***Investigation of sorption
interactions between organic and
mineral phases of processed oil
shale***

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INVESTIGATION OF SORPTION INTERACTIONS BETWEEN ORGANIC AND MINERAL
PHASES OF PROCESSED OIL SHALE

By
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November 1987

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By
Western Research Institute
Laramie, Wyoming

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SUMMARY

Minerals and organic compounds representative of oil shale processing wastes were analyzed for potential sorption interactions. The analysis consisted of fourier transform infrared spectroscopy, high performance liquid chromatography, thermogravimetric and differential scanning calorimetry, and laser raman spectroscopy. Montmorillonite clay was used as a representative of the smectites found in raw and spent shales, and hematite was used as a representative of iron oxide found in spent shales. Benzene 2,2,4-trimethylpentane, benzoic acid, sodium benzoate, and pyridine were used as representatives of oil shale process organic wastes. In addition, isopropylamine and dimethyl methylphosphonate, a pesticide model, were studied. A preparation methods comparison study was performed and established the validity of the solid state KBr sample preparation technique upon FTIR spectral quality. Fourier transform infrared analysis showed chemisorption between the montmorillonite clay and pyridine, isopropylamine, and dimethyl methylphosphonate. There were no indications of sorption between the montmorillonite clay and benzene, 2,2,4-trimethylpentane, benzoic acid, or sodium benzoate. Fourier transform infrared analysis of the hematite dimethyl methylphosphonate complex showed chemisorption in addition to possible degradation. Fourier transform infrared analysis of the hematite isopropylamine complex showed chemisorption. No sorption was observed between the hematite and benzene, 2,2,4-trimethylpentane, benzoic acid, sodium benzoate, or pyridine. The high performance liquid chromatographic study showed no interaction between montmorillonite clay and benzene, 2,2,4-trimethylpentane, benzoic acid, sodium benzoate, or dimethyl methylphosphonate in a dynamic aqueous system. Some interaction was observed between the pyridine and the montmorillonite clay in the high performance liquid chromatographic system. Thermogravimetric and differential scanning calorimetry analysis techniques were not sensitive enough to detect the established sorption interaction between the montmorillonite clay and the dimethyl methylphosphonate. A custom fiber-optic laser raman spectrometer, constructed for use in this project, detected carbon tetrachloride in water. The results of this study illustrate the utility of fourier transform infrared spectroscopic analysis to establish and describe the potential for sorption interactions between inorganic and organic phases of oil shale processing wastes. Experimentation with the laser raman system shows promise for significant contributions in this field of research.

INTRODUCTION

Overview

Western Research Institute has been conducting basic research on complex chemical solutions associated with oil shale processing waste products. Reviews of past research, both WRI's and others' sources, have demonstrated a need for improved methods of predicting contaminant/substrate interactions (Hounslow 1983). The ability to predict these interactions will provide needed information on the transport of organic contaminants by the groundwater through the oil shale substrate.

The goals in this research included the identification of the interaction mechanisms between the organic contaminants and the oil shale substrates using vibrational spectroscopic methods and then the determination of the strengths of these interactions using a variety of experimental methods. For this study three goals were specified. The first was the infrared characterization of the sorption mechanisms of organic compounds common in oil shale with mineral phases in the oil shale substrate. Second, Raman vibrational spectroscopy was used to characterize organo-mineral sorption. This method is complementary to infrared but can be used in the presence of liquid water. The instrument is still being constructed, but some data have been acquired using the preliminary version.

The third goal was the chromatographic analysis of these interactions to determine the retention times of the model organic contaminants and thus to determine the strengths of the interaction. These data were to be supported by adsorption isotherm studies and a study of thermogravimetric and differential scanning calorimetric analyses of the interactions.

In addition to these specified goals, an additional study was necessary to validate the method used for infrared analysis. This comparison of sample preparation techniques used for solid state FTIR analysis was necessary to allay any doubts that the methods used for the FTIR study were acceptable to the spectroscopic community at large.

Infrared Spectroscopic Study

The use of infrared spectroscopy for the determination of the sorptive interactions between organic compounds and solid substrates is a widespread and useful technique. This technique often has been used to establish the mechanisms of interaction between chromatographic substrates and organic compounds (Basila et al. 1964; Bernstein et al. 1982; Morrow and Cody 1976). The petroleum refining industry has used infrared spectroscopy to study catalyst/organic compounds relationships (Parry 1963; Parfitt et al. 1970). Soils scientists have used infrared spectroscopy to study soil structure and sorptive relationships between pesticides and soils components (White 1971; Farmer and Russell 1964; Shoval and Yariv 1979; Saltzman and Yariv 1975).

Of the methods available to study sorption interactions between organics and solids, infrared spectroscopic methods have the potential to rapidly determine the origins and functional groups responsible for the sorptive interactions. This is the method that WRI used in this study. Fourier Transform Infrared (FTIR) spectroscopy, a method of infrared analysis which is much more precise than dispersive IR analysis, will be used to analyze shifts in the vibrational bands of the organo-mineral complex versus the original band positions of the pure organic compound. The band that is shifted corresponds to the portion of the molecule that is undergoing bonding, and the direction and magnitude of the particular band shift indicate the extent of involvement of the molecule with the substrate.

The importance of clay-contaminant interactions has been well documented (Mortland 1986; Warren 1986). Mechanisms including ion exchange, protonation, hydrogen bonding, coordination, and catalytic degradation may be involved in the interaction between clays and pollutants. The use of infrared spectroscopy to study such clay/organic relationships has been described (Farmer and Russell 1964).

Many researchers have investigated interactions between clays and organic compound types (Mohamed 1978; Mortland 1986). In addition, much infrared research has been done to describe the mechanisms of these interactions (Saltzman and Yariv 1975; Yariv 1966; Mortland 1976; Huang 1977).

The infrared investigations of interactions between dimethyl methylphosphonate (DMMP) and montmorillonite clay illustrate the propensity for polar molecules to associate with the interlamellar cations in the clay (Rockley and Rockley 1987; Bowen 1986; Mortland 1975). Compounds containing nitrogen, oxygen, sulfur, or olefinic functional groups have electron pairs which may be donated to electrophilic exchange cations to form complexes on the clay surface. However, the energy of ligand formation of an organic molecule with an exchange cation must be greater than the solvation energy of the cation with water in order for displacement of water molecules and direct organic-cation coordination to take place.

Soon after the beginning of the study, organic compounds and minerals characteristic of those found in oil shale were substituted for those originally specified in the 1987 research plan. FTIR was used to investigate interactions of benzene, 2,2,4-trimethylpentane, benzoic acid, sodium benzoate, pyridine, isopropylamine, and DMMP with montmorillonite clay. These compounds, with the exception of isopropylamine and dimethyl methylphosphonate, were chosen because they more accurately represent some of the functional group types found in organic products and wastes in shale oil production processes (McKay 1984; McKay and Blanche 1985; McKay and Blanche 1987). Isopropylamine was chosen because its polar functionality should be sufficient to displace the water from the interlamellar cations in the clay. Dimethyl methylphosphonate was chosen because its mechanisms of interaction are well described. The minerals, montmorillonite (a smectite) and hematite (an iron oxide), are also found in various phases of oil shale production processes (Essington et al. 1987).

Preparation Methods Comparison Study

Since methods of solid state infrared analysis of organo-mineral complexes are varied and seldom agreed upon, a study was conducted to establish the best method(s) to use in this work. First, a comparative study on the effects of different sample preparation techniques on the infrared spectra of a model montmorillonite clay-dimethyl methylphosphonate adsorption complex was conducted. This interaction is well described in the literature, and the spectral characteristics of the complex are described (Bowen in press; Rockley and Rockley 1987).

The use of alkali-halides as supportive substrates for infrared analysis may affect the quality of the spectra (D. Compton 1987; Farmer 1957). Some work has been done to investigate the effects of sample preparation on the spectra of minerals and organic compounds (Farmer 1957; Yariv 1966; Rockley and Rockley 1987).

As the sorption interactions between montmorillonite clay and dimethyl methylphosphonate have been investigated, this system was used to compare the effects of sample preparation on the spectral quality of the adsorption mechanism. This study compared the unsupported thin film, supported thin film, pressed disk, photoacoustic (PAS), and diffuse reflectance (DRIFT) techniques of sample preparation and analysis.

As described in the methods and materials section, the unsupported and supported thin film preparation techniques are time consuming. The very nature of the preparation schemes lends itself to non-reproducible data: the film itself is made by applying a sample/water suspension to a support, usually a plastic sheet, making it very difficult to control the thickness of the dried film. The thickness of the sample affects the spectrum. However, these techniques are approved because there is no chemical interaction between the sample and the support.

The use of alkali halides as support for solid state infrared analysis is widespread. However, the use of the pressed disk has been discouraged in the soil sciences because the possibility exists for the exchange of cations between the alkali halide and the mineral phase of the sample (Bowen 1986). This exchange would be difficult to observe in the infrared spectrum because the bands associated with the metal ions are broad and not well defined (Parfitt et al. 1970; Gadsden 1975).

The use of photoacoustic (PAS) detectors for FTIR spectroscopy is cited in the literature (Krishnan 1980; McClelland 1983; Tam 1986). The application of PAS techniques to the analysis of solids is also documented (Vidrine 1980; Low and Parodi 1980). Several studies have used PAS to study pesticide/soil component interactions (Bowen 1987; Rockley and Rockley 1987; Shoval and Yariv 1979; Lowry 1982). Diffuse reflectance spectroscopy (DRIFT) has been cited in the literature, usually in comparison with PAS (Childers and Palmer 1986).

High Performance Liquid Chromatographic Study

Another method used to study organic/substrate relationships is high performance liquid chromatography (Braumann 1986). The expulsion of a solute from its aqueous solution due to its energetically unfavorable interaction with the water molecule network (hydrophobicity) is the driving force for liquid-liquid distribution processes, soil sorption, and bioconcentration of environmental pollutants. Since the development of high performance liquid chromatography (HPLC), it has become apparent that this technique might produce retention data which, when using the appropriate stationary and mobile phases, could relate to a solutes hydrophobicity and potential sorption interactions. Some solids and organic compounds used in the FTIR portion of this study were applied to a high performance liquid chromatographic system in an attempt to correlate retention data from the HPLC with data obtained from the FTIR band shifts.

Since the FTIR data will be used to establish the potential for sorption interactions between the solid and organic compound, HPLC will be used to investigate the interactions in a dynamic aqueous system.

Adsorption Isotherm Study

Because this portion of the study was dependent upon completion of the HPLC study, it was not accomplished.

Thermogravimetric and Differential Scanning Calorimetric Study

This study was undertaken to directly determine the strength of the sorption bond between the organic contaminant and the mineral phase. The method for both techniques is to heat the sample of the organo-mineral complex and to detect the amount of energy that is required to break the sorption interaction. Several thermogravimetric (TGA) and differential scanning calorimetry (DSC) experiments were run on the DMMP-montmorillonite complex.

Laser Raman Spectroscopic Study

A laser Raman instrument coupled with fiber optics for the remote in situ detection of organic compounds, sorption complexes, and mineral substrate analysis is being constructed in a joint venture between Western Research Institute and the Department of Chemistry at the University of Wyoming. Raman spectroscopy is a form of vibrational spectroscopy similar to, and complementary with, infrared spectroscopy. Like infrared spectroscopy, Raman spectroscopy produces a fingerprint spectrum capable of both qualitative and quantitative analyses, but unlike infrared spectroscopy, Raman spectra of organo-mineral complexes can be analyzed in the presence of water.

The instrument consists of a laser, the optical fiber light channel to the sample cell, a monochromator, and a photomultiplier detector. In the preliminary version of the instrument, an Ar+ visible

continuous wave (cw) laser was used. In the future version, which is under construction, a Neodymium:YAG pulsed laser coupled with a dye laser will be used. The device will have the capability of both cw and pulsed operation at wavelengths between the ultraviolet and the near infrared. This will accommodate research into the analysis of organic compounds using resonance Raman, surface enhanced, and surface enhanced resonance Raman spectroscopy. Preliminary analysis of carbon tetrachloride diluted with n-hexane was performed to test the instrument.

EXPERIMENTAL

Instrumentation and Materials

The infrared spectrometer used in this study was the Nicolet MX-1 Fourier Transform Infrared Spectrometer (FTIR). This study tested two recently developed solid state sampling/analytical techniques: Photoacoustic (PAS) and Diffuse Reflectance (DRIFT) spectroscopy. The PAS and DRIFT analyses were performed by Digilab (division of BIORAD Corporation) on an FTS 65 spectrometer in their research laboratories in Cambridge, Massachusetts. The PAS cell was provided by Digilab, and the DRIFT cell was manufactured by Spectra-Tech Inc.

The HPLC system consisted of a Spectra Physics SP8700 solvent delivery system, a Spectra Physics SP8750 organizer, a Spectra Physics SP8400 uv/vis detector, and a Hewlett Packard 3393A integrator.

Montmorillonite Clay (SAZ-1) was obtained from the Clay Minerals Society Repository, University of Missouri, Department of Geology. Hematite was an in-house standard, verified by published infrared spectral information (Gadsden 1975).

All reagents used were distilled-in-glass, high purity solvents obtained from commercial supply houses. The water used was deionized and double distilled in house.

The solid state FTIR substrate, potassium bromide (KBr), was high purity spectroscopic grade obtained from a commercial vendor and subsequently stored in a dry box with dessicant.

Thermogravimetric and Differential Scanning Calorimetry studies were done with a Dupont 990 Modular Thermal Analysis system equipped with a standard differential thermal analysis cell and a Dupont 951 thermogravimetric analysis cell. Thermal measurements were aided by a Dupont model 942 Thermomechanical Analyzer.

The Raman instrument used was a custom built instrument made up of a Lexel Ar⁺ laser, a Spex monochromator, and Polymicro optical fibers. Detection was by a coiled photomultiplier tube and photon counting electronics.

Due to a difficult coupling problem, and in order to collect data for this report, a second instrument was used temporarily. This instrument consists of a Czerny-Turner monochromator optically coupled to a subtractive monochromator which completely subtracts the Rayleigh line from the spectrum. Both instruments are custom built. The detection system of this instrument consists of an intensified Tracor Northern diode array system TN-1701. This water-cooled system is capable of obtaining an instantaneous Raman spectrum 40 nm in width, thus making optical coupling with the sample easy. The system was originally set up with the standard 90 degree Raman sampling configuration in order to provide a real comparison with the optical fiber system. The laser used for this experiment is the Argon ion laser previously described.

A second laser system to be used for the resonance Raman experiments consists of a Quanta Ray Tuneable Laser system. It is supported by a Quanta Ray Nd:YAG laser equipped with doubling crystals for two visible emission wavelengths. The second part of the system is a Quanta Ray PDL dye laser which, when equipped with selected dyes, can produce any wavelength in the visible and near IR spectrum. This is coupled with the Quanta Ray WEX, which is a doubling-mixing crystal system. The WEX enables the system to be tuned into the ultraviolet. A Raman shifter provides further tuneability to the WEX. This is one of the most advanced systems in the country, and the only one dedicated to DOE environmental research.

Procedures

A clay with calcium interlamellar cations and a second clay with potassium cations were made from raw montmorillonite clay by ion exchange.

The clay was suspended in a 1-M solution of the appropriate chloride salt, and the suspension was rinsed with deionized, double-distilled water. The rinse continued until AgNO_3 established the absence of chloride ions in the supernatant. The exchanged clays were allowed to stay suspended in the final rinse water until used. At the time of experimentation, the clays were dried at room temperature in air for 48 hours.

Organic compounds were applied to solids either neat by vapor transfer or in solvent mix. Subsequent drying prior to sample preparation was at room temperature in air with dessicant under glass.

The pressed disks were made by weighing approximately 0.1 gram of substrate and adding approximately 0.0010 gram of sample; all weights were recorded to .0001 grams. The substrate-sample mixture was then placed in a stainless steel vial with stainless steel ball and milled for 30 seconds. The mixture was then transferred to a disk die where it was pressed at 16,000 psi for 1 minute. This formed a disk 13 mm in diameter.

A supported thin film of montmorillonite was made by depositing a clay/water suspension on a zinc selenide (ZnSe) plate and allowing it

to dry in air at room temperature. The dimethyl methylphosphonate was then vapor transferred to the sample under mild heat with dessicant under glass.

Unsupported thin films were made by depositing clay water suspensions on a sheet of polystyrene plastic and drying in air at room temperature. The films were removed from the plastic sheet using a razor blade, being careful not to remove any plastic with the film. Once again the dimethyl methylphosphonate was applied by vapor transfer as previously described.

All pressed disks, supported thin films, and unsupported thin film spectra were produced by the Nicolet MX-1 Fourier Transform Infrared spectrometer at 1 cm^{-1} resolution, 160 scans in a nitrogen purged sample compartment.

The diffuse reflectance data were collected using a Digilab FTS 65 Fourier Transform Infrared spectrometer at 1 cm^{-1} resolution for 152 scans, using diamond powder for the background and diluent.

The photoacoustic data were collected on a Digilab FTS 65 FTIR spectrometer at 2 cm^{-1} resolution, 5 KHz mirror speed, at 152 scans, using carbon black for the background and diluent.

All spectra recorded, by both WRI and Digilab, were transferred to flexible disks for storage and retrieval.

RESULTS AND DISCUSSION

Infrared Spectroscopic Study

Preparation Methods Comparison Study

This study compared five techniques of solid state infrared preparation-analysis and their effects on the spectral quality of a DMMP montmorillonite sorption complex. The techniques used were the unsupported thin film, supported thin film, KBr pressed disk, diffuse reflectance, and photoacoustic. Pressed disk analysis was performed to ensure that the KBr powder was not contributing to the spectra of the DMMP, Ca montmorillonite, or the K montmorillonite. The study showed that the KBr pressed disk is a valid technique of solid state infrared preparation and analysis.

To ensure that the substrates and techniques used to prepare pressed disks did not alter the spectrum of pure DMMP, a blank was prepared by applying the neat compound to powdered KBr and pressing at 8 tons for 1 minute. FTIR analysis showed the absorption bands to correspond with those found in the literature (Pouchert 1985).

The FTIR spectra of the Ca-exchanged and the K-exchanged montmorillonite were indistinguishable using the KBr pressed pellet technique (Figure 1).

Figure 1. FTIR Spectra of K-Exchanged and Ca-Exchanged Montmorillonite

The dimethyl methylphosphonate (DMMP) was applied to the unsupported thin film of the Ca-exchanged clay. The P=O stretch of pure DMMP occurs at $\sim 1245\text{ cm}^{-1}$; this band shifted to $\sim 1211\text{ cm}^{-1}$ in the Ca-exchanged clay. This result concurs with results reported in the literature (Bowen et al. 1987; Rockley and Rockley 1987).

The ZnSe supported thin film showed similar results. The spectrum of the Ca-exchanged clay with DMMP shifted the P=O stretch band to $\sim 1212\text{ cm}^{-1}$.

Pressed disks of the clay-DMMP complex were prepared using both Ca- and K-exchanged clays. The Ca-exchanged, clay-DMMP complex showed a shift of the $\sim 1245\text{ cm}^{-1}$ P=O stretch band to 1213 cm^{-1} , which agreed with the supported and unsupported thin films. The K-exchanged, clay-DMMP complex showed a shift of the $\sim 1245\text{ cm}^{-1}$ P=O stretch band to $\sim 1223\text{ cm}^{-1}$. This spectrum illustrates the change in shift expected if the K cations of the KBr substrate were to exchange with the Ca interlamellar cations of the prepared clay.

Photoacoustic and diffuse reflectance analyses of the clay, DMMP, and clay-DMMP complex were also similar to those produced by the methods described above. However, the photoacoustic spectra show some residual water vapor as the clays de-gas: gases are more easily detected by PAS than by the other methods, and the trace amount of water vapor gives an enhanced spectrum (S. Compton 1987). The diffuse reflectance spectra showed a major portion of the P=O band shifted to $\sim 1210\text{ cm}^{-1}$ and revealed a minor unshifted $\sim 1244\text{ cm}^{-1}$ P=O band. The DRIFT technique had detected labile DMMP, but the other methods did not.

The wavenumber assignment comparing the P=O region for these techniques are shown in Table 1.

To ensure that no long term ion exchange was taking place between the KBr and the clay, spectra of a KBr disk of clay-DMMP were taken at 1, 3, 4, 6, and 10 days. As the stacked spectra in Figure 2 illustrate, no changes in the shifted P=O band occur to indicate K exchange for the Ca interlamellar cations in the clay.

The unsupported thin film, PAS, and DRIFT methods of analysis ensure no substrate/sample interaction. When these spectral results are compared with the supported thin film and KBr disk spectra, it is conclusive that the KBr is not influencing the clay-DMMP sorption interaction. This is further supported by the spectrum of the K-exchanged, clay-DMMP complex, which illustrates the result of such an exchange. The time study also shows that this exchange is not time dependent.

Montmorillonite Sorption Study

In this portion of the study FTIR is used to investigate interactions of benzene, 2,2,4-trimethylpentane, benzoic acid, sodium benzoate, pyridine, and isopropylamine with montmorillonite clay.

Figure 2. FTIR Spectra of Time Lapse DMMP/Montmorillonite Complex Study

Table 1. Infrared Wavenumber Assignments for Preparation Methods Comparison Study

pure DMMP KBr disk	~1245 cm ⁻¹
pure DMMP PAS	~1241 cm ^{-1a}
pure DMMP DRIFT	~1243 cm ⁻¹
Ca clay-DMMP unsupported thin film	~1211 cm ⁻¹
Ca clay-DMMP supported thin film	~1212 cm ⁻¹
Ca clay-DMMP KBr disk	~1213 cm ⁻¹
K clay-DMMP KBr disk	~1223 cm ⁻¹
Ca clay-DMMP PAS	~1210 cm ^{-1a}
Ca clay-DMMP DRIFT	~1211 cm ⁻¹

^a All wavenumber assignments are based upon 1 cm⁻¹ resolution spectra excepting the photoacoustic (PAS) spectra which were produced at 2 cm⁻¹ resolution. All wavenumbers are rounded off to the next highest whole number.

Benzene and 2,2,4-trimethylpentane were directly applied to the montmorillonite clay as a neat liquid using the method previously described. Using the KBr pressed disk method, solid state FTIR analysis indicated no sorption of either compound on the clay. If the compound is labile on the clay, then an undisturbed spectrum of the compound appears. In this case, no evidence of either compound was observed by FTIR analysis. This indicates that (1) the compounds were still in a neutral state and thus sufficiently volatile to evaporate from the clay or (2) not present within the limits of the instrument's capacity to detect and identify the interaction.

Ordinary organic salts, such as sodium benzoate, are predicted to adsorb on clays by displacing the cations present in the interlamellar spaces (Mortland 1975). The sodium benzoate was mixed in water (1.0%

by weight) and added to the montmorillonite clay. The resulting solid state FTIR analysis revealed no sorption of the compound on the clay. Again, if the compound was indeed present, it was in insufficient quantity to be detected by the instrument.

A study of the relationship between benzoic acid and montmorillonite clay has revealed both labile and adsorptive associations (Yariv 1966). However, this work used carbon tetrachloride and cyclohexane as carrier solvents for the benzoic acid. The solvent also acted as a transporting medium to remove water from the interlamellar spaces, thus preparing for the interaction between the benzoic acid and the cation.

Benzoic acid was added to water (1.0% by weight) and after 24 hours was rinsed to remove any benzoic acid not associated with the clay. The results of solid state FTIR analysis were not consistent. The majority of the samples analyzed indicated no benzoic acid in the spectrum. However, in two cases, bands appeared which cannot be ascribed to either the benzoic acid standard or the montmorillonite standard. The infrared analysis of one sample produced a sharp, well-defined band at $\sim 1317 \text{ cm}^{-1}$. The nearest band of pure benzoic acid is at $\sim 1327 \text{ cm}^{-1}$ and is associated with the C-O stretch of the dimer (Pouchert 1985). When the absorption intensity of the $\sim 1327 \text{ cm}^{-1}$ band is compared with that of the ring substitution band at $\sim 707 \text{ cm}^{-1}$ and the C=O band at $\sim 1687 \text{ cm}^{-1}$, it seems likely that they would also appear in the spectrum of the complex, but they do not. The only interference the clay spectrum has in these areas is the $\sim 1635 \text{ cm}^{-1}$ O-H band of water. Another sample analysis produced a well-defined band at $\sim 1810 \text{ cm}^{-1}$. This band cannot be ascribed to either the acid or the clay. Further experimentation is needed to substantiate these results. Table 2 shows wavenumber assignments and comparisons.

Table 2. Benzoic Acid/Montmorillonite Sorption Wavenumber Assignments

Benzoic Acid	Benzoic Acid/Montmorillonite
1688 cm^{-1}	1605-1640 cm^{-1}
1453 cm^{-1}	*
1426 cm^{-1}	1418 cm^{-1}

*No corresponding absorption band

Infrared spectroscopic research has described the mechanisms of interaction between pyridine and solids (Basila et al. 1964; Bernstein et al. 1982; Morrow and Cody 1976; Parry 1963). In addition, the sorption bands between pyridine and montmorillonite have been previously described (Farmer and Mortland 1966).

Pyridine was applied as a neat liquid to the montmorillonite, and the mixture was allowed to dry at room temperature as previously described. The solid state FTIR analysis shows a band at $\sim 1596\text{ cm}^{-1}$, the C=N stretch band region. This band, in the absence of the $\sim 1583\text{ cm}^{-1}$ band, indicates that the pyridine is hydrogen bonded to water or coordinately bonded pyridine to the interlamellar cations (Parry 1963; Farmer and Mortland 1966). The difference between hydrogen-bonded and coordinately bonded pyridine is not clearly defined in this region (Parry 1963.) Two shifted bands are present in the C=C stretch region at $\sim 1442\text{ cm}^{-1}$ and $\sim 1490\text{ cm}^{-1}$. These shifts are from the $\sim 1439\text{ cm}^{-1}$ and the $\sim 1482\text{ cm}^{-1}$ bands of pure pyridine and are ascribed to both hydrogen-bonded and coordinately bonded pyridine (Parry 1963; Farmer and Mortland 1966). Table 3 shows wavenumber assignments and comparisons.

Table 3. Pyridine/Montmorillonite Sorption Wavenumber Assignments

Pyridine	Pyridine/Montmorillonite
1583-1596 cm^{-1}	1596 cm^{-1}
1482 cm^{-1}	1490 cm^{-1}
1439 cm^{-1}	1442 cm^{-1}

Isopropylamine was applied to the clay as a neat liquid and allowed to dry, as previously described. Solid state FTIR analysis indicates changes in the spectra of both the montmorillonite clay and the pure isopropylamine. Both water bands of the clay (O-H stretch at $\sim 3400\text{ cm}^{-1}$ and O-H band at $\sim 1635\text{ cm}^{-1}$) show reduced intensity in the isopropylamine-montmorillonite complex. This indicates that isopropylamine is displacing water from the clay. A broad, yet well-defined band, appears at $\sim 3255\text{ cm}^{-1}$ in the spectrum of the complex; the NH_2 stretch band of pure isopropylamine appears at $\sim 3281\text{ cm}^{-1}$. This downfield shift indicates an interaction with the NH_2 .

The FTIR spectrum of the isopropylamine-montmorillonite complex also reveals two sharp bands at $\sim 1385\text{ cm}^{-1}$ and $\sim 1400\text{ cm}^{-1}$, whereas the spectrum of pure isopropylamine shows absorption at $\sim 1337\text{ cm}^{-1}$ and $\sim 1380\text{ cm}^{-1}$. These absorption bands are assigned to the $\text{C}(\text{CH}_3)_2$ stretch of the isopropylamine (Shoval and Yariv 1979). A broad band appears at $\sim 1500\text{ cm}^{-1}$ and is assigned to the protonation of the NH_2 group to NH_3^+ (Shoval and Yariv 1979). This frequency depends on whether the clay is hydrated or not, and in this case the clay was hydrated. Air-dried clay should produce bands at $\sim 3255\text{ cm}^{-1}$, $\sim 1620\text{ cm}^{-1}$, and $\sim 1500\text{ cm}^{-1}$, which are assigned to the NH_3^+ symmetric deformation of the isopropylammonium ion (Shoval and Yariv 1979). This indicates that the isopropylamine is protonated in the interlamellar spaces of the clay before it can displace the associated water and associate with the cations. Table 4 shows wavenumber assignments and comparisons.

Table 4. Isopropylamine/Montmorillonite Sorption Wavenumber Assignments

Isopropylamine	Isopropylamine/Montmorillonite
3281 cm^{-1}	3255 cm^{-1}
1600 cm^{-1}	1500 cm^{-1}
1380 cm^{-1}	1400 cm^{-1}
1337 cm^{-1}	1385 cm^{-1}

Hematite Sorption Study

Hematite is found in soils and is a weathering product of iron-bearing minerals. The crystalline structure of hematite is comprised of layers of oxygen ions and layers of iron ions (Deer et al. 1972). The chemical composition of hematite is Fe_2O_3 with traces of MnO and FeO .

Dimethyl methylphosphonate (DMMP) was used in this portion of the study because its sorption interactions are well understood. In addition, it is a pesticide-like material of environmental importance. Hematite was placed in pure DMMP for 24 hours. The excess DMMP was then decanted, and the hematite was dried in air under glass with dessicant for 48 hours.

Solid state FTIR analysis of the DMMP-hematite complex shows a lack of well-defined P=O stretch in the 1200 to 1245 cm^{-1} region of the infrared spectrum. It is known that the P=O group of the molecule coordinates with metal cations and that a downfield shift results (Farmer and Russell 1964). Bands ascribed to CH_3O and CH_3P are well defined and only slightly perturbed, with the exception of the ~914 cm^{-1} CH_3P band which has shifted to ~905 cm^{-1} . A band appears at ~1128 cm^{-1} that is unidentified. Pure DMMP has two P-O_2 bands at ~788 cm^{-1} and ~822 cm^{-1} , which appear to have shifted to ~804 cm^{-1} and ~842 cm^{-1} , respectively. The C-O bands of pure DMMP occur at ~1032 cm^{-1} and ~1059 cm^{-1} , but only one band appears in this area in the spectrum of the DMMP-hematite complex, at ~1045 cm^{-1} .

After six days another sample from the original application of DMMP to hematite was prepared and analyzed. Both the ~3400 cm^{-1} O-H and ~1635 cm^{-1} O-H bands of water showed reduced intensity. The ~1417 cm^{-1} and ~1313 cm^{-1} CH_3P bands from the day one analysis had shifted further downfield to ~1398 cm^{-1} and ~1307 cm^{-1} , respectively. The sharp ~1045 cm^{-1} C-O band of the initial analysis had split into a triplet ~1043 cm^{-1} , ~1085 cm^{-1} , ~1128 cm^{-1} band. The ~1045 cm^{-1} band of the initial analysis had lost intensity and definition.

In light of the differences between the initial and day six sample analyses, another sample was drawn and prepared at day eight

for FTIR analysis. The main feature of this spectrum is the significant loss of band definition and intensity throughout all infrared regions from 650 cm^{-1} to 4000 cm^{-1} . Most noticeable is the loss of absorption at the $\sim 2999\text{ cm}^{-1}$ area, the C-H stretch of the CH_3P of the pure compound. In turn, the CH_3P band at $\sim 2923\text{ cm}^{-1}$ has become more intense and better defined. The water bands at $\sim 3400\text{ cm}^{-1}$ and $\sim 1635\text{ cm}^{-1}$ are more pronounced and intense. The only recognizable band above $\sim 1150\text{ cm}^{-1}$ is $\sim 1308\text{ cm}^{-1}$, a CH_3P band. The $\sim 1043\text{ cm}^{-1}$, $\sim 1085\text{ cm}^{-1}$, and $\sim 1128\text{ cm}^{-1}$ bands of the day six analysis have lost both definition and intensity. Table 5 is a list of wavenumbers.

Table 5. DMMP/Hematite Sorption Wavenumber Assignments

DMMP Neat		DMMP/Hematite Complex	
<u>Initial Spectrum</u>			
2999 cm ⁻¹		2999 cm ⁻¹	
1417 cm ⁻¹		1417 cm ⁻¹	
1314 cm ⁻¹		1313 cm ⁻¹	
1245 cm ⁻¹		*	
1185 cm ⁻¹		1128 cm ⁻¹	
1033-1060 cm ⁻¹		1045 cm ⁻¹	
913 cm ⁻¹		*	
822 cm ⁻¹		842 cm ⁻¹	
788 cm ⁻¹		804 cm ⁻¹	
<u>Day Six Spectrum</u>			
<u>DMMP</u>		<u>DMMP/Hematite Complex</u>	
2999 cm ⁻¹		2999 cm ⁻¹	
1418 cm ⁻¹		1398 cm ⁻¹	
1314 cm ⁻¹		1307 cm ⁻¹	
*		1128 cm ⁻¹	
1033-1060 cm ⁻¹		1085 cm ⁻¹	
*		1043 cm ⁻¹	
<u>Day Eight Spectrum</u>			
<u>DMMP</u>		<u>DMMP/Hematite Complex</u>	
2999 cm ⁻¹		not present	
1314 cm ⁻¹		1318 cm ⁻¹	

*No corresponding absorption band

The comparison of the three time-lapsed spectra indicates sorption and even possible degradation of the DMMP. Additional experimentation is needed to describe the relationship between DMMP and hematite.

Benzene, 2,2,4-trimethylpentane, and pyridine were deposited on hematite as neat liquids and allowed to dry, as previously described. The subsequent solid state FTIR analysis of the samples revealed no sorption of either compound. As with the montmorillonite clay, the compounds did not associate with the mineral matrix of hematite and probably evaporated. If either compound was present on the hematite, the quantity was too small to be detected by the FTIR analysis.

Benzoic acid was applied to the hematite in the same manner as previously described for its application to montmorillonite. The solid state FTIR analysis of the sample indicated a broad C=O band (doublet) at $\sim 1605\text{ cm}^{-1}$ to $\sim 1640\text{ cm}^{-1}$, whereas the spectrum of the pure benzoic acid had a sharp, strong C=O band at $\sim 1688\text{ cm}^{-1}$. A C-OH band appeared at $\sim 1418\text{ cm}^{-1}$ in contrast to a sharp doublet at $\sim 1426\text{ cm}^{-1}$ and $\sim 1453\text{ cm}^{-1}$ in the benzoic acid spectrum. Analysis of other samples still maintained the sharp $\sim 1418\text{ cm}^{-1}$ band; the bands in the mid- 1600 cm^{-1} area were of variable intensity and definition. The downfield shift of the bands indicates that the sorption reaction results in lowering the energy of the assigned bonds.

Sodium benzoate was applied to hematite as a 1.0% solution in water and allowed to dry in air for 48 hours. Subsequent FTIR analysis of the dried mixture showed that the sodium benzoate was present in the spectrum, but in an undisturbed state.

Isopropylamine was applied to hematite as a neat liquid and allowed to dry under the conditions described previously. Solid state FTIR analysis reveals a band at $\sim 1728\text{ cm}^{-1}$ which is not assigned to hematite or isopropylamine. A $\sim 1450\text{ cm}^{-1}$ band appears, which has been ascribed to CH_3 , and a $\sim 1384\text{ cm}^{-1}$ band, which has been assigned to $\text{C}(\text{CH}_3)_2$ (Shoval and Yariv 1979). Indications of C-N stretch appear at $\sim 1275\text{ cm}^{-1}$ and $\sim 1290\text{ cm}^{-1}$, the closest bands in isopropylamine being at $\sim 1250\text{ cm}^{-1}$ and $\sim 1337\text{ cm}^{-1}$. A sharp band appears at $\sim 1123\text{ cm}^{-1}$, shifting from either $\sim 1140\text{ cm}^{-1}$ or $\sim 1170\text{ cm}^{-1}$ in the isopropylamine spectrum. Peaks at $\sim 1090\text{ cm}^{-1}$ and $\sim 1075\text{ cm}^{-1}$ are possible C-N stretches; isopropylamine has a band at $\sim 1040\text{ cm}^{-1}$. Considering the clean baseline of the spectra produced and the relative absorbances of the bands, the absence of the intense NH_2 wagging doublet band at $\sim 804\text{ cm}^{-1}$ and $\sim 854\text{ cm}^{-1}$ is noticeable. The spectrum of hematite has no intense absorbance bands in this region. In general, the directions of the band shifts are not easily assigned because of the complexity of the spectra. However, the lack of NH_2 wag bands and the perturbed C-N bands indicate possible interactions involving either the H of the NH_2 group or the N of the NH_2 group. Table 6 is a list of wavenumbers.

Table 6. Isopropylamine/Hematite Sorption Wavenumber Assignments

Isopropylamine	Isopropylamine/Hematite
not present	1728 cm^{-1}
1380 cm^{-1}	1450 cm^{-1}
1337 cm^{-1}	1384 cm^{-1}
1250 cm^{-1}	1275 cm^{-1}
1170 cm^{-1}	*
1140 cm^{-1}	1123 cm^{-1}
*	1090 cm^{-1}
*	1075 cm^{-1}
854 cm^{-1}	
804 cm^{-1}	

*No corresponding absorption band

High Performance Liquid Chromatographic Study

In order to identify the retention time of an organic compound within the HPLC system and thus help determine the strength of the interaction, procedures were established for packing a suitable column. Montmorillonite clay was placed in an aqueous slurry of CaCl_2 (10 ppm) and allowed to filter and pack under mild pressure at a flow rate of 1 milliliter per minute. Because smectite clays are less than 2 microns average particle size, packing a column with an even flow was time consuming and difficult to maintain. Most attempts resulted in flow pressures exceeding the capacity of the system, 4500 psi.

One four-inch column was successfully packed. Solutions of benzene and 2,2,4-trimethylpentane were injected at concentrations of 100 ppm in the CaCl_2 eluent. The resulting chromatograms indicated direct flow through the columns with no retention other than that expected from the void volume of the column. The information obtained from the FTIR analysis predicted this result since it showed no capacity for interaction between the compounds and the clay.

Benzoic acid and sodium benzoate showed the same result as the hydrocarbons: no interaction with the clay column was observed. FTIR indicated the possibility of interaction between these compound types and the clay, but the results were inconclusive.

FTIR analysis showed interactions between the montmorillonite clay and dimethyl methylphosphonate. The HPLC system indicated no interactions between the clay and the DMMP in a dynamic aqueous system. Other researchers have noted that DMMP, once sorbed onto the clay, is easily displaced by liquid water (Bowen et al. 1987). Even though the FTIR does indicate the possibility for interaction between

the clay and the DMMP, the HPLC system demonstrates the lack of interaction in a dynamic aqueous system.

The FTIR analysis of pyridine and montmorillonite clay showed possibilities for hydrogen bonding to water associated with the interlamellar cations and direct coordination with the cations. At initial injection of the pyridine into the system, retention of pyridine indicated an interaction between the clay and the pyridine. Subsequent injections onto the same column showed no further interaction. This indicated that if pyridine did interact with the clay on the first injection, it saturated the system.

Adsorption Isotherm Study

Since this portion of the study was dependent upon completion of the HPLC study, it was not accomplished.

Thermogravimetric and Differential Thermal Calorimetric Study

In this study, an attempt was made to directly determine the bonding strength of the DMMP with the montmorillonite by determining the amount of heat energy required to drive the organic compound off. A sample of the DMMP/montmorillonite complex was prepared and analyzed using the MX-1 FTIR spectrometer. A total of twelve samples, six of which were pure montmorillonite for comparison with six of the DMMP-montmorillonite complex, was run using the two analytical methods. The samples ranged in weight from 15.9 to 16.9 mg. The results, when compared each time with the background analysis of the montmorillonite clay with no adsorbed DMMP, showed that neither technique was sensitive enough to detect the loss of the DMMP. At that point, research was terminated.

Laser Raman Spectroscopic Study

Several spectra of neat carbon tetrachloride were run on the Raman spectrometer as equipped with the cw laser. Carbon tetrachloride is used as a standard to check for band wavelengths and intensity of signal. The carbon tetrachloride was also diluted with n-hexane in order to confirm that the intensity of the signal was linear with concentration (Figure 3).

A tuneable laser system was adapted to the Raman spectrometer. This system allows experiments to be conducted at different laser wavelengths, enabling resonance Raman experiments to be conducted. Again, carbon tetrachloride standards were run to confirm band location and wavelength linearity. In order to make this adaptation, the Raman monochromator was equipped with computer-controlled stepper motors and a cooled RCA 31034 photomultiplier tube. Several spectra of compounds of environmental interest were run, including toluene and JP-4 jet fuel. These spectra confirmed that toluene is a major component of the JP-4 fuel, as indicated by the analytical division report accompanying the sample. These experiments also indicated that the optical coupling between the optical fiber and the monochromator, although adequate for the analysis of neat compounds, was inadequate

Figure 3. Laser Raman Spectra of Serial Dilutions of Carbon Tetrachloride

for the analysis of compounds in water at environmental concentrations. Other investigators have shown that Raman spectra of compounds of environmental concern can be obtained in low ppm concentrations (Marley et al. 1985). Likewise, low concentrations were obtainable when using the optical fiber bundle and the McCreery tube using Raman scattering and resonance Raman methods (Schwab and McCreery 1987). A decision was made to use a second existing instrument equipped with an intensified diode array detector capable of producing instantaneous Raman spectra with a spectral width of 40 nm. It also permitted spectral addition and averaging in order to detect small signals and to extract these signals from noise. This system enabled facile preliminary coupling of a sample and the monochromator but without the optical fiber system. Spectra of phenol in water at 500 ppm were acquired. It is expected that concentrations at low ppm levels will be accessible with the use of this instrument after it is equipped with the optical fiber-McCreery tube sampling system.

It should be emphasized that this is a highly technical experimental technique that is being built on site, and as such is susceptible to unforeseen problems. Because it is not a proven commercial instrument, a great deal of time has been spent to make the system operational. Based on the literature cited in this report and the capability of this method to work in an aqueous environment, it is apparent that Raman spectroscopy will provide a most valuable technique for future environmental and energy related analyses.

CONCLUSIONS

The results of this study illustrate the capability of fourier transform infrared spectroscopic analysis to establish and describe the potential for sorption interactions between inorganic and organic phases of oil shale processing wastes.

The conclusions of this study are as follows:

- The comparison of preparation methods supports the applicability of the KBr pressed disk technique for solid state FTIR analysis of sorption interactions. The results, however, suggest increased detection sensitivity using the diffuse reflectance and photoacoustic methods of solid state FTIR analysis.
- Fourier transform infrared analysis of benzene, 2,2,4-trimethylpentane, benzoic acid, and sodium benzoate deposited on montmorillonite clay revealed no sorption interaction.
- Fourier transform infrared analysis of pyridine deposited on montmorillonite clay revealed a probable interaction between the nitrogen of the compound and the interlamellar cations or water associated with the cations. This interaction can be either a

hydrogen bond between the hydration spheres surrounding the interlamellar cations or a direct coordination between the pyridine and the cation. The capability of the pyridine to displace water associated with the interlamellar cations determines the extent of this sorption interaction.

- Fourier transform infrared analysis of isopropylamine deposited on montmorillonite reveals formation of the isopropylammonium ion. This indicates that the isopropylamine is protonated in the interlamellar spaces of the montmorillonite before it can displace the water associated with the interlamellar cations and form a direct association with the cation. Whether or not the isopropylammonium is free to exit the interlamellar spaces and to transport is not yet known.
- Fourier transform infrared analysis of benzene, 2,2,4-trimethylpentane, sodium benzoate, and pyridine deposited on hematite revealed no sorption interaction.
- Fourier transform infrared analysis of the dimethyl methylphosphonate-hematite complex indicates initial sorption reactions and possible degradation of the dimethyl methylphosphonate over a period of eight days. Absence or perturbation of the phosphonate bands indicates interaction between hematite and the polar constituent of the molecule.
- Fourier transform infrared analysis of the benzoic acid-hematite complex revealed sorption interactions between the C=O and C-OH groups of the acid. Infrared information indicates a relaxation of these stretches, possibly due to association with the positive charges associated with the iron (Fe) of the hematite.
- Fourier transform infrared analysis of isopropylamine deposited on hematite revealed sorption interactions. However, the spectral shifts were too complex to assign any specific mechanism to the interaction. The C-N bands were all perturbed, and a noticeable lack of NH₂ wagging was revealed, indicating possible interactions involving either the H or the N of the NH₂ group.
- High performance liquid chromatographic studies using a montmorillonite clay column revealed additional sorption information on the dimethyl methylphosphonate and pyridine complexes. Even though FTIR analysis described sorption interactions between montmorillonite clay and dimethyl methylphosphonate, HPLC analysis revealed that this interaction is of limited strength because it is displaced by liquid water. The HPLC analysis of pyridine on the montmorillonite column indicated sorption interaction in a dynamic aqueous system, as revealed by retention time. It also indicated the capability of pyridine to saturate the sorption sites, as indicated by the lack of interaction when additional injections of pyridine were made.
- Thermogravimetric and differential thermal calorimetry were not sensitive enough to detect the sorption mechanism between

montmorillonite clay and dimethyl methylphosphonate that FTIR analysis had revealed.

- Based upon preliminary experimentation, cited literature, and compatibility in aqueous environments, laser Raman spectroscopy will provide a valuable and unique technique for future environmental and energy related analyses.

MANAGEMENT IMPLICATIONS

Of primary concern in the disposal of oil shale processing wastes is the solubilization and mobilization of organic contaminants in the groundwater aquifer. Methods to predict the quality of water associated with oil shale processing and the development of mitigation techniques require a comprehensive understanding of the partitioning of organic contaminants between aqueous and solid phases. The purpose of this study was to determine the mechanisms of interaction between the organic and inorganic phases of oil shale wastes using vibrational spectroscopic methods and to determine the characteristics of these interactions using a variety of experimental methods.

The results of this study suggest that fourier transform infrared (FTIR) analysis can predict potential sorption interactions between the organic and inorganic phases of oil shale. In conjunction with high performance liquid chromatographic (HPLC) studies, the validity of those predictions in a dynamic aqueous system can be investigated. The potential for interaction between the two phases seems to be influenced by the functional groups present in both the organic and inorganic phases, the polarity of the organic and its hydrophobic character. Even though the findings of this report are limited to a small number of compounds, they are significant in showing that FTIR and HPLC analyses can reveal the potential for sorption interactions and thus aid in predicting the transport and fate of the organic phase.

The utilization of mass transport models appears questionable for predicting the transport and fate of organic contaminants in a waste disposal environment. During this research, it has become increasingly apparent that the organic and inorganic constituents of the soil and deeper subsurface play an important part in the sorption and thus retardation of introduced organic chemicals. The greater the retardation of the contaminant, the greater will be the time during which biotic or abiotic degradation of the contaminant will occur. Even though the present transport models do take these factors into account, the methods used to obtain data for input into these models lack parameters based on solid experimental data. This program will generate data based upon functional groups of the organic versus the mineral phase and will be more amenable to site specific applications. In addition, this research will establish and compare laboratory methods for input of data into current transport models.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular make or brand.

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INVESTIGATION OF SORPTION INTERACTIONS BETWEEN ORGANIC AND MINERAL
PHASES OF PROCESSED OIL SHALE

DOE