

Precise Multicomponent Quantification of Solid Materials using Attenuated Total Reflection: Calcium Carbonate and Kaolin Minerals

Introduction

Fourier transform infrared (FT-IR) spectroscopy has long been used in the quantification of materials. A big advantage of the Infrared (IR) spectroscopy technique is that it can be used to analyze materials in any physical state – vapor, liquid, and solid. However, quantification of solids presents special challenges. First there is the physical mixing of the materials under study, influenced by the particle size and distribution uniformity. Next there is the aspect of pathlength, the pathlength must be known or kept constant, or an additive standard used. Typical FT-IR quantification methods applied to solids include transmission measurements using mulls or KBr pellets, diffuse reflectance, or attenuated total reflection (ATR). ATR methods are desirable due to the ease in sample presentation to the device, generally less sample preparation required, and a pathlength that is constant, governed by the refractive index ratio of the sample to the internal reflection element (IRE) for a given polarization and incident angle. However, when analyzing solids, slight changes in force applied to the sample to contact the IRE can lead to differences in the degree of contact and by extension, the observed absorbance intensities.

In this report, an example mineral quantitative analysis is demonstrated for calcium carbonate (calcite) and kaolinite. The quantitative analysis of minerals is important to grade the productivity of mining operations and mineral composition is an important indicator in petroleum reservoir quality.

Experimental

The MicromATR_Q[™] ATR accessory from CziTek (Fig. 1) was used with a commercial FT-IR spectrometer for all data presented in this report. Spectra were recorded using 4 cm⁻¹ resolution and 30 seconds of data collection time. An l-alanine doped, deuterated triglycine sulfate (DLATGS) pyroelectric detector was used to measure double-side,



Figure 1: MicromATR_Q with digital force readout

bidirectional interferograms that were transformed using strong Norton-Beer apodization. MicromATR_Q is designed with fixed alignment optics, ensuring a constant, reproducible incident angle of the IR wavefront with the IRE. A continuous force press coupled to a digital force readout was used, enabling the reproduction of constant contact force between the sample and the IRE. The design incorporates both a continuously adjustable force as well as an upper force threshold to safeguard the ATR crystal. For all of the data measured for this report 200 Newtons (45 lbs) of force was applied to samples contacted on a three-reflection diamond/zinc selenide (ZnSe) composite ATR disk. Two component mineral mixtures were prepared using powders of both Kaolin clay and Calcium Carbonate in concentrations from 1-99 %wt. Samples were thoroughly mixed before being analyzed. Partial Least Squares (PLS) models for the two components were built using software included with the instrument. Prediction of concentrations were then evaluated using separate samples.

Results and Discussion

The IR spectra of a partial CaCO_3 / Kaolin data set are displayed in Fig. 2. The CO_3^{2-} $\nu\text{C-O}$ stretching band is strongly observed near 1400 cm^{-1} . Kaolin is an aluminosilicate clay mineral with the molecular formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The $\nu\text{Al-O}$ and $\nu\text{Si-O}$ stretching absorption bands are observed strongly in the $1100\text{-}900\text{ cm}^{-1}$ range. Some peak shifting is observed, particularly in the case of the CO_3^{2-} absorption. This shifting can be attributed to the varying amounts of CaCO_3 in contact with the IRE and the effective refractive index differences due to mixing with the kaolin. A similar effect can be seen in the IR spectra of Kaolin over the same concentration range. These effects are common in samples with strong absorption bands (large changes in refractive index over the band) like CaCO_3 and kaolin. The use of univariate (simple peak height) methods with data of this type does not always yield optimum results. A multivariate method, like PLS, can use this variation to model concentration and is more immune to these physical effects. Using commercially available quantification software, a PLS model was developed, and used to study the potential for multicomponent quantitative analysis of these minerals. To test the full capabilities of the model, an independent set of samples were made and spectra recorded under the same conditions. The new samples were subjected to the models' estimation feature and the results shown in Figs. 3 and 4 below.

The average error of prediction is $\pm 0.4\%$ over all the samples predicted using the model, with the largest error seen in the $99\% \text{ CaCO}_3 / 1\% \text{ Kaolin}$ sample. The correlation between the gravimetrically measured and predicted concentrations is excellent, with r^2 values exceeding 0.99999 . The data in Figs. 3 and 4 show that even over a wide range of concentrations, the method is capable of predicting the appropriate concentrations. By narrowing the concentration range, higher accuracy in the predicted results might be achievable.

Conclusion

FT-IR spectroscopy has long been used as both a qualitative and quantitative analysis technique. Using an ATR platform for quantitative analysis simplifies sample handling, but can introduce additional variables into the quantitative measurement. Those additional variables have been minimized through implementation of a fixed optical geometry, a continuous force sample press and digital force readout. This enables the analyst to "dial in" the desired force and repeated measurements can be made without significant differences in contact pressure. The results above illustrate the effectiveness in analyzing solid mixtures over a wide concentration range. Although FT-IR spectroscopy is not a trace technique and suitable for all applications, it can be well suited for the quantitative analysis of a wide range of solid materials.

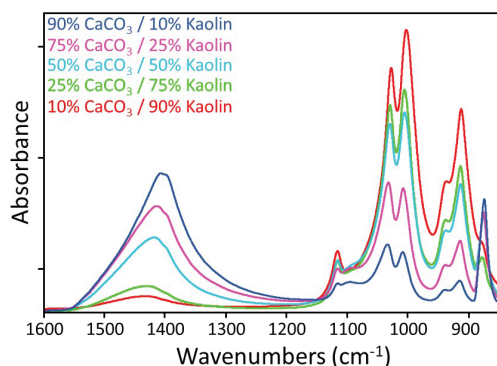


Figure 2: Infrared spectra of Calcium carbonate (CaCO_3) and Kaolin mineral mixtures

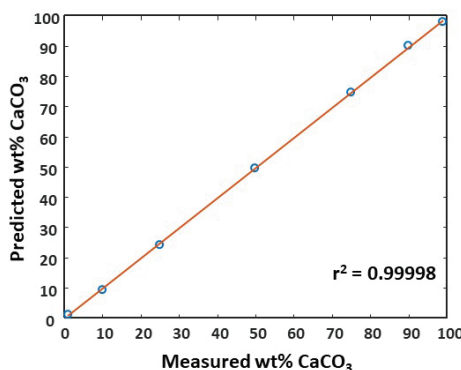


Figure 3: PLS model predicted concentration (wt%) vs. measured concentration (wt%) of Calcium Carbonate

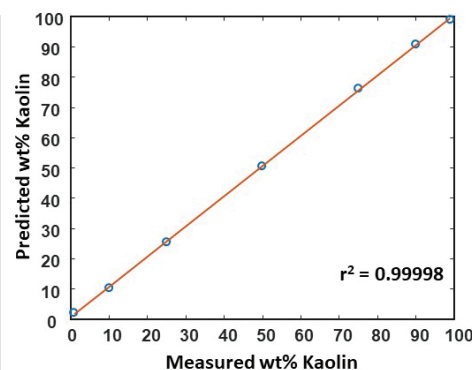


Figure 4: PLS model predicted concentration (wt%) vs. measured concentration (wt%) of Kaolin