Handheld FTIR spectroscopy applications using the Agilent ExoScan 4100 FTIR with diffuse sample interface

Onsite, non-destructive analysis for geological, fabric, paint and plastic applications

Application Note

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Abstract

The Agilent 4100 ExoScan FTIR spectrometer with a diffuse reflectance sample interface enables powerful onsite, non-destructive, qualitative and quantitative infrared analysis of samples that are difficult to analyze with other handheld FTIR interfaces. Efficient collection optics and a long field depth facilitate easy analysis of geological, fabric, paint and plastic samples, overcoming the challenges associated with external reflectance, attenuated total reflectance and grazing angle reflectance techniques.

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Introduction

The Agilent 4100 ExoScan FTIR spectrometer provides infrared (IR) spectral analysis in a handheld package. This has made possible many applications for onsite, non-destructive analysis by IR spectroscopy, such as analysis of heat or UV damage on composites, identification and thickness measurements of anodized coatings, first article qualification, identification of paints, surface contamination measurements and thickness measurements of thin primers. The 4100 ExoScan FTIR is available with these sample interfaces:

- External reflectance, suitable for coating thicknesses and specular reflectance measurements;
- Diamond attenuated total reflectance, suitable for identification of soft and liquid materials; and
- Grazing angle reflectance, suitable for measurement of thin coatings or contaminants on metal surfaces.

Agilent also offers a diffuse reflectance sample interface for the 4100 ExoScan FTIR. This creates further opportunities for measurement of samples that were previously difficult to analyze by a handheld FTIR.

According to Snell's Law, when light strikes a surface, some portion is directly reflected at the same angle to normal as the incident light; this light is commonly referred to as specular reflectance. For a mirror smooth surface, over 90% of the light experiences specular reflectance. For non-mirror surfaces, the uneven surface causes light to be reflected at all angles; this light is called diffuse reflectance.

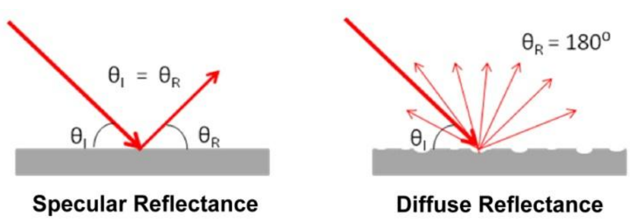

Figure 1. Specular reflectance versus diffuse reflectance

An accessory for measuring the spectra in a diffuse reflectance geometry by laboratory FTIRs was first described by Fuller and Griffiths in 1978 [Fuller and Griffiths, Anal. Chem., 50, 1906 (1978)]. The accessory focused the incoming light normal to the sample surface and collected the diffusely reflected light by a circular ellipsoidal mirror collinear with the incoming beam. Since that time, a variety of diffuse reflectance accessories have been used in laboratory spectrometers. In the near-infrared region, diffuse reflectance is the primary method of analysis for solid samples.

Agilent has designed a diffuse reflectance sample interface for use with the handheld 4100 ExoScan FTIR spectrometer. The 4100 ExoScan's interface uses a lens design that illuminates the sample with normal incidents, then collects the beam collinear. This is similar to the original design by Fuller and Griffiths, but it uses refractive optics and brings the beam back along the same axis as the incoming beam. Figure 2 shows a representation of the 4100 ExoScan diffuse reflectance optics.

Figure 2. The diffuse reflectance sample interface provides a large collection angle to effectively collect diffusely scattered light. Additionally, the slow focus provides a large depth of field, enabling data collection even when the sample is several millimeters from the beam focus. The combination of these two features enables easy measurement on real samples, which are not always flat or smooth.

Application examples

Sample identification

The 4100 ExoScan FTIR with diffuse reflectance provides high quality data on a variety of surfaces. The ease of sampling and high data quality makes it easy to identify samples with a short measurement time. Three sample types that were conventionally difficult, but can be easily identified with the 4100 ExoScan Diffuse Reflectance are fabrics, plastics and geological samples.

Mineralogy

Field identification of minerals is an important branch of geological sciences. Many minerals can be identified by their IR spectra. The covalent bonds in minerals due to silicates, carbonates, oxides, sulfates and other polyatomic groups provide strong IR bands. The frequencies of these IR bands are due to the mineral's molecular structure; in addition, the bands are often shifted due to the mineral's crystal structure. This combines to make IR spectroscopy a powerful tool for mineral identification. Even minerals that have similar elemental structures will have a different molecular or crystal structure, which enables even similar minerals to be distinguished.

Figure 3 shows spectra of three minerals that commonly occur together: franklinite, esperite and willemite. These samples were each measured from natural rocks using the 4100 ExoScan FTIR with diffuse reflectance. The spectra were collected at 8 cm^{-1}, co-adding 32 scans for an 8 second data collection time. These materials clearly have different spectra, which would be easy to identify with a library search. Large differences can even be seen between the esperite and willemite, both of which have a zinc silicate.

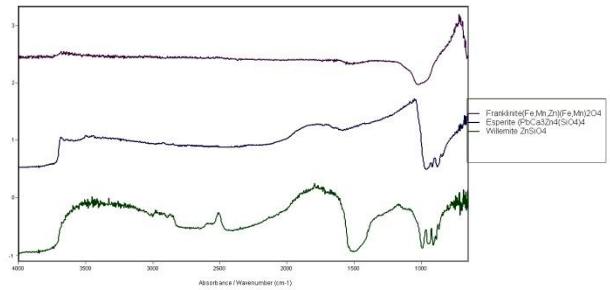

Figure 3. IR spectra of franklinite, esperite and willemite minerals collected on the 4100 ExoScan FTIR with diffuse reflectance

Figure 4 shows another three minerals that can be easily distinguished by field measurement with the 4100 ExoScan FTIR with diffuse reflectance: calcite, margarosanite and wollastonite. These spectra were measured with the same instrument parameters as those in Figure 1, directly from the rock surface with the 4100 ExoScan with diffuse reflectance.

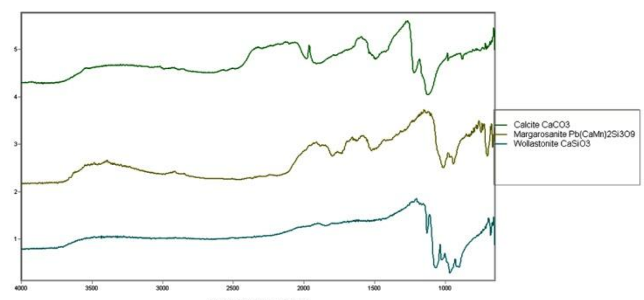

Figure 4. IR spectra of calcite, margarosanite and wollastonite minerals collected on the 4100 ExoScan FTIR with diffuse reflectance

The spectra in Figures 1 and 2 have both positive and negative bands. The negative bands are due to the minerals' high molar absorbtivity. In reflectance measurements, strongly absorbing bands can turn negative. In a laboratory setting, samples may be crushed and mixed with a non-absorbing matrix, such as potassium bromide, to eliminate the negative bands. In order to accomplish field measurements, the sample must be measured without preparation; therefore, the reflectance spectra are measured directly. Although this produces unconventional looking data, the spectra are still characteristic of the sample measured. This means that library matching can be accomplished with the same accuracy as laboratory data.

Plastic identification

Similar to the mineralogy identification presented above, the 4100 ExoScan FTIR with diffuse reflectance can also be used to identify many synthetic materials, such as plastics and fabrics. Identification of raw materials and finished products is an important aspect of any manufacturing operation. Increasingly, raw materials are purchased from a variety of sources. Even with the best vendors, materials are occasionally mislabeled or incorrectly shipped. For critical applications that require specific materials of construction, certification of incoming materials can prevent both scrapped parts and possibly accidents due to improperly manufactured parts.

Identification of raw materials is easily accomplished using mid-infrared spectroscopy. Until recently, however, spectroscopy was limited to measurement by laboratory equipment. The development of handheld IR spectrometers, such as the 4100 ExoScan FTIR with diffuse reflectance, now enables materials to be measured in a factory or loading dock setting. The 4100 ExoScan with diffuse reflectance has the added advantage of being able to measure both the raw material and finished products. The long depth of field enables the diffuse reflectance to measure samples with a shape that prevents them from being placed in direct contact with the front of the instrument. In addition, the non-contact sampling enables finished products to be measured without marking or affecting the product.

As an example, a customer had four different polymer coatings. The coatings are difficult to determine visually, but they have different properties with respect to weather resistance and paint adhesion. Figure 5 shows the Agilent MicroLab software Results screen for a library search from the customer library developed for this application. The measurement was from a finished product and was made in less than 15 seconds.

Figure 5. Library match showing identification of a polymer coating on finished product

Quantitative measurements — Geology

In addition to identification of minerals and soil types using a library search, the relative amounts of minerals in a given sample can be quantified using the 4100 ExoScan FTIR with diffuse reflectance. As was mentioned above, many minerals have a high absorbance, which produces negative bands at frequencies below 1500 cm^{-1}. Most minerals, however, have other bands at higher frequencies, which can be used for quantitation.

The measurement of sulfate in soil is key to construction of roads in some area. Excess sulfate can cause buckling of completed road surfaces. Though easy to measure by laboratory techniques, accurately mapping a proposed road site requires that samples are taken at close intervals. This lead to backups in the lab and slows the construction process. A method was created using the 4100 ExoScan FTIR with diffuse reflectance to measure sulfate in soil. The measurement is made in less than 10 seconds of sample acquisition time, making mapping of a proposed road site fast and accurate. Figure 6a shows spectra of soil samples containing different amounts of sulfate measured on the 4100 ExoScan with diffuse reflectance. Although the primary sulfate bands between 1000 and 1200 cm^{-1} are negative due to a high absorbance, the overtone of that band near 2200 cm^{-1} is linear. A calibration plot of the band area near 2200 cm^{-1} versus the concentration of sulfate is shown in Figure 6b.

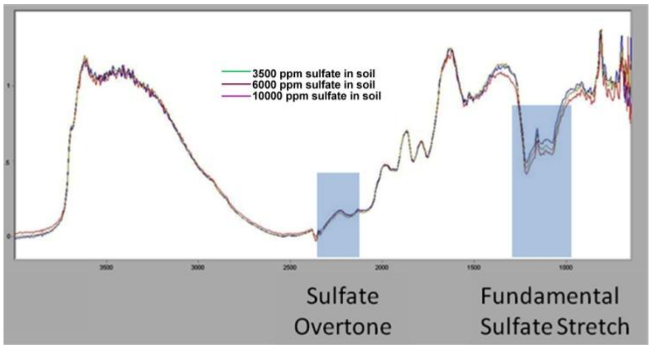

Figure 6a. IR spectra of soil samples containing 3500, 6000 and 10,000 ppm sulfate

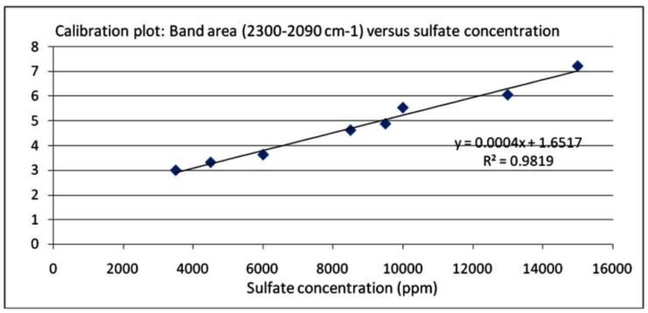

Figure 6b. Calibration curve showing correlation of sulfate overtone at 2200 cm^{-1} to sulfate concentration

In a second example, a method was developed to measure the relative amounts of five minerals as well as organics in soil using the 4100 ExoScan FTIR with diffuse reflectance. The method can measure carbonate, quartz, gibbsite, kaolinite, gypsum and organics in soils. Using a variety of bands, each of these can be determined individually from a single sample measurement. Figure 7 shows an example of a Results screen in the MicroLab software using this method.

Figure 7. Sample results of quantitative method measuring 6 components from a single soil sample

Conclusion

The Agilent 4100 ExoScan FTIR with diffuse reflectance creates a variety of possibilities for measurement of difficult samples using a handheld FTIR spectrometer. Both qualitative and quantitative methods have been demonstrated on samples that are traditionally difficult to measure in the field. The combination of efficient collection optics and a long depth of field make the 4100 ExoScan FTIR with diffuse reflectance easy to use and forgiving on rough sample surfaces. Combining these sample optics with the power of the 4100 ExoScan handheld mini-infrared spectrometer provides a powerful package for field measurement.

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Published May 1, 2011
Publication Number 5990-7793EN

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