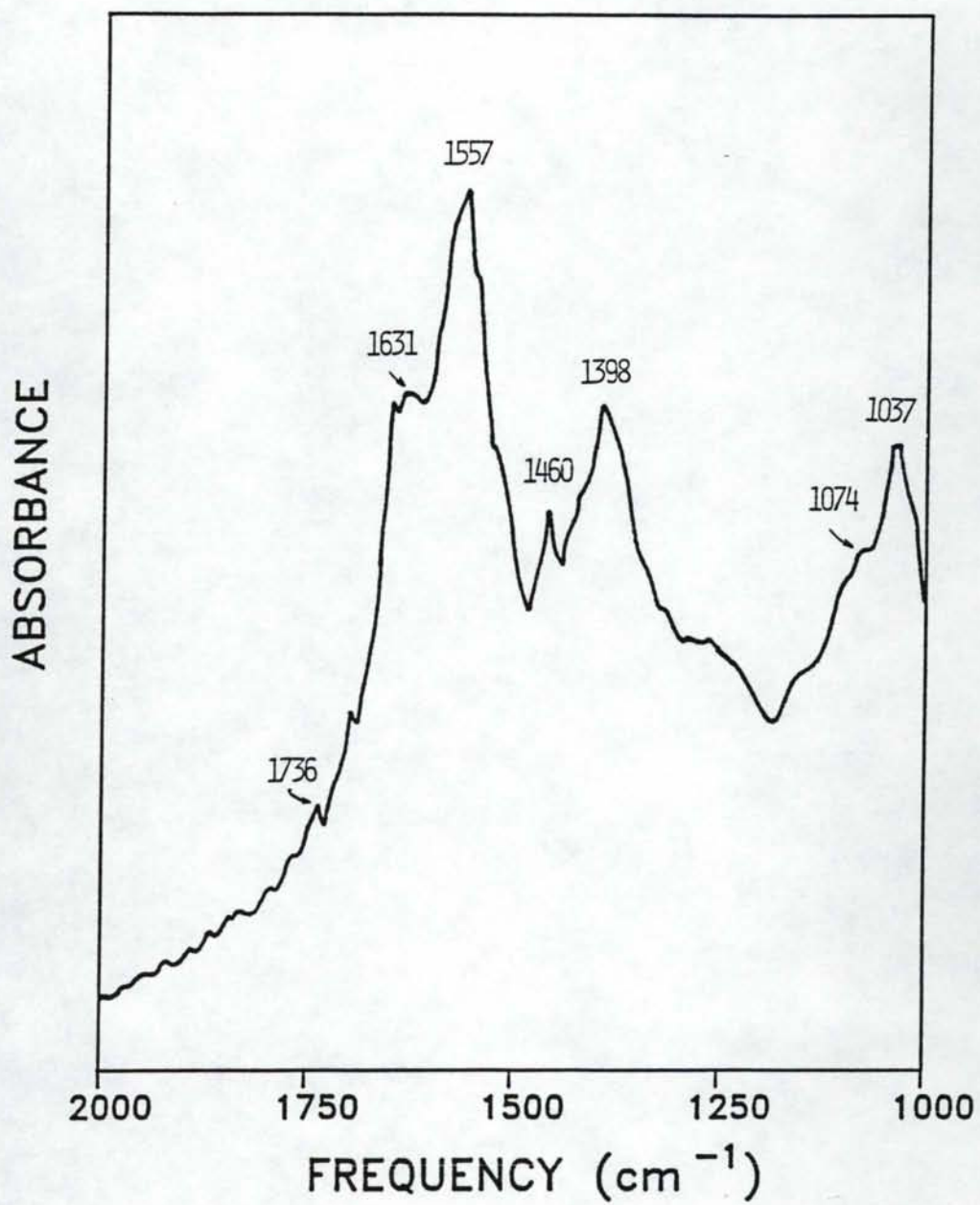Fig. 15. CIR spectrum of Fenn humic acid extract after freeze drying.

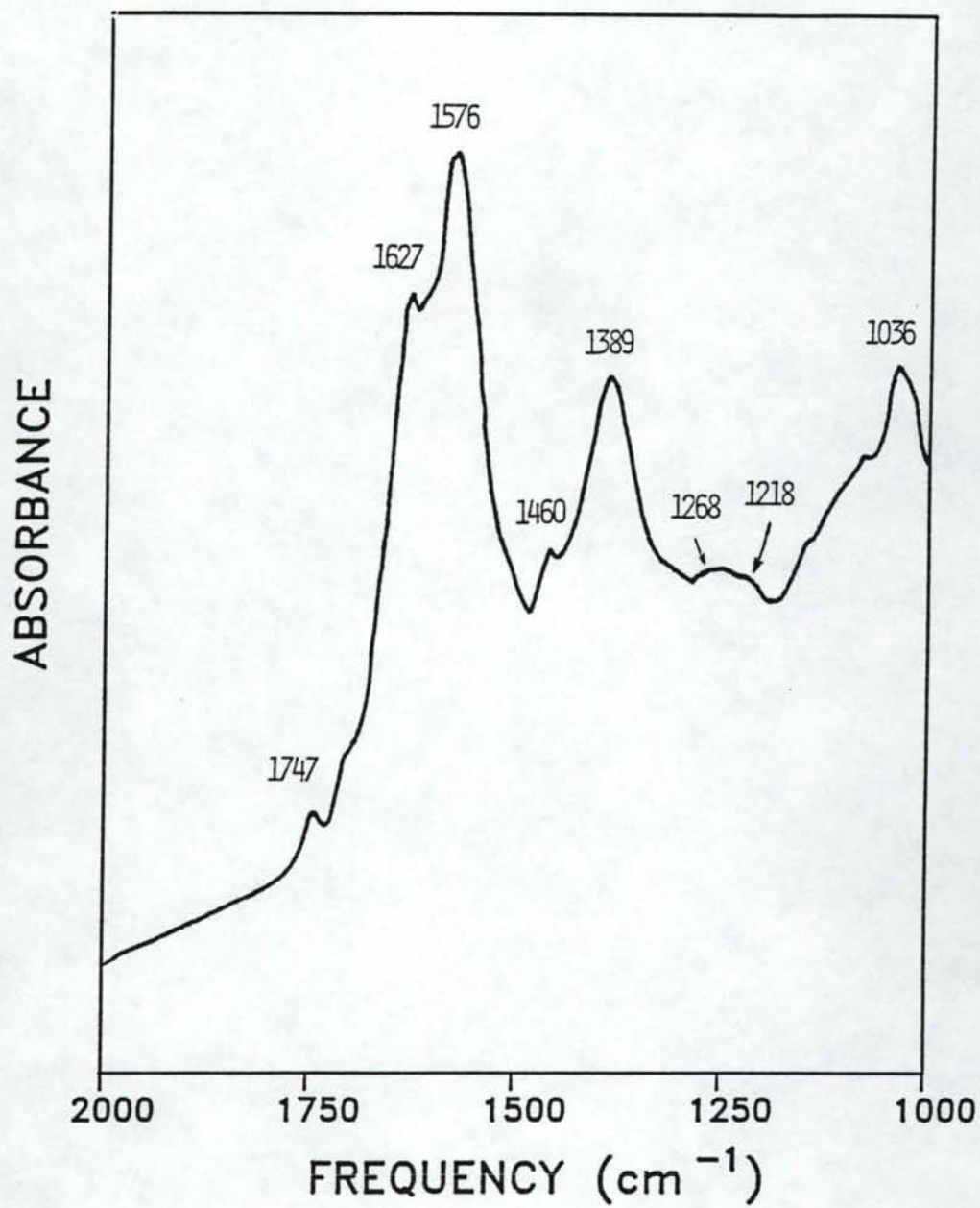Fig. 16. CIR spectrum of Sudduth humic acid extract prior to freeze drying.

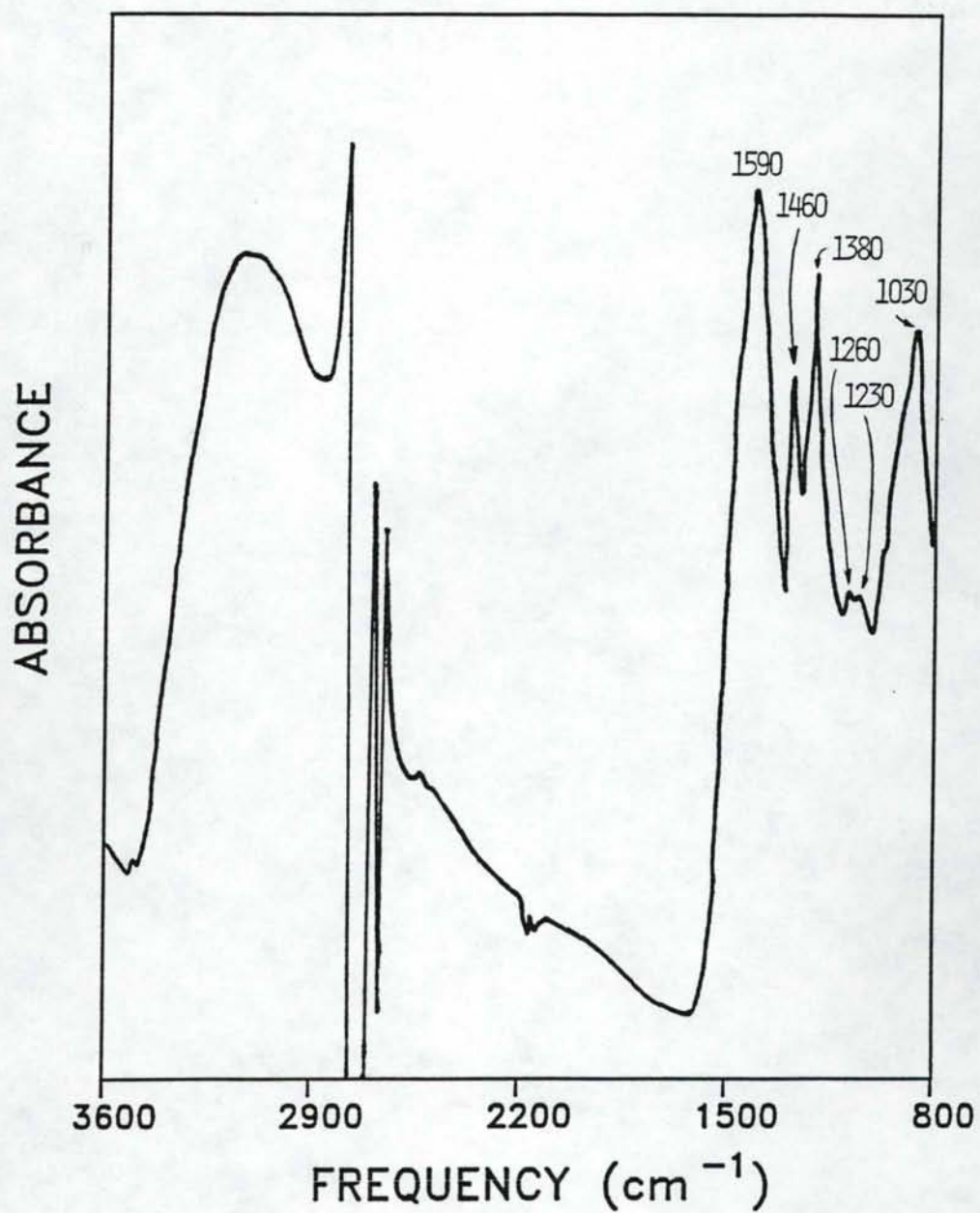Fig. 17. CIR spectrum of Sudduth humic acid extract after freeze drying.

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Fig. 18. Nujol mull spectrum of Fenn humic acid.

of nonaqueous preparations would thus inaccurately represent the extent of potential functional groups available for pesticide interactions.

Water extracts from Fenn and Sudduth soils produced similar CIR spectra, in that the most predominant absorbance peaks occur in the 1000 to 1100 cm^{-1} region (Figs. 19, 20). Baham and Sposito (1983) reported the spectrum of a water extract from sewage sludge, showing major absorbance peaks at 1120 and 1150 cm^{-1}. However, the spectra were obtained using a nonaqueous sample preparation technique which could have shifted the peaks. Solid sampling techniques have also been used in obtaining infrared spectra of water extracts from soil-sludge mixtures (Schaumberg et al., 1980). Absorbance readings in the 1000 to 1100 cm^{-1} region were attributed to C-O in polysaccharides, Si-O, SO_3^-, PO_4^{3-}, or SO_4^{2-}. The presence of inorganic constituents in the present solutions is possible. Water extracts from Sudduth soil produced spectra with minor absorbances indicating polysaccharides (1044 and 1101 cm^{-1}), carboxyl groups (1377, 1543, 1585, and 1706 cm^{-1}), and aliphatic C-H groups (1460 cm^{-1}) (Fig. 20). Although some of these absorbance peaks occur in fulvic acid extracts, water extract spectra differ significantly. Fulvic acid extracts cannot be used to simulate pesticide interactions with water soluble organic materials, because of the distinct chemical differences evident in the respective materials infrared spectra.

Water extract spectra for Feltham soil displays different absorbance characteristics than either Fenn or Sudduth water extract spectra (Fig. 21). Absorbance intensity in the 1000 to 1100 cm^{-1} region is reduced as compared to Fenn and Sudduth soils indicating less polysaccharide content. Predominant absorbances occur at 1367, 1390,
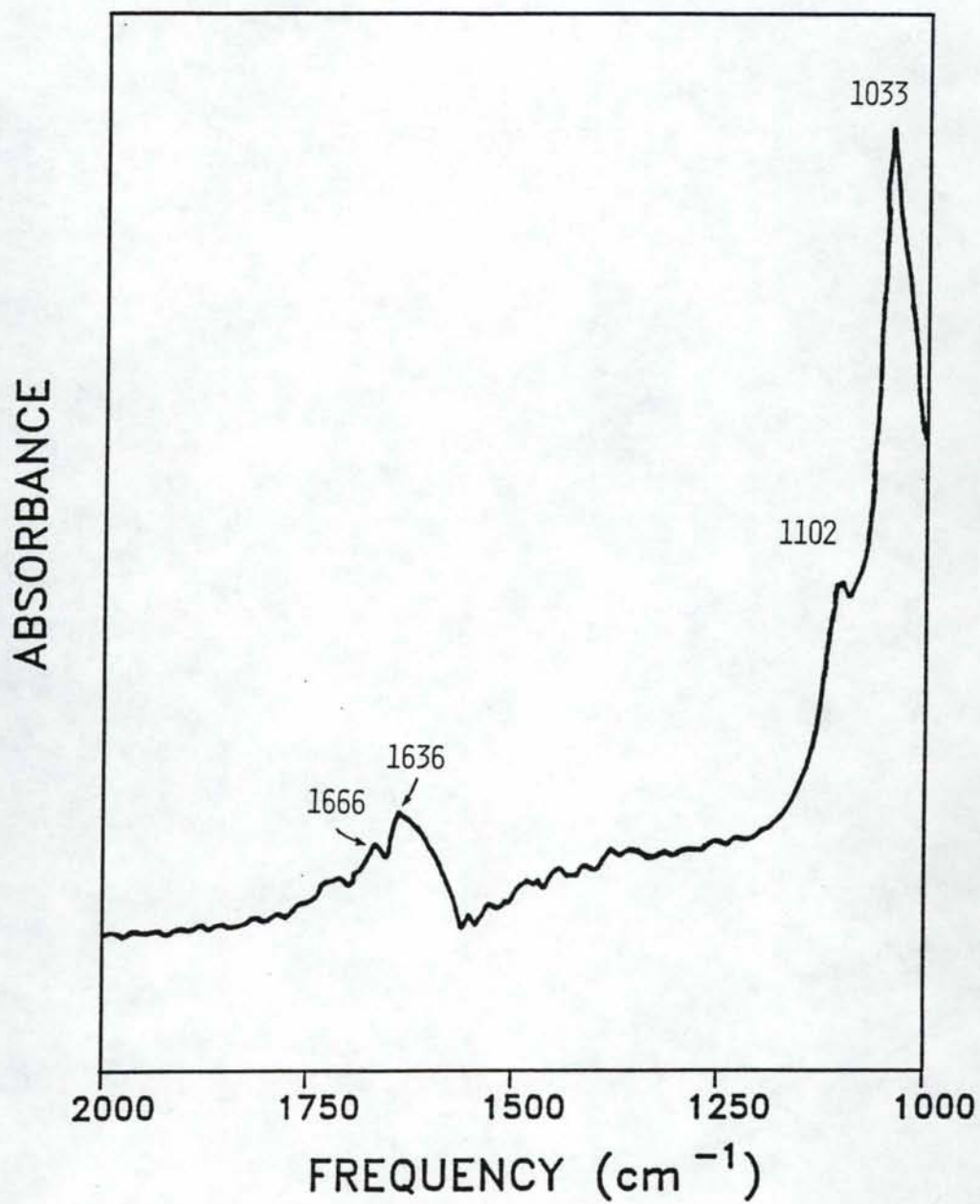
35

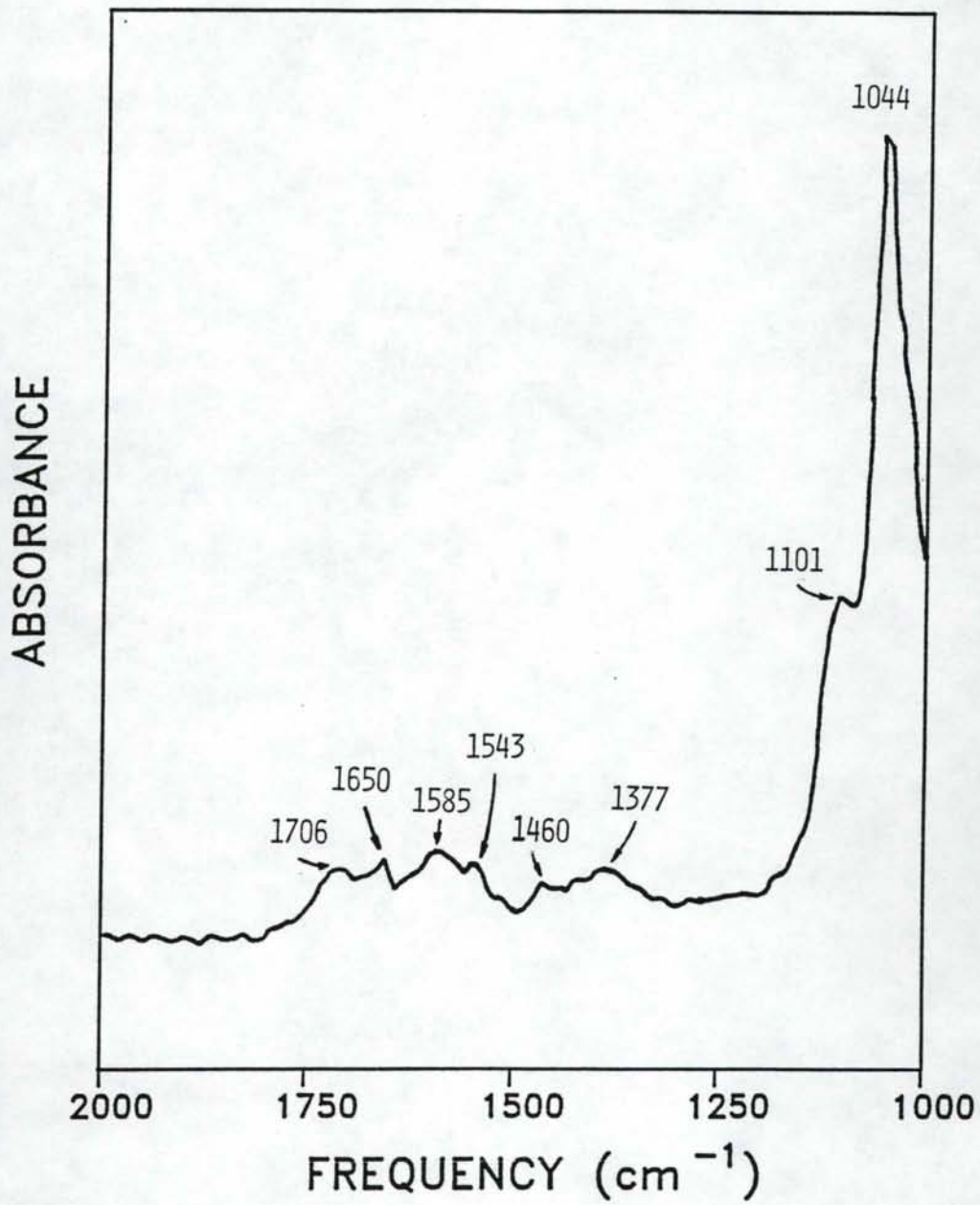Fig. 19. CIR spectrum of water extract from Fenn soil.

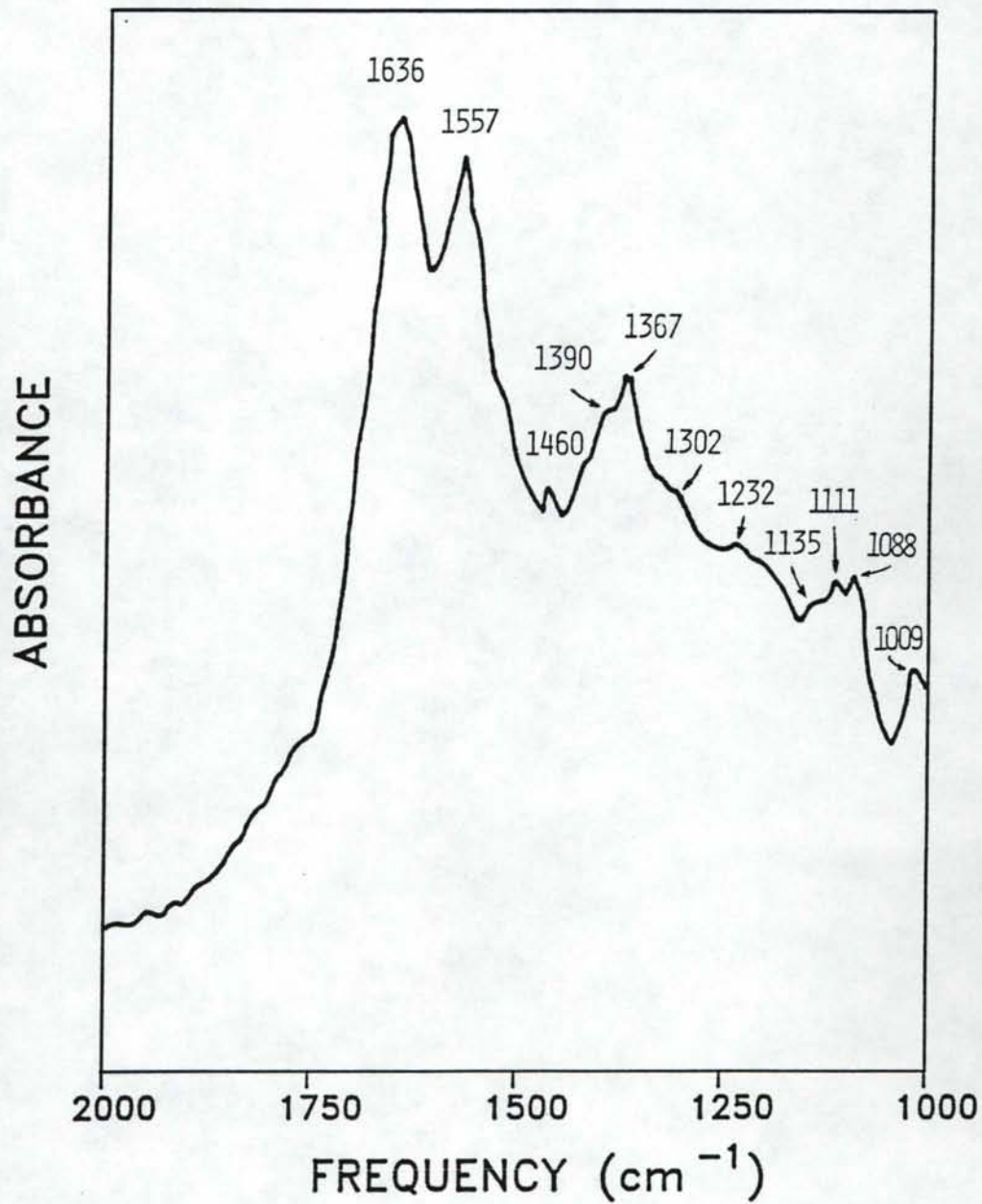Fig. 20.   CIR spectrum of water extract from Sudduth soil.

Fig. 21. CIR spectrum of water extract from Feltham soil.

and 1557 cm^{-1} indicating relatively high levels of carboxyl groups as compared to other functional groups. Soil characteristics indicate that lower organic matter content for the Feltham soil may be responsible for this difference (Table 1).

CONCLUSIONS

Recent development of the Cylindrical Internal Reflectance (CIR) sample cell has made infrared analysis of solutes in highly infrared-absorbing solvents such as water possible. Fourier Transform Infrared spectroscopy (FT-IR) has been combined with a CIR sample cell to determine the spectra of Aldrich humic acid in water at concentrations as low as 0.5 g L^{-1}. Spectral scans from 670 to 4000 cm^{-1} indicate that the region of greatest resolution for observing characteristic humic acid absorbance bands occurs from 1000 to 2000 cm^{-1}. Absorbance bands reflecting ester-bonded polysaccharides (1050, 1088, and 1164 cm^{-1}), aliphatic C-H groups (1450, 2860, and 2920 cm^{-1}), and carboxyl groups (1380, 1565, and 1713 cm^{-1}) were detected. Comparison of CIR spectra with a Nujol mull spectrum demonstrated increased C-H peak intensities and near total elimination of ester absorbance peaks in the mull preparations. Solution phase parameters were altered to illustrate that the spectra of humic acid in water varied with humic acid concentration, ionic strength, and pH as explained by humic acid conformational changes and functional group protonation. The ability to determine the infrared spectra of humic materials in their native wet state will prove advantageous in determining humic material interaction with inorganic and organic pollutants such as trace elements and pesticides.

CIR can be used to obtain the spectra of soil extracts in the form of dissolved humic or fulvic acids as well as water soluble materials.

Advantages with fulvic acid extracts result from the ability to avoid artifacts occurring through freeze drying. Distinct differences between fulvic acid extracts and water soluble organic material extracts are indicated through comparison of the respective spectra. Pesticide interactions with water soluble organic materials are therefore best studied using a water extract.

Aqueous interactions cause distinct differences between spectra obtained using CIR and nonaqueous Nujol preparations. CIR is thus an infrared sampling technique which more accurately depicts soluble materials. CIR should prove useful as a key tool in studying pesticide interactions with water soluble soil organic materials. Studies in this area are currently in progress.

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