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Comparison of Sample Preparation Methods for the Fourier Transform Infrared Analysis of an Organo-Clay Mineral Sorption Mechanism

John M. Bowen,* Senja V. Compton,¹ and M. Sterling Blanche

Western Research Institute, P.O. Box 3395, University Station, Laramie, Wyoming 82070

Several methods of sample preparation and Fourier transform infrared (FT-IR) analysis techniques for the observation of a sorption interaction between a clay mineral and an organophosphonate were compared to determine if spectral changes induced by these methods would change the interpretation of the sorption interaction. The methods of sample preparation included the traditional free-standing (unsupported) thin clay films, supported thin clay films, and KBr disks. The FT-IR analysis techniques examined were photoacoustic spectroscopy (PAS) and diffuse reflectance spectroscopy (DRIFT). The organo-mineral interaction used as a model for this study was between dimethyl methylphosphonate and calcium saturated montmorillonite. The results showed that none of the methods affected the interpretation of the sorption interaction. It was found that the spectra obtained by using the KBr disk method, the method most likely to affect the interaction, did not change with time. Thus, interpretation of the sorption mechanism due to the loss of interlamellar water or the exchange of the clay interlamellar cation with K^+ from the KBr matrix did not change as a function of preparation method or detection method.

INTRODUCTION

The transport of organic contaminants through porous media, and the computer modeling of that transport, are of great importance for the prediction of groundwater quality at present (1). Germane to this is the characterization of interactions between mineral surfaces and organic compounds that are implicated as environmental contaminants (2-4). Through the use of Fourier transform infrared (FT-IR) spectroscopy, the mechanism of an organo-mineral sorption interaction can be determined by an analysis of the direction and magnitude of band shifts and intensity variations when the spectrum of the organic compound is compared against that of the organo-mineral complex (5-7).

The methods traditionally used in the analysis of organo-mineral interactions have included KBr disks and unsupported clay films. The use of KBr disks has been discouraged, especially when the mineral is a swelling clay such as montmorillonite, to avoid possible artifacts caused by the supporting material, which could change the interpretation of the interaction (8-11). Interactions between a support material and a sample affect the positions or intensities of the vibrational bands in the infrared spectrum of the organo-mineral complex. Thus, the method of choice for the infrared analysis of organo-mineral interactions has been the use of a thin unsupported film of the mineral cast from a smooth surface, treated with the organic compound, and suspended in the IR beam. This ensured that no unwanted interactions would take

place between the organo-mineral complex and the support material (8, 12, 13). However, thickness reproducibility is difficult to attain with the unsupported film method, causing problems with spectral replication and signal to noise levels. If the films are thick enough to be self-supporting, the result can often be total absorption of the IR energy below about 1100 cm^{-1} . In addition, any instrumental nonlinearity on the absorbance scale results in a poor comparison of band ratios observed for thick and thin films. It is of interest, therefore, to determine the effects of various sample preparation techniques on a particular organo-mineral interaction.

For this study, four sampling methods were compared against the recommended thin unsupported clay film methodology. These included thin clay films supported on a ZnSe plate, KBr disks, and two newer methods of detection that utilize little or no sample preparation, photoacoustic spectroscopy (PAS) and diffuse reflectance spectroscopy (DRIFT). The organo-clay complex used in this study is the interaction between dimethyl methylphosphonate (DMMP) and calcium saturated montmorillonite (SAz-1). Spectral quality, ease of sample preparation, and changes in the interpretation caused by sample preparation effects are discussed in this study.

EXPERIMENTAL SECTION

Two infrared spectrometers were used in this study. The thin-film and KBr studies were performed on a Nicolet MX-1 FT-IR equipped with a room-temperature deuterated triglycine sulfate (DTGS) detector. The thin-film and KBr disk data were collected at 1-cm^{-1} resolution at 160 scans. A Digilab FTS-65 spectrometer equipped with a room-temperature DTGS detector was used for the photoacoustic (PAS) and diffuse reflectance (DRIFT) studies. The Bio-Rad PAS accessory consisted of a sample cube, microphone, and associated electronics, was equipped with a KBr (potassium bromide) window, and was fitted with a 9-mm-deep sample cup. Carbon lamp black powder (Fisher Scientific Co., Fair Lawn, NJ) was used as the background reflectance material. The spectra were recorded at 2-cm^{-1} resolution with a measurement time of 8 min. The Spectra-Tech (Stamford, CT) diffuse reflectance accessory was used for the DRIFT studies. Diamond powder (Spectra-Tech) was used as the background reference material as well as the sample diluent to minimize any effects of cation exchange or hydration, which could possibly arise from the use of alkali halide diluent. The spectra were recorded at 1-cm^{-1} resolution, with a measurement time of 15 min. Details of the experimental procedures for PAS and DRIFT are discussed elsewhere (14). Although the spectra showed differences between instruments, as different methods of detection and detectors were involved, the spectra derived from each instrument were internally consistent.

Montmorillonite clay (SAz-1) was obtained from the Clay Minerals Society Repository, University of Missouri, Department of Geology. The SAz-1 montmorillonite was saturated with Ca^{2+} or K^+ . The clay was suspended in a 1 M CaCl_2 or KCl solution for a day. After saturation, the sample was washed repeatedly with deionized water, and dried at room temperature.

The dimethyl methylphosphonate was acquired from Alfa Chemicals (Danvers, MA). After FT-IR validation of its spectrum for positive identification (15), the DMMP was used without further purification.

* Author to whom correspondence should be addressed.

¹ Bio-Rad, Digilab Division, 237 Putnam Ave., Cambridge, MA 02139.

Reference DMMP spectra were acquired by each of the methods for comparison among the techniques. A KBr reference blank was prepared by dispersing the neat compound into powdered KBr pressed at 8 tons for 1 min to produce a KBr disk with interspersed DMMP. FT-IR analysis showed that the DMMP absorption bands correspond to those frequencies reported for neat smears of DMMP (15, 16). The DRIFT measurement was done by intimately mixing the DMMP in diamond powder, while the PAS measurement is of the DMMP in the PAS sample cell. In the case of the PAS spectrum of the DMMP, the P=O band appeared to be 4 cm⁻¹ lower than the same band from the KBr method. This effect may be due to the fact that PAS is also observing the vapor-phase DMMP in the PAS sample chamber in addition to the neat liquid form (17).

In all cases, the organo-clay complex was made by vapor deposition of the DMMP at 40 °C. The samples were separated and analyzed in triplicate by each method. The KBr disks were made from an approximate weight of 0.1 g of a mixture prepared as a 100:1 ratio of infrared grade KBr to organo-clay complex. The disks were examined immediately upon manufacture. Time study samples were stored under desiccation and were reexamined at intervals of 1, 3, 4, 6, and 10 days.

Unsupported thin clay films were made by deposition of the clay slurry onto a sheet of polystyrene. After air-drying at room temperature, the thin films were removed by bending the coated sheet across a sharp edge. Supported clay films were manufactured by depositing a clay-water slurry on a ZnSe plate and allowing the clay slurry to air-dry at room temperature. These procedures were followed by vapor deposition of DMMP.

Spectra of the Ca²⁺ and K⁺ saturated montmorillonite and the organo-clay complexes were collected in triplicate by using each of the five techniques mentioned previously. KBr disk spectra of these materials and the corresponding organo-clay complexes were obtained in order to compare the effect of the cation exchange of K⁺ for Ca²⁺ on the spectra.

RESULTS AND DISCUSSION

The model interaction, which is described in detail elsewhere (7, 12) has been determined with some certainty to proceed through d- π backbonding between the P=O moiety of DMMP and the interlamellar cation of the montmorillonite clay. This apparent mechanism is deduced from the observation of shifts in the vibrational bands of the DMMP molecule from their position in the FT-IR spectrum of the pure compound. Although all of the band shifts were considered to determine the interaction mechanism, for the purpose of this comparison, only the P=O band shift is considered. This band undergoes the largest shift, approximately 32 cm⁻¹ to lower frequencies for the Ca²⁺ saturated SAz-1 and 22 cm⁻¹ for the K⁺ saturated clay, and is slightly dependent upon detection technique. In order for a sample preparation effect to change the interpretation of the organo-clay sorption mechanism, this band shift would have to undergo a change in magnitude or direction. Possible sample preparation effects that might cause changes in the shift of the organo-mineral complex bands include exchange of K⁺ ions from the KBr for the interlamellar cations in the clay mineral. If a significant amount of cation exchange were to take place, the P=O band shift would be expected to decrease to about 22 cm⁻¹, the shift observed for K⁺ saturated SAz-1 montmorillonite. A similar decrease in band shift could be expected if the interaction were to proceed through a hydration sphere. Another change that could affect the interpretation would include a change in the amount of the interlamellar water, inclusive of the cationic hydration sphere. This could be observed by a change in the magnitude of the OH stretch region around 3600 cm⁻¹, as well as in the magnitude of the P=O shift.

After the organo-mineral complexes were prepared, the position of the P=O band was determined. The band shifts were calculated from the P=O band position of the organo-clay complex compared against that of the DMMP found from the same instrumental technique, as described above.

Table I. P=O Band Positions and Shifts for Each of the Five Sample Preparation Techniques or Detection Methods

method	P=O position, ^a cm ⁻¹		
	DMMP	DMMP-clay complex	shift, cm ⁻¹
KBr disk	1245 ^a	1213	32
unsupported thin film	1245 ^a	1211	34
supported thin film	1245 ^a	1212	33
FT-IR/PAS	1241 ^b	1210	31
	1245 ^a		35
FT-IR/DRIFT	1243 ^c	1211	32
KBr disk of K ⁺ -SAz-DMMP	1245 ^a	1223	22

^a Location of P=O band of DMMP smeared on KBr disk.

^b Location of P=O band obtained with PAS cell. As this results in a vapor spectrum, this is also compared against neat DMMP.

^c Location of P=O band obtained with DRIFT cell. ^d FT-IR/PAS wavenumber assignments were 2-cm⁻¹ resolution; all others were 1-cm⁻¹ resolution. Wavenumbers listed refer to the highest datum point.

The positions and related shifts of the P=O band for each technique have been listed in Table I. It is apparent from these results that the magnitude of the shift of the P=O band in the Ca²⁺-clay-DMMP complex is in all cases 32.4 \pm 3 cm⁻¹ compared with a shift of 22 cm⁻¹ for the K⁺-clay-DMMP complex. The high value was obtained from the unsupported thin clay film and diffuse reflectance methods while the low value was obtained by PAS, measured from the PAS position of neat DMMP. However, it is well-known that PAS tends to enhance the spectra of gases and otherwise weak bands. The PAS spectrum of neat DMMP is mainly due to the vapor phase of the sample in the PAS cell rather than the condensed phase (12, 17). Therefore, the P=O band shift given in Table I has also been compared against the position of neat DMMP smeared on a KBr disk, as it would be inappropriate to compare the complexed DMMP band position with that of vapor-phase DMMP. It is apparent from the wavenumber shifts that all of the sample preparation techniques provide equivalent data, enabling the identical interpretation to be made from each of the techniques.

Of the sample preparation techniques studied, the KBr disk technique offers the greatest potential to affect the shift of the P=O band through the reaction with the KBr supporting material, due to the intimate contact between the sample and the support. Therefore, the organo-clay complex prepared as the KBr disk was subjected to a time study where the sample was sampled periodically over a 10-day period. It can be seen in Figure 1 that the location of the P=O band did not change during the period of the study. A gradual loss of water in the sample, with time, was seen to take place through the observation of the decrease in the intensity of the O-H stretching region around 3300 cm⁻¹, indicating a slow loss of water associated with the clay mineral by the KBr or desiccant. Whatever the cause of the reaction, it is quite slow compared to the time required to obtain a spectrum. Thus, spectra obtained quickly are unlikely to be affected by dehydration effects. Presumably, most investigators would be able to obtain a spectrum of the sample before this effect became significant.

Figure 2 shows representative spectra obtained from the unsupported thin clay film, the clay film supported on a ZnSe window, and the KBr disk technique. The unsupported clay film shown was the thinnest that could be made self-supporting, but was still thick enough to almost completely absorb the IR energy below about 1100 cm⁻¹. Due to this effect, the P=O band is nearly saturated, making the determination of the peak position difficult. The spectrum of the supported film is thin enough that saturation of the in-plane Si-O stretch

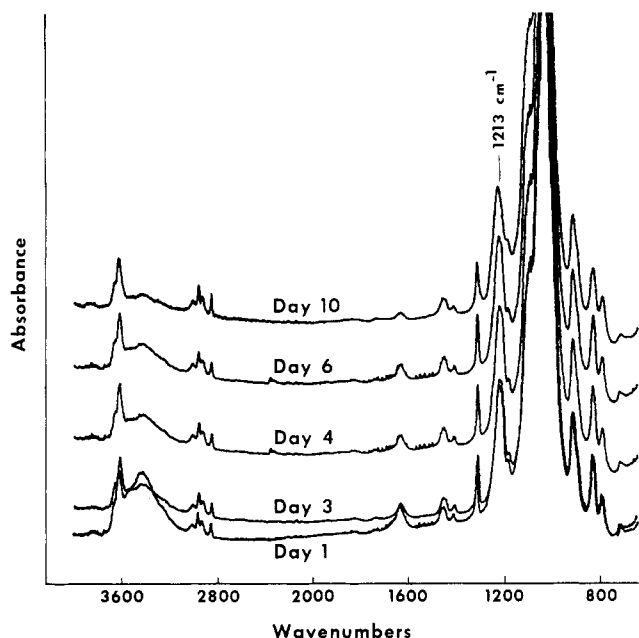


Figure 1. FT-IR spectra of DMMP-Ca montmorillonite in a KBr disk taken with time.

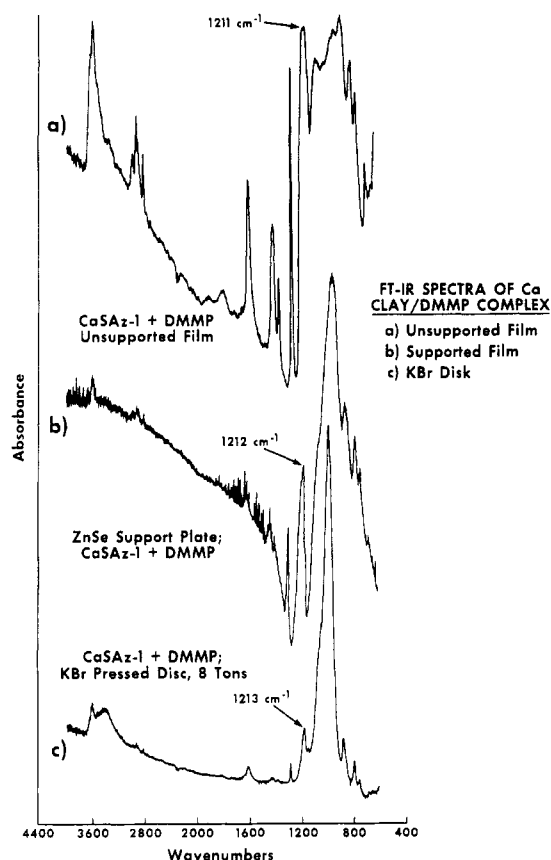


Figure 2. FT-IR spectra of DMMP-Ca montmorillonite complex obtained by differing methods: a, unsupported film; b, thin film supported on a ZnSe disk; c, in a KBr disk.

at $\sim 1100\text{ cm}^{-1}$ is not significant. However, even after desiccation, the spectrum around 1650 cm^{-1} is obscured by the rotational spectrum of water vapor, indicative of free water desorbing from the surfaces of the clay mineral. As sufficient time was allowed for nitrogen to purge the sample compartment, the water vapor in the spectrum is assumed not to come from the atmosphere. The OH stretch region is also obscured by these vapor bands and exhibits very low intensity when compared to the KBr disk spectrum. Both of the thin clay

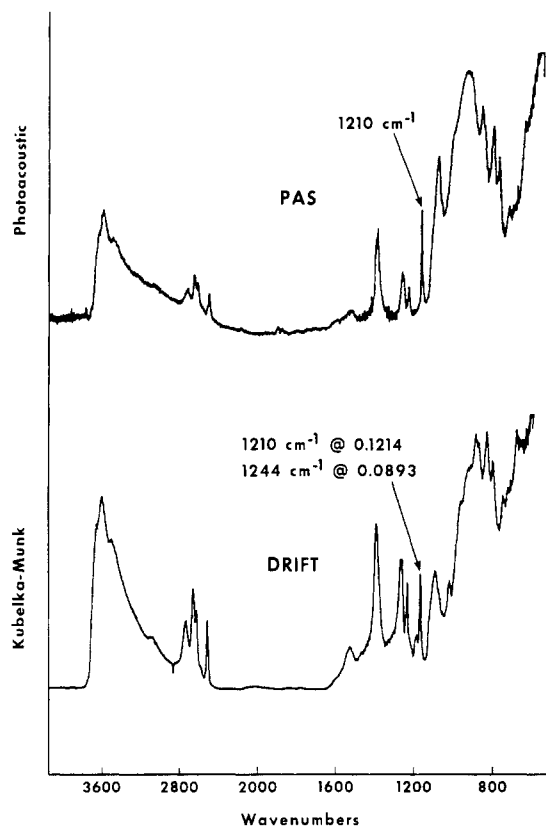


Figure 3. FT-IR spectra of the DMMP-Ca montmorillonite complex obtained by PAS and diffuse reflectance (DRIFT).

film samples required overnight drying, while the KBr disk sample was run immediately upon preparation. Of these three traditional techniques, the KBr disk method provided the most reproducible spectra due to the ability to precisely control the amount of the organo-clay complex in the sample examined.

Figure 3 illustrates spectra of the DMMP-clay complex obtained by PAS and diffuse reflectance. These techniques require little sample preparation and provide reproducible spectra. Further, it has been shown that PAS will provide equivalent information for this sorption mechanism (12). These spectra are similar to those produced by the methods described above but differ in the mechanism of energy detected. As photoacoustic spectroscopy is much more sensitive to gases than the other methods (14), the fine structure of water vapor, outgassed into the PAS cell during the data collection period, is observed in the OH stretch region at around 3300 cm^{-1} and the HOH bending regions around 1635 cm^{-1} . Although these spectra were not spectrally subtracted from spectra of the pure mineral phase for this study, this practice can be used to enhance the spectrum of the organo-mineral complex. Rockley and Rockley (12), using this method, reported that PAS spectra underwent spectral subtraction more reliably than spectra from the KBr disk method.

The diffuse reflectance spectra were also valuable in determining surface interactions not detected in the other methods. They showed that although the major portion of the P=O band was shifted to about 1210 cm^{-1} , a small P=O band exists at around 1244 cm^{-1} possibly due to the presence of uncomplexed DMMP on the surface of the clay mineral.

CONCLUSIONS

The interpretation of a particular sorption interaction mechanism between an organophosphonate and montmorillonite, a swelling clay mineral, is independent of the sample preparation technique or instrumental detection method used to obtain a spectrum. Within the detection ability of FT-IR,

the use of KBr as a supporting substrate did not influence the interpretation of this sorption interaction over a period of 10 days.

Of the five techniques, the most satisfactory in terms of spectral quality and ease of use were the PAS and diffuse reflectance methods. As with the thin-film techniques, these methods absolutely ensure that no sample/substrate interactions can take place. Interactions severe enough to change the interpretation of the sorption mechanism appear to be unlikely with even the KBr disk method if the samples are analyzed in a timely fashion. These techniques also provide information concerning the surface of the samples, such as the presence of unadsorbed organic compound as evidenced by diffuse reflectance.

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Enhanced Analysis of Poly(ethylene glycols) and Peptides Using Thermospray Mass Spectrometry

Saul W. Fink and Royal B. Freas*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

The effects of a needle-tip repeller electrode on thermospray mass spectra of poly(ethylene glycols) and peptide samples have been studied. A significant increase in ion current was observed for increased repeller potentials in the low-mass region (m/z 300 to m/z 1100) and the high-mass region (m/z 1100 to m/z 1900). The change in ion current is due to a change in ion extraction efficiency because of increased ion diffusion rates. The amount of peptide sample needed for direct injection studies was decreased 1 to 2 orders of magnitude by using an ion source with both a needle-tip repeller electrode and a restricted vaporizer probe tip.

INTRODUCTION

Liquid chromatography/mass spectrometry (LC/MS) facilitates analyses of polar, nonvolatile, and thermally labile compounds. The thermospray technique has proven to be a useful and practical methodology as an LC/MS interface (1-4). Thermospray is an ionization technique as well as an interface for LC/MS (5-7). Ions can be generated with and without supplemental ionization (5). Thermospray ionization (without supplemental ionization) is a "soft" ionization process. That is, the mass spectra exhibit abundant molecular ions and little or no fragmentation. Therefore, molecular weight information of a sample can be obtained, although structural information is often unavailable.

Thermospray and other soft ionization techniques have expedited the use of mass spectrometry to analyze biomolecules (8). Rapid peptide sequencing with sensitive detection using thermospray mass spectrometry has been reported using on-line column enzymatic hydrolysis by immobilized car-

boxypeptidase Y (9). Hemoglobin variants have been identified in peptide mapping studies by using thermospray mass spectrometry (10). Other studies of peptides and proteins using thermospray have been conducted (11).

The thermospray ion source has been modified recently to increase the versatility and sensitivity of the technique. These modifications include a smaller desolvation chamber, an auxiliary tip heater, and a repeller electrode inside the ion source block (12). Several repeller electrode geometries have been designed and studied (12-18). A blunt-tip repeller electrode has been used to induce fragmentation of several compounds (12-15). A needle-tip repeller electrode has been shown to improve high mass sensitivity (greater than m/z 1100) (16-18).

We have constructed a needle-tip repeller electrode to study the effect it has on the thermospray mass spectra of poly(ethylene glycol) (m/z 300 to m/z 1900) and peptide and protein samples. In addition, a smaller orifice for the vaporizer probe tip has been used to increase sensitivity. The smaller orifice produces smaller droplets, which increases ion abundances by increasing ion evaporation (12, 16-18). By use of the needle-tip repeller electrode and a smaller vaporizer probe tip orifice, the detection limits for the peptide samples studied on our instrument have been lowered. We discuss the results of these improvements in this paper.

EXPERIMENTAL SECTION

A thermospray ion source (Vestec Thermospray LC-MS Model 721A) was used to interface a liquid chromatographic gradient system (Scientific Systems, Inc., Model 230) to a quadrupole mass spectrometer (Hewlett-Packard Model 5988A). The poly(ethylene glycol) (PEG) samples were introduced into the mass spectrometer