Moisture effects on diffuse reflection infrared spectra of contrasting minerals and soils: A mechanistic interpretation

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A B S T R A C T

Moisture can impact on infrared spectra of soils, with implications for field analysis. The basis for these effects needs to be explained. This study aims to describe the basis for the impact of moisture content on soil spectra and to use this information to suggest a method to predict the limiting moisture contents in various soil types. Reference minerals and soils were spiked with water, typical of field conditions. Their infrared spectral band intensities were non-linearly related to moisture contents and showed severe distortion in the mid-infrared (MIR) near 3400 cm^{-1} at critical moisture contents. Distortion was not observed in the near-infrared (NIR) spectra due to the lower spectral absorbances compared to the MIR. The extent of spectral distortion appears to depend on the refractive index of water, associated with specular reflection from free water films on the particle surfaces and on the total absorbance from internal water in major soil components. The key mechanisms impacting on the spectral distortion were the limiting absorbance near 1.5 absorbance units being reached and the rapidly changing refractive index of water films in the MIR region. It was shown that the onset of spectral distortion could be predicted for a range of soils from specific soil properties such as quartz and smectite contents, particle size, and moisture retention. From this study, it could be concluded that high clay soils cause minimal distortion of infrared spectra but high sand soils pose significant risk of distortion for moisture contents typical of field conditions.

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1. Introduction

In-field prediction of soil properties from infrared (IR) diffuse reflection[1] spectra is increasingly being seen as a practical means of acquiring analytical information rapidly and inexpensively. However, soils may vary widely in their moisture contents under natural environmental conditions and intense spectral bands of water in the soils can have an adverse impact on the reflection profiles of the IR spectra, particularly in the mid-infrared (MIR) region. The fundamental H—O—H stretching vibration for water has a very strong, broad, stretching vibration in the MIR near 3450–3250 cm^{-1} and a weaker bending vibration near 1630 cm^{-1}. Overtones of these vibrations are observed in the near-infrared

(NIR) near 7000 cm^{-1} (1430 nm) and 5200 cm^{-1} (1923 nm). At high moisture contents, these bands can overlap with or mask those of soil organic matter and soil mineralogy [1].

A non-linear NIR response to water content has been reported by Weidong et al. [2]. Their results showed that for low soil moisture levels, the reflection decreased with increasing moisture, but after a "critical point" (approximately 30–40% moisture content), the reflection increased. The influence of numerous soil characteristics on reflection, such as primary and secondary minerals, organic matter, and physical structure (e.g., water-holding capacity, aggregation, surface roughness), has also been reported [2]. While the study by Weidong et al. [2] used the visible-NIR spectral range to characterise the reflection behaviour for a number of representative soils, they did not report any distortion of the water peaks apart from slight band shifts but identified a "critical point" for reflection from water films on particle surfaces.

It has been suggested that the problem of moisture in IR spectra of soils is much more severe in the MIR than the NIR spectral range due to the higher sensitivity of MIR for water [3,4]. Spectral absorbances in the MIR are much stronger than in the NIR,

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particularly for major soil minerals with intercalated water, leading to severe intensity non-linearity effects and a comparative lack of signal for minor soil components such as soil organic matter. This is particularly evident as the spectral intensities approach ~1.5 absorbance units whereby minor bands become almost eliminated. Hazel et al. [5] discussed the observed non-linearity of spectral response of petroleum hydrocarbons in the vicinity of the MIR water peak, but did not explain the reflection mechanisms responsible for this non-linearity. Furthermore, there has been very little explanation of the spectral aberrations in the MIR observed at relatively high moisture contents.

A number of approaches have been proposed to account for the effect of water in field-based NIR spectra (e.g. [4,6–11]). Before attempting to develop regression methods to account for the presence of water in the IR spectra, however, there should be an understanding of the underlying optical mechanisms responsible for the effect of water in various soil types and IR spectral ranges. For example, in some soil types, moderate moisture content may not be a problem, while in others there may be a very strong effect, requiring some attention to sampling strategy for analytical determinations using IR spectroscopy. In this way, the range of moisture contents that can be tolerated in the spectroscopic analysis of a range of soil types collected as field samples can be established.

Multivariate models and careful inspection of the resulting spectral features can help us understand the mechanisms behind the effect of moisture in analytical applications, bearing in mind that this effect is expected to be different for varying soil compositions and particle sizes [2,3,5,12,13]. Sand particles are relatively large (often >50 μm) and impervious to moisture, so the water merely fills the inter-particle voids or covers the particle surfaces as films of varying thickness [5,14]. At high moisture contents the water films are relatively thick and so only the reflected signal is observed, with the radiation being completely absorbed within the water. In the case of the MIR, often little or no radiation from within the water layer reaches the quartz grains. This water absorbance is less affected by the much weaker absorbance in the NIR [14].

In view of the paucity of mechanistic interpretations in previous reports, there is the need to conduct more detailed research on the effect of water in IR spectra across a wide range of soil compositions and spectral ranges (MIR and NIR). This study aims to describe the basis for the impact of moisture content on soil spectra and to use this information to suggest a method to predict the limiting moisture contents in the various soil types.

1.1. Theory of infrared diffuse reflection from wet powders

When IR radiation is applied to a sample, it can be either reflected from the sample surface as specular reflection (R_s), or it can pass into the sample and then be partly absorbed and re-emitted as volume reflection (R_v) [15–17]. A combination of these two effects gives rise to diffuse reflection infrared spectroscopy (DRIFT), whereby the observed radiation emanating from dry powders is a mixture of R_s and R_v [15]. Specular reflection can be described as a combination of the absorption coefficient (k) defining the volume reflection, and the complex refractive index (n^*) defining the specular reflection [5]. The mean optical path length in a particle is approximately inversely proportion to the square root of the absorption coefficient [18]. Thus, the stronger the absorber, the less IR photons will penetrate through the bulk of the sample. In the case of the reflection spectrum of water, the values of k and the real part of n^* (n) are large in the region of the MIR water absorbance, and impact on the observed diffuse reflection spectra [14].

Plots of n and k for water over the NIR and MIR ranges (7500–400 cm^{-1}) are depicted in Fig. 1. In this case, the optical constants were calculated from a DRIFT spectrum of water by using the Kramers-Kronig transformation function [19]. Curves of these derived optical constants strongly resemble those shown by other authors [18,20]. For low moisture contents, where specular reflection is minimal, the DRIFT spectrum appears similar to sample absorbance and resembles k. For higher moisture contents, specular reflection dominates and the DRIFT spectrum resembles n for water.

In the case of dry powdered or granular samples, the R_s component of the incident radiation results from successive reflections from the surfaces of the individual sample particles, with the remainder of the radiation continuing through the sample and partly absorbed as it travels through each particle (R_v) [15]. For a wet sample, the reflection mechanism will depend on the particle size of the sample, and also to the extent of coverage of the sample particles by water and the thickness of the water films [14]. In very wet soils (water content greater than field capacity) the incident radiation in the MIR would be dominated almost entirely by the specular reflection from the water surface (R_{sw}) [5,14] (illustrated in Fig. 2a). The net effect is that only the specular reflection R_{sw} is re-emitted from the sample surface and none from the sample, so that the measured diffuse reflection is then simply the mirror-like surface reflection (known as "*Reststrahlen*" [16,17] from water rather than an absorption process. For thinner water films on non-absorbing particles (e.g. as in Fig. 2b), the diffuse reflection would be expected to be a composite of R_{sw} and R_{vw} from water, and R_s and R_v. from the particles [14].

In highly porous soils such as those with high clay contents, and thus high field capacities, moisture is absorbed into the interior of the matrix, thus partly shielding the water from the incident radiation (Fig. 2c). For these soils, it can be assumed that the components from water surfaces (R_{sw} and R_{vw}) would become small, and R_s and R_v become strong due to the relatively thin water film on the sample grain surfaces. This difference in behaviour has consequences on the optical properties of different soil types such as those high in clay and those with high sand contents [16,14].

2. Experimental and methods

2.1. Samples

Three soil minerals (quartz, kaolinite and smectite), common in Australia, and seven contrasting soils were selected for spiking with
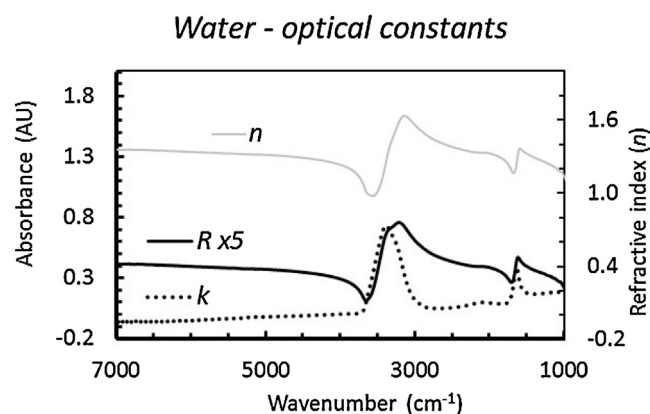

Fig. 1. The DRIFT spectrum of water (R) (scaled x5) and the optical constants (refractive index n and absorption index k) for water in the NIR and MIR spectral regions. The optical constants were calculated in this study using the Kramers-Kronig transformation function and strongly resemble those shown by Clark and Roush (1984).