HARRICK SCIENTIFIC PRODUCTS

No. 10809

# Temperature Induced Changes in Clays Measured by Diamond ATR FTIR Spectroscopy

**Marie-Jo Nassar**
**Harrick Scientific Products, Inc, Box 277, Pleasantville, NY 10570**

Figure 1. Diamond Single Reflection ATR MVP-Pro Star™.

Figure 2. Heated Crystal Holder.

Figure 3. Temperature Controller

## Introduction

In some types of experiments, it becomes important to analyze samples at a variety of temperatures. Increasing temperature could cause a chemical change, speed up an ongoing reaction, concentrate an aqueous sample, or dry an analyte which absorbs or contains water. In the last case, heating guarantees that no important peaks will be obscured by water's typical broad absorption band in the 3200 $cm^{-1}$ region. Any of these experiments can be carried out using a temperature controller, and an accessory equipped to elevate sample's temperature, such as a MVP-Pro Star™.

This note explores the use MVP-Pro™ to analyze clay samples and how they are affected by heating. The analytes ranged from mineral clays such as smectite, to "modeling clays" such as Sculpey III, many of which are actually polymers.

## Experimental

The measurements were carried out using a diamond single reflection ATR, the MVP-Pro™ (Figure 1) with its heated diamond crystal holder (Figure 2), and a temperature controller (Figure 3), along with a commercial FTIR spectrometer. The temperature controller was autotuned for operation to 200°C. Then the desired set point was selected as needed. Spectra were collected at an 8 $cm^{-1}$ resolution, a gain of 8, and signal averaged over 32 scans. The spectrometer was equipped with a DTGS detector.

A small mound of each sample was pressed against the diamond ATR using the maximum force delivered by the built-in pressure applicator. The spectra were collected over a wavenumber range of 4000 $cm^{-1}$ to 400 $cm^{-1}$. Of the six samples examined, two were mineral clays: otay, and smectite; and four were modeling 'clays': Model Magic®, Play-Doh™, Sculpey® III, and terra cotta.

## Results and Discussion

Some clays such as otay and smectite are hygroscopic, easily absorbing water at room temperature. The resulting water peak in the 3000 $cm^{-1}$ to 3400 $cm^{-1}$ region can interfere with characteristic C–H peaks near 3000 $cm^{-1}$. The water and its corresponding peak can be easily eliminated by heating the

# Temperature Induced Changes in Clays Measured by Diamond ATR FTIR Spectroscopy

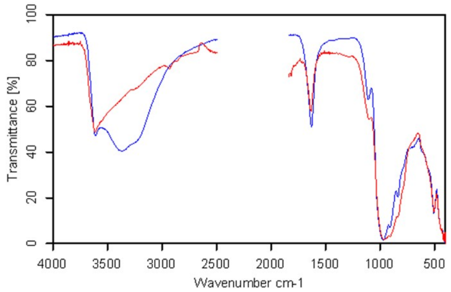


Figure 4. Otay spectra at 26°C (blue) and 200°C (red).

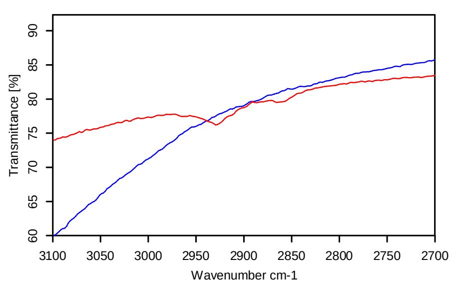


Figure 5. Expanded view of the C–H region for otay.

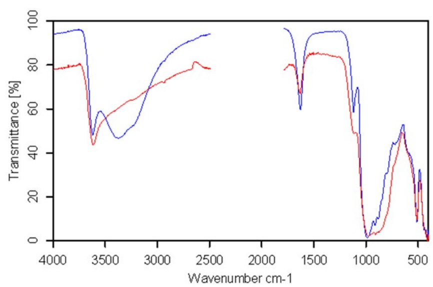


Figure 6. Smectite spectra at 25°C (blue) and 200°C (red).

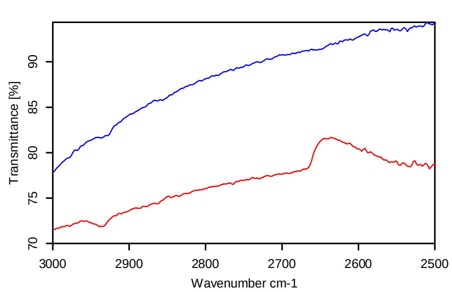


Figure 7. Expanded view of the 3000 $cm^{-1}$ to the 2500 $cm^{-1}$ region.

sample to 200°C for 5 minutes. The C–H peaks in these samples emerge or become more clearly defined as a consequence (Figures 4 through 7). In all of the figures, blue signifies room temperature spectra while red denotes heated spectra. The portion of the spectrum in the 2500 $cm^{-1}$ to 2000 $cm^{-1}$ region is not shown because the high noise level in that area due to the absorbance of diamond.

The second portion of the experiment tested to see if the same held true for wet modeling clays. Most of these substances are not actually made from clay or clay-like minerals. Some are complex mixtures, while others are plastic polymers. These samples were heated to 150°C for 10 minutes, as recommended for curing the baked clays. Many of these 'clays' such as Play-Doh™ Model Magic®, and terra cotta exhibit a similar O–H peak to otay and smectite. However the effect of heating on these compounds varies drastically. Despite being composed primarily of paper, terra cotta exhibits the same drying phenomenon as the mineral clay samples (Figure 8). Heating drives off the water and makes the other spectral features more clearly delineated. Model Magic® and Play-Doh™ initially display a slight decrease in peak strength in the 3200 $cm^{-1}$ region, but no new peaks appear

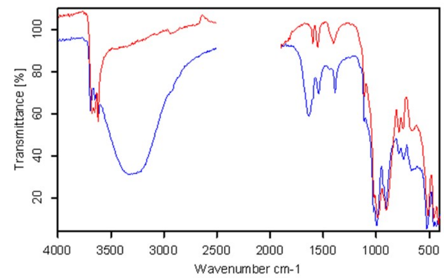


Figure 8. Terra Cotta spectra at 26°C (blue) and 150°C (red).

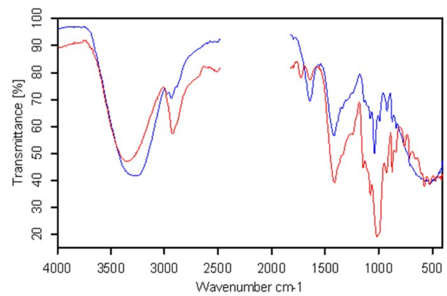


Figure 9. Model Magic® spectra at 26°C (blue) and 150°C (red).

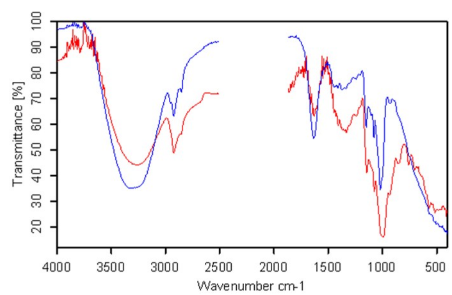


Figure 10. Play-Doh™ spectra at 26°C (blue) and 150°C (red).

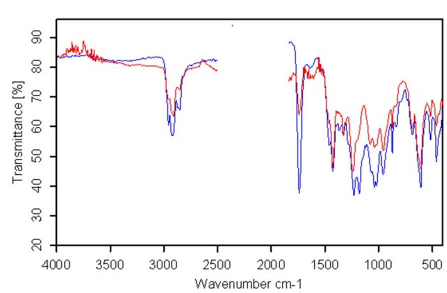


Figure 11. Sculpey® III spectra at 26°C (blue) and 150°C (red).


HARRICK SCIENTIFIC PRODUCTS
141 Tompkins Ave., 2nd floor • PO Box 277 • Pleasantville, NY 10570
www.harricksci.com • E-mail: info@harricksci.com
Phone (international): 914-747-7202 • Phone (in USA): 800-248-3847 • Fax: 914-747-7209

in either case (Figures 9 and 10). These results are consistent with the standard usage of each modeling material. Terra cotta is meant to oven-harden, Model Magic™ air dries over days, and Play-Doh should only becomes hard if improperly stored.

Overall, the most unusual results came from Sculpey® III. This modeling clay, actually a polymer, exhibits no O–H peak even at room temperature. Even the reaction that causes this clay to harden with heat modifies the infrared spectrum only slightly (Figure 11).

## CONCLUSION

Sampling accessories, such as the MVP-Pro™, coupled with a thermostated crystal holder or cell are effective in removing water from samples that absorb it. This also makes them valuable in detecting chemical changes that occur upon heating.