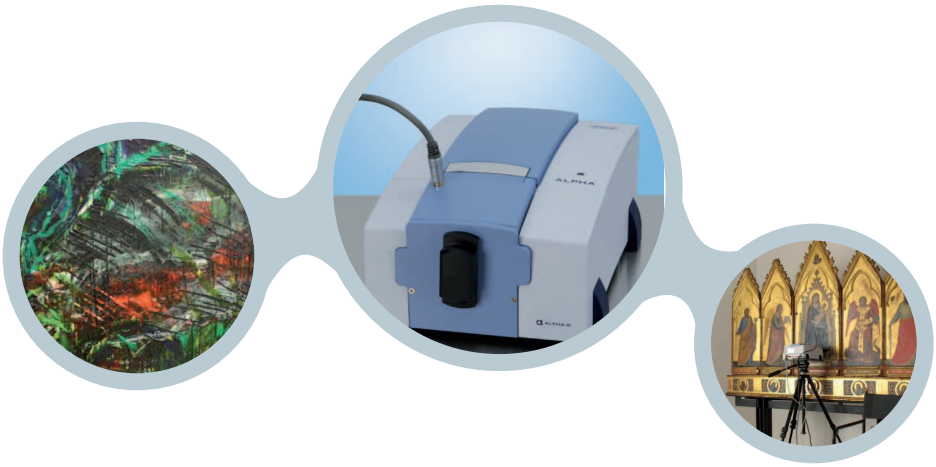

Application Note AN #95

Contactless analysis of paintings with FT-IR spectroscopy

The restoration of works of art is a very complicated task and there is often the risk to inflict damage on the object itself. In particular, paintings - which should be on canvas, murals, papers or parchments - are very heterogeneous objects.

Therefore it is mandatory to gather as much information as possible about the nature of the constituent materials and the subsequently applicated ones, in the forefront of the restoration work. For example, in order to find an appropriate cleaning agent to remove surface impurities or an altered varnish layer from a painting, information about the chemical identity of all components is fundamental. Another task where knowledge about the chemical nature of a certain paint is required is the reproduction of historic paints for scientific reasons.

An ideal technique for the analysis of paint and paintings is the Fourier transform infrared (FT-IR) spectroscopy. Typical absorption patterns in the IR-spectrum allow the identification of substances present in the sample. Until recently, a major drawback of this technique was the fact that an on-site measurement of the artwork was not possible. For example, measurements on murals or big paintings required destructive sampling because pieces of the sample had to be transferred to the laboratory. In many cases this is of course not an option and a non-destructive measurement technique

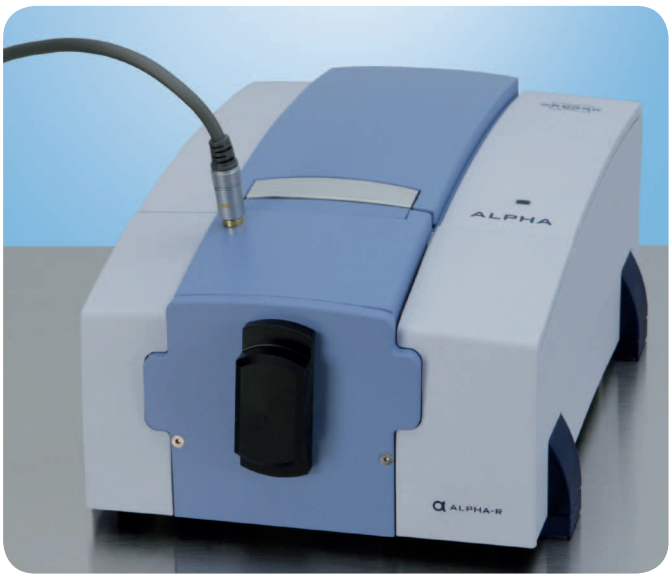

Figure 1: ALPHA-R with forward looking reflection unit including video.

is the only alternative. Now the ALPHA FT-IR spectrometer in combination with the front reflection module offers a fast and easy method to measure infrared spectra of mural paintings or paintings on-site and in a contactless and non-destructive manner.

Instrumentation

The very compact ALPHA FT-IR spectrometer is a robust and affordable system that is very easy to operate. Due to its rugged design, the ALPHA is insensitive to vibrations and can be operated almost anywhere. With a weight of only 7 kg and a footprint of a laboratory notebook it can be moved easily and is immediately operational without any need for alignment. Its patented RockSolid™ interferometer design is wear free and guarantees reproducible results even under harsh measurement conditions. In combination with the front reflection module the ALPHA allows an on-site measurement that is contactless and does not alter the sample in any way. The built in video-camera gives the user a direct impression of the measurement area and allows an exact positioning of the spectrometer. With a working distance of about 15 mm between the ALPHA and the object, an unwanted accidental contact is safely prevented. The sample spot size is about 5 mm in diameter and can optionally be reduced to 3 mm when a higher spatial resolution is needed. Furthermore, the ALPHA can be operated completely cordless by means of a Wi-Fi connection and a battery pack for the spectrometer.

Figure 2: Nottetempo by Mario Schifano with a tripod mounted ALPHA-R in the front.

Surface analysis of a painting by Mario Schifano[1]

The painting "Nottetempo" (CSAC - Centro Studi e Archivio della Comunicazione – Parma) was created in 1986 by the Italian artist Mario Schifano and is an ideal example to show that even complex modern paint compositions can be analyzed via FT-IR spectroscopy. The measurement setup is shown in figure 2 with the ALPHA-R has been mounted on a tripod to facilitate that measurements on various positions of the painting.

Figure 3 shows the raw reflectance spectra measured on two different spots of the painting covered with a blue and white pigment respectively. On a first glance, both spectra look very complicated and expose artifacts that usually do not appear in infrared-spectra. In reflection spectra, these effects can happen due to anomalous dispersion that occurs in highly specular samples in spectral regions which exhibit a strong light absorption. As a result the bands of the spectra are distorted and look similar to those of a first derivative curve. These distortions can be converted into absorption bands by means of the Kramers Kronig transformation (KKT) that is included in Bruker's spectroscopic software OPUS.

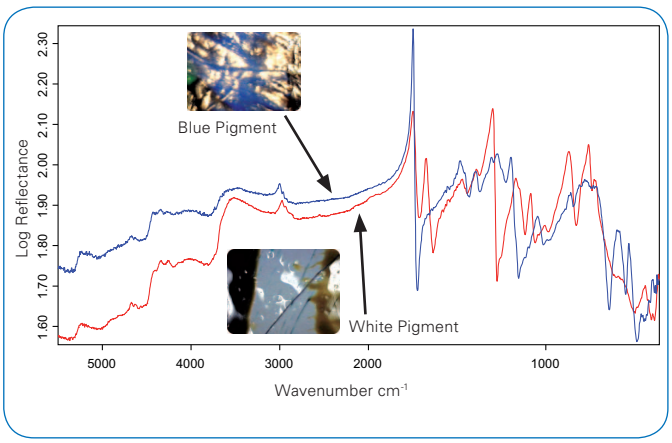

Figure 3: Raw reflection spectra of two different measuring points with two different pigments (blue pigment = blue spectrum, white pigment = red spectrum).

The corrected spectrum of the white pigment is shown in figure 4 as the black curve. It is obvious that the spectrum now looks like a "normal" absorption-spectrum. Analysis was then performed with the assistance of the library search function of OPUS and dedicated libraries. Additionally to the sample spectrum, figure 6 shows the sum spectrum of the reference components that were identified. For its calculation, reference spectra of nitrocellulose (used as a binder), alkidic resin and titanium white pigment were used. It is remarkable how much both spectra resemble each other since even small bands of the sample spectrum have a counterpart in the sum spectrum. This is a clear indication that all the main components of the paint were correctly identified.

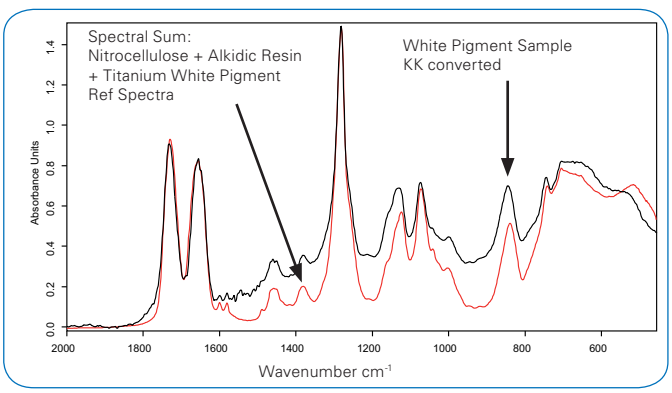

Figure 4: KKT transformed sample spectrum of a white pigmented area (black curve) and sum spectrum of different reference spectra (red curve).

In figure 5 a similar evaluation has been performed with the blue pigment sample. The KKT transformed spectrum of the pigment is shown as a black curve; again it is obvious that all derivative like bands have been convertes into absorption bands completely. The chemical composition is again evident when the spectrum is compared against a sum spectrum

of two reference spectra: Poly(methyl methacrylate:ethyl acrylate),3:2 and cobalt blue. There is again a striking similarity between both spectra which means that all important constituents of the paint have been determined.

This case study shows a real benefit of this technique, i.e. the wide spectral range accessible. Here, the option to investigate wavenumbers down to about 400 cm^{-1} gives up the opportunity to identify also the inorganic pigments and not only the organic binders or ground layer. In fact, Titanium White and Cobalt Blue have fingerprint signals only below 800 cm^{-1}, a region that cannot be accessed by spectrometers using MIR calcogenide fiber optics.

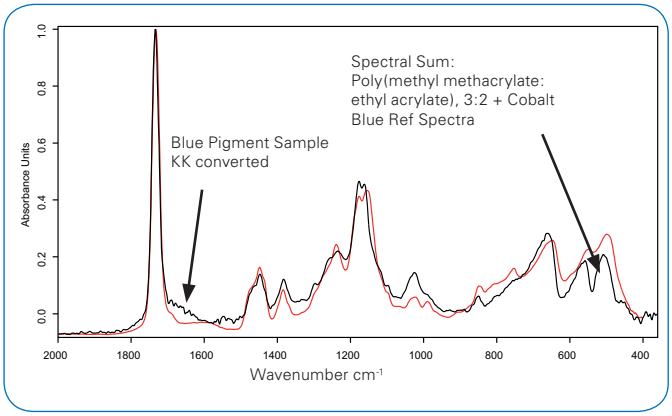

Figure 5: KKT transformed sample spectrum of a blue pigmented area (black curve) and sum spectrum of different reference spectra (red curve).

Surface analysis of a painting by Giotto[2]

The measurement can also be used for the analysis of ancient paintings. Figure 6 shows a really famous painting by Giotto (Polittico, about 1330, Pinacoteca Nazionale di Bologna, Italy) during the FT-IR measurements with a setup consisting of a tripod mounted ALPHA spectrometer in combination with a laptop computer.

As an example the result of the analysis of a region on the wing of the angel located on the second panel from the left (Arcangelo Gabriele) is shown in figure 7. The small inset-picture shows the camera-view of the measuring point. In this case the ground layer (gold foil) gives a so called transflectance spectrum, already similar to an absorbance spectrum, so it is not necessary to apply a KKT. In addition to the sample spectrum the reference spectra of terpenic varnish, calcium sulfate and calcium oxalate are shown. The combination of these three reference spectra accounts for all major absorbance bands in the sample spectrum indicating that all important constituents have been detected[3].

Figure 6: Polittico di Giotto with a tripod mounted ALPHA-R and a laptop PC.

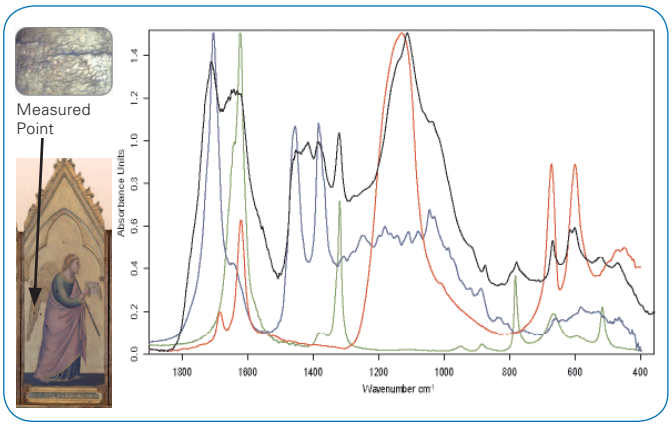

Figure 7: Detail of panel and video image of the measurement point (left). Right: Sample spectrum (black) and reference spectra of terpenic varnish (blue), calcium sulfate (red) and calcium oxalate (green).

Summary

The ALPHA FT-IR spectrometer with the front reflection module is a flexible and easy to use instrument for the identification of all kinds of materials like pigments or varnishes. The analysis can be performed on-site and is contactless and non-destructive. For the post-processing and analysis of the measured spectra Bruker´s OPUS software is offering a wide range of powerful tools which are still easy to use. In conclusion, FT-IR spectroscopy can provide crucial information about all kinds of paints for conservation and restoration alike.

[1] In cooperation with D. Bersani, A. Casoli and P. P. Lottici, *University of Parma,* Italy
[2] In cooperation with D. Cauzzi, *Soprintendenza BSAE di Bologna,* Italy
[3] Il Polittico di Giotto nella Pinacoteca di Bologna - Nuove letture, *D. Cauzzi e C. Seccaroni,* Centro Di (2009)

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