Specular Reflection and Diffuse Reflectance Spectroscopy of Soils

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Studies on the occurrence and effects of specular reflection in mid-infrared spectra of soils have shown that distortions due to specular reflection occur for both organic (humic acid) and non-organic fractions (carbonates, silica, ashed fraction of soil). The results explain why the spectra of $CaCO_3$ in limed soils do not match published spectra and offer an explanation as to why the presence of inorganic C interferes with the development of calibrations for organic C. These results may also have implications for the use of mid-infrared spectra for quantitative and qualitative analysis of soils. For example, libraries of spectra collected by means other than diffuse reflectance would be largely useless for comparing mineral spectra to soil spectra. To obtain the best results with forages and grains, it is necessary to develop separate calibrations for different products, but this has not seemed to be a problem for diverse sets of soil samples with C contents of 0 to 5%. Mid-infrared calibrations have also appeared to be more robust than the corresponding near-infrared calibrations in that fewer outliers are found. However, the results discussed here indicate that at least for some soil types (e.g., large differences in mineralogy or C contents), separate calibrations may be necessary.

Index Headings: **Mid-infrared; Near-infrared; Carbonates; Soils; Specular reflection.**

INTRODUCTION

It has long been held that diffuse reflectance infrared spectroscopy (DRIFTS) in the 400 to 4000 cm^{-1} spectral region requires the dilution of samples with KBr, or similar materials, or that the sub-region of the mid-infrared (MIR) spectra used must be carefully considered[1] in order to avoid spectral distortions caused by specular reflection.[2,3] This has been one of the advantages cited for near-infrared (NIR) spectroscopy in the 25 000 to 4000 cm^{-1} spectral region where such dilution is not necessary for quantitative analysis. However, recent work on materials ranging from forages[4] and grains[5] to soils[6–8] have shown that sample dilution is not necessary for quantitative analysis of these materials using DRIFTS. It should also be noted that in these efforts, which employed partial least squares regression (PLSR), the entire MIR spectra have been used, i.e., spectral sub-regions were not chosen to avoid artifacts due to specular reflection. With forages, it has been found that while specular reflection does cause spectral distortions in non-diluted samples, the distortions are generally small and are either ignored or compensated for during the development of quantitative calibrations using methods such as PLSR.[9] However, it was also found that such distor-
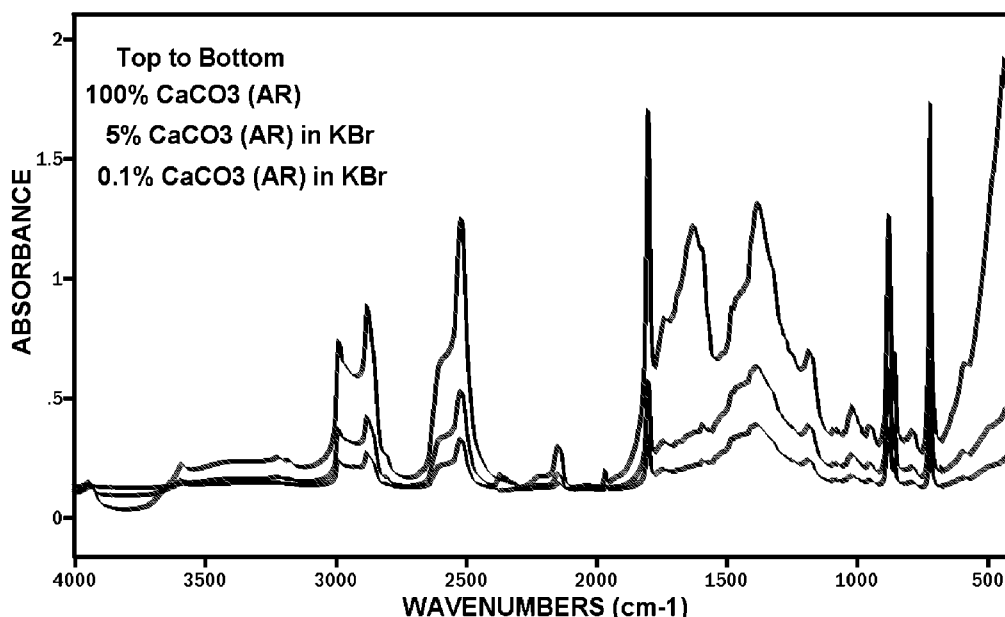

FIG. 1. Mid-infrared diffuse reflectance spectra of ground, neat, reagent-grade calcium carbonate, 5% and 0.1% diluted in KBr.
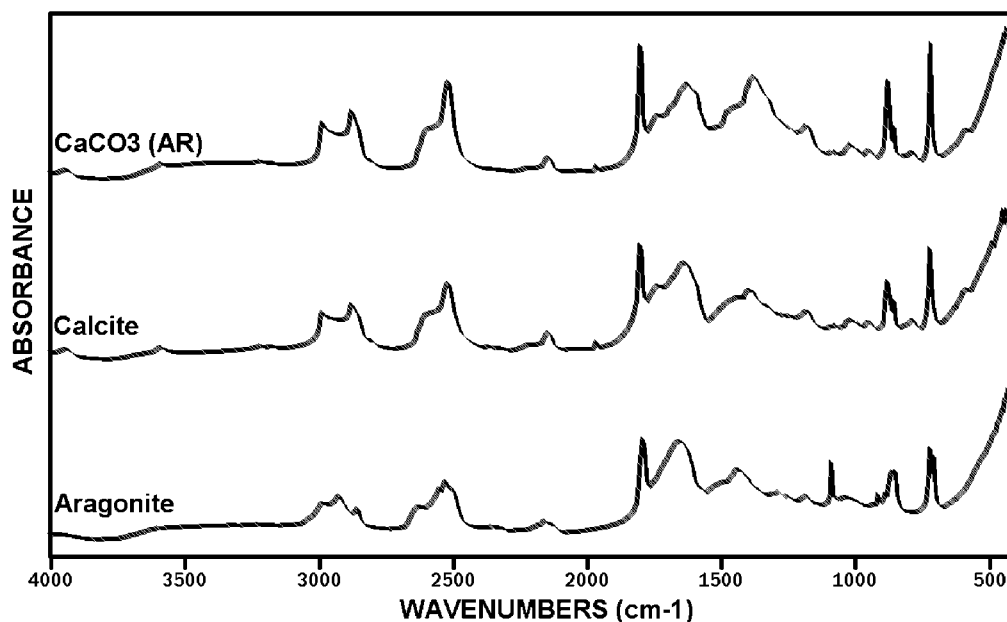
FIG. 2. Mid-infrared diffuse reflectance spectra of ground, neat, reagent-grade calcium carbonate and ground, neat calcite and aragonite purchased from a local rock shop (each scaled to window slot).

tions were more intense for humic acid than for many of the components of forages such as cellulose or proteins,[9] implying greater potential problems for soil calibrations. Tremblay and Gagné were able to quantitate humic substances and organic matter in sediments using DRIFTS on non-diluted samples, but they carefully chose the spectral sub-region they used.[1] Also, in soils, the inorganic C can exist in equal or greater concentration than the organic C, presenting an interference that is not pertinent to forages or grains. In earlier work, it was found that the presence of carbonate minerals in soils interfered with the development of PLSR calibrations for organic soil C when using MIR spectra, but not when using NIR spectra. This was despite the fact

that the MIR based calibrations for organic C outperformed the NIR based calibrations.[7] The objective of this study was to examine the effects of specular reflection on the MIR and NIR spectra of calcium carbonates mixed with soils and the possibility for their interference in the determination of organic C in soils.

MATERIALS AND METHODS

Samples. Samples were obtained from various sources including reagent grade calcium carbonate (Fischer Scientific), mineral specimens purchased at local rock shops, and a soil collected from Garrett County, Maryland. In addition, calcite and dolomite mineral samples
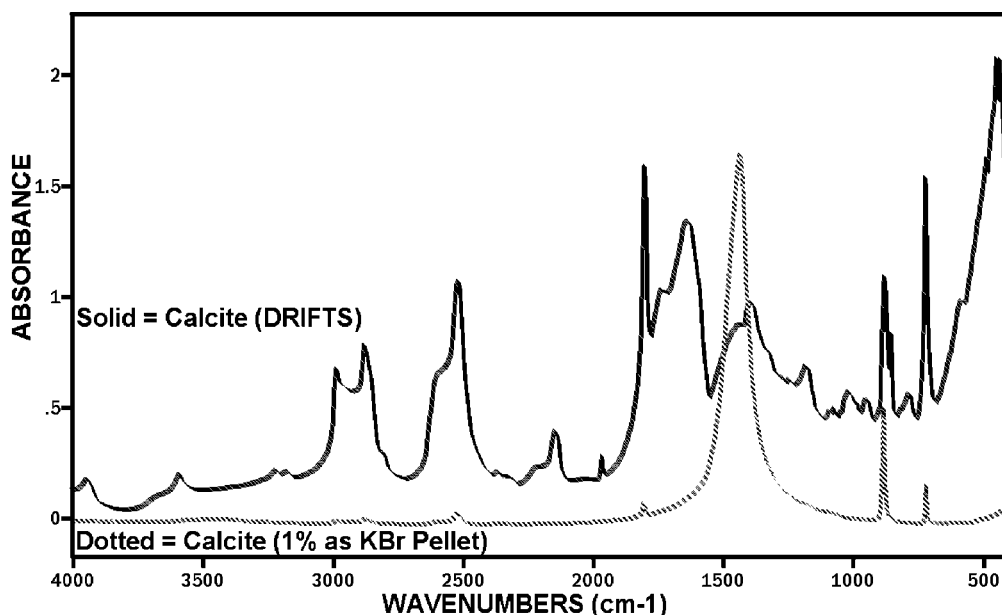

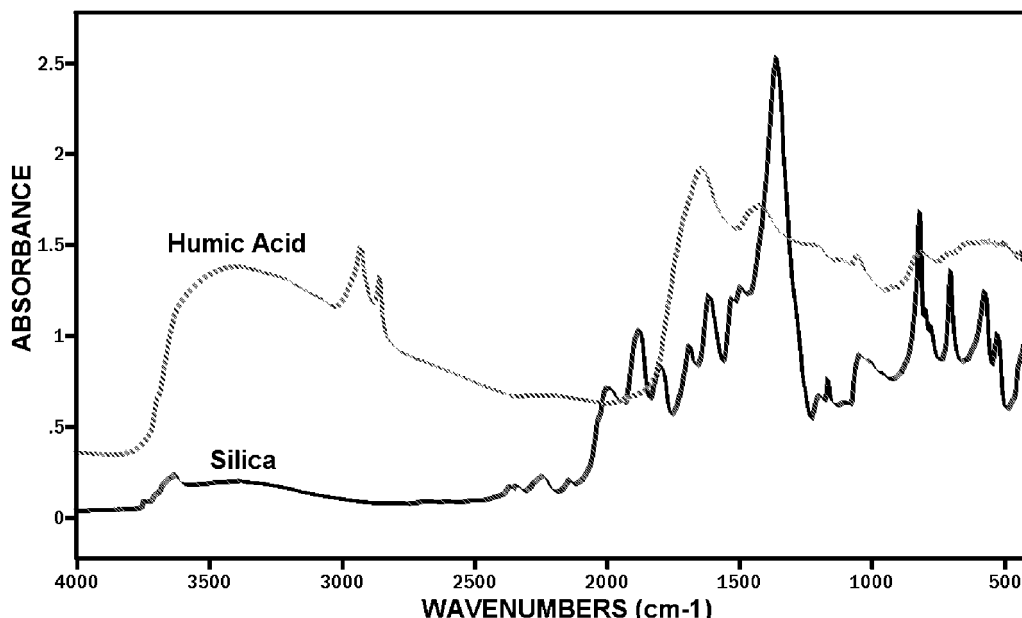FIG. 3. Mid-infrared diffuse reflectance spectra of ground, neat calcite and 1% calcite as a KBr pellet.

FIG. 4.   Mid-infrared diffuse reflectance spectra of ground, neat silica and humic acid.

were purchased from Ward's Natural Science Establishment, Inc. The calcite (Ward's 49-5860) was collected from Santa Eulalia, Chihuahua, Mexico, and the dolomite (Ward's 49 E 5871) comes from Butte, Montana. The mineral samples were finely ground with a mortar and pestle after removing any obvious contaminants; the purity of the oven-dried, ground samples was estimated at 92–94% based on measurement of CO_2 evolution in a pressure calcimeter;[10] the identity of the remaining mass is unknown. Silica (silica sand) was obtained from Fischer Scientific and humic acid from Sigma Scientific. Spectroscopic-grade KBr was used for all dilutions.

Mid- and Near-Infrared Spectroscopy. All spectra were acquired using a DIGILAB (DIGILAB USA, Ran-

dolph, MA, 02368) FTS 7000 Fourier Transform spectrometer equipped with a Peltier cooled DTGS detector, KBr beam splitter and Pike Technologies (Pike Technologies, Madison, WI 53719) AutoDiff autosampler equipped with aluminum-coated mirrors. Samples were scanned from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution with 64 coadded scans per sample unless otherwise noted. Samples were similarly scanned on the same instrument in the near-infrared from 10 000 to 4000 cm^{-1} at 4 cm^{-1} resolution with 64 coadded scans per sample, but using a quartz beam splitter and liquid N_2 cooled InSb detector. Spectra were converted to Grams format (.spc file) for processing using GRAMS/386 for Windows (Galactic Industries, Corp., Salem, NH 03079).
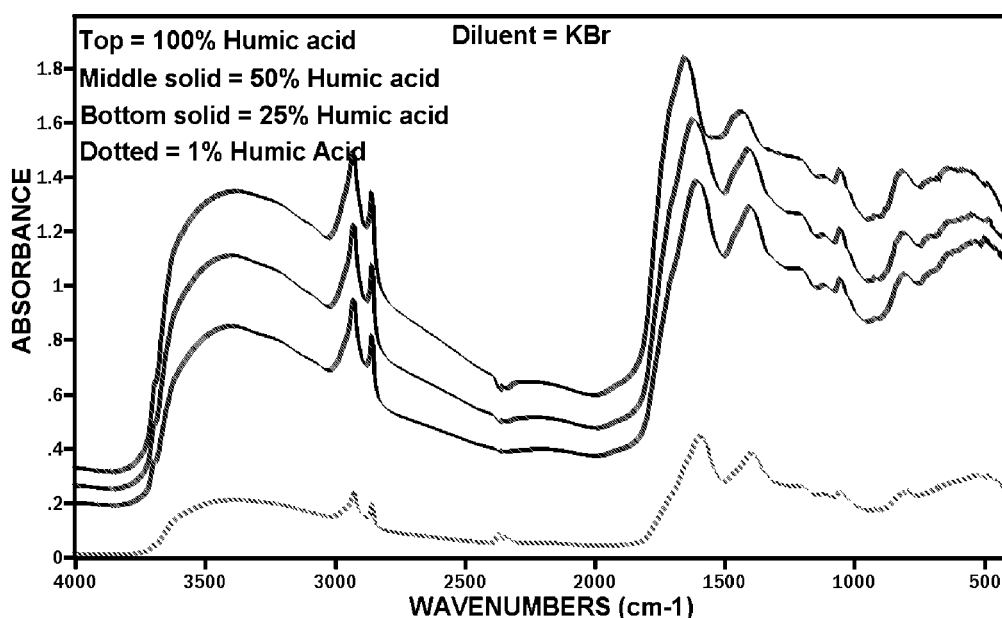

FIG. 5.   Mid-infrared diffuse reflectance spectra of humic acid at concentrations of 100%, 50%, 25%, and 1% (top to bottom) in KBr (all materials ground).
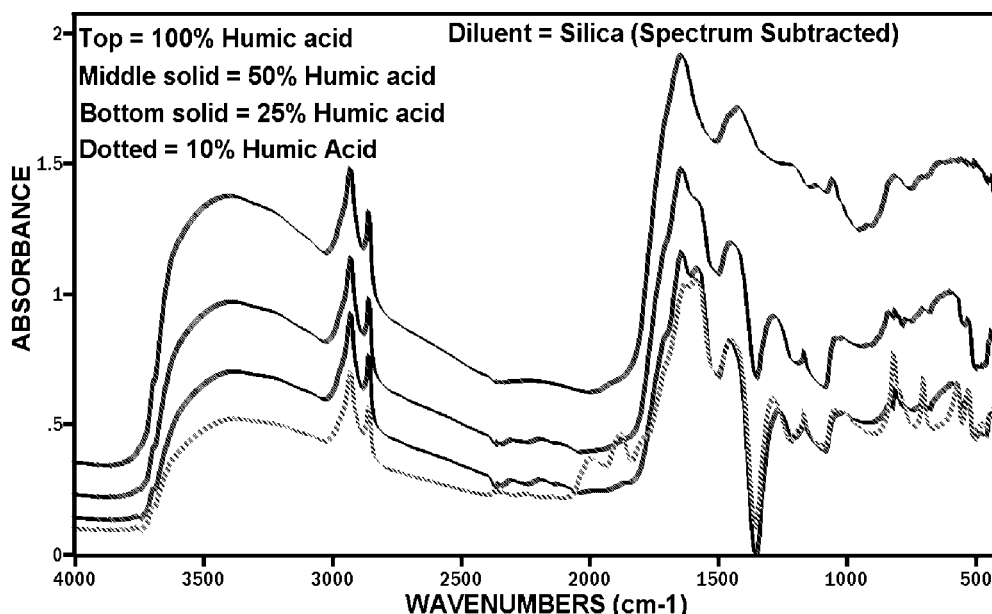
FIG. 6. Mid-infrared diffuse reflectance spectra of humic acid at concentrations of 100%, 50%, 25%, and 10% (top to bottom) in silica after subtraction of silica spectrum (all materials ground).

RESULTS AND DISCUSSION

The MIR spectra of 100% (neat) $CaCO_3$ and 0.1% $CaCO_3$ in KBr are shown in Fig. 1. As shown, the two spectra are quite different, particularly in the region from 1750 to 1550 cm^{-1} and again in the region from 550 to 400 cm^{-1}. Although the spectra of different forms of inorganic carbonates (Fig. 2) show some differences, the differences among forms are nowhere near as great as those caused by specular reflection in neat samples. As demonstrated in Fig. 3, the method by which the spectrum is obtained can also greatly influence the spectral signature, with transmission spectra having vastly different signatures than those obtained using diffuse reflectance.

As a result of the observation of differences in spectral signatures for the carbonate samples, other likely components of soils were examined to better understand exactly when specular reflection might cause problems in the development of quantitative calibrations for soil carbon content and forms. The spectra of neat silica (Silica sand from Fischer Scientific) and humic acid (Sigma Scientific) are shown in Fig. 4. These two components were chosen for study to represent major inorganic and organic components of many soils. As shown, the two have very different spectra. In Fig. 5, the spectrum of humic acid at various dilutions in KBr is shown. As shown, spectral distortions occur as the concentration increases, particularly in the bands between 1400 and 1700 cm^{-1}. In Fig.
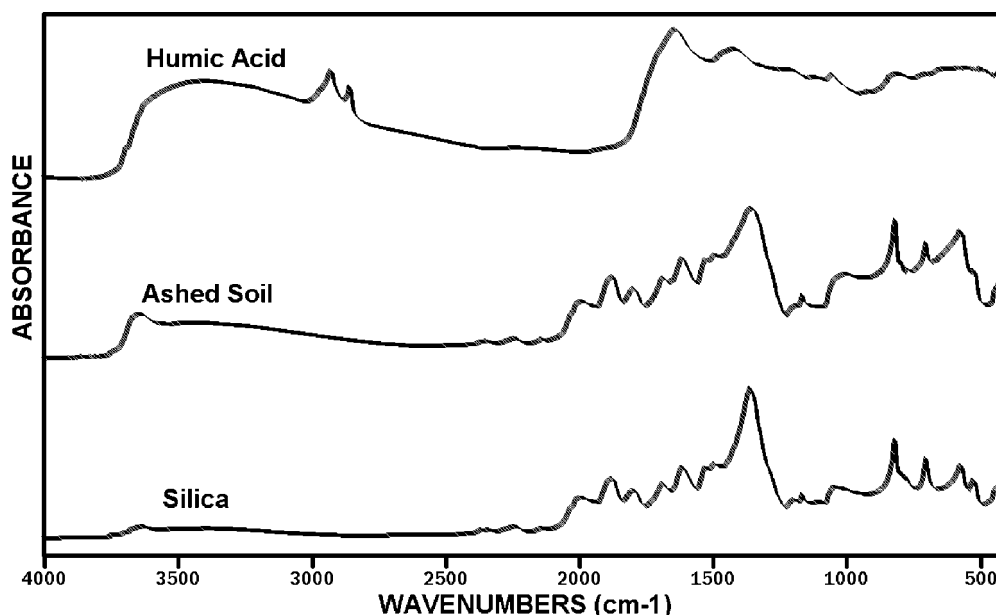

FIG. 7. Mid-infrared diffuse reflectance spectra of ground, neat silica, ashed Garrett County soil, and humic acid.
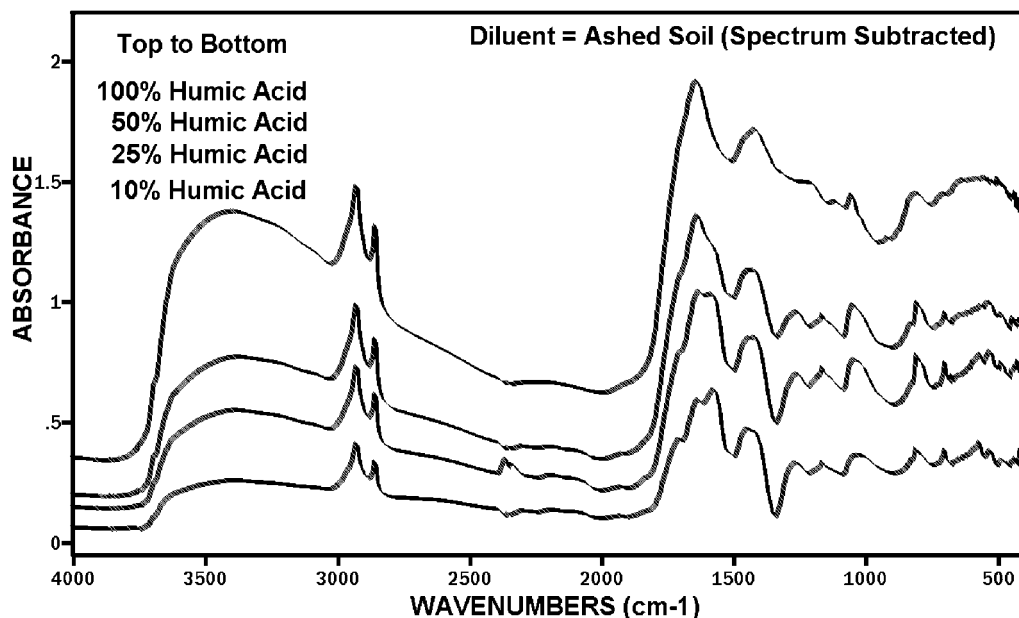
FIG. 8.   Mid-infrared diffuse reflectance spectra of humic acid at concentrations of 100%, 50%, 25%, and 10% (top to bottom) in ashed Garrett County soil after subtraction of soil spectrum (all materials ground).

6, the spectra of neat humic acid and humic acid at concentrations of 10, 25, and 50% by weight in silica are shown (the diluent spectrum of silica was subtracted out using GRAMS software). The results show a large derivative-like artifact in the humic acid spectra at ~1350 cm^{-1}. This is very close to the peak at 1360 found in silica (Fig. 4), thus indicating over-subtraction of the silica spectrum. However, the subtraction factors used did remove the silica bands found at ~1800, 1900, and 2000 cm^{-1}, without creating negative artifacts, for all but the 10% humic acid mixture. Also, with the subtraction factors used, the humic acid spectra for the 25 and 50% mixtures otherwise resemble the spectrum for neat humic acid. While it is difficult to say from these data alone if

the humic acid spectrum is changing with concentration or if it is the silica spectrum that changes, or more likely both, the fact remains that the spectral signatures available for quantitative analysis are changing in ways not consistent with simple dilution.

Soils consist of more than just silica as the inorganic fraction, as shown in Fig. 7. Note that while the three bands at 2000 to 1800 cm^{-1} match quite well for the silica and ashed soil sample, the same is not true elsewhere, with differences at 3750–3550, 1080–950, and 650–550 cm^{-1}. Even the large silica band at 1360 cm^{-1} does not appear to be in proportion to the three previously discussed bands (ratio of band at 1360 to band at 1880 ~2 to 1 for ashed soil and ~1.4 to 1 for silica), indicating
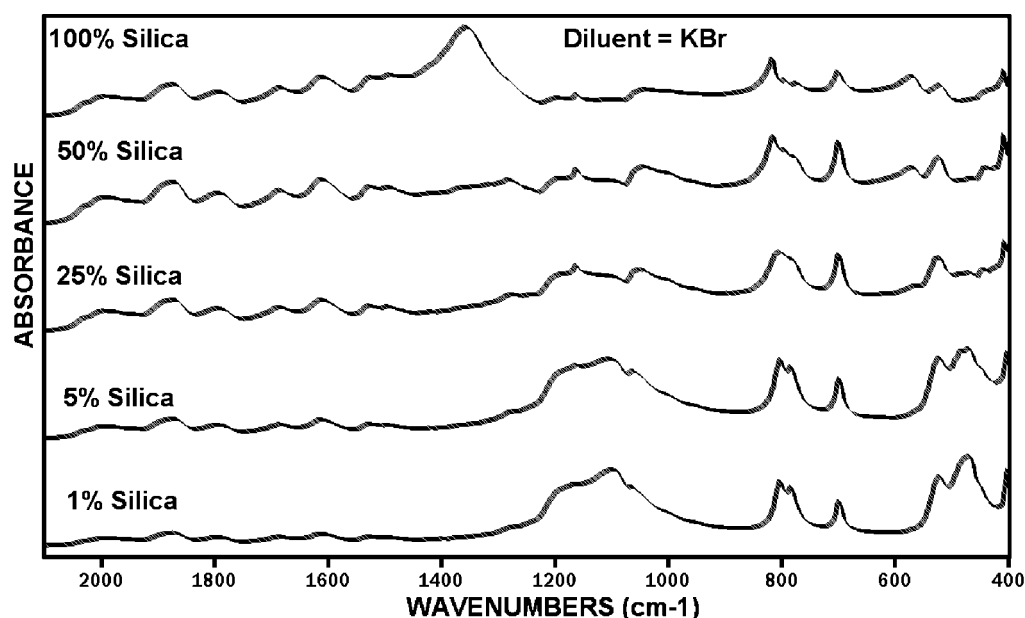

FIG. 9.   Partial mid-infrared diffuse reflectance spectra of silica at concentrations of 100%, 50%, 25%, 5%, and 1% (top to bottom) in KBr (all materials ground).
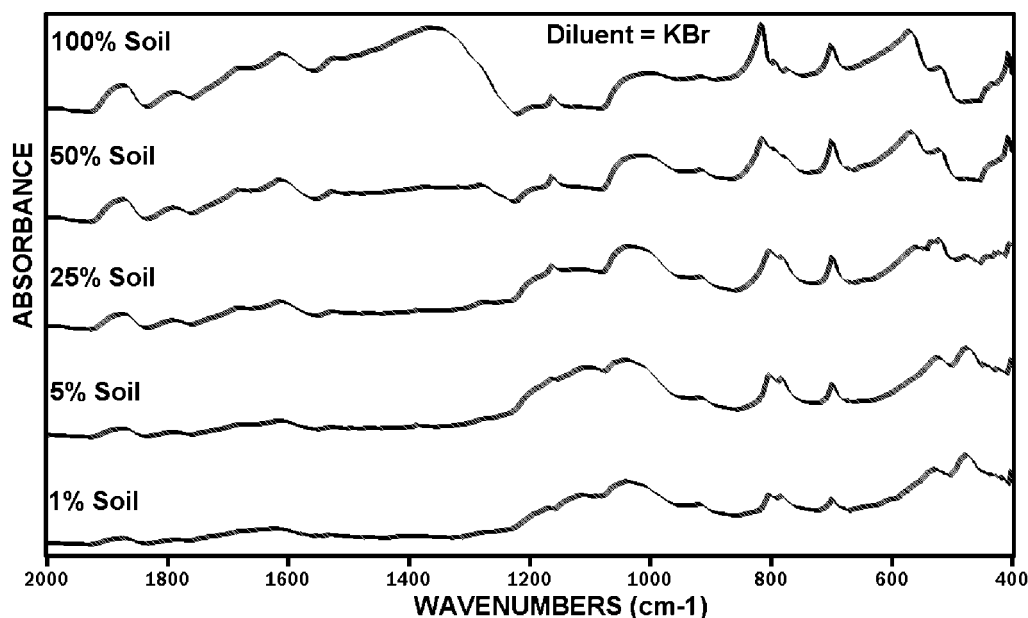
FIG. 10. Partial mid-infrared diffuse reflectance spectra of Garrett County soil at concentrations of 100%, 50%, 25%, 5%, and 1% (top to bottom) in KBr (all materials ground).

the possibility that specular reflection alters the silica bands depending on the degree to which the silica is diluted by other inorganic components in the soil. Figure 8 shows that humic acid diluted in an ashed soil behaves the same as previously seen for dilution in pure silica. In Fig. 9, partial spectra of silica diluted to concentrations of 1, 5, 25, and 50% with KBr and 100% silica are shown. These spectra demonstrate that the spectrum of silica undergoes large changes at 1360 cm^{-1} with dilution. Even 75% silica in KBr (data not presented) looked largely like the 50% spectrum at 1360 cm^{-1}. However, careful examination shows that changes elsewhere show a continuum with slight but discernable differences even between 1 and 5% silica in KBr. As previously published

work[8] has shown that humic acid diluted with KBr shows changes with concentration due to specular reflection, it is apparent that the spectral signatures of both the organic and inorganic components undergo changes with concentration. This can be seen in Fig. 10 for a soil diluted with KBr. Careful examination of the KBr diluted soil spectra shows a continuum of changes in virtually all areas of the spectra shown. Even when peak shapes are relatively constant, the relative intensity of one peak or region continuously changes relative to other regions. Finally, in Fig. 11, the spectra of reagent-grade CaCO$_3$ (1% in KBr) and 1, 10, 20, and 50% diluted with soil are presented (spectra shown are after subtraction of the soil spectrum). Assuming no spectral changes due to specular reflection,
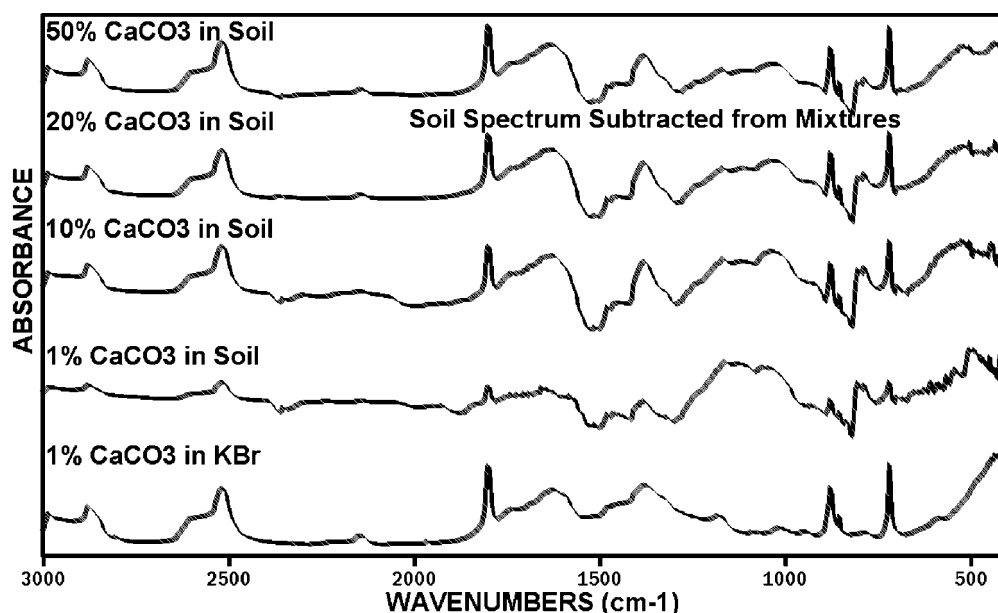

FIG. 11. Partial mid-infrared diffuse reflectance spectra of calcium carbonate at concentrations of 50%, 20%, 10%, and 1% (top to bottom, after subtraction of the soil spectrum) in ashed Garrett County soil and 1% in KBr.
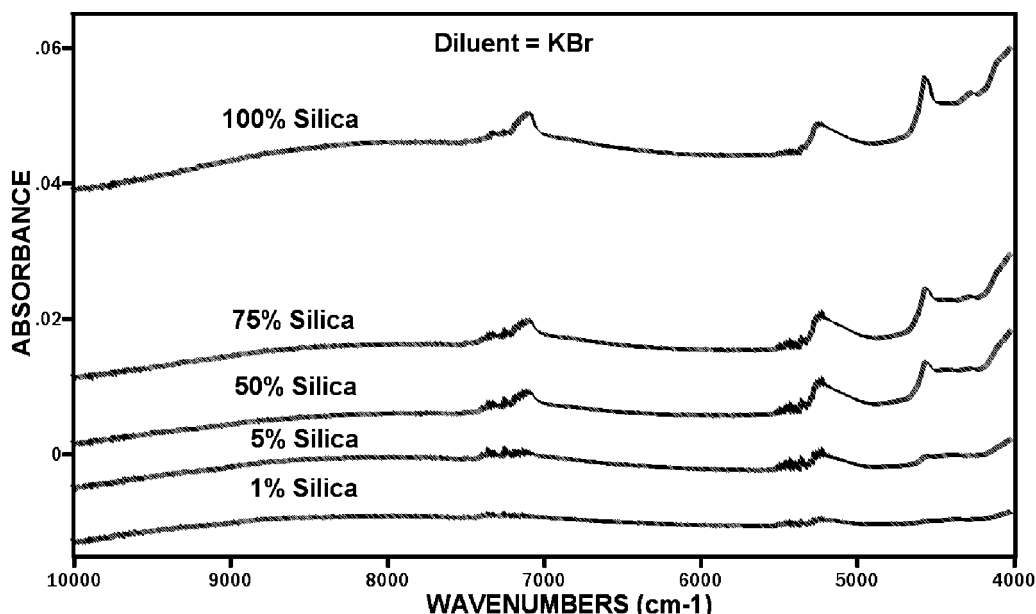
FIG. 12. Near-infrared spectra of silica in KBr (all materials ground).

the CaCO$_3$ spectra shown in Fig. 11 should all look alike, e.g., resembling the 1% CaCO$_3$ in KBr, but they obviously do not. While the CaCO$_3$ spectra at dilutions of 10 to 50% are similar to one another, there are differences in the spectra in the region from 1200 to 1000 cm^{-1} compared to the KBr diluted sample. Also, the 1% CaCO$_3$ in soil, while resembling the other CaCO$_3$ spectra in the 1200 to 1000 cm^{-1} region and in the 800 to 750 cm^{-1} region, shows marked differences at 1800, 950, and 700 cm^{-1}.

While these studies were initiated as a result of comparing spectra of soils where lime had been added (data not presented) to textbook spectra of CaCO$_3$, the results discussed may also help explain calibration results found for carbonate-containing soils that had been acidified.[7] In

that study, it was found that the presence of carbonates reduced the accuracy of calibrations for organic C when MIR spectra were used, i.e., calibrations for organic C were better for samples acidified to remove the carbonates. However, the same was not true for calibrations using NIR spectra, i.e., calibrations for organic C were about the same for the acidified and non-acidified samples. This then brings up the question of whether there are any similar effects for NIR spectra.

As shown in Fig. 12, the spectra of silica in KBr is, with the exception of becoming noisy, the same at all dilution concentrations, indicating no specular reflection effects. As shown in Fig. 13, silica absorbs very little in the NIR compared to organic matter such as humic acid, and thus any effects on silica spectra would be very lim-
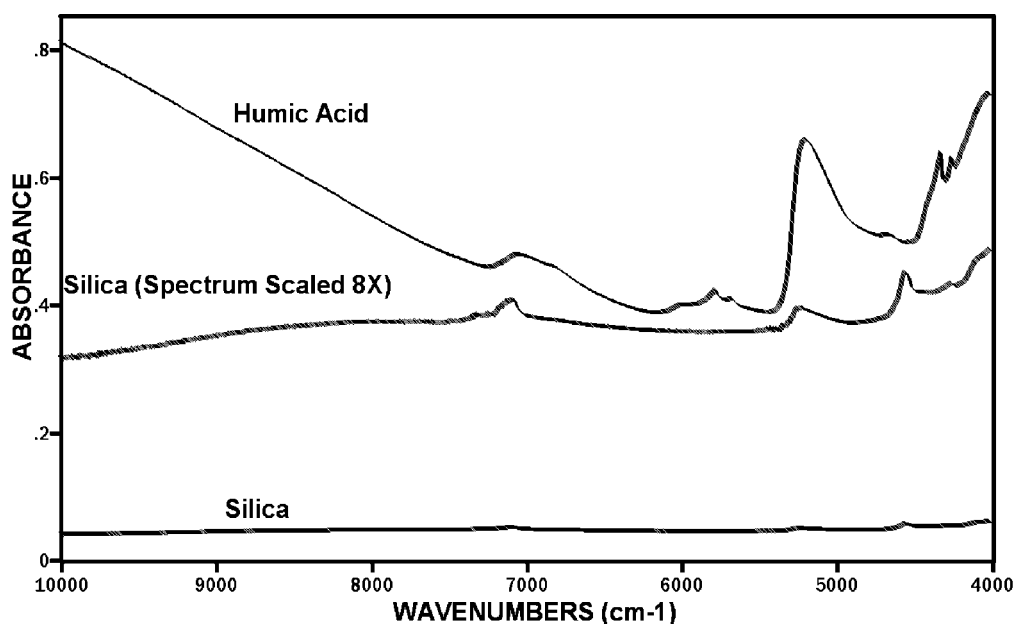

FIG. 13. Near-infrared spectra of ground, neat silica and humic acid with silica spectra also displayed with 8× scaling.
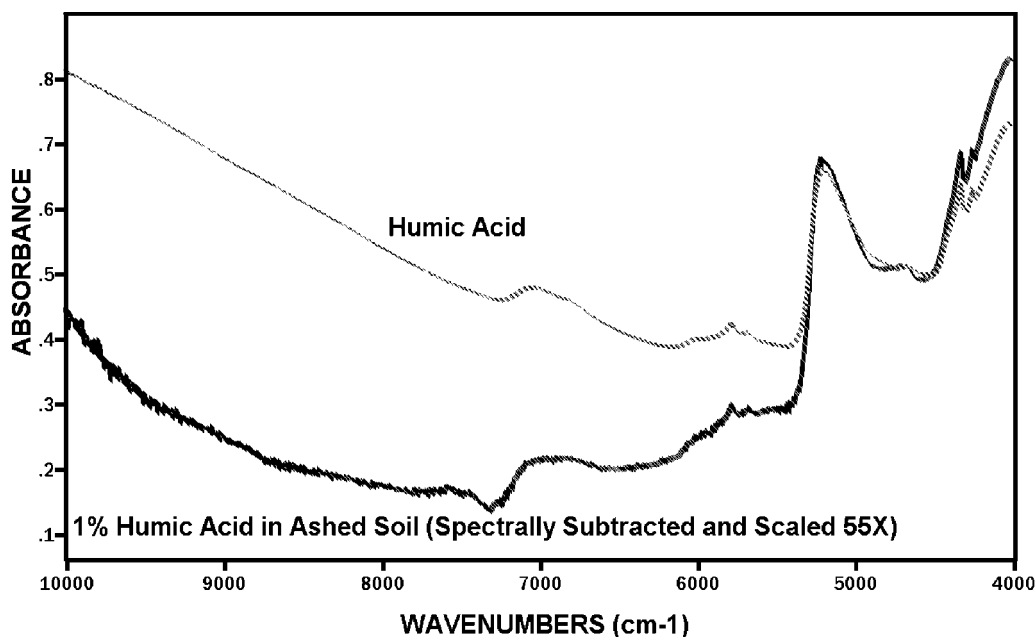
FIG. 14. Near-infrared spectra of humic acid and 1% humic acid in ashed Garrett County soil after subtraction of soil spectrum.

ited in their effects on calibrations. Also, as seen in Fig. 14, the spectra of humic acid and 1% humic acid in soil are close to identical. Thus, the effects of specular reflection seen with the MIR spectra are not present to any significant degree in NIR spectra, and are in agreement with the effects seen in calibrations.

IMPLICATIONS

While the results demonstrated explain why the spectrum of $CaCO_3$ in limed soils did not match that of published spectra and also offer an explanation as to why the presence of inorganic C interferes with the development of calibrations for organic C in soil for the MIR but not for the NIR, they also have far-reaching implications for the use of MIR spectra for quantitative and qualitative analysis of soils. For example, as demonstrated by the spectra in Fig. 3, commercial libraries of spectra of minerals collected by means other than diffuse reflectance would be largely useless for comparing mineral spectra to soil spectra. Even libraries obtained by diffuse reflectance might need to have spectra of the same material at various concentrations in KBr to be of maximum use (see silica spectra in Fig. 9). Also, correlations of spectra in the MIR to NIR spectra (two-dimensional correlation) have been used with forages to help interpret the NIR spectra.[11,12] The question is: how would the presence of a mineral component such as $CaCO_3$, at both high and low concentrations (0.1% and 5 or 10%), affect the correlation plots and the spectral interpretation that follows? Finally, in a previous study (data not presented), it was found that MIR calibrations for organic C fit a quadratic function very well, with high organic C samples being consistently under-predicted by a linear fit, e.g., the calibration was nonlinear. One explanation for this would be that the organic C in samples with high organic C levels has a different spectral signature than the organic C in samples with low

organic C levels, as in the results discussed for humic acid (Figs. 5, 6, and 8), making it impossible for linear PLSR to develop proper calibrations.

With forages and grains it is necessary to develop separate calibrations for different products in order to obtain the best results. With soils, this has not seemed to be a problem for many diverse sets of samples with C contents in a range of 0 to 5%, making it appear that the development of calibrations for soils might be easier than for products such as forages.[7,8] Mid-infrared calibrations have also appeared to be more robust than the corresponding NIR calibrations in that fewer outliers have been found even when using the same samples and analyte values. However, the results discussed here indicate that at least for some soil types (e.g., large differences in mineralogy or C contents), separate calibrations or the use of nonlinear PLSR or other nonlinear calibration methods will be necessary.

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