Fiveash Data Management, Inc.

Application Note 01

March 6, 2023

Comparing Variable Angle ATR/FTIR spectra of two brands of black crayons.

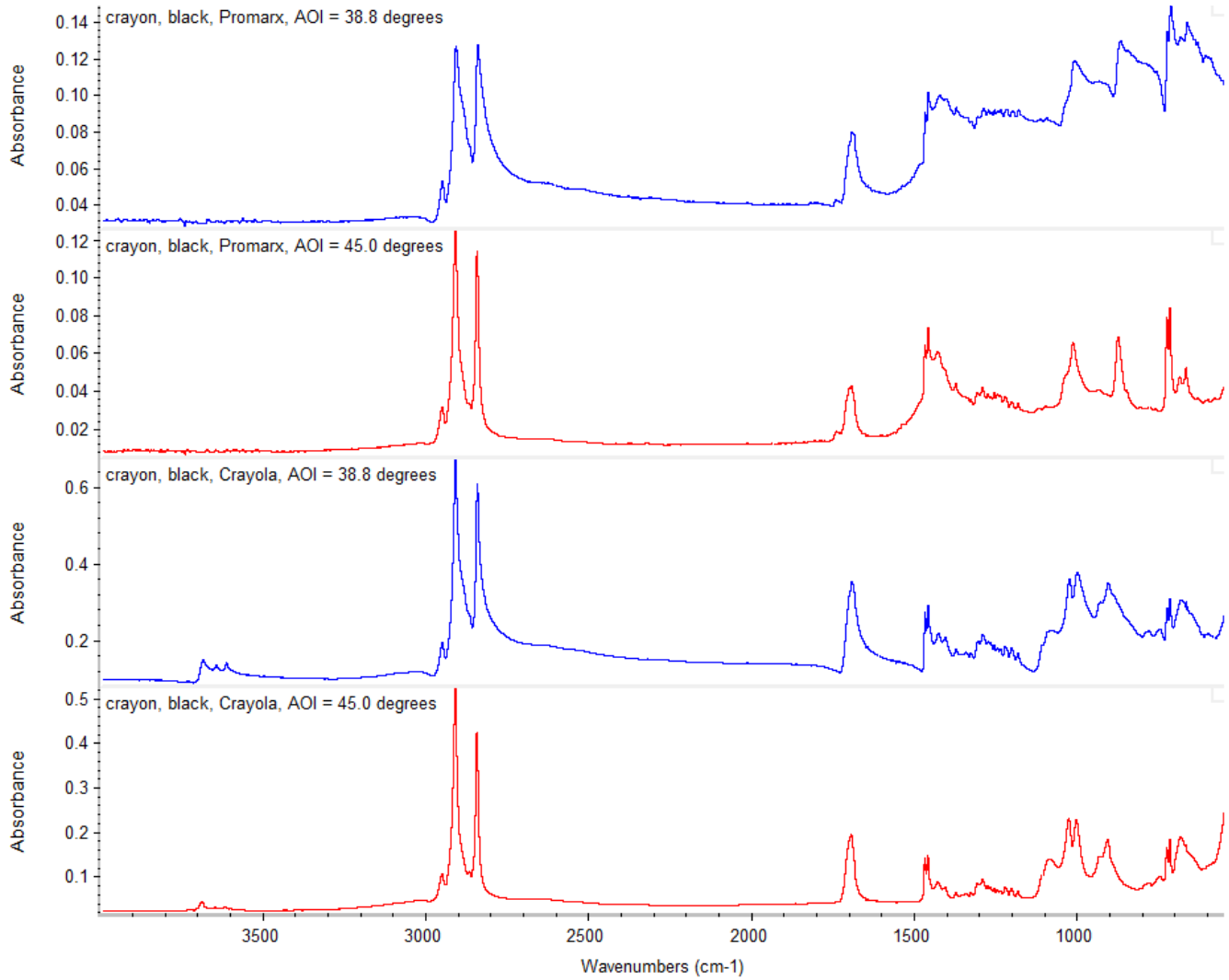


Figure 1: Two brands of black crayons at 38.8 degrees and 45.0 degrees AOI on a 45 degree ZnSe ATR crystal.

The spectra of the crayons were obtained by drawing directly on the face of the 20 mm diameter ZnSe ATR crystal. The angle was varied from 38.8 degrees to 58.8 degrees in approximately 0.8 degree increments. The ATR accessory is a PIKE VeeMAX™ III, fully automated. Background and sample spectrum data collection where driven by the PIKE AutoPro 7 software. The spectral range is 550 cm-1 to 4000 cm-1 at 4 cm-1 resolution.

AOI = Angle of Incidence.

Several observations can be made from figure 1.

1) Both 38.8 degree spectra have distortions suggesting partial specular reflectance especially at lower wavenumbers. This means those peaks are being measured below their critical angle.

2) At 38.8 degrees, the Promarx crayon appears to have considerable carbon black pigment given the strong background similar to many black plastic and black rubber materials.

3) The Crayola crayon has kaolinite[1], as easily seen from the peaks in the range of 3600 cm-1 to 3700 cm-1 and the peak at 1028 cm-1. Kaolinite is a common polymer additive. While the 1028 cm-1 peak is present in both spectra, the highly characteristic peaks in the range of 3600 cm-1 to 3700 cm-1 are clearly more pronounced in the 38.8 degree spectrum.

4) Both crayons have stearic acid[2] (common in some candle waxes) as indicated by the two sharp doublets at about 725 cm-1 and 1470 cm-1, the fine structure in the range of 1180 cm-1 to 1320 cm-1, and the carbonyl peak at 1699 cm-1. Stearic acid accounts for most of the fine structure. Note that those doublets are virtually the same as those that appear in the spectrum of LDPE[3,4], which would also account for the small peak at 1377 cm-1 in the Crayola sample. It is plausible both crayons contain stearic acid and LDPE. And kaolinite is in the Crayola.

5) At 45.0 degrees, both baselines are improved relative to the 38.8 degree spectra.

6) At 45.0 degrees, the Promarx spectrum no longer shows a specular reflectance contribution, which obscured the true position of the doublet at about 725 cm-1.

7) All spectra were run on a ZnSe ATR crystal, providing greater signal and a wider spectral range than on a Ge crystal. Going from 38.8 degrees to 45.0 degrees offers similar benefits to running at 45.0 degrees on a Ge crystal with respect to eliminating specular reflectance contributions.

8) Automating the AOI with the PIKE VeeMAX III and the PIKE AutoPro 7 software is easier than switching crystals and does not risk opening up the ATR accessory to internal dust and damage or dropping either crystal.

9) Automating the ATR's AOI expands the spectroscopic scope of any FTIR.

10) The 45.0 degree spectrum acts as an automatic key for working with multiangle ATR/FTIR data sets. It is a key to human understanding because 45.0 degree spectra are the most transmission like.

11) The automation itself links the 45.0 degree spectra to spectra measured at other angles without the sample being moved. In this way, with no effort, any spectroscopist's view can be expanded to multiple angles while linked to a perspective they know well. Furthermore, while lower angle spectra maybe have peaks shapes that many are unfamiliar with or chose to avoid, they can now be safely accessed. For analytical purposes, all AOI can be put to good use.

Conclusion

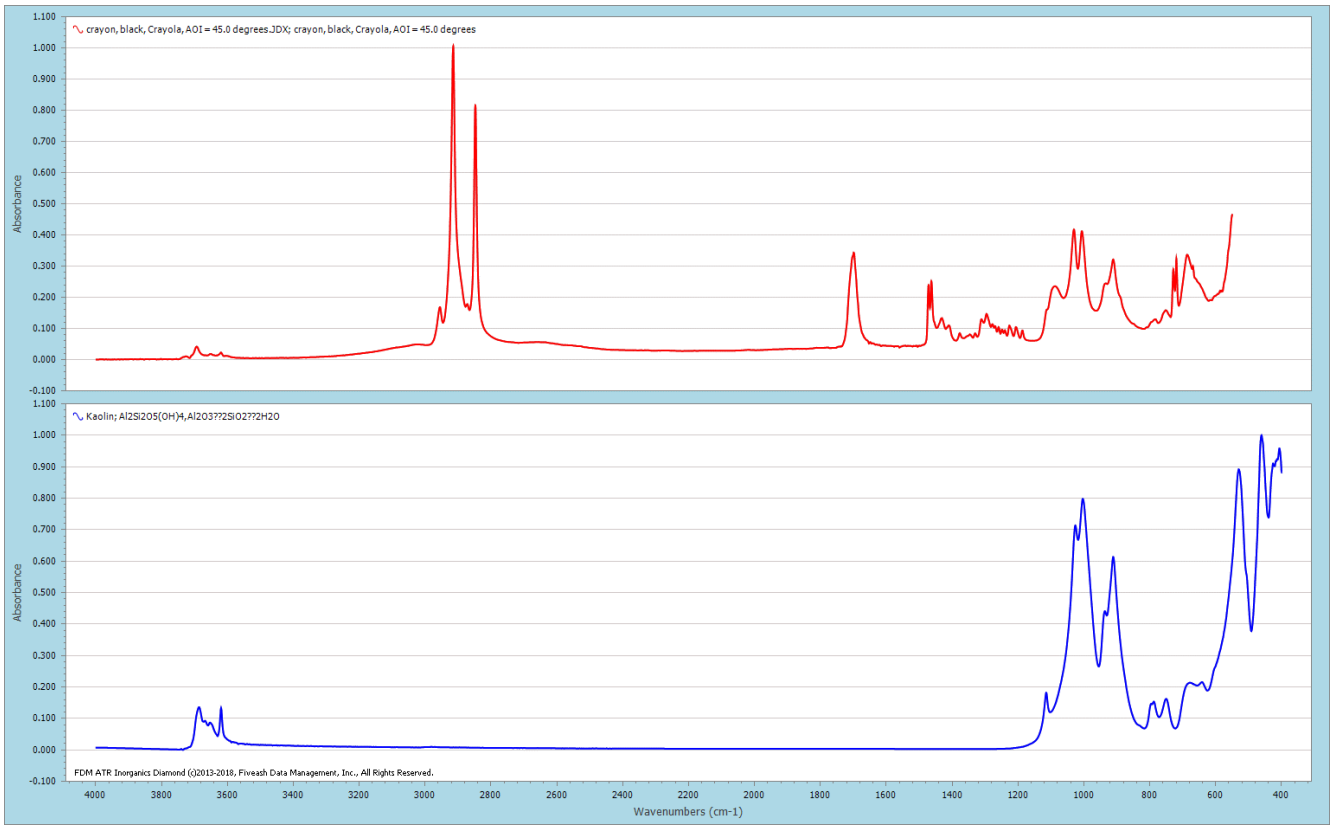
Working with multiangle ATR/FTIR spectra from a variable angle ATR accessory presents the opportunity to have one spectrum inform the other(s) and to benefit from the data set as a whole.

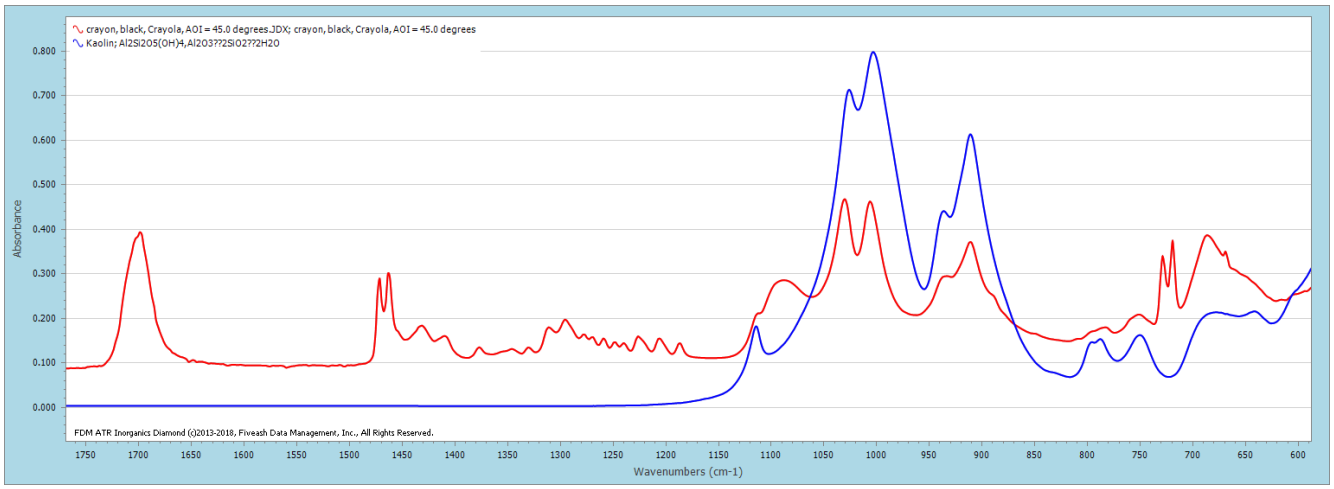
Definitions

The term "Variable Angle ATR" describes the accessory. This is fitting because users can control the angle of incidence. Example: the PIKE VeeMAX™ III is a variable angle ATR available with turnkey automation. The term "Multiangle ATR" describes the data sets recorded by a variable angle ATR accessory. This is fitting because there is nothing variable about recorded data. Example: the FDM Multiangle ATR Polymers is a spectral library.

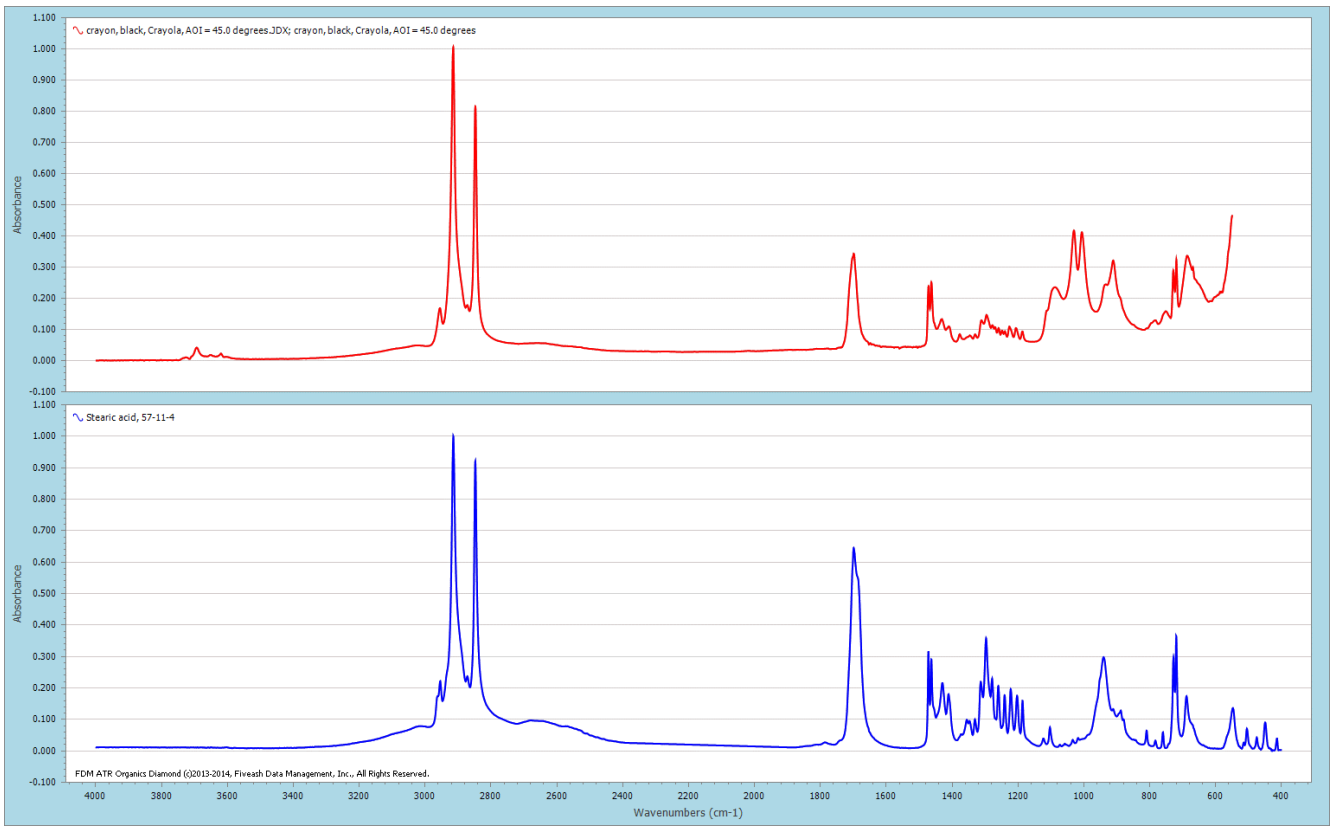
References

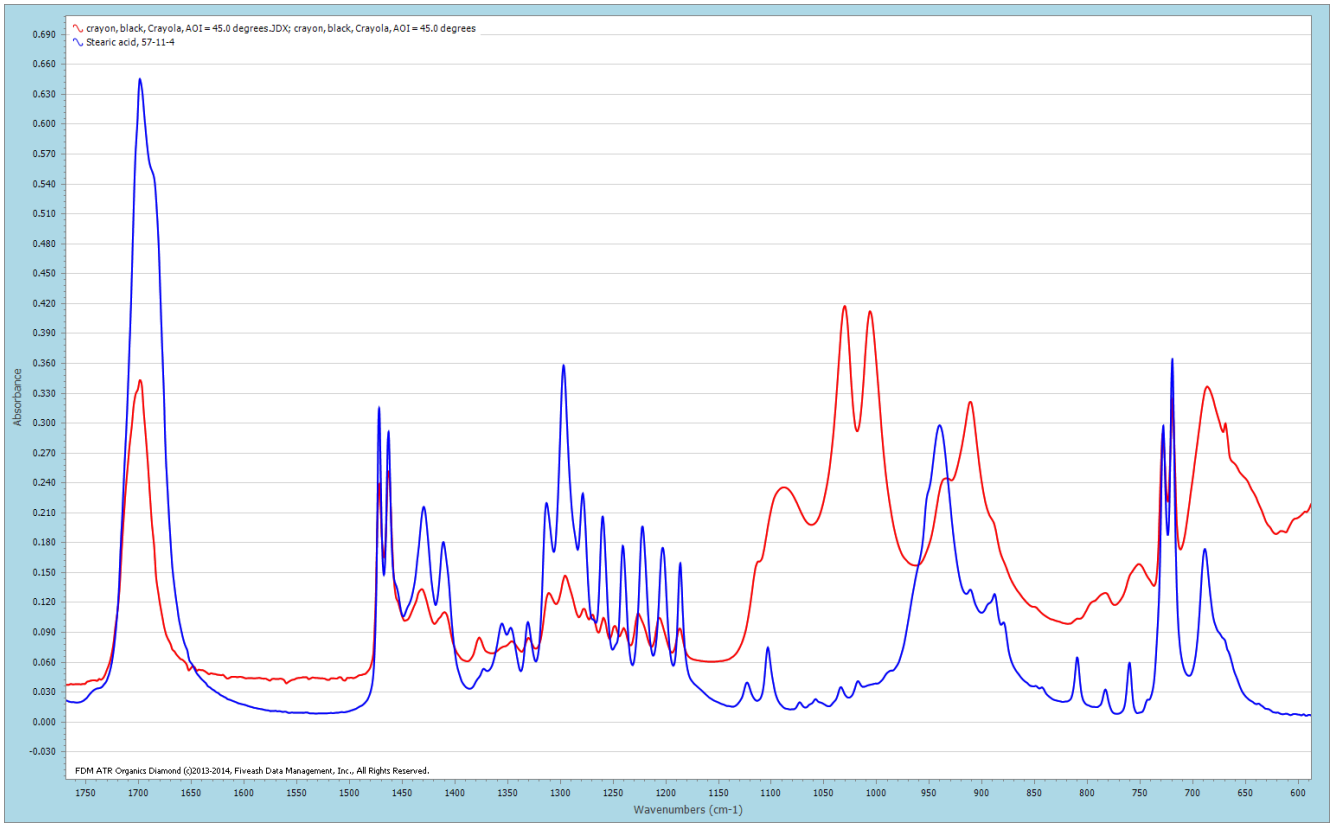
[1] Kaolinite, from the FDM ATR Inorganics Diamond, Fiveash Data Management, Inc.



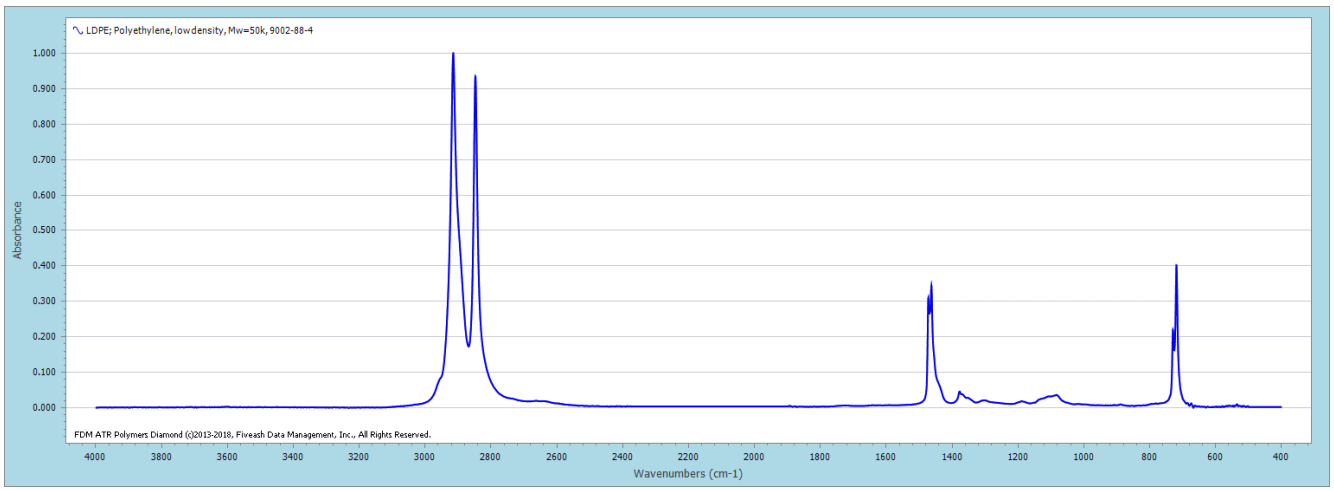


[2] Stearic acid, from the FDM ATR Organics Diamond, Fiveash Data Management, Inc.





[3] LDPE, from the FDM ATR Polymers Diamond, Fiveash Data Management, Inc.



[4] Stearic acid and LDPE have a pair of overlapping doublets.