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DVS Application Note 110

# DVS-NEAR IR Technique for Investigating Clay Minerals

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*Near-IR spectroscopy has been combined with gravimetric sorption methods to allow for the acquisition of NIR spectra from an important industrial mineral, sepiolite which was subjected to in situ hydration.*

## Introduction

Sepiolite is an important industrial mineral characterized by its modulated structure consisting of alternating tunnels and ribbons. Mild thermal treatments facilitate the removal of surface and zeolitic $H_2O$ from the material. Owing to its unique structure, morphology and chemical inertness, sepiolite demonstrates an expanding range of applications, traditionally as a specialty absorbent, carrier, filler or viscosity modifier, and more recently as a template or host matrix in the development of functionalized hybrid nanomaterials [1,2].

Sepiolite exhibits high surface areas both internally and externally, which can be enriched with various forms of $H_2O$. The sepiolite structure contains $OH_2$ species coordinated to outer Mg cations in a discontinuous octahedral sheet, tunnels containing zeolitic $H_2O$, physisorbed $H_2O$ and $H_2O$ adsorbed on the external surface. Excluding the $Mg_3OH$ structural groups of the trioctahedral sheet, there are numerous terminations in the tetrahedral sheet that result in the formation of abundant surface SiOH groups. As a result, sepiolite has a complex dehydration profile, with various low-temperature $H_2O$ desorption processes activated below ca. 150 °C. In turn the external and internal surfaces of sepiolite are exposed, significantly increasing the specific surface area of the material (from ≈200 $m^2/g$ to >300 $m^2/g$) and rendering the tunnels open and accessible to small molecules [3].

The combination of dynamic vapor sorption and Near Infrared spectroscopy (DVS-NIR) has enabled the real-time observation of sepiolite's dehydration and hydration processes, a novel technique capable of analyzing various material's sorption/desorption properties. Quantification of the effect of relative humidity on the sepiolite's structure and water uptake is traditionally derived from experiments on samples pre-conditioned over saturated salt solutions. The central focus of this work demonstrates $H_2O$ and OH can function as very sensitive probes for determining sepiolite's structure, composition and interaction with various chemical species. Such a detailed structural investigation of the sepiolite–water interactions is needed to support future efforts in understanding the adsorption of chemicals on sepiolite [3].

## Methods

The clay mineral sample was Spanish sepiolite SepSp-1 from the Clay Minerals Society repository [4].

The sample was ground to less than 250 µm using a hammer mill (Retsch**)**.

DVS water sorption experiment was performed by drying the sample at 0% relative humidity for 120 minutes to remove any residual moisture. A sorption cycle from 0-90% RH was carried out at 25 °C, using 2% RH increments up to 30% RH and 10% RH steps after this (up to 90% RH). The sorption cycle was followed by desorption from 90- 0% RH in a similar manner. The weight change during the sorption cycle was monitored, allowing for the hygroscopic nature of the sample to be determined. The %RH was maintained by a mixture of saturated water vapor and dry air (flow rate of 200 sccm) and the percentage of mass change per minute (dm/dt) was set as 0.002 %/min. The rate at which the material equilibrates at each humidity level, as well as the adsorption and desorption isotherms were studied.

For this study, the DVS was coupled with a B&W Tek near infrared spectrophotometer (Sol 1.7), using a thermoelectric (TE) cooled 512 element, linear InGaAs array detector. NIR spectra were recorded using a fiber-optic probe positioned approximately 4 mm below the flat quartz glass sample pan. Measurements were collected at ~4 nm spectral resolution (FWHM), with NIR spectra for all samples recorded in the range of 900–1700 nm (a subset of the typical NIR range of 700-2500 nm). The specifications of the NIR system (detector and spectrometer) and experimental parameters for this study are detailed in Table 1. It should be noted that the DVS instrument can be interfaced with any NIR systems, provided the NIR probe dimensions are compatible with the DVS adapter.

## Results and Discussion

DVS water vapor sorption characteristics over 0-90% RH are illustrated in Figure 1, showing a significant mass change at 25 °C due to the uptake of moisture by the clay sample. This change appears to be reversible post desorption, as the sample has returned to dry state.

The water sorption isotherms are shown in Figure 2. The type II isotherms confirm a significant uptake at low partial pressures followed by small adsorption at intermediate vapor concentration. A high uptake of water occurs at elevated partial pressures, which is consistent with monolayer and multi-layer vapor sorption mechanisms.

The NIR spectra shown in Figure 3 confirms the changes in the sample at different relative humidity conditions. The NIR spectrum of sepiolite generally exhibits several characteristic bands related to its chemical structure and water content. These bands arise primarily from the vibrational modes of various bonds within the mineral. In the 0-30% RH range, the absorbance band around 1375 nm disappears, and there is a shift in the absorbance band from ~1391 nm to ~1387 nm. Additionally, a broader absorbance band appears in the region between 1415 nm and 1523 nm. As RH increases to 40%-90%, this broader absorbance feature in the 1415-1523 nm range becomes more pronounced.

The specific NIR spectrum of sepiolite can be influenced by factors such as purity, particle size, and hydration state. However, the most prominent features in the NIR spectra are associated with water content and the presence of hydroxyl groups, reflecting the clay's hydrous, magnesian silicate structure.

The 1400–1500 nm region is a key diagnostic region for many clay minerals, as it reflects the stretching and bending modes of the hydroxyl group .

Water-related absorption bands at around 1440 nm are typically associated with H-O-H bending and stretching vibrations of the adsorbed water or structural water in the mineral. The 1440 nm band often corresponds to the O-H bending mode, and the 1930 nm band corresponds to the H-O-H stretching mode (water molecules).

The range at around 2320-2400 nm is associated with the hydroxyl groups (OH) bonded to aluminum or magnesium in the mineral structure. This band typically appears due to O-H bending or stretching vibrations.

Table 1. NIR detector, spectrometer, and light source specifications from B&W Tek (https://bwtek.com/products/modular-spectrometers/sol/).

| System | | |
|---|---|---|
| **Measurements** | **Transmittance, Reflectance, Absorbance Fiber Optic Probes and Sampling Accessories Required (sold separately)** | |
| **Connections** | **Illumination and Collection SMA905 ports for fiber optic coupling** | |
| **Triggering** | **Triggering Front panel connection for use with sampling probes with triggering feature** | |
| **Computer Interface** | **USB 2.0/1.1** | |
| **Software** | **B&WSpec®** | |
| **Software Options** | **Software Developer's Kit (SDK) Sample Code: C#, C++, Visual C++, Visual Basic, VBA, Labview, VB.NET** | |
| **Instrument Dimensions** | **9.5 (H) x 6.7 (W) x 13.7 (D) in 242 (H) x 170 (W) x 347 (D) mm** | |
| **Weight (model dependant)** | **7.9 - 10.8lbs 3.6 - 4.9kg** | |
| **Power** | **12V DC @ 10.8 Amps, Battery Option Available** | |
| **Operating Temperature** | **0°C to 45°C** | |
| **Spectrometer** | | |
| **Optical Design** | Crossed Czerny-Turner Spectrographs | |
| **Digitization Resolution** | 16-bit or 65,535 to 1 | |
| **Integration Time** | 250ms - 5ms (Min. Spectrometer Dependant), 63,535ms x multiplier (Max.) | |
| **Light Source** | **Tungsten Halogen 5W** | **Tungsten Halogen 20W** |
| **Spectral Output Range** | 350 to > 2600nm | 350 to > 2600nm |
| **Color Temperature** | 2800 K | 2900 K |
| **Warm Up Time** | ~40 Minutes | ~40 Minutes |
| **Rated Life** | 10,000 Hours | 2,000 Hours |

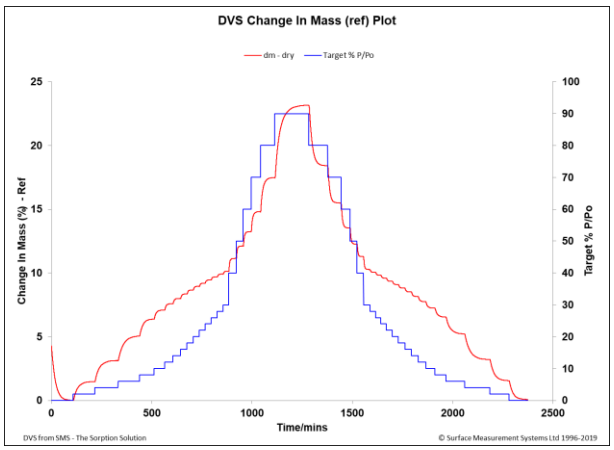


*Figure 1: Water vapour sorption kinetics for Sepiolite at 25 ℃.*

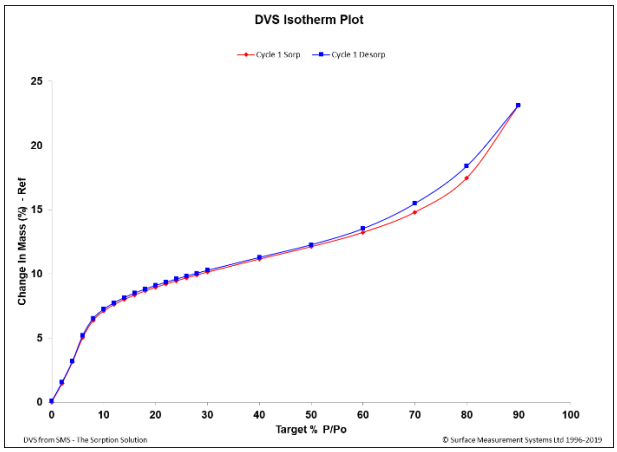


*Figure 2: Sorption and desorption isotherms for Sepiolite at 25 ℃.*

From the DVS-NIR it is therefore possible to conclude that the water uptake process for the Sepiolite sample is reversible. This is confirmed by the closed loop in the sorption desorption isotherms.

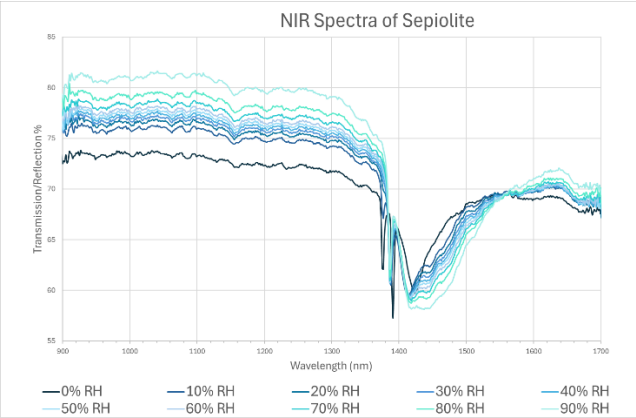


*Figure 3: NIR Spectra of Sepiolite recorded at 0-90% RH and 25 °C. The changes in NIR spectra are consistent with the DVS change is mass data and reflect the progressive hydration of sepiolite.*

This study had been performed in the past with separate NIR and sorption experiments using saturated salt solutions. The DVS sorption data is in excellent agreement with the published results [3], with the added advantage of establishing a much faster equilibration, where the total experimental time is reduced from 30 days (for equilibration over saturated salt solutions) to 1.7 days. The molecular weight shows each water molecule contributes 1.56 mass % to the dry sepiolite. DVS sorption isotherms (Figure 2) show the changes in water uptake occur in three discrete states of hydration for sepiolite at room temperature: a steep increase in water uptake up to 10% RH, followed by a slower increase, before a sharp increase above 60% RH. Sepiolite is in a hydrated state (7-8 molecules of water per molecule of sepiolite) above 30% RH and a dry state (0–1 molecules of water per molecule of sepiolite) below 3% RH, with an intermediate state (4–5 molecules of water per molecule of sepiolite) in the 3–10% RH range which is identified in the near-infrared spectra at 1384.7 nm.

## Conclusion

The NIR data reproduced the published findings well, albeit at a much lower spectral resolution and over a smaller frequency range. This comes from the characteristics of the relatively basic NIR instrument, which is ideal for detecting broad-brush trends, but not suitable for a detailed analysis of structure and bonding. In the latter case, the DVS would need to be coupled to a FT spectrometer operating via optical fibers.

## References

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