Mid-Infrared Fiber-Optic Reflection Spectroscopy (FORS) Analysis of Artists' Alkyd Paints on Different Supports

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Mid-infrared Fourier transform fiber-optic reflection spectroscopy (mid-IR FORS) is a noninvasive and flexible spectroscopic technique. It is ideal in the art conservation field because of its portability for on-site and in situ analysis of art objects, analyses that require delicate handling, or analyses of objects that cannot be sampled. This paper studies the applicability of mid-IR FORS for the characterization of commercial artists' alkyd paints cast on different supports. As predicted, the quality of the spectra and intensity of characteristic peaks varied according to reflectivity, roughness, and materials used in the supports. The presence of organic binder was best identified by its carbonyl peak (the most intense) and CH_2 stretching peaks; however, this was not sufficient to distinguish between oil and alkyd binders. The differentiation and identification of alkyds and oils must rely on the unique fingerprint peaks. However, in some cases, the fingerprint peaks were difficult to interpret because of strong absorptions caused by inorganic paint fillers, often present in modern paint formulations, resulting in anomalous dispersion and *reststrahlen* distortions.

Index Headings: Art conservation; Cultural heritage conservation science; Artists' alkyd paints; Fiber-optic reflection spectroscopy; FORS; Noninvasive investigations.

INTRODUCTION

In the science of the conservation of cultural heritage a good understanding of the materials used by artists is essential for choosing the correct conservation treatments, storage, and display conditions. Because the integrity of the piece of art is essential, both in preserving the artists' intentions and for display to the public, noninvasive and nondestructive techniques are highly encouraged in the field of conservation science. Mid-infrared fiber-optic reflection spectroscopy (mid-IR FORS) has been used in the conservation field for over 10 years[1] and continues to gain popularity. It is a flexible technique that allows one to investigate delicate objects, art objects in galleries and museums, or objects that cannot be moved from their locations. The fiber-optic probe contains a bundle of fibers with a portion of them dedicated to directing the radiation to the object and the others dedicated to directing the radiation reflected back from the object to a detector. It is designed to be coupled with a Fourier transform infrared (FT-IR) bench; in situ measurements are possible if the fibers are coupled with a portable FT-IR spectrophotometer. The analyses can be done with or without contact with the surface of the material (at different distances) and perpendicular or at an angle, as desired, for optimizing the collected spectrum.[1,2] The possibility of operating the probe at different angles, with and without contact, also overcomes issues posed by sampling requirements in awkward and restrictive areas on the work of art, such as odd angles in sculptures and modern painting installations.

In this study, artists' alkyd paints on different supports were investigated in order to assess the suitability of this technique for the identification of these materials in an artistic setting, but also with the hope that the results could be extended to alkyds in industrial settings.

An alkyd resin is an oil-modified alkyd polyester made by condensation polymerization of polyols (at least three hydroxyl groups), polybasic acids, and a source of fatty acids (either siccative oils or free fatty acids). Artists' alkyd paints use an alkyd resin with a high weight percent of fatty acids (56 to 70 weight percent) and they dry through catalyzed auto-oxidation reactions (chemical drying) after carrier solvent evaporation (physical drying). Auto-oxidation is a chain reaction that proceeds by a free-radical reaction mechanism, described in terms of initiation, propagation (by peroxy radicals and hydrogen abstraction), and termination. Typically, ether cross-links are created in alkyds; however, carbon–carbon and peroxy cross-links can also be formed.[3]

As mentioned, mid-IR FORS is a relatively new and useful tool in the conservation science field.[1,2,4–10] However, the spectra obtained by this technique can be complicated and difficult to interpret; the spectra are low in intensity and noisy because the reflected energy is usually in the range of 1–2% due to the surface topography, geometry, and composition.[4] Distortions in the spectra, such as peak shifts (to higher wavenumbers) and changes in peak shapes, make it difficult or impossible to compare these reflection spectra with those from transmission and attenuated total reflection (ATR) techniques.[2,5] Many of these distortions originate from specular reflection and variations in refractive indices;[2] these distortions, including *reststrahlen* (residual energy) bands and bands affected by anomalous dispersion resembling first derivatives (bipolar bands), must be carefully interpreted and can be corrected in some circumstances. In particular cases, the Kramers–Kronig transform[1,2,6] allows a specular reflection spectrum to be converted to the optical constants, i.e., the absorption index and refraction index. The specular component of the reflection can be modulated by the inclination of the fibers; this inclination reduces the specular component and shifts the balance in favor of the diffuse component of the reflected radiation; however, this leads to signal loss.[2]

This technique may appear to be only partially suitable for the detection of organic binders, but currently it is the most ideal, effective, and totally noninvasive technique available. Other portable and noninvasive techniques, such as Raman spectroscopy, handheld ATR devices, or portable FT-IR benches, suffer from drawbacks and limitations. Poor spectra

APPLIED SPECTROSCOPY **429**

Sample	Polyol	Polybasic acid	Filler
Winsor & Newton			
Titanium white	PE	PA	Dolomite
Alizarin crimson	PE	PA	Gesso
Ferrario			
Titanium white	PE	IPA	Calcium carbonate + barium sulphate
Rosso magenta	PE	IPA	
Da Vinci Paint Co.			
Titanium white	PE	IPA	Calcium carbonate
Alizarin crimson	PE	IPA	Talc

and large interference from fluorescence are often present when analyzing artistic organic materials with the Raman technique. Portable benches offer better mid-IR spectra than FORS, but they present many problems for the measurements due to the encumbrance and weight of the device, which make positioning difficult, particularly in the case of three-dimensional objects. Handheld ATR devices require close contact between the IRS element and the substrate for a good instrumental response, which can induce superficial modifications or damage to the works of art.

The first step of this work was a general comparison between alkyd and oil binders in order to determine whether FORS allows differentiation between these two binders, which are widely used in modern paintings. When successful, this technique could be used for a rapid, initial, and totally noninvasive surface survey of the work of art in order to significantly reduce sampling. This is possible because of the relatively limited number of binding media commonly used by artists, which simplifies characterization. The bulk of this research focuses on the mid-IR FORS characterization results of titanium white and alizarin crimson artists' alkyd paints from three different commercial artists' paints manufacturers—Winsor & Newton, Ferrario, and Da Vinci Paint Co.—cast on four different substrates (aluminum, raw canvas, glue-gesso ground, and an acrylic ground). Also discussed are the complications encountered during analyses and data interpretation. It was difficult in several cases to identify the binder of the paints. A number of spectral distortions and interferences (fillers, substrate, atmospheric, and spectral) were present in many of the spectra, and previous knowledge or some information about the materials was helpful when interpreting the spectra. The overall goal is to determine whether the differences between the pure oil and alkyd media remain detectable under a variety of different conditions and formulations.

EXPERIMENTAL

Reflection spectra were acquired using a Thermo Nicolet FT-IR NEXUS spectrophotometer connected to a Remspec fiber-optic immersion probe and liquid nitrogen cooled MCT (photoconductive HgCdTe) detector. The Y-shaped fiber-optic probe had a tip length of 10 mm with fibers made of chalcogenide (500 μm each in diameter), with a glass core matrix of an As-Se-Te mixture, which is clad in an As-Se-S mixture and coated with a polymer buffer for mechanical protection. The probe contained a 19-fiber bundle; seven fibers

send the radiation to the sample, and the other 12 are dedicated to guiding the reflected energy back to the detector. Spectra were collected from 4000 to 1000 cm^{-1} at a resolution of 4 cm^{-1} over 128 scans. Beyond 128 scans, there was little improvement in the noise in the spectra. A polished piece of aluminum was used as the reference material for the background spectrum. The probe, securely mounted with a retort stand and clamps, was kept at 90° (0°/0°) to the sample surface and a small distance was left between the probe and sample. Data was collected and analyzed in OMNIC 6.1a software. The reported spectra are all smoothed using the Savitzky–Golay algorithm with 25 points (48.212 cm^{-1} frequency range), reducing the resolution of the spectra. Comparing peak maxima of 4 cm^{-1} resolution and smoothed spectra is an issue; data are reported as approximate maxima and take these different resolutions into account. Ideally, a conservation material database of FORS spectra should be created for spectra comparisons and facilitation of spectral interpretation.

The limitations of the fibers and technique include undesired absorptions; the fibers show a Se–H stretching absorption in the 2050 to 2250 cm^{-1} range, rendering this region unusable, and it was cut in all the spectra. Environmental CO_2 at 2350 cm^{-1} can also cause interference in this region[5] if the ambient air conditions around the instrument change.

Fourier transform infrared–attenuated total reflection (FT-IR-ATR) spectra were measured with a Smart Endurance single-reflection diamond ATR accessory and DTGS detector, from 4000 cm^{-1} to 600 cm^{-1} with 32 scans and 4 cm^{-1} resolution.

The titanium white and alizarin crimson samples were painted as thin patches (2 cm × 2 cm, less than 100 μm thickness) using a flat paint brush, on a sheet of aluminum, an un-prepared canvas, a canvas prepared with an acrylic ground (Reeves™ Artist Gallery Canvas), and a canvas prepared with a glue-gesso ground, according to the method described by Gottsegen,[11] i.e., using rabbit-skin glue, titanium white pigment, and *gesso di Bologna* (Bologna chalk, $CaSO_4 \cdot 2H_2O$). Artists' alkyd paints from three different manufacturers were studied: Griffin Alkyd (Winsor & Newton), Colore Alchidico (Ferrario), and Leonardo Oil with Alkyd (Da Vinci Paint Co.). The linseed oil was supplied by Lanfranc & Bourgeois (Huile de lin clarifiè). It should be noted that Ferrario magenta (rosso magenta) was used, and not an alizarin crimson, because the latter was not available in this brand. The Da Vinci Paint Co. paint is an artists' oil paint, pre-mixed with an alkyd resin, as opposed to the alkyd resin paints such as the Winsor & Newton and Ferrario brands. Table I describes the compositions of the paints.[12]

RESULTS AND DISCUSSION

The quality of the spectra depended on the substrate on which they were cast. The noise and some of the spectral distortions present in all the spectra varied in strength between each substrate sample set. The behavior of the binders and an example of an alkyd paint on each of the three substrates will be highlighted below. The FORS spectra of the different binders were compared in order to assess the presence of specific markers. Due to noise and spectral distortions, accurate comparisons between spectra were quite difficult. The approximate points of inflection of the characteristic bipolar bands of the binders on each of the different supports were

TABLE II. The approximate inflection points (±5 cm⁻¹) in the FORS spectra of the reference materials on the different substrates (for the ATR spectra, the peak maxima are reported). Comments explain interferences from the substrates.

	Free film	Glue-gesso	Acrylic	Canvas
	ATR	FORS	FORS	FORS
	$\tilde{\nu}$ (cm⁻¹)	$\tilde{\nu}$ (cm⁻¹)	$\tilde{\nu}$ (cm⁻¹)	$\tilde{\nu}$ (cm⁻¹)
Alkyd				
CH_2 sym.	2925	2930	2940	2940–2840[a]
CH_2 asym.	2855	2853	X	
C=O	1726	1732	1739	1734[b]
C–O phthalic	1258	1271	1281	1234[b]
C–O	1120	1121	1134[b]	X
C–H arom.	1071	1068	1071[b]	X
Oil				
CH_2 sym.	2924	2929	2938	2974–2804[a]
CH_2 asym.	2854	2851	2860	
C=O	1743	1740	1738	1725
CH_2 bend.	1462	1455	1445[b]	X
C–O	1168	1160	1160	X

[a] Range of bipolar bands; noise prevents the exact determination of the inflection points.
[b] Noise can complicate band determination.

obtained and are listed in Table II. It should be noted that in the binder spectra collected on the glue-gesso ground, there is the possibility of interferences from the gesso between 1150 and 1000 cm⁻¹, and in the spectra collected on the acrylic ground, there is the possibility of interferences due to the calcium carbonate filler at approximately 2525 cm⁻¹ and 1795 cm⁻¹, as well as *reststrahlen* interference between 1590 and 1450 cm⁻¹.

The mid-IR FORS spectra of the thin alkyd films cast on the aluminum substrate resembled transmission spectra in form, due to a transflection effect.[9] Transflection results from the passing of the infrared energy though the thin film, which is then reflected off the aluminum substrate and back through the sample. In some cases, sinusoidal distortions in the spectra were observed from the interference of the two reflected signals, one from the alkyd paint film and the other from the substrate back through the sample.[13]

The mid-IR FORS spectra collected on the other substrates were more difficult to interpret. In order to investigate whether it was possible to use FORS to distinguish alkyds from classical oil binders, the spectra of the two types of binders cast on a traditional support were collected and compared. The comparison of the two binders (see Fig. 1) was carried out on a classic rabbit-skin glue ground, containing *gesso*. In the case of the alkyd binder, six signals† have been identified: two weak bands related to CH_2 stretching around 2930 and 2850 cm⁻¹, a strong bipolar band related to C=O stretching at 1732 cm⁻¹, a strong bipolar band of the phthalic C–O bond at 1271 cm⁻¹, and two weak bipolar bands at 1121 cm⁻¹ and 1068 cm⁻¹ related to C–O stretching and C–H aromatic bending, respectively (see Fig. 1). Only three of these bipolar bands can be associated specifically with the alkyd binder because the methylenic and the carbonyl distortions are too close to those of oil. In the case of linseed oil, five characteristic absorptions

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† The wavenumber value reported for each peak is the approximate inflection point of the bipolar band obtained by visual observation. This is used instead of the upper cusp of the bipolar band because it best represents the absorption maximum reported with more traditional FT-IR techniques.

have been identified. Two distorted signals of the symmetric and antisymmetric stretching of the CH_2 bond are clearly detected at 2929 cm⁻¹ and 2851 cm⁻¹, respectively, as well as a strong carbonyl bipolar band around 1740 cm⁻¹, a strong C–O bipolar band around 1168 cm⁻¹, and a weaker CH_2 bending bipolar band around 1455 cm⁻¹ (see Fig. 1). This indicates that the signals specifically related to the oil are the strong C–O and the weak CH_2 bending bipolar bands only.

The two binders have also been tested on a modern canvas prepared with an acrylic ground containing calcium carbonate ($CaCO_3$). The alkyd and oil marker signals, as described above, all remained detectable; however, it is important to note that it is difficult to distinguish between the oil and acrylic ground because they have relatively similar fingerprint regions in the noisy and distorted mid-IR FORS spectra. For both binders, distorted peaks around 1450 and 1160 cm⁻¹ are expected.

Given the possibility to differentiate between the pure alkyd and oil binders, as shown above, a series of commercial artists' alkyd-based paints were analyzed on different grounds to determine whether it was possible to characterize the binders when present in a paint formulation.

The spectra of the Winsor & Newton titanium white alkyd paint cast on the glue-*gesso* ground (Fig. 2) showed the CH_2 stretching bands around 2923 cm⁻¹ and 2846 cm⁻¹, as well as the bipolar carbonyl (C=O) stretching signal at approximately 1732 cm⁻¹. The fingerprint regions (below 1500 cm⁻¹) were more difficult to interpret because of the strong interferences of the absorption bands of the filler materials in the paint formulation and by the ground layer, in particular in the region of the amide and sulfate ion signals.[9,10] Even though the complicated signal between 1700 and 1400 cm⁻¹ is partially due to the carbonate ion in the paint formulation and the water in the *gesso* of the ground layer, the amide bands of the protein in the glue (around 1625 and 1540 cm⁻¹) are distinguishable from the carbonyl peak of the alkyd and oil (between 1740 and 1730 cm⁻¹). The signal from the titanium white pigment below 700 cm⁻¹ was not detected because of the instrumental limitations below 1000 cm⁻¹.

The intense spectral distortion due to the stretching of carbonate ion present in the formulation does not permit the detection of the phthalic group of the alkyd but the binder can be assessed by the presence of the aromatic C–O bending signal (bipolar band) at 1120 cm⁻¹. The presence of the carbonate filler in the Winsor & Newton formulation was also proved by the absorptions of the ($\nu_1 + \nu_3$) and the ($\nu_1 + \nu_4$) combination modes of the carbonate ion (CO_3^{2-}) around 2524 cm⁻¹ and 1800 cm⁻¹ (shoulder), respectively. Because in reflection spectra the main ν_3 vibration mode cannot be used, as it heavily distorts the spectrum,[5] the combination modes of the carbonate ion are helpful in its identification.[9]

It was observed that the combination bands of the carbonate ions present in the paint as filler were much higher in intensity in the mid-IR FORS spectra than those obtained using other infrared spectroscopic techniques. The CO_3^{2-} combination bands appear as very weak absorption bands in ATR and in transmission infrared spectroscopy because the transitions are forbidden, while they are more visible in reflection spectroscopy and moreover are not affected by spectral distortions such as the *reststrahlen* effect[9] or anomalous dispersion. Also, it has been found that surface roughness strongly affects the reflection features of calcium carbonate; the intensity of the combination bands and distorted features decreases when
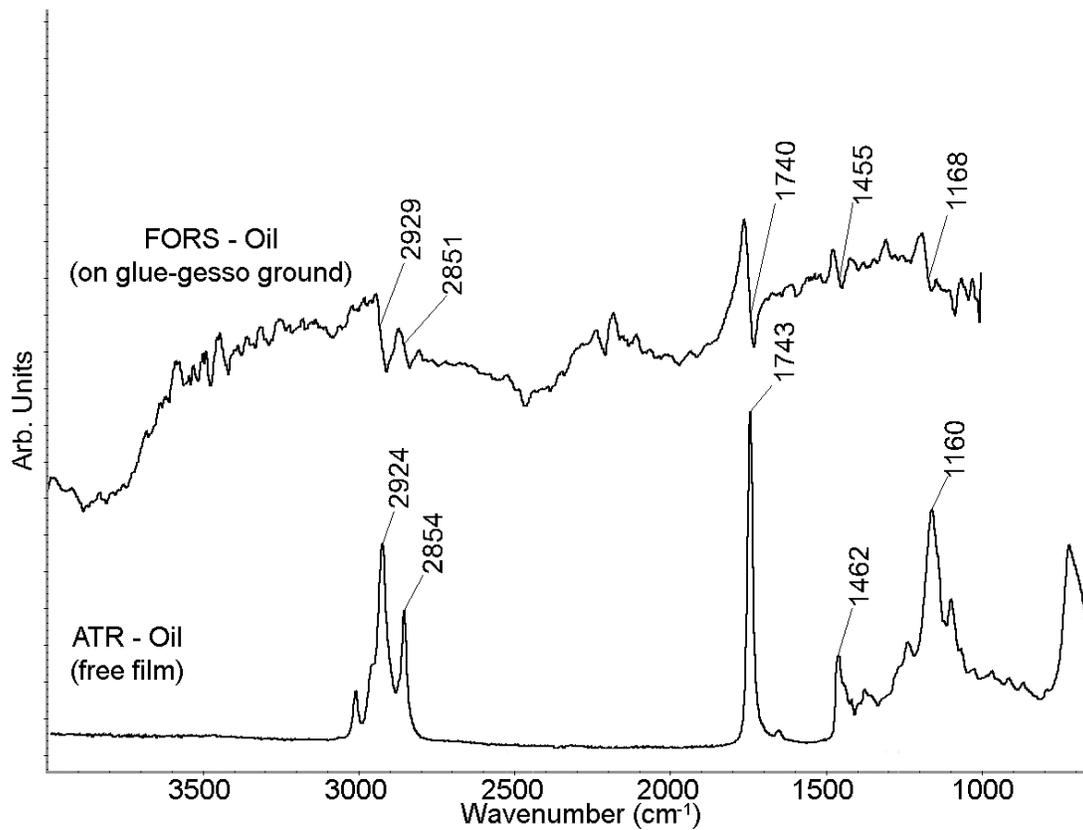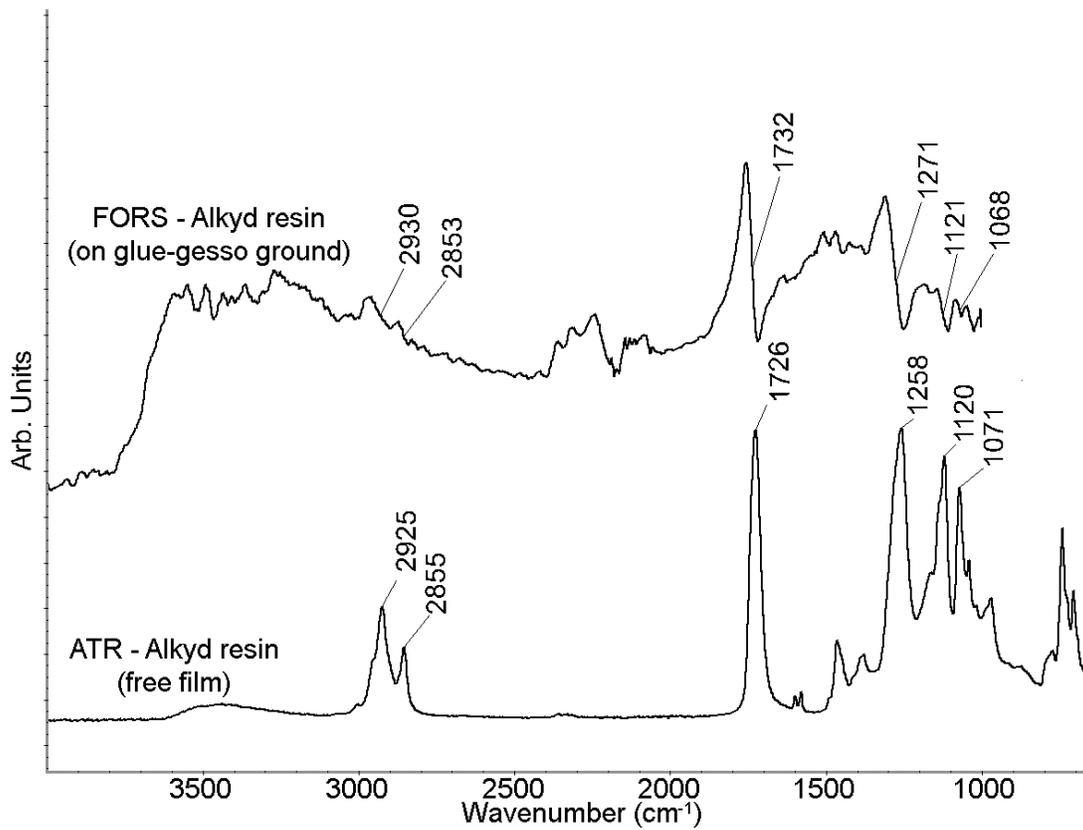
FIG. 1. Comparison of mid-IR FORS alkyd and oil reference spectra on a prepared canvas with a rabbit-skin glue and gesso ground and free-film reference spectra using FT-IR-ATR.
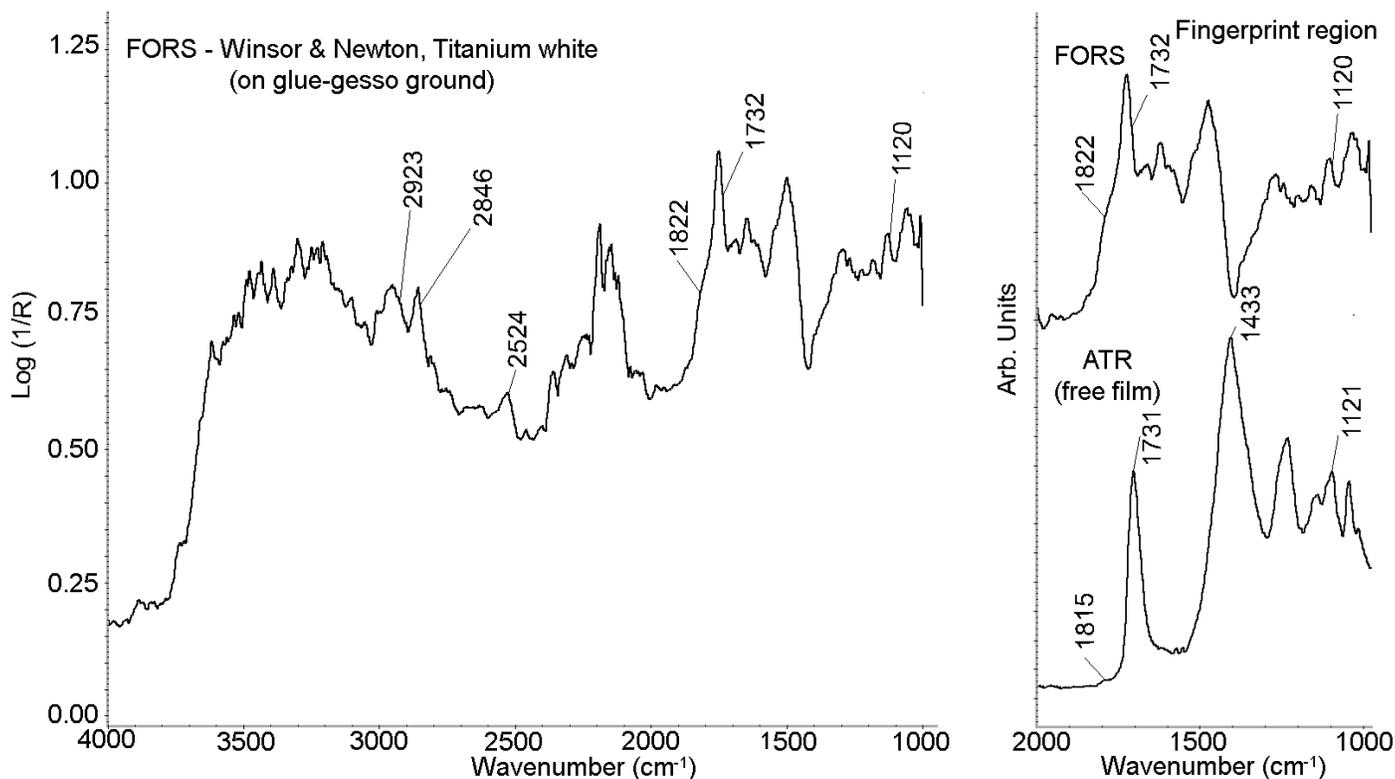
FIG. 2. (**Left**) Mid-IR FORS spectrum of Winsor & Newton, Titanium White cast on a prepared canvas with a rabbit-skin glue and gesso ground. (**Right**) The fingerprint region compared to the FT-IR-ATR spectrum of the Winsor & Newton, Titanium white free film.

surface roughness matches the wavelength of incident radiation.[10] In these types of samples much of the signal is from the inorganic filler materials and not from the organic component of the paint films, as demonstrated by the spectra dominated by large distortions caused by the ν_3 vibrational mode of the carbonate ion. Unfortunately, it was not possible to distinguish the specific carbonate filler based on the combination band shifts; the shifts related to the substitution of Ca^{2+} (calcium carbonate, $CaCO_3$) by Mg^{2+} (dolomite, $CaMg(CO_3)_2$) were not differentiable in our working conditions[14] and the bending absorptions occurred below the investigated spectral range.

The spectra of the same paints on the acrylic ground were less clear and more difficult to characterize than those cast on the glue-*gesso* substrate. The signals of the alkyd are the same; however, the two weak bipolar bands at 1124 cm^{-1} and 1072 cm^{-1} (C–O stretching and C–H bending) in the fingerprint region cannot be attributed exclusively to the alkyd because of the absorption at 1145 cm^{-1} of the acrylic binder in the substrate. The strong bipolar band of the phthalic C–O bond at 1258 cm^{-1} is here again the best marker of alkyd binders. Also present in all the spectra were the $(\nu_1 + \nu_3)$ and $(\nu_1 + \nu_4)$ combination modes of the calcium carbonate filler in the acrylic ground and a specular distortion between 1600 cm^{-1} and 1490 cm^{-1}, corresponding well to the ν_3 vibration mode of the carbonate ion in the filler. This indicates the simultaneous sampling of the painting and the substrate layer causing interferences in the alkyd spectra. Due to noise and distortions, the mid-IR absorption pattern collected for the acrylic ground and the oil binder are relatively similar, thus not permitting the confident differentiation of the binders. This is evident in Fig. 3, which shows the mid-IR FORS spectrum of Da Vinci Paint

Co. alizarin crimson paint film cast on the canvas prepared with an acrylic ground. Da Vinci Paint Co. paints are oil paints with a very low amount of alkyd resin added[8] (oil absorptions dominate the ATR spectra of the free films) and they are not clearly distinguishable from the acrylic substrate.

In this case, the paint does not contain a calcium carbonate or dolomite filler, as confirmed through other analyses,[12] so the combination modes of the carbonate ion present at 2514 cm^{-1} and 1800 cm^{-1} and the distortion in the fingerprint region between 1460 cm^{-1} and 1590 cm^{-1} present in the spectrum are exclusively attributable to the acrylic ground. Interference from the substrate complicates spectral interpretation and should be taken into consideration. The principal bipolar band around 1028 cm^{-1} is not related to the binder or to the pigment, but to talc, which is present as a filler/extender material in the paint formulation.

The mid-IR FORS analyses of alkyd paints cast on the unprepared canvas produced poor spectra; they were very noisy and low in intensity. The loss of signal can be explained by the combination of two factors: (1) a higher diffuse spectral component from the roughness of the cotton canvas threads (with individual fiber diameters ranging between 15 and 35 μm) and (2) the noise in the spectra from low-intensity reflected signal, due to the weave and weft morphology of the canvas.

Oil and alkyds applied to raw canvas were completely or partially absorbed into the substrate, complicating the identification of these binders. In most of the spectra the methylenic stretching bands were present, but it was hard to determine the correct approximate inflection point because of the noise and interference of the cellulose signals. The carbonyl (C=O) stretching band was present in all the spectra; however, it was
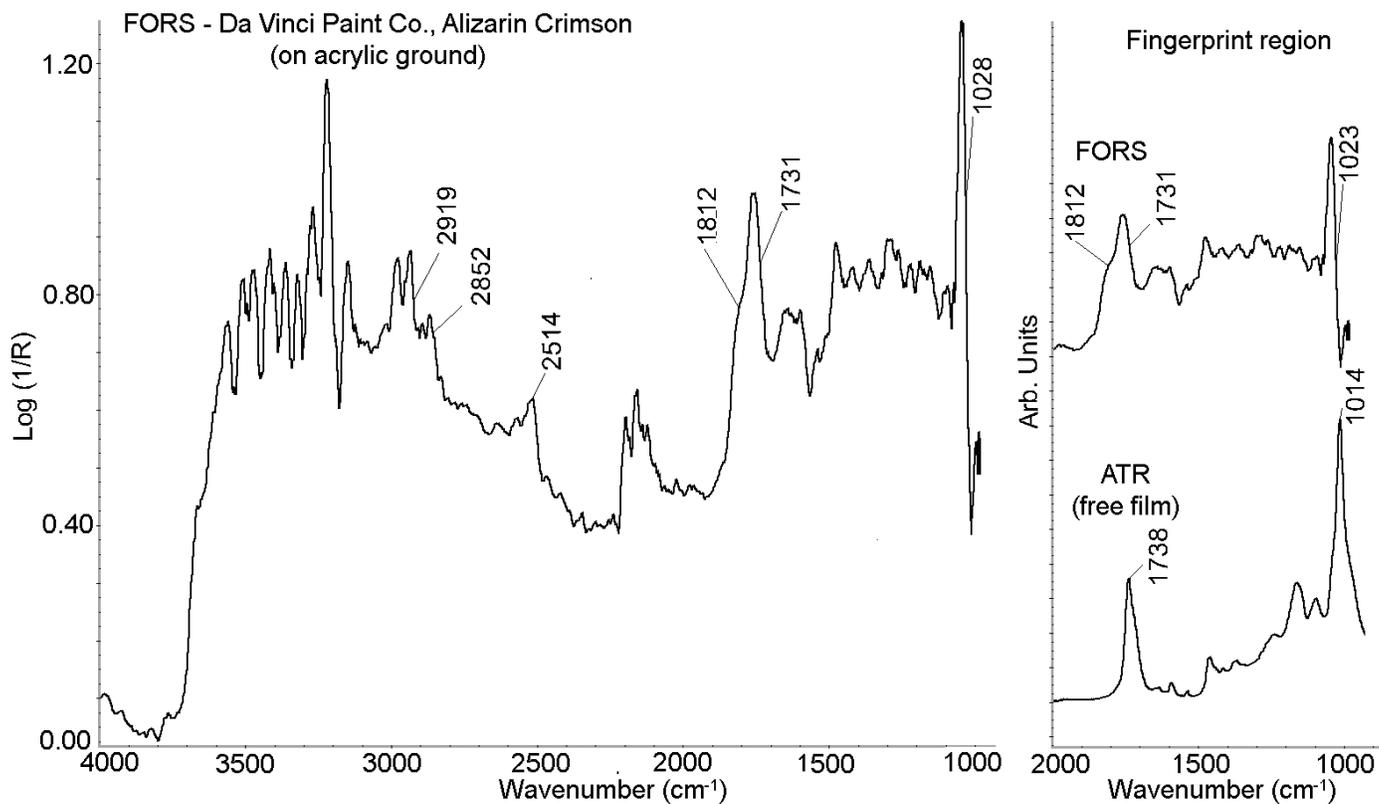
FIG. 3. (**Left**) Mid-IR FORS spectrum of Da Vinci Paint Co., Alizarin Crimson cast on a commercially prepared canvas with an acrylic ground. (**Right**) The fingerprint region compared to the FT-IR-ATR spectrum of the Da Vinci Paint Co., Alizarin Crimson free film.
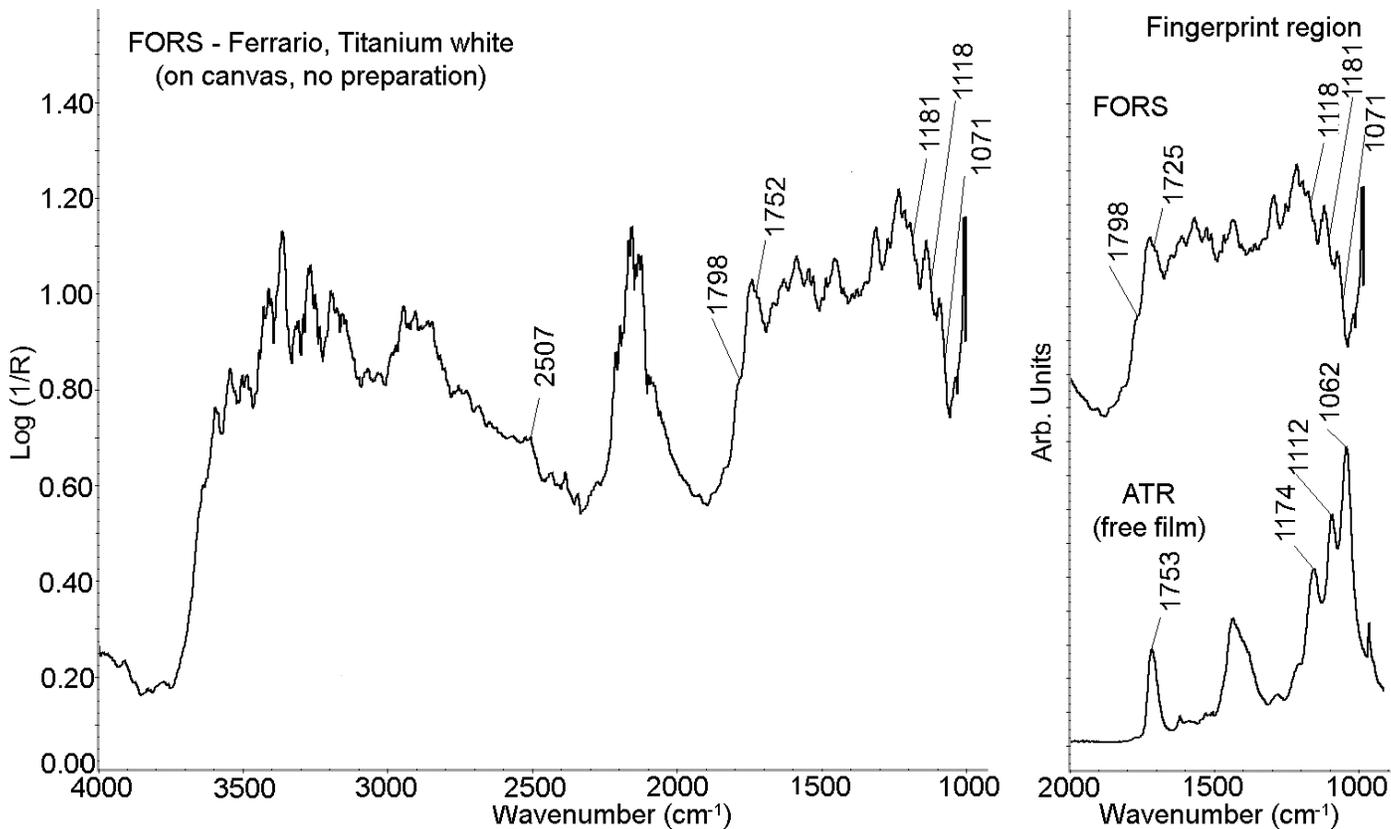

FIG. 4. (**Left**) Mid-IR FORS spectrum of Ferrario, Titanium White cast on an unprepared canvas. (**Right**) The fingerprint region compared to the FT-IR-ATR spectrum of the Ferrario, Titanium White free film.

not as pronounced as in the spectra collected on other substrates.

This behavior is shown in Fig. 4 by the mid-IR FORS spectrum of Ferrario titanium white cast on the unprepared canvas. It can be seen that the spectrum is noisy and it is hard to assess the inflection point of the bands. Again, the main bands in the spectrum are due to the filler, in this case, barium sulfate ($BaSO_4$), with distortion bands between 1076 ± 6 cm^{-1}, 1118 cm^{-1}, and 1172 ± 20 cm^{-1}. Barium sulfate has three characteristic bands in this area at approximately 1189 cm^{-1}, 1124 cm^{-1}, and 1080 cm^{-1}.[15] This three-peak combination was consistent between all the Ferrario samples regardless of the supporting substrate. As observed with the pure oil and alkyd binders applied on raw canvas, it is likely that most of the binder in the paints has been absorbed into the canvas threads, leaving a film surface enriched in inorganic components.

CONCLUSIONS

In this paper the application of mid-IR FORS was investigated for the noninvasive characterization of alkyd binders cast on different supports. Mid-IR FORS spectra are often difficult to compare to those of classic transmission spectroscopy; this makes it necessary to perform a preliminary study, not only on the original materials, but also on the interactions between these products and their substrate. Because it is a noninvasive, nondestructive, and flexible technique, it is ideal for the study of cultural heritage but can be easily extended to industrial paint applications, even if there are some restrictions associated with the instrumental limitations, such as the smaller spectral range (detection limit is 1000 cm^{-1}), the *reststrahlen* and anomalous dispersion effects, and noisy reflection signals. The operator must optimize the instrument and measurement for every surface by modifying the angle of incidence and the working distance in order to regulate the ratio between specular and diffuse components and to maximize the response.

Moreover, the quality of the paint spectra varies depending on the support on which the paint films are cast and the thickness of the paint layer. It was noted that oil was more difficult to identify, while it is easier to identify an alkyd due to its phthalic C–O bipolar band around 1258 cm^{-1}. Attention must always be paid to the painting substrate because it can influence the reflected signal by either interfering with the paint film signal (simultaneous sampling of both the ground and thin paint layer), by absorbing the binding media leaving a film enriched with the inorganic paint components, or by dispersion of the signal due to its roughness and surface morphology.

Summarizing, methylenic and carbonyl stretching bands indicate the presence of an organic binder. The phthalic C–O stretching (inflection point around 1271 cm^{-1}) of alkyds is shifted enough from that of fatty acid-triglyceride C–O stretching (inflection point around 1168 cm^{-1}) that they can be differentiated, even in complex conditions. When the signal is clean, the presence of a medium can be assessed also considering the aromatic C–H bending (inflection point around 1068 cm^{-1}) in the case of an alkyd and the methylenic bending (inflection point around 1454 cm^{-1}) in the case of a drying oil. The phthalic C–O stretching is very important in the identification of the alkyd binder for its high intensity and spectral position, which is relatively free of interferences.

The signals of the fillers, extenders, and pigments are often the most intense and can dominate the spectrum, especially when the porosity of the substrate has impoverished the paint film of the binder. The fillers and extenders, despite their major interferences in the paint spectra, can be used to advantage, since they vary between different brands (talc, barium sulfate, calcium carbonate, etc.), aiding in their identification; one can narrow down a range of potential paints based on which formulations contain which fillers and extenders.

Based on the results, the use of mid-IR FORS for identification of paint binders is not straightforward; however, it could still be useful as a fast and first-step analysis of a work of art if sampling is difficult or undesirable.

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