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NON-INVASIVE MID-INFRARED FIBRE OPTIC REFLECTANCE SPECTROSCOPY ANALYSIS OF PAINTED GLASS MAGIC LANTERN PLATES

Rebecca Ploeger, Dominique Scalarone, Oscar Chiantore
Department of Chemistry I.P.M. and
NIS, Nanostructured Surfaces and Interfaces Centre of Excellence
University of Torino – Via Pietro Giuria, 7 – 10125 – Torino (TO) - Italy

ABSTRACT
A series of painted glass magic lantern plates from the Museo Nazionale del Cinema, Torino (Italy), were studied using mid-infrared (Mid-IR) fibre optic reflectance spectroscopy (FORS), a non-invasive technique, to test its potential in the identification of the types of binding media and pigments used in the paints. A magic lantern is the ancestor of the modern slide for a slide-projector; an image was carefully painted on glass plate which was then placed in front of a light source and projected onto a screen or wall. Mid-IR FORS is gaining popularity in the conservation field due to its non-destructive nature and relative simplicity in use; however, this technique gives complicated and relatively low intensity spectra, because it relies on the reflected beam from the sample and, in some cases, also the substrate. The reflection within the range of 4000 cm^{-1} and 1000 cm^{-1} at a resolution of 4 cm^{-1} was measured at several points of interest on the magic lantern plate surfaces and also on a series of reference samples prepared on glass. This paper will discuss some of the findings and complications of the use of this technique on several magic lantern plates from the collection of the museum from the second half of the 19th century . The results from the Mid-IR FORS analyses correlate well with the results from other techniques in previous analyses on the magic lantern plates; it is found that different types of binding media can be distinguished from each other and characterised.

INTRODUCTION
Mid-IR fibre optic reflectance spectroscopy (FORS) is a non-invasive and flexible technique allowing one to examine unique objects and materials. This technique has been used in the conservation field for about 10 years [1] and continues to gain popularity. The fibre optic probe contains a bundle of chalcogenide fibres, transparent in the mid-IR spectral region, with a number dedicated to directing the radiation to the object and the others dedicated to directing the radiation reflected back from the object, and is designed to be coupled with a Fourier transform infrared (FTIR) bench. *In-situ* mid-IR measurements on objects are possible if the fibers are coupled with a portable FTIR spectrophotometer. The analyses can be done with or without contact with the surface of the material and perpendicular or angled, as desired for optimizing the collected spectrum [1, 2, 3].

Particularly delicate objects, for which mid-IR FORS is ideal, are painted glass magic lantern plates (Figure 1). Described as the ancestors of the modern slides for slide projectors, the plates consisted of a carefully painted image on a clear glass surface which was held in place by wood or another type of support. The slide image was then projected onto a suitable screen by the magic lantern, by passing a bright beam of light through the slide and an enlarging lens, and was for an early form of entertainment [4]. Due to the fragile nature of the painted glass magic lantern plates, a non-invasive and flexible technique is ideal for the analysis of the binding materials of the paints used.

Though the 15th to 19th centuries, before photography, the images on the magic lantern slides were painted by hand; these delicately and elaborately hand-painted glass slides are considered to be miniature masterpieces of their own. The main painting techniques described in the literature involve watercolour and oil and often both on the same piece of glass. Also sometimes used was tempera (animal glue). To help realize the design, sometimes a very thin layer of varnish, diluted gelatin or a solution of water and sugar was placed on the glass, allowing one to lightly draw on top the design with a thin brush and black pigments or a neutral colour, with a pencil or with chalk or calcium carbonate. A more simple method, with lower quality results, was to trace a design on a sheet of gelatin using a thin point and carefully scattering a fine powder of lead on the surface which is deposited in the incisions. Another method frequently used, especially to obtain realistic images, was to place a clean glass over a design and copy it directly using coloured paints without originally creating an outline. Three coloured layers were applied, each one with a varnish, the first one for the background and the subsequent for details [4].

Figure 1: Panoramic glass showing the story of Noah's Ark from the early 19th century, United Kingdom, currently in the collection of the Museo Nazionale del Cinema, Torino, Italy

The oil colour technique used the more transparent traditional oil colours. The paint was added in layers, at least three; the second and third layers were painted with more luminous and pure colours. Once complete, the paint surfaces were cleaned and varnished where necessary with a very dilute mastic varnish to give the final retouches. For the painting glass magic lantern plates, where fine details and clarity were essential, a fine design was first laid out on a flat piece of glass and coloured in with watercolours over which was spread a layer of varnish to give the necessary transparency to the image. This method was established and used by the accomplish British microscopist Rev. Dr. D. Dallinger in the 19th century [4].

As mentioned, Mid-IR FORS is currently making its way into the conservation science field [2, 3, 5, 6]. It's main advantages of being non-invasive and flexible (and portable) makes it ideal for *in-situ* analysis of art objects in galleries and museums or on objects which cannot be moved from their locations. However, the spectra obtained by this technique are complicated and difficult to interpret. Due to surface topography and geometry, the reflected energy is usually in the range of 5-10% [7] and the spectra obtained are low in intensity and noisy [2]. Distortions in the spectra, such as shifts in absorption frequencies and peak shapes are also observed in mid-IR FORS spectra making it difficult or impossible for comparison purposes with transmission and ATR spectra [3]. Many of these distortions originate from specular reflection; these distortions, including *Reststrahlen* (residual energy) bands and peaks which resemble first derivatives, must be carefully interpreted and corrected, when possible. Saying this, a good understanding of the reflected energy is required for the employment of the correct spectral correction; for some peak ratio changes caused by diffuse reflection the Kubelka-Munk correction can be used, and for some spectral distortions caused by specular reflection the Kramers-Kronig correction can be used [3, 5]. Some mid-IR FORS spectra require the use of both corrections for correct interpretation. The specular component of the reflection can be decreased by the inclination of the fibres; however, this leads to signal loss [3]. Deviations from transmission spectra in diffuse spectra manifest themselves in changes peak ratios, because of the differences in the penetration of the wavelengths in to the sample and sample surface roughness. Specular distortions are observed as peak shifts (to higher wavenumbers) and changes in shape; peak shape distortions include first order derivative peaks or r*eststrahlen* bands (the complete inversion of the peak) [3].

Presented in this paper are mid-IR FORS characterisation results of the binding materials used in the painted images on the glass magic lantern plates from the Museo Nazionale del Cinema's collection in Torino, Italy. The two magic lantern glass plates studied were *Ponte del diavolo giorno* and *Ponte del diavolo notte* and are described in more detail in the experimental section. Characterization results will be discussed, as well as the results of the studies of the spectra collected with various probe to surface angles.

EXPERIMENTAL

Reflectance spectra were acquired using a Thermo Nicolet FTIR NEXUS spectrophotometer, connected to a Remspec fibre optic immersion probe and liquid nitrogen cooled MCT (photoconductive HgCdTe) detector. The Y-shaped fibre optic probe had a tip length of 10 mm with fibres (500μm each in diameter) made of chalcogenide, with a glass core matrix of a As-Se-Te mixture and a As, Se, S glass cladding mixture. The probe contained a 19 fibre bundle; seven fibres sent the radiation to the sample, and the other 12 were dedicated to guiding the reflected energy to the detector. Spectra were collected from 4000 to 1000 cm^{-1} with 4 cm^{-1} resolution and 128 scans. A polished piece of aluminium was used as the reference material for the background spectrum. The probe, securely mounted with a retort stand and clamps, was kept at a 90˚, 88°, 85° and 80° to the sample surface and a small space of approximately 1 to 2 mm was left between the probe and sample surface. Data was collected and analysed in OMNIC 6.1a software. Employed in some cases to help with the interpretation of the spectra, but not discussed in this work, were the Kubelka-Munk and Kramers-Kronig corrections. The spectra were all smoothed to 11 cm^{-1} smooth points twice.

Some limitations of the fibres and technique were undesired absorptions; the fibres show an Se-H stretching absorption in the 2050 to 2250 cm^{-1} range blinding the regions and the environmental moisture at 3100-3500 cm^{-1} and CO_2 at 2250 cm^{-1} also caused interference, blinding the regions [1, 5]. These areas were considered as blind areas and blacked out during the interpretation of the spectra collected in this study.

The painted glass magic lantern plates were *Ponte del diavolo giorno* (The devil's bridge, day) and *Ponte del diavolo notte* (The devil' bridge, night). Both plates are from Germany and were made in the second half of the 19^{th} century. They are designed to be "dissolving views", both having the same scene, a bridge and country-side surroundings, at two different moments during the day; one with the light of the sun (day) and the other with the twilight of night. Placed over one another during the projection gives the effect of the transition between day and night. Figure 2 shows the *Ponte del diavolo giorno* and the probe setup.

Reference samples were prepared on glass microscope slides and measured the same manner as the glass magic lantern plates. Thin film reference samples of clarified linseed oil (used to represent an oil paint in general, from Lefranc & Bourgeois, France), rabbit skin glue (bulk from Rima, a local art supplies store), gum Arabic (for Water Colour from Winsor & Newton, England) and Venetian turpentine (oil colour, from Talens, Holland) were prepared and analysed for comparison purposes.

Figure 2: Left: Ponte del diavolo giorno (painted side of glass plate), second half of the 19th century, Germany, currently in the collection of the Museo Nazionale del Cinema Torino, Italy.
Right: Ponte del diavolo giorno (painted side of glass plate) and probe setup

RESULTS

The reference materials were necessary in the interpretation of some of the spectra collected on the painted glass magic lantern plates. It was noticed that oil (linseed oil), watercolour (natural gums) and tempera (animal glues) were the most widely used painting materials for glass magic lantern plates, so reference samples of these materials were prepared. A reference sample for Venetian turpentine was also prepared, since varnishes were also historically used in the preparation of the glass magic slides. Linseed oil (uncorrected) had a characteristic C=O vibration peak at 1754 cm^{-1}; however, this peak shows a first order derivative specular distortion. Also present, were the CH_2 stretching peaks at approximately 2951 cm^{-1} and 2850 cm^{-1} and in the noisier fingerprint region were peaks at 1465 cm^{-1} and 1257 cm^{-1}. Gum Arabic (uncorrected) had a very characteristic C-O peak at 1162cm^{-1} and peaks at 1454 cm^{-1} and 1680 cm^{-1}. Rabbit skin glue (uncorrected) had a very characteristic peak at 1700 cm^{-1} from the C=O in the amide group in the glue protein. Also observable was the peak around 1574 cm^{-1} likely from the C-N-H bending vibration of the protein. Venetian Turpentine reference (uncorrected) had a characteristic C=O peak around 1727 cm^{-1} and fingerprint peaks at approximately 1467 cm^{-1}, 1265 cm^{-1}, 1146 cm^{-1} and 1064 cm^{-1}. The reference spectra can be seen in Figure 3.

An important observation to note is the shifting of the peaks to longer wavenumbers compared to the values reported for transmission and attenuated total reflectance spectra. This is likely due to the contribution of the specular reflection [5]. Other phenomena observed were the distortions of some of the main peaks into a peaks resembling first order derivatives and *reststrahlen* bands due to the intense reflectance maxima. Table 1 describes the absorption of the most characteristic peaks in the uncorrected mid-IR FORS spectra compared to the absorptions noted using the same instrument, with an ATR accessory.

Ten areas were examined on each piece (Figure 4), with the probe at 90° to the sample surface, and there were variations of the paint binder composition; however the components remained the same. On the Ponte del Diavolo Giorno and Notte the binding materials identified were oil and watercolour, gum Arabic or a gum with a similar infrared spectrum. The gum material identified is likely part of a preparatory layer, which could explain why it is more prevalent in areas without much colour. Also suspected was a resin-oil paint binding material or a varnish layer or layers. Also present in some spectra were distortions resembling *reststrahlen* bands, that distorted much of the finger-print region making binder identification difficult or impossible.

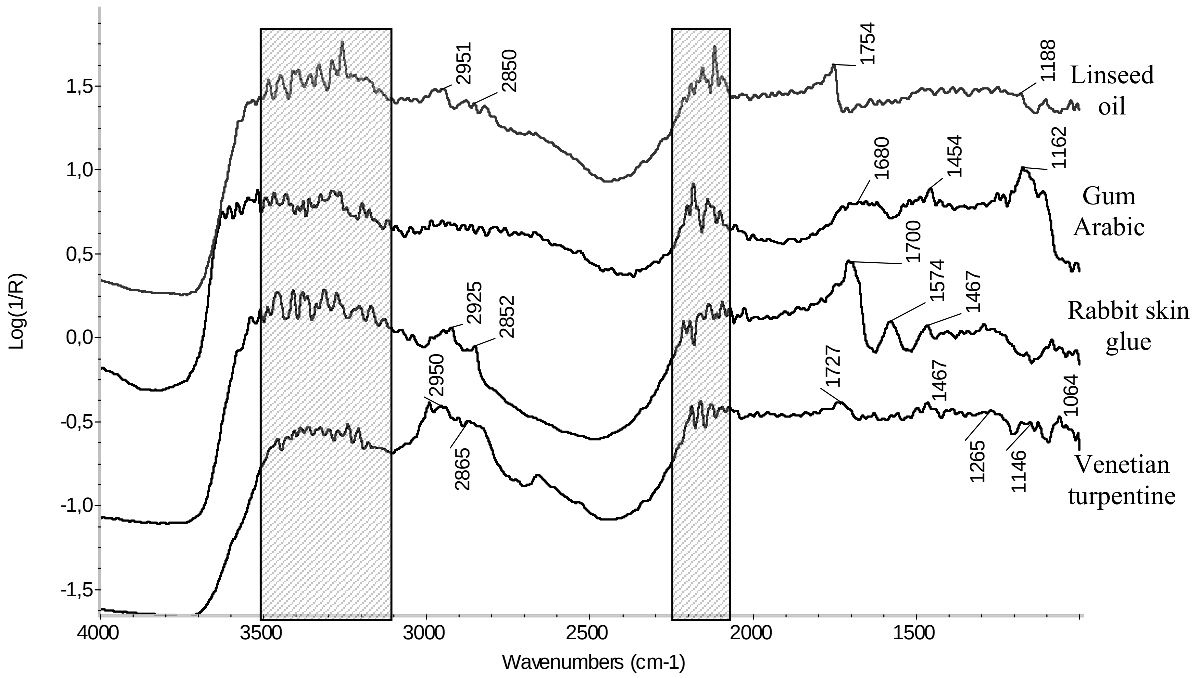

Figure 3: Mid-IR spectra (uncorrected) of the four reference materials. From top to bottom: linseed oil, gum Arabic, rabbit skin glue and Venetian turpentine. Taken at a 90° angle to the sample surface. Arbitrary axis, smoothed 11 cm^{-1} twice.

Linseed oil	C-H	C-H	C=O	C-H	C-O	C-O
Mid-IR FORS	2951	2850	1754	1465	1257	1188
ATR	2924	2854	1743	1462	1238	1160

Gum Arabic	O-H	C-H	C-O
Mid-IR FORS	1680	1454	1162*
ATR	1601	1413	1021

Rabbit skin glue	C-H	C-H	C=O	C-N-H	C-H
Mid-IR FORS	2925	2852	1700	1574	1467
ATR	2920	2848	1634	1538	1455

Venetian turpentine	C-H	C-H	C=O	C-H	C-O	C-O	C-O
Mid-IR FORS	2958	2865	1742	1467	1265	1146	1064
ATR	2932	2856	1694	1447	1248	1131	1038

Note: The peaks reported are approximate values, since noise and spectral distortions sometime limit the accuracy of determining the peak maxima.

* It is likely that this intense absorption peak in ATR is distorted in the reflectance spectrum, and what is observed is the edge of the distortion (either forming a first derivative distortion or a reststrahlen band) or what is observed is a shoulder in the absorption peak

Table 1: Comparison of the maxima of the absorption peaks between mid-IR FORS and FTIR-ATR of the same samples

Figure 4: The sample points on the Ponte del diavolo giorno (left) and Ponte del diavolo notte (right)

In certain areas the main composition of the binder material was identified as a gum, possibly gum Arabic, in other areas the main binder material was identified as a oil-resin mixture, or mixed layers, and in the rest of the areas a combination of the gum and oil-resin mixture. Figure 5 shows the spectrum of point 8, a pinkish part of the sky above the roof, taken on the *Ponte del diavolo giorno* with the gum Arabic reference sample, showing that they correspond relatively well with overlapping peaks at approximately 1687 cm^{-1} 1449 cm^{-1} and 1136 cm^{-1}. Also Figure 5 shows the spectrum of point 10, blue water, sampled on the same magic lantern plate with the oil reference sample for comparison. It can be seen that the carbonyl peak of the oil at 1754 cm^{-1} corresponds well to the peak found in the sample at 1752 cm^{-1}; the carbonyl peak present in point 10 shows a first order derivative specular distortion. Finally, the spectrum of point 2, the brown area on the building, showed additional peaks at 1466 cm^{-1}, 1256 cm^{-1} and 1064 cm^{-1}, which likely evidence of a resin, the specific one unknown. All these peaks correspond well with the resin reference. The carbonyl peak around 1727 cm^{1} is not observed because of the first order derivative specular distortion of the carbonyl peak of the oil or because the carbonyl peak of the aged resin has shifted to a absorption similar to that of the oil. The presence of a resin material matches the literature which states that a varnish layer was often painted over the dried coloured paint layers [4]. The same results of mixed media over the magic lantern plate was observed for the *Ponte del diavolo notte*; Table 2 shows the binders which have been identified for each point on both glass magic lantern plates.

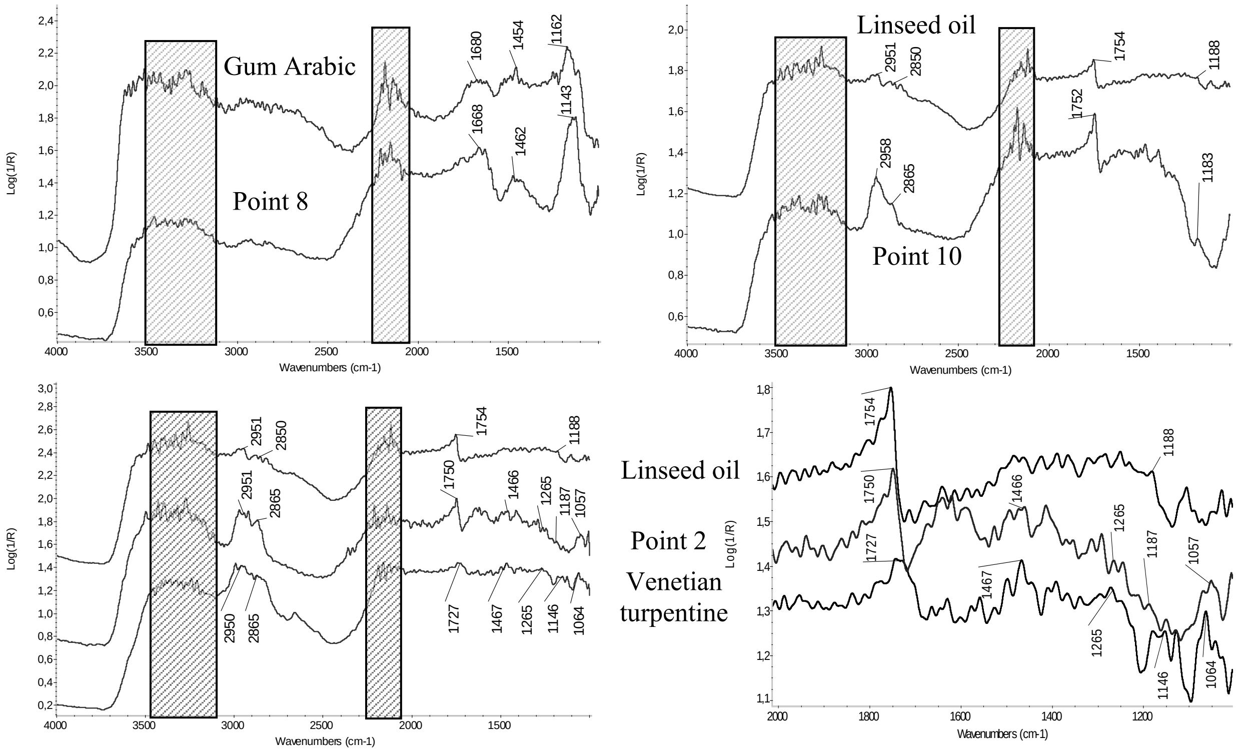

Figure 5: The different binders used in the painting of the Ponte del diavolo giorno. Upper left: sample point 8 has a main composition of a gum with a spectrum similar to gum Arabic; upper right: sample point 10 has a main composition of oil; lower left: sample point 2 has a main composition of oil and resin (perhaps a varnish) and lower right: an enlargement of the fingerprint region of sample point 2. Taken at a 90° angle to the sample surface. Arbitrary axis, smoothed 11 cm^{-1} twice.

	Points	1	2	3	4	5	6	7	8	9	10
Ponte del Diavolo Giorno	Gum			√	◊	◊		*	√	◊	◊
	Oil	√	√		√	◊	√	√		√	√
	Resin	*	√			◊	*				
Ponte del Diavolo Notte	Gum	◊	*	√	*						◊
	Oil	◊	√		√	◊	◊	√	√	√	◊
	Resin				√	◊	◊	*	*	*	
√ present, ◊ likely present, but noise in spectra masks several peaks, * possibly present in small amount											

Table 2: Binders identified with mid-IR FORS in at the various points (as indicated in Figure 4) for the two glass magic lantern plates studied

These results correspond well with the results from previous FTIR-ATR studies of the binding materials on these painted glass plates [4]. The plates were gently placed over the ATR window and lightly pressed down to ensure minimal contact and invasiveness.

To study the changes in the intensity of the reflected energy and corresponding spectra, the probe angle was changed slightly. By angling the probe, the specular reflection component of the reflected energy, which can severely distort the spectra, can be gradually removed. The points 2, 8 and 10 on the *Ponte del diavolo giorno* were studied since they gave relatively clear spectra of the binding materials. There was little difference observed in the spectra when the probe was angled 88° to the surface. At 85° a significant amount of the specular first order distortion had been decreased; however, there was also a notable loss of signal, especially observed by the intensity of the C-H stretching peaks at approximately 2860 cm^{-1} and 2930 cm^{-1}. At an 80° probe angle to the surface, the signal loss was high and in some cases the noise was so high that it was very difficult to impossible to identify the binding materials. Figure 6 shows the spectra collected at point 2 at 90°, 88°, 85° and 80° and the subsequent decrease of the first order derivative specular reflection distortion and signal. From this, an optimal angle for working lies between 88° and 85°, if one wishes to work with limited specular reflection and with an adequate amount of signal. It show be noted, that the specular distortion of the carbonyl peak only decreased, meaning it did not shift the peak to the expected absorbance wavelength, but only minimized the first order derivative shape of the peak.

CONCLUSIONS

Although Mid-IR FORS has some limitations, including blind spots in the spectra, noisy reflection spectra, spectral distortions and difficulties in spectra interpretations, it has been successfully used to non-invasively characterise the binding media used in the creation of painted magic lantern glass plates from the collection of the Museo Nazionale del Cinema, Torino, Italy. Being delicate and fragile artefacts, a non-invasive technique such as Mid-IR FORS was ideal for the analysis of the binding materials. Oil and watercolour binding materials were identified, as well as a possible resin material. This suggests that an oil-resin painting medium or an oil medium with a resin varnish layer were used, as well as a gum preparation layer, or painting medium, in the decoration of the glass plates. The presence of all these materials correspond to documented painting methods of glass slides for magic lanterns, in which varnish layers were applied over the coloured paint layers. Spectra recorded at 90° to the sample surface showed a specular distortions, as expected, and by angling the probe with respect to the surface these distortions were decreased significantly, unfortunately with the subsequent decrease in signal. The optimal angle for spectral collection with minimal specular reflection and signal loss lies between a probe angle of 88° and 85° to the sample surface.

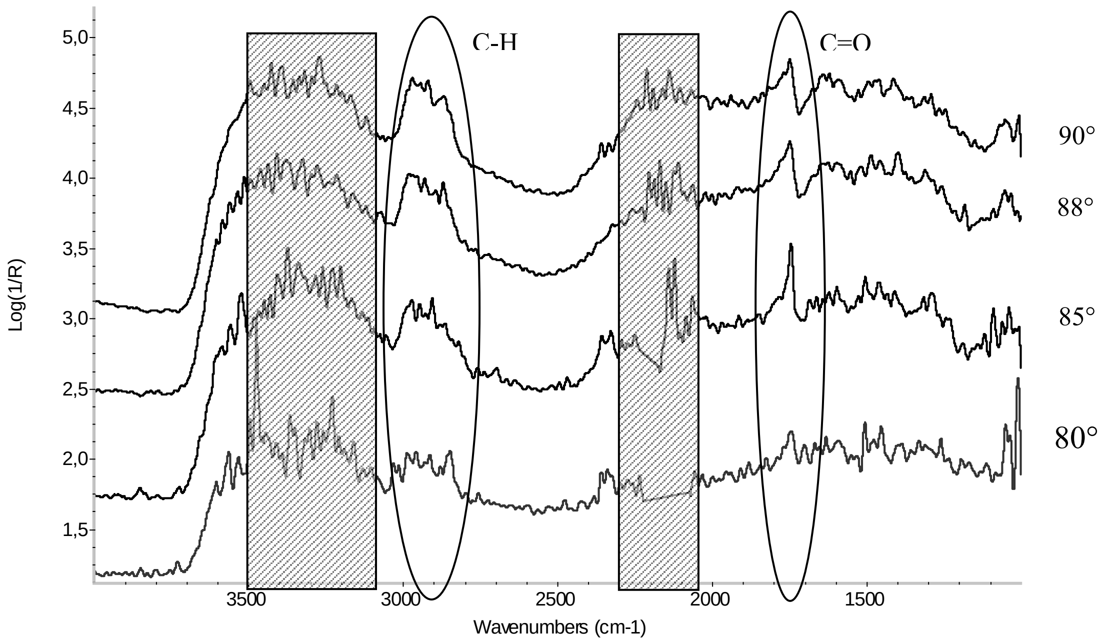

Figure 6: The changes in the reflected energy with probe angle with respect to the sample surface. From top to bottom the angle decreases from 90° to 80°. It can be seen that the signal is lost as the angle is decreased by observing the C-H stretching peaks at 2921 cm^{-1} and 2865 cm^{-1}. As the angle is decreased the specular distortion of the carbonyl peak at 1750 cm^{-1} is also decreased.

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