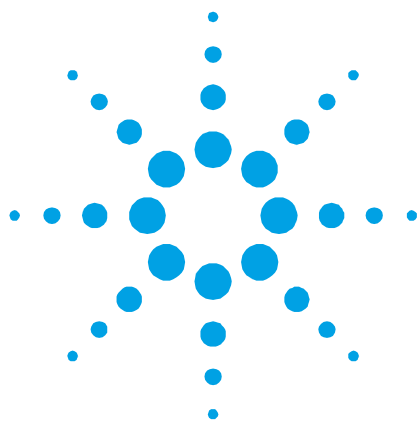




Elucidating rock and mineral composition with handheld Agilent FTIR analyzers

Onsite, diffuse reflectance measurement

Application Note

Authors

Alan Rein and Frank Higgins
Agilent Technologies
Connecticut, USA



Abstract

Agilent handheld FTIR analyzers are optimized for geological sample measurements, with an integrated diffuse reflectance sample interface. The instruments can be used on samples in the field, with little or no sample preparation. FTIR provides information about how the elements are bonded to form a mineral's chemical composition. When used in conjunction with x-ray fluorescence analyzers, which determine what elements are present, geoscientists are equipped with a powerful onsite identification system.



Agilent Technologies

Introduction

Agilent has introduced a new capability to scientists involved in the geosciences, with the development of field-ready Fourier transform infrared (FTIR) analyzers that have been optimized for the measurement of rocks, minerals and soil. These analyzers have an integrated diffuse reflectance sampling interface to enable molecular spectra to be obtained with little or no sample preparation required; that is, they can be used directly on the specimen in the field.

FTIR is a natural complement to the x-ray fluorescence (XRF) field analyzers that have been used for years by geoscientists. Whereas the latter analyzers provide information about what elements are present, FTIR provides information about how the elements are bonded to form the mineral's chemical composition. Thus, by using both XRF and FTIR, the geoscientist has a far more complete understanding of the specimen or site.

Diffuse reflectance mid-IR spectroscopy of rocks and minerals

FTIR spectroscopy provides information on covalently bonded molecules and therefore a variety of rocks and minerals can be analyzed using this technique. For example carbonates, nitrates, sulfates, oxides, hydroxides, silicates, aluminosilicates, phosphates, borates, vanadates, tungstates, arsenates, molybdates and uranates all have covalently bonded atoms and thus are amenable to infrared (IR) analysis. Rocks and minerals often contain trace elements or impurities that are unique to a specimen or locale, so the ability of the user to build their own on-board library is a valuable asset to these field FTIR analyzers. The spectra of a variety of mineral classes are shown in Figure 1, which include talc (magnesium silicate), vanadinite (lead chloride vanadate), gypsum (calcium sulfate dihydrate), phosphate rock (calcium phosphate) and calcite (calcium carbonate). The spectra are all unique and indicate the characteristic 'fingerprint' functional groups that are evident in the spectra, such as gypsum with the SO_4 asymmetric stretch at 1140 cm^{-1} and its

first overtone at 2240 cm^{-1} (broad). Though diffuse reflectance IR spectra look different to classical transmittance spectra (see 'Reflectance measurements of rocks and minerals'), the spectra are reproducible and the mineral can be readily identified from the Agilent diffuse reflectance FTIR library of rocks and minerals.

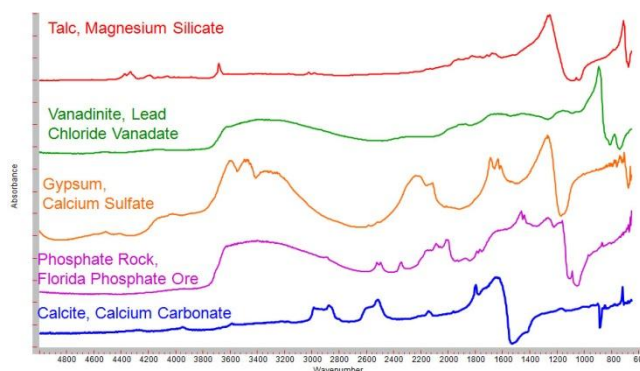


Figure 1. Stacked plot of different chemical classes of minerals carbonates, sulfates, and phosphates

Accurate mineral identification

A 4100 ExoScan FTIR system equipped with a diffuse reflectance sampling interface was used to investigate a collection of over 1000 Canadian and worldwide minerals. As examples, four white minerals specimens present in the collection had been identified as gypsum (calcium sulfate), celestite (strontium sulfate), barite (barium sulfate), and calcite (calcium carbonate). The IR spectra of the specimens in this collection revealed that many were either mislabeled or relatively impure. The spectrum of each of these specimens (Figure 2) all matched each other quite well, clearly containing a strong band arising from a carbonate contribution. In contrast, the spectrum (Figure 3) of a reference barite sample (verified by other analyses), shows the correct position of the sulfate vibration. Via library identification, all four specimens from the large collection were identified as predominately calcite.

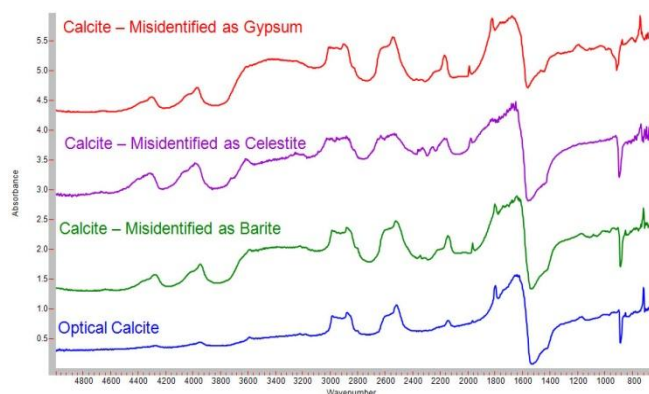


Figure 2. Photos and stacked spectra of white minerals

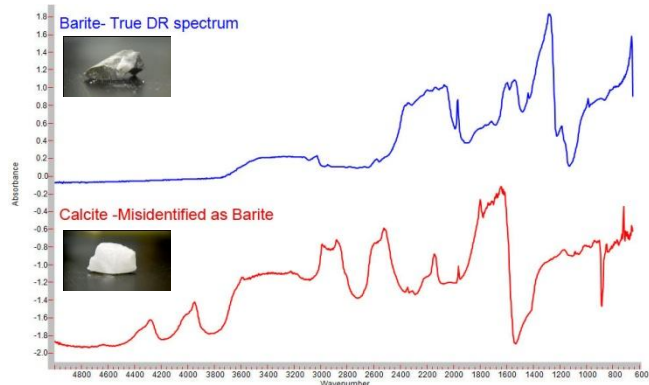


Figure 3. True barite spectrum versus misidentified spectrum

Identification of secondary components in a specimen

The 4100 ExoScan FTIR system was used to investigate the composition of lignite coal. Lignite is a soft, inexpensive, low quality form of coal that is typically used for powering steam engines. The amount of water and secondary inorganic components present can affect the power output of the coal as well as negatively contribute to environmental factors. In this example, we found that the FTIR could readily determine the water level present in the lignite and also show that, in specimens from a specific locale, there was kaolin clay

(hydrous aluminum silicate) present, which was not expected by the geologists who provided the samples (Figure 4). The unexpected kaolin clay in lignite is an example of an unknown contaminant that dilutes the quality of an economically important mineral. Such contaminants in minerals can be extremely difficult to identify by any other technique, even for an expert geologist, since the appearance and other identifying physical properties can be inconclusive. Many geoscientists rely heavily on XRF for the identification of minerals, which is very sensitive to heavy elements but insensitive to light elements such as aluminum, magnesium, and silicon present in many silicates. A specimen's FTIR spectrum can in most cases be a fingerprint for its identity and purity. For kaolin clay and other crystalline silicates (that is, talc, muscovite, biotite, and so on) the metal cations have covalently bonded hydroxyl groups (Me-OH), which are unable to hydrogen bond to each other or to any other atom, and therefore give rise to sharp highly characteristic 'Free OH' stretching bands at 3700 to 3600 cm^{-1} (Figure 4). The relative amounts of hydrocarbons and other organic substances can also be observed (3000 to 2800 cm^{-1} , usually sharp bands) from the IR spectra and assist in qualifying similar minerals such as anthracene, bitumen, oil sands, and industrial coal.

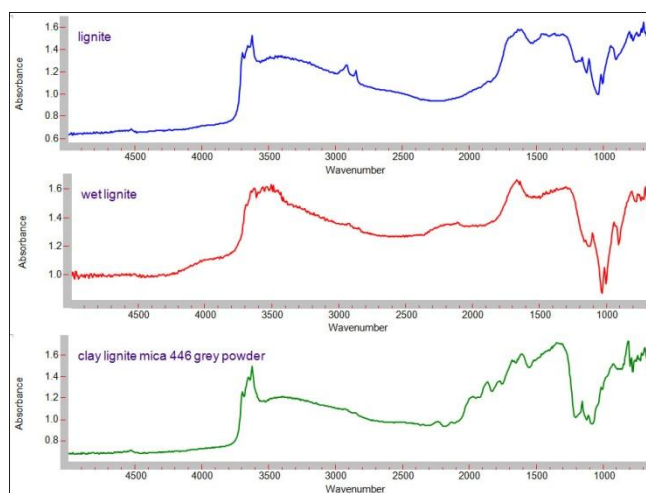


Figure 4. The lignite spectra (lignite, wet lignite, kaolin lignite)



The value of field-ready FTIR analyzers

FTIR analysis of rocks and minerals provides valuable information to the geoscientist including the ability to determine:

- The chemistry of the specimen or formation, providing insight into its origin.
- The relative purity of a mineral and the presence of secondary minerals.
- Relative amounts of minerals present in matrix.
- Inorganic and organic constituents such as water (and how it is bonded) and the presence of hydrocarbons (oil in rocks, sediments, and shale).
- Differences in crystal structure, polymorphic changes (that is, sodalite to cancrinite), crystallinity (amorphous versus crystalline silica).
- Identification of hydration states of minerals, such as calcium sulfate dihydrate (gypsum), calcium sulfate hemi-hydrate (plaster of paris), and calcium sulfate anhydrous (anhydrite).

Field-based FTIR analysis is a natural complement to field-based XRF (x-ray) analysis:

- Map areas of site based on chemical information and identify those areas that are most important and relevant.

- Eliminate the need to send irrelevant samples back to the lab for analysis.
- Make real-time decisions on where to concentrate efforts.
- Matching FTIR and XRF data together makes absolute mineral identification possible.
- Most XRF instruments cannot measure light elements (H to S on the periodic table) like sodium, magnesium, lithium, silicon, or aluminum. This makes absolute identification of rocks and soils difficult for most XRF instruments. Higher end XRF instruments can measure elements Mg to U but still do not give molecular structure information (for example, whether sodium is from a carbonate or a borate salt).
- FTIR is highly sensitive to most minerals composed of light elements, including all silicates, which compose 90% of the earth's crust. FTIR is also very sensitive to carbonates, sulfates, quartz, and borates.
- XRF is highly sensitive to heavy metals and is great at alloy identification.
- FTIR is insensitive to pure metals, but is sensitive to most metal oxides and metal carbonates, sulfates, and silicates.

Reflectance measurements of rocks and minerals

Spectra of rocks and minerals measured without sample preparation contain both positive and negative absorbance bands. Negative absorbances, also known as restrahlen bands, are due to a change in refractive index concurrent with the absorbance band; these are especially apparent with strongly absorbing (optically opaque) bands. Due to these effects, diffuse reflectance spectra of undiluted minerals look different to absorbance spectra of the same minerals; however, the spectra still contain information specific to covalent chemical bonds within the minerals. By building either a quantitative or library search method based on the undiluted diffuse spectra, pertinent information can be obtained.

In a laboratory experiment, these features would be minimized by grinding the sample with dry potassium bromide (KBr) powder. This has the effect of both reducing particle size and reducing the concentration, thereby eliminating restrahten bands. Another way to accomplish these goals is to sand the sample with silicon carbide paper, and directly measure the sample on the silicon carbide paper. This is an easy sample preparation that can be accomplished in the field, and still produces a dilute sample of small particle size. In the example shown in Figure 5, a calcite sample was measured both directly, and with the silicon carbide method, on the 4100 ExoScan FTIR. In both cases, absorbance bands appear at the same frequency, but the silicon carbide method provides smaller intensity, all positive bands.

Both measurements can be made with the 4100 ExoScan; methods for mineral identification and quantitation can be made with either technique.

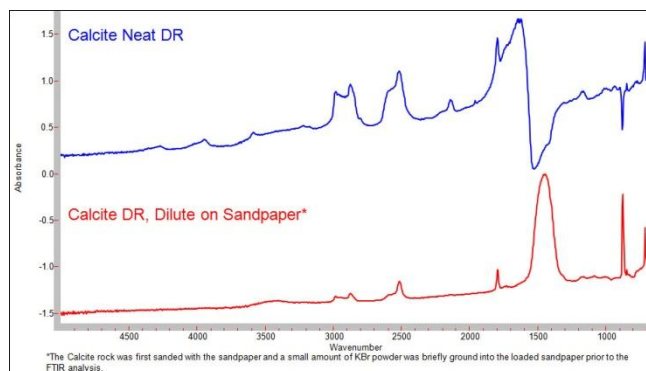


Figure 5. A calcite specimen was first sanded with sandpaper and a small amount of KBr powder was briefly ground into the loaded sandpaper prior to the FTIR analysis

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