Introduction

FTIR spectroscopy has long been used for the analysis of art and historical objects in support of efforts to conserve, restore and validate authenticity of these rare objects. The value of the technique for this application lies in its inherent sensitivity, specificity and non-destructive capabilities. Typical applications include analysis of paint pigments and binders, lacquers and finishes. FTIR can analyze the degree of oxidation of protective coatings used to protect objects, and the efficacy of those coatings. Measurement of chemical changes that result from aging is also a significant area of use for FTIR in support of art conservation efforts.
To date, virtually all FTIR spectrometers are located in labs and though the technique is non-destructive, the measurement often requires a small amount of the material of interest to be removed from the artifact. In order to ensure the minimum amount of damage to the object of interest, these samples are typically very small and often examined by microspectroscopic FTIR methods. This is positive, as only a small sample is required, but still the valuable object is being altered by sampling. Moreover, sampling such a small amount may not be representative of the chemical makeup of the larger area from which it has been removed. Furthermore, continuous monitoring of the restoration process is not desirable, as this would require a continuing sampling of the object, and thereby greater alteration.

**Agilent 4100 ExoScan and 4200 FlexScan FTIR analyzers**

The availability of handheld FTIR analyzers such as the Agilent 4100 ExoScan and 4200 FlexScan FTIR systems is important for several reasons. Firstly, the FTIR analyzer is small enough and compact enough to bring the system directly to the object of interest whether it is located in a lab, on a museum floor or at a field site. Secondly, no sample needs to be removed to analyze the object, and in fact, a number of areas on the object can be analyzed quickly in a truly non-destructive manner. Critical to getting useful information, the Agilent FTIR analyzers possess performance equivalent to that of traditional benchtop systems. This means that data obtained will be of high quality and information content.

Agilent handheld FTIR analyzers can:

- Analyze paintings, papers, documents and manuscripts, historical photographs, statuary, architecture, tapestries, tiles, mosaics, wood, and so forth.
- Be used at archeological or historic sites where cave art, ceiling paintings, mosaic tiles or large immovable objects are located; that is, at sites where objects are too large or too valuable to send to a lab or to remove samples for lab analysis.
- Determine the identity of natural and synthetic organic and inorganic pigments, colorants and dyes, siccative binders, lacquers, resins, coatings, adhesives, fibers, and so forth.
- Determine the effect of aging, including damage caused by UV, thermal and environmental pollution.
- Support cleaning and restoration efforts of rare and historical objects.
- Identify counterfeit objects or objects that have been restored.

**Application examples**

Some objects are too large and/or too historically significant to remove to a lab for analysis. Removing small samples from an object for lab analysis is not desirable, particularly if many areas on the artifact need to be investigated. For this reason, using a handheld FTIR analyzer at the object site is most valuable.

As an example, the 4100 ExoScan FTIR system equipped with Diffuse Reflectance sampling accessory was used to investigate the painted doors of the Beigans Chao-Tian temple doors in Taiwan (Figure 1). The infrared spectra of the aged paint on these doors indicate differences in the amounts of oxalates, calcium carbonate and cellulose present. The oxalates are a common by-product of microorganisms such as fungi and algae that feed off of the paint, pigments and cellulose and excrete oxalic acid, which can attack the paint pigments. The infrared spectra of a light red region of the doors shows little oxalate present, however a blackened region shows much higher levels of oxalate (Figure 2).

Analysis of a number of other spots on the painted doors showed different levels of oxalates, plus identified the major chemical components of the paint mixture including calcium carbonate, talc, kaolin clay and cellulose. This was accomplished without removing samples, nor disturbing the artifacts.
Two regions of a 17th century painting were analyzed with the 4100 ExoScan FTIR system (Figure 3). The painting was in poor condition, discolored from aging and years of dirt accumulation, and was primarily used for testing restoration techniques. An area of the painting that was not cleaned was measured by the FTIR analyzer; a second area that had undergone mild cleaning was also analyzed by the FTIR. The spectra of the two areas are shown in Figure 4.

The spectrum of the uncleaned area shows a baseline shift due to scattering of dirt particles on the surface as well as a signature of silicate, which likely arises from the dirt particles present on the surface.

The spectrum of the cleaned area shows far less baseline shift as well as absence of the silicate spectral band indicating that the mild cleaning procedure indeed removed some of the grime on the painting.

Ancient glues are produced from a variety of sources such as animal hides, bone or fish, whereas modern glues are typically synthetic such as cyanoacrylates or resin based. At archeological sites, antiquity scavengers may attempt to repair broken pottery in order to maximize the sale value of the object. Thus, the type of glue that may have been used to repair pottery can be an indicator of when the repair was made. Glues are also used to repair parchment manuscript or historic paintings and the type of glue used again is an indicator of when and who made the repair. FTIR is quite useful for identifying types of glue used in these repairs and...
thus can be a useful tool for aiding in the authentication of objects. Using handheld FTIR at archeological sites allows investigators to decide which objects should be sent to a lab for further evaluation. The infrared spectra of examples of ancient glues and modern glues, recorded using a 4100 ExoScan FTIR system equipped with a spherical ATR sampling accessory, are shown in Figure 5. The ancient glues exhibit the telltale protein bands in the 1500 cm\(^{-1}\) to 1700 cm\(^{-1}\) spectral region indicating that they are sourced from animals, whereas the modern glues show the strong carbonyl vibrations associated with the ester moiety in the synthetic glues. The presence of the fish/hide glues on potter shards, or in parchment repair materials, can be confirmed by searching the infrared spectra of the unknown glue against an onboard library containing the spectra of these glues.

As an example, a shard of pottery (Figure 6) found at Skaill on the Orkney Islands was suspected of being a piece of an ancient glue pot. The exterior and interior surfaces of this artifact were examined by the 4100 ExoScan FTIR system equipped with Diffuse Reflection sampling accessory. The interior and exterior portions of the artifact showed similar spectra (Figure 7a and 7b). Using the real-time mode, the 4100 ExoScan scanned the interior surface and located an area of the shard that exhibited a high level of animal bone glue (Figure 7c). This enabled verification that this shard is indeed a small portion of an ancient glue pot.

The infrared spectra contained in Figure 8 are ancient pigments and dyes derived from natural sources — Tyrian purple from mollusks, carmine red from cochineal, alizarin orange from plant roots and indigo woad from the isatis plant. These are very common ancient natural pigments and dyes used in a variety of paintings and historical objects, and FTIR analysis enables investigators to identify these pigments. FTIR has advantages for the measurement of pigments when compared to conventional handheld Raman spectroscopy. Fluorescence of the pigments induced by
the laser source used in Raman spectroscopy swamps the weak Raman signal. Moreover, the laser can cause burning and bleaching of sample areas, that is, may be destructive. Also, organic colorants have very high tinting power and may be found in low concentrations in art objects. Conventional Raman spectroscopy is not particularly amenable to low concentration analysis and coupled with strong fluorescence, it makes the analysis of pigments far more difficult. More advanced Raman methods such as SERS require removal of a sample from an object and specialized sample preparation methods, and thus is less amenable to at-site analysis.

As an example, the diffuse reflectance spectrum of stone tile on which carmine red pigment had been applied (Figure 9) shows bands that clearly indicate the presence of the pigment, as well as the bands of the underlying stone. The infrared radiation penetrates the pigment layer and measures a portion of the tile below. Diffuse reflectance infrared spectroscopy permits the degree of pigment loading to be determined and the effect of ambient light on the degree of fading as a function of pigment load to be investigated. FTIR spectra can be acquired without contacting the object or painting by placing the 4100 ExoScan FTIR system approximately 5 mm from the surface of the object.

Figure 9. The infrared spectrum of carmine red pigment on stone correlates quite well with the amount of pigment on the surface and also shows the bands from the underlying stone matrix.

Archeologists wished to determine if clay pottery artifacts found on the Orkney Islands had been heat-fired, and at what temperature. To do so, clay from the same locale was obtained and fired at increasing temperatures varying from 200 °C to 800 °C. The diffuse reflection FTIR spectra of the clays (Figure 10), recorded using the 4100 ExoScan FTIR system, shows significant changes in the bound and free OH region, which are linear with increasing temperature, as well as changes in other regions of the spectrum. Comparison of these fired samples to the actual clay shard (Figure 11) indicates that it was fired at roughly 500 °C. This result allows the researchers to determine the degree of heat that was applied, and insight into the firing process.
Figure 11. The infrared spectra of Orkney Island unfired clay and clay fired at 800 °C are compared to that of a clay fragment found at the site. The latter spectrum indicates that the pottery was fired at between 400 and 600 °C.

Major cities throughout the world encourage contemporary artists to paint remarkable murals on the sides of large buildings or structures. These cities are interested in preserving these murals, which are exposed to sunlight, pollution and the elements. Organizations such as Rescue Public Murals! in the U.S. are actively involved in bringing public attention to murals, documenting their artistic and historic significance, and obtaining expertise and funding to preserve them.

For example, the mural in Figure 12, entitled “Dr. J”, is located in Philadelphia, which has a significant collection of outdoor murals. In order to preserve this mural, as well as others, conservationists are exploring the use of various coatings that include UV stabilizers and other additives.

Figure 12. The Agilent 4100 ExoScan FTIR will be used to evaluate the condition of the “Dr. J.” mural to determine when re-coating/restoration is required.
Image courtesy of The City of Philadelphia Mural Arts Project and Amanda Norbutus, University of Delaware Preservation Studies Doctoral Program.

To do so they are carrying out accelerated aging experiments using coupons covered in various types and shades of paint that are typically used in outdoor murals. Different surface coatings are applied and then tested for their suitability for preserving these paints. FTIR spectroscopy is used to test the changes in both the paint and the coatings as a function of time — this is done by following changes in the carbonyl band (Figure 13) of the methacrylate-based polymer used as coatings. The plan is to use the 4100 ExoScan FTIR system to evaluate the condition of both the coating and the paint on the outdoor mural in order to determine its condition and when recoating/restoration is required.

Figure 13. The infrared analysis of the lower leg of the “Dr. J.” mural recorded with the Agilent 4100 ExoScan FTIR shows spectral contributions from both the polymer coating and the underlying paint. By following changes in these bands, conservationists hope to be able to determine when restoration is required.

Conclusion

FTIR spectroscopy is useful for a wide range of applications in the conservation and restoration of art and historical objects. With the availability of handheld FTIR analyzers such as the Agilent 4100 ExoScan and 4200 FlexScan FTIR systems, the spectrometer can be brought directly to the object to be analyzed. Advantages of the 4100 ExoScan and 4200 FlexScan handheld, portable FTIR for art and historical conservation and authentication are:

- Large objects, or objects that cannot be brought to a lab can be measured in situ.
- The compact size of the system and its sampling interface configuration enables the analysis of less accessible spots (Figure 14) and/or analysis of curved surfaces of an object.
- Agilent analyzers can be used in any orientation, thus art that is located on ceilings, in caves, and so on can be analyzed as easily as those on flat walls.
- Agilent handheld FTIR systems allow larger areas to be scanned in real-time mode to locate areas of interest for more thorough infrared investigation.
• In restoration processes, it is not necessary to remove particles from rare objects for analysis, and therefore the handheld FTIR systems are excellent for following complex restoration processes.

• Since Agilent handheld FTIR systems are on-board battery operated, local power supply is not an issue at ancient conservation sites where cave art, ceiling paintings and other immovable ancient objects may be located.

• The handheld 4100 ExoScan FTIR system offers interchangeable sampling accessories and thus the optimum sampling method, whether ATR, diffuse or external reflectance, can be selected to carry out the analysis.

• Since FTIR does not use a laser as the measurement source, as handheld Raman spectrometers require, there is no danger of burning or bleaching the sample. Sample fluorescence is also a significant negative issue in Raman spectroscopy, and does not pose an issue with FTIR.

• Allows investigators to make informed decisions at the locale on what and where to analyze, thus reducing the number of less important samples that need to be sent to a lab.

Figure 14. Compact size and ideal sampling interface configuration allow Agilent handheld FTIR systems to investigate curved, less accessible areas of this Egyptian sarcophagus. Image courtesy of Glasgow Museum