

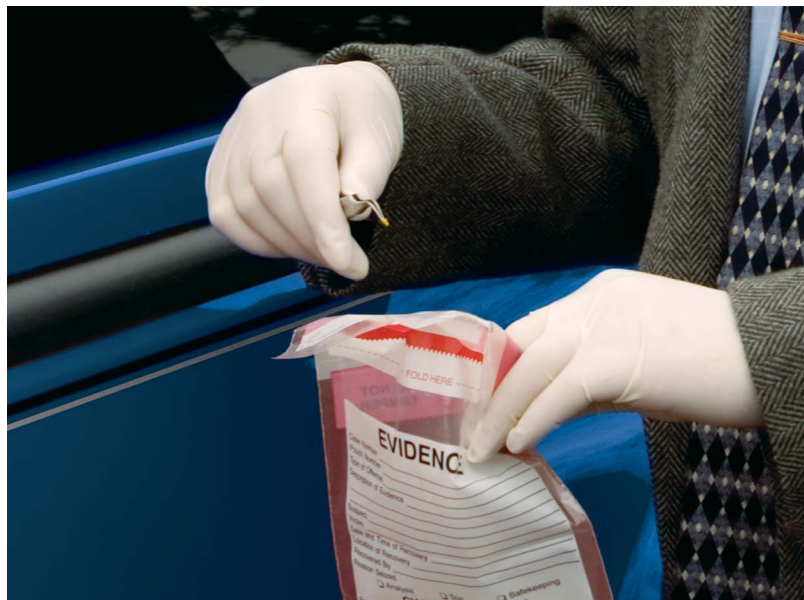
Analyzing automotive paints with extended range ATR: 1800–100 cm^{-1}

Key words

Automotive paint, far-infrared, forensic science, infrared spectroscopy, inorganics, paint analysis

Infrared (IR) spectroscopy is used extensively to characterize the chemical composition of trace evidence such as paints, fibers and adhesives as well as seized drugs and related chemicals. Attenuated Total Reflectance (ATR) has become the sampling technique of choice for many of these measurements. The advent of diamond ATR crystals has allowed spectral data to be collected over an extended range. The Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer offers a novel approach to ATR sampling with the Thermo Scientific™ Nicolet™ iS50 ATR Module that is integrated into the spectrometer. This ensures that the ATR module is always available for rapid analysis of unknown materials even with another accessory mounted in the sample compartment. The built-in ATR combines an optimized optical design with a diamond ATR crystal and a broad range DTGS detector to provide high-sensitivity infrared spectroscopy from 4000 cm^{-1} to 100 cm^{-1} . The enhanced stability, resulting from mounting the ATR within the sealed section of the spectrometer, makes it possible to acquire spectra down to 200 cm^{-1} even with a desiccated system.

Infrared spectroscopy is one of the few analytical techniques considered by the forensic science community to have the highest discriminating power required to provide confirmatory evidence about the chemical composition of a material. FTIR is used extensively in most forensics laboratories to identify materials such as seized drugs and possible evidence from a crime scene. One area where FTIR has proven particularly valuable is analyzing automotive paint chips. A number of forensics laboratories have reported the significance of the infrared spectral range below 400 cm^{-1} in helping to identify specific inorganic pigments or minerals in a paint sample.¹⁻⁵



Traditionally these measurements have been performed with a diamond compression cell or diffuse reflectance accessory on an FTIR system that uses Cesium Iodide (CsI) optics to acquire spectra down to 225 cm^{-1} . Suzuki et al. have published a paper in the *Journal of Forensic Science* describing the application of extended range FTIR to the analysis of pigments in automotive paint.⁴ Another excellent resource for analyzing automotive paints and pigments is the *International Forensics Automotive Paint Data Query (PDQ) database* developed by the Royal Canadian Mounted Police Forensics Laboratory Services. Much of the infrared spectral data in this database contains peak information down to 225 cm^{-1} .⁶

While the advantages of extended range FTIR may be clear, obtaining high-quality transmission spectra requires a great deal of experience and careful sample preparation. The CsI optics typically used to scan this range are delicate and hygroscopic, so great care must be taken to maintain a low humidity environment within the instrument and handle the beamsplitter with extreme caution. Also, preparing a paint sample that is sufficiently thin and fringe-free to work in a diamond anvil cell form can be challenging to an inexperienced examiner. The diamond windows not only compress the sample but are transparent in both the mid- and far-IR spectral region.

In this application note, we will discuss a novel feature of the Nicolet iS50 FTIR Spectrometer that provides a rapid, easy way to acquire spectra down to 100 cm^{-1} . The system that we used was configured with the built-in iS50 ATR module and an Thermo Scientific™ Nicolet™ iS50 ABX Automated Beamsplitter exchanger. With this configuration, both a mid-IR and far-IR spectrum can be acquired from a sample with a single operation. In this report, extended range far-IR spectra were acquired from 1800 cm^{-1} to 100 cm^{-1} with the solid substrate beamsplitter and the integral diamond ATR shown in Figure 1 below. High-quality spectra were acquired at 4 cm^{-1} resolution in a couple of minutes.



Figure 1: The Nicolet iS50 FTIR Spectrometer configured with the iS50 ABX Automated Beamsplitter exchanger, the built-in iS50 ATR module, and the iS50 Raman module

Infrared spectroscopic analysis of inorganic pigments: ATR spectra from 1800 to 100 cm^{-1}

As mentioned, one of the important advantages of extended range FTIR is the ability to detect the peaks from inorganic pigments and fillers found in many paints, coatings, and plastics. The first sample analyzed was a small piece of white plastic. The best match found with the spectral search was the spectrum of rutile, which is a TiO_2 compound used as a whitener. Figure 2 shows a comparison of the ATR spectrum and the transmittance reference spectrum from the Washington State Crime Laboratory (WSCL) library. The two reference peaks described in Dr. Suzuki's paper for rutile are clearly present in this sample.

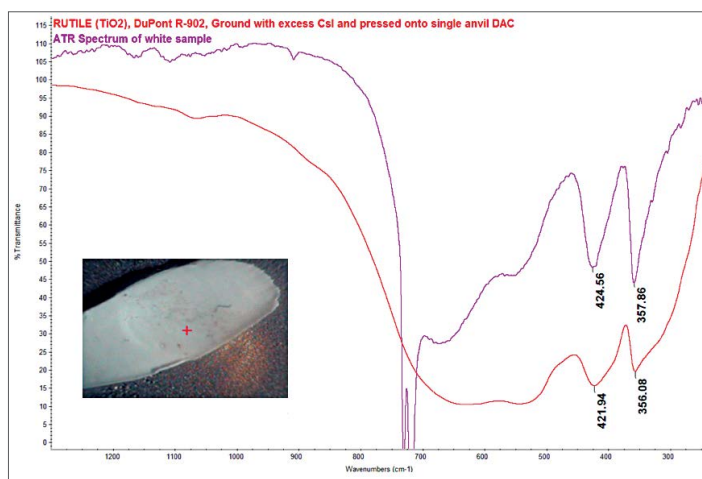


Figure 2: Extended range ATR spectrum compared to reference rutile spectrum acquired in transmittance with a diamond anvil cell

A second example is actually a bright yellow plastic material with two large peaks below 400 cm^{-1} . While it may be possible to identify the calcite with the peaks above 400 cm^{-1} , as in Figure 3, the only peak in the reference spectrum of cadmium yellow is near 250 cm^{-1} and matches nicely with the strong feature in our extended range ATR spectrum.

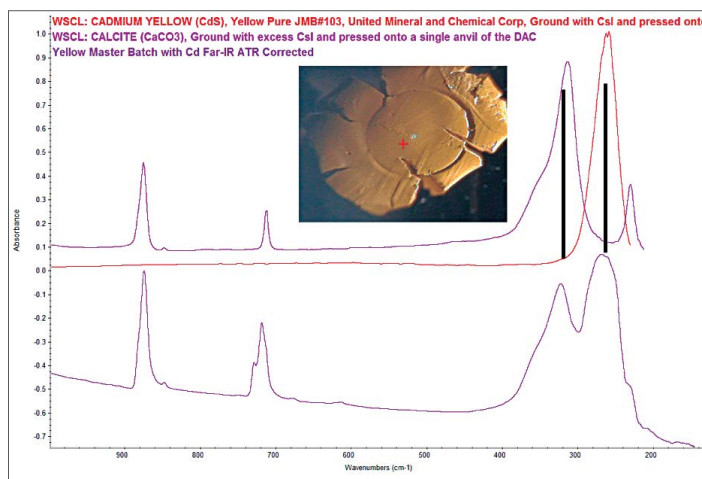


Figure 3: Comparing the spectrum from a yellow material to reference spectra of calcite and cadmium yellow

The analysis of automotive paint with extended range FTIR: ATR spectra from 1800–100 cm⁻¹

One unique feature of ATR spectroscopy is the limited depth of penetration into the sample. The depth of penetration is dependent on the wavelength of the infrared light and the refractive index of the sample. While the depth of penetration in the far-IR region may be several microns, this may still be smaller than the thickness of the paint layers. Figure 4 shows the spectra acquired from both sides of a paint sample. The spectra from the two sides are clearly different, indicating that we have at least two paint layers present in the sample. Spectral subtraction can often be employed to sort out the different spectral features and avoid having to manually separate the paint layers. Because all of the components in the built-in ATR module were optimized specifically for the Nicolet iS50 Spectrometer, the sensitivity is excellent. Although the Nicolet iS50 instrument is not designed as a microspectrometer, excellent infrared spectra can be rapidly obtained from samples smaller than 1 mm. This sensitivity is shown in the ATR spectra from a small sliver of paint in Figure 5.

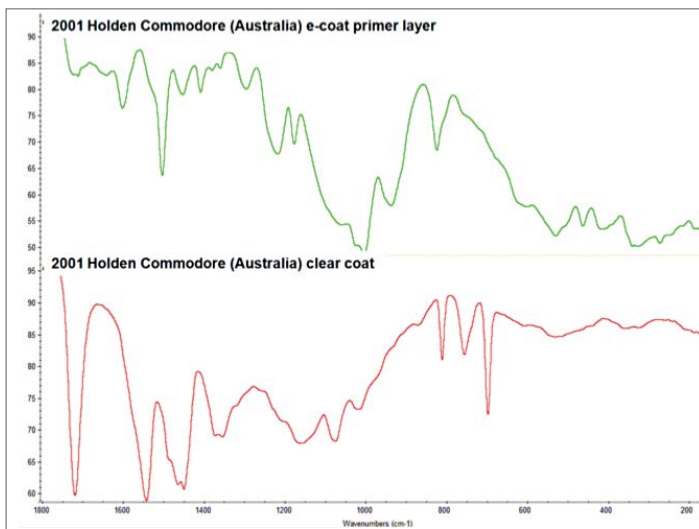
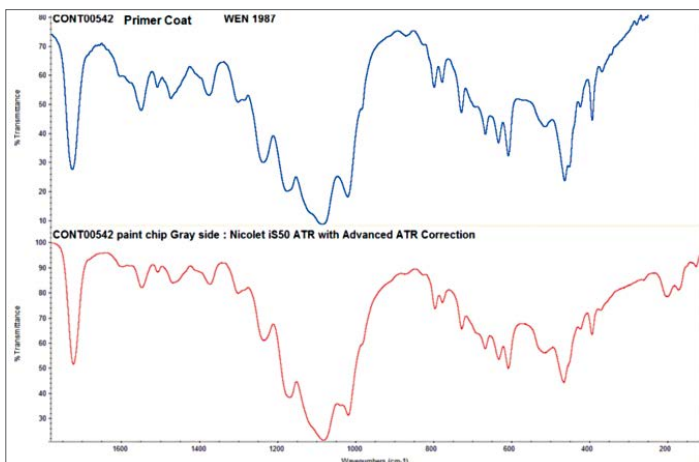


Figure 4: Spectra acquired from two sides of a paint chip showing obvious differences



Comparing ATR and transmission spectra

A spectrum acquired with the extended range, built-in ATR from a second paint chip is compared to the corresponding transmission spectrum. Although the sample preparation methods were different as well as the measurement techniques, the spectra are quite similar after applying the Thermo Scientific™ OMNIC™ Software advanced ATR-correction function. In addition, the ATR spectrum shows a few significant features below the 220 cm⁻¹ cutoff of the transmittance spectrum acquired with CsI optics.

Conclusion

In this report, we have shown a number of spectra acquired with the Nicolet iS50 Spectrometer and the new extended range, built-in ATR module. The integrated ATR module makes it easy to rapidly obtain infrared spectra all the way down to 100 cm⁻¹ from small amounts of sample. This report demonstrates that a high-sensitivity extended range, built-in ATR can play a significant role in the forensics laboratory.⁷ We believe that with proper validation the extended range ATR can provide a complementary method to characterize materials of interest to the forensic scientist. Building the Nicolet iS50 Spectrometer with the integrated iS50 ATR module offers the user an instrument with two sampling stations. The sample compartment remains available for transmission analysis or for inserting other accessories and modules. Combining the built-in ATR with the Nicolet iS50 Raman module with an infrared microscope creates a strong foundation for molecular spectroscopy in the forensics laboratory.⁸

Figure 5: A comparison of a transmittance spectrum acquired with CsI optics to a spectrum acquired with the built-in Nicolet iS50 ATR and the solid substrate beamsplitter

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