

Article

An SWIR-MIR Spectral Database of Organic Coatings Used on Historic Metals [†]

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[†] This article is an expanded version of a paper entitled "Non-destructive characterization of organic patinas on Renaissance bronzes using short-wave infrared and mid-infrared spectroscopy," which was presented at Metal 2025, Cardiff, Wales, UK, 1–5 September 2025, and published under the same name in the proceedings: *METAL 2025: Proceedings of the International Conference on Metals Conservation*, Nicola Emmerson, Johanna Thunberg, and David Watkinson, eds, 2025. In addition, select figures and writing, as well as the full scope of the research project, are published in an internal, non peer-reviewer thesis at Queen's University.

Abstract

Surface organic coatings (SOCs) composed of drying oils, resins, and bitumen were commonly applied to small Renaissance bronze sculptures to enhance their visual and physical properties, producing dark, lustrous surfaces that were both esthetic and protective. Yet, the identification of these coatings remains challenging due to aging, conservation interventions, and the damage caused by physical sampling. This study presents a reproducible, non-destructive protocol for characterizing SOCs on metal substrates using external reflection Fourier transform infrared spectroscopy (ER-FTIR) and fiber optic reflectance spectroscopy (FORS). Twenty-seven reference coating mock-ups of linseed oil, walnut oil, mastic resin, pine resin, and bitumen were stoved onto bronze coupons and artificially aged. Spectra were analyzed across the visible/near-infrared (VIS-NIR) (~400–1000 nm), short-wave-infrared (SWIR) (~1000–2500 nm), and mid-infrared (MIR) (~2.5–25 μ m) ranges, with key diagnostic features identified for each component and blend, including primary absorptions, combination bands, and overtones. ER-FTIR proved highly effective in detecting oil–resin mixtures and later wax coatings through characteristic bands in the MIR, while FORS, enhanced by first-derivative processing, successfully differentiated triterpenoid and diterpenoid resins and identified multi-component SOCs in the SWIR region. The reference spectral database generated in this study is intended to serve as a comparative tool for future non-invasive analysis of organic coatings on metal surfaces and to demonstrate that ER-FTIR and FORS, used in tandem, offer a practical and scalable framework for the non-destructive identification of SOCs.

Keywords: sculpture; metal; Renaissance; spectroscopy; non-destructive; FORS; ER-FTIR; SWIR-MIR



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1. Introduction

In the late fifteenth century, reflecting a revived interest in classical art, small bronze sculptures became highly sought after by Renaissance collectors [1,2]. Beyond their varied iconographies, forms, and uses, Renaissance bronzes also exhibited diverse visual effects, achieved through adjustments in alloy composition, mechanical finishing techniques, and the application of different surface coatings [3–8].

In a 2010 article published in the *Metropolitan Museum Journal*, conservator Richard Stone noted, “Most, if not all, Renaissance patinas are organic” [2] (p. 107). Two subsequent studies at the MET and Kunsthistorisches museums using gas chromatography–mass spectrometry (GC-MS) revealed coatings comprising drying oils, tree resins, mineral bitumen, and occasionally, pigment additives, yielding colors from translucent reds to deep, opaque blacks [9,10]. Building on these findings, this research aims to correlate non-invasively derived spectral features from various surface organic coating (SOC) compositions using diagnostic spectral markers in reflectance and first-derivative spectra. Fiber optic reflectance spectroscopy (FORS) and external reflection Fourier transform infrared spectroscopy (ER-FTIR) across the visible/near-infrared (VIS-NIR) (~400–1000 nm), short-wave-infrared (SWIR) (~1000–2500 nm), and mid-infrared (MIR) (~2.5–25 μm) ranges were used (Table 1). Both ER-FTIR and FORS have demonstrated effectiveness in identifying organic materials in paintings and illuminated manuscripts [11–25], as well as inorganic copper corrosion products [26–28].

Table 1. Spectral ranges of NIR, SWIR, and MIR regions, with corresponding absorptions and characteristic features relevant to spectroscopy and cultural heritage analysis.

Region	Instrument	Wavelength (nm)	Wavenumber (cm^{-1})	Features
NIR	FORS	780–2500	12,820–4000	Overtones/combination bands
SWIR	FORS	1000–2500	10,000–4000	Overtones/combination bands
MIR	ER-FTIR	2500–25,000	4000–400	Fundamental vibrations

In the NIR and SWIR, absorption bands arise primarily from vibrational overtones and combination bands rather than fundamental vibrations, which dominate the MIR region of ER-FTIR. An overtone occurs when a molecule absorbs enough energy to excite a vibration to a higher harmonic level, typically the second (2ν) or third (3ν) vibrational state. Combination bands result from the simultaneous excitation of two or more fundamental vibrations, as explained by Badr Eldin [29]. Because overtones and combinations involve higher energy transitions, they tend to be weaker and broader than fundamental bands in the MIR and often overlap substantially. Nevertheless, they provide valuable information about functional groups that are abundant in organic coatings. Combining ER-FTIR and FORS expands the spectral range from the visible to the mid-infrared, enabling more precise surface characterization of SOCs by capturing both vibrational fundamentals and electronic or overtone absorptions.

To date, invasive and micro-invasive techniques like GC-MS, attenuated total reflectance, and transmission infrared spectroscopy have been used to characterize the surfaces of Renaissance bronzes, particularly investigating SOCs and some aspects of metal corrosion [10,19,30–34]. However, the small size and often pristine condition of indoor Renaissance bronzes make sampling restrictive, as even minor sampling can leave noticeable flaws. Non-destructive, portable methods are increasingly favored for their ability to analyze cultural heritage on-site without compromising physical integrity, making ER-FTIR and FORS ideal options.

The characterization of surface coatings on bronzes is of high importance to art conservators, whose treatment approaches depend on understanding the surface chemistry of an artefact. Despite historic and modern interventions common to Renaissance bronzes—including tinted shellac, beeswax, or other materials applied to meet changing tastes or to mimic antiquities, as seen with selenium-based coatings applied to European collections in the 19th and 20th centuries [10,35]—small bronzes have maintained traces of robust patinas, with original SOCs often entirely preserved. Knowledge of an original surface coating not only guides appropriate conservation strategies but also cautions

against treatments that could irreversibly alter or destroy these layers, such as the use of heat during waxing or the use of aggressive approaches to cleaning (e.g., scrubbing or abrading the surface in preparation for preservative coatings).

2. Materials and Methods

2.1. Coupon Preparation

Leaded red brass (C83600) was selected as the base alloy based on a literature survey of 237 published data points from Renaissance bronze alloy analysis. The results are summarized in Table 2.

Table 2. Data from 237 data points of Renaissance bronze alloy analysis [8,36,37] (p. 552; pp. 236–237; pp. 88–89, 90–91, 116, 130, 199) compared to C836/C83600 leaded red brass.

Element	Min (%)	Max (%)	Average (%)	C83600 (%)
Copper	59.25	96	85.59	84–86
Tin	0.12	14.36	4.27	4.0–6.0
Lead	0	41.64	4.09	4.0–6.0
Zinc	0	31.1	4.94	4.0–6.0
Antimony	0	3.29	0.42	0.25
Iron	0	5.5	0.70	0.30
Nickel	0	1.18	0.27	1.0
Silver	0	0.41	0.14	-
Arsenic	0	2	0.52	-
Silicon	0	0.16	0.15	0.005
Phosphorus	-	-	-	1.50
Aluminum	-	-	-	0.005
Sulfur	-	-	-	0.08

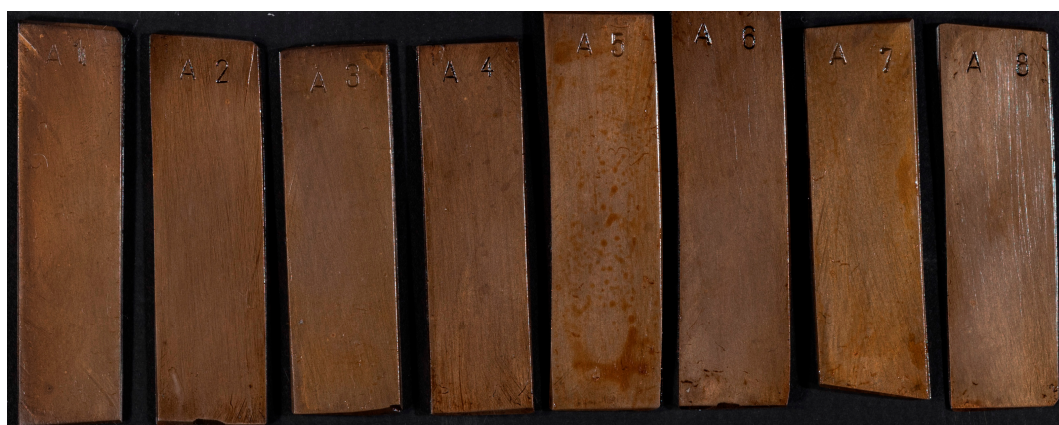
Metal coupons ($\sim 2\text{ cm} \times 5\text{ cm} \times 3\text{ mm}$) were cut and sequentially wet-sanded using 240, 300, and 600 grit paper. An oxide passivation layer was induced by heating the coupons at 500 °C for 20 min. The passivation layer increases corrosion resistance and encourages metallic cross-linking with the SOC [38].

Twenty-seven coatings of pure standards and mixtures (Table 3) were prepared with equal *w/w* ratios. Oil–resin mixtures were prepared by crushing the resin tears or chunks and dissolving them in oil in a double boiler for 1.5–2 h with intermittent stirring. For pure resin standards, the resins were solubilized in 99% ethanol (equal *w/w*); the ethanol was evaporated prior to stoving. Coatings and coupons were heated with a heat gun until $\sim 49\text{ }^{\circ}\text{C}$ before the coatings were applied with a brush. The surface was immediately burnished with a cheesecloth to create a thin, uniform layer. A duplicate of each mock-up was prepared. Mock-ups were “stoved” for 1.5–5 h at 120–150 °C, coated again, and “stoved” for an additional 1.5–3 h until the mock-ups were dry to touch.

To determine if SOCs can be characterized beneath later conservation treatments and maintenance, two maintenance coatings were applied to coated mock-ups. Renaissance wax polish—a microcrystalline wax developed by the British Museum in the 1950s and since used worldwide in museum conservation—was applied to the linseed oil mock-up using a cotton rag and burnished using a cheese cloth. Shellac flakes were dissolved (1:8 *w/w*) in 100% isopropanol using a magnetic stirrer for 5 h. The solution was applied with a cheese cloth to the walnut oil mock-up and left to airdry. After analysis, Renaissance wax was removed with odourless mineral spirits and shellac was removed with 100% isopropanol.

Table 3. Oil, resin, and bitumen combinations applied to metal coupons.

Linseed Oil-Based Mock-Ups (Figure 1)	Walnut Oil-Based Mock-Ups	Linseed–Walnut Oil-Based Mock-Ups	Other Mock-Ups
Linseed	Walnut	Linseed–walnut	Bitumen
Linseed–bitumen	Walnut–bitumen	Linseed–walnut–bitumen	Mastic
Linseed–mastic	Walnut–mastic	Linseed–walnut–mastic	Pine
Linseed–mastic–bitumen	Walnut–mastic–bitumen	Linseed–walnut–mastic–bitumen	
Linseed–pine	Walnut–pine	Linseed–walnut–pine	
Linseed–pine–bitumen	Walnut–pine–bitumen	Linseed–walnut–pine–bitumen	
Linseed–mastic–pine	Walnut–mastic–pine	Linseed–walnut–mastic–pine	
Linseed–mastic–pine–bitumen	Walnut–mastic–pine–bitumen	Linseed–walnut–mastic–pine–bitumen	

**Figure 1.** Linseed oil-based stoved mock-ups. Coatings: A1: linseed; A2: linseed–bitumen; A3: linseed–mastic; A4: linseed–mastic–bitumen; A5: linseed–pine; A6: linseed–pine–bitumen; A7: linseed–mastic–pine; A8: linseed–mastic–pine–bitumen.

2.2. Accelerated Aging

Duplicates of the 27 mock-ups were mounted on a plastic tray at an inclination of $\sim 30^\circ$. Samples were subjected to 30 artificial aging cycles (24 h each) in a humidity cabinet. Aging conditions were selected based on the protocol outlined by Oliveira (2015), following the PROMET guidelines [39,40]. Temperature (T) and relative humidity (RH) parameters are detailed in Table 4.

Table 4. Artificial aging conditions per 24 h cycle.

Aging Cycle		Cycle Periods and Conditions	
1 cycle of 24 h	Normal conditions	time = 8 h	T = 23 °C RH = 55%
	Extreme conditions	time = 16 h	T = 35 °C RH = 90%

2.3. ER-FTIR and FORS Analysis

ER-FTIR spectra were collected in reflectance mode using a ConservatIR external reflection accessory coupled to a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA USA) from 6000 to 400 cm^{-1} with an average of 64 scans at 4 cm^{-1} spectral resolution. Backgrounds were acquired every four measurements using a standardized

reflection mirror. Noise from carbon dioxide and water vapour was minimized for some spectra by subtracting spectra from a blank metal coupon. The FTIR was equipped with a fast recovery DTGS detector. Data was processed using OMNIC® (Thermo Fisher Scientific, v9.12.928) and Spectragryph™ software (v1.2.16.1) programmes.

FORS spectra were acquired using an oreXplorer™ Portable UV-Vis-NIR Spectrometer (Spectral Evolution, Haverhill, MA, USA). The instrument has three detectors: a 512-element extended TE-cooled InGaAs detector (350–1000 nm), a 512-element TE-cooled InGaAs detector, and a 1024-element UV-enhanced Silicon detector. The spectrometer operated in the range of 350–2500 nm with an integrated fiber optic input for reflectance measurements. The instrument has a spectral resolution of 2.7 nm at 700 nm and 5.5 nm at 1400 nm and 5.8 nm at 2100 nm. The illumination source was a Spectral Evolution contact probe. The fiber optic cable produced a ~1 cm diameter spot size with the illumination source at 90° and the detector at 30° relative to the sample surface at ~5 mm standoff distance. Calibration was performed using a 2'' × 2'' 98% reflectance white reference plate made of polytetrafluoroethylene. Dark field readings were taken internally prior to each measurement. Each scan averaged 80 spectra. Data was collected in the DARWin SP software (v1.5) and processed using the Spectragryph™ software. All spectra were smoothed using the Savitsky–Golay smoothing option at an interval of 9 and polynomial order of 3.

3. Results and Discussion

To demonstrate the results of ER-FTIR and FORS, pure standards (linseed oil, walnut oil, pine resin, mastic resin, and bitumen) and select mixtures will be discussed. Artificially aged mock-up spectra yielded less spectral information, with band weakening and broadening observed in all samples. As such, data prior to artificial aging is presented in the main results, while all spectra and band assignments for the 27 mock-ups before and after aging can be found in Supplementary Materials. ER-FTIR and FORS spectra were collected over a combined range of 28,000–400 cm^{−1} (equal to ~350–25,000 nm); presented spectra are cropped to areas of observed absorption. The metal substrate and its oxide layer did not significantly affect the absorption features, which thus originate from the organic materials alone.

3.1. ER-FTIR

ER-FTIR analysis successfully classified oils, resins, and bitumen. Band assignments of pure standards are presented in Table 5. Spectra for linseed oil, mastic resin, and bitumen are shown in Figure 2, Figure 3, and Figure 4, respectively.

Table 5. ER-FTIR band assignment (cm^{−1}, with an error margin of ±10 cm^{−1}) for stoved reference materials on metal coupons prior to artificial aging [22,41–45]. (Underlined assignment indicates strong absorption; ν : stretching; δ : bending; a : asymmetric; s : symmetric; sh: shoulder.)

	$\nu_a(\text{CH}_2) + \delta(\text{CH}_2)$	$\nu_s(\text{CH}_2) + \delta(\text{CH}_2)$	νOH	$\nu_a\text{CH}$	$\nu_s\text{CH}$	$\nu\text{C=O}$	δCH	$\nu\text{C-O}$
Linseed oil	4339	4259	<u>3468</u>	3011 sh, <u>2926</u>	<u>2852</u>	<u>1743</u>	<u>1532–1387</u>	<u>1166</u>
Walnut oil	4347	4259	3468	3015 sh, <u>2924</u>	<u>2852</u>	<u>1736</u>	<u>1523–1391</u>	1164
Mastic resin	4412	4347	<u>3473</u>	3079 sh, <u>2949</u>	<u>2869</u>	<u>1707</u>	<u>1457, 1382</u>	<u>1247–1033</u>
Pine resin	~4389		<u>3434</u>	3070 sh, <u>2943</u>	<u>2870</u>	2638 sh, 2529 sh, <u>1717, 1696</u>	<u>1460–1387</u>	<u>1247–1032</u>
Bitumen				2952 sh, <u>2925</u>	<u>2852</u>			

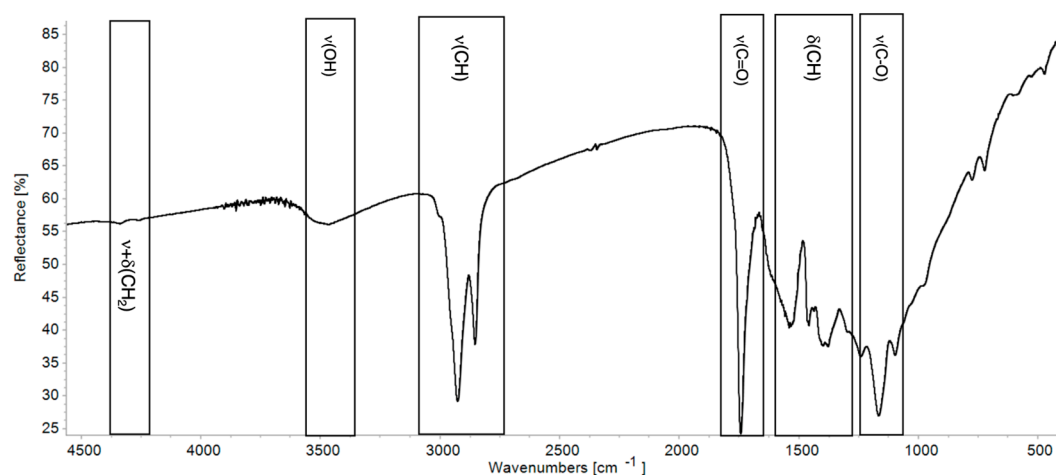


Figure 2. Linseed oil stoved on metal coupon ER-FTIR spectrum with assigned bands.

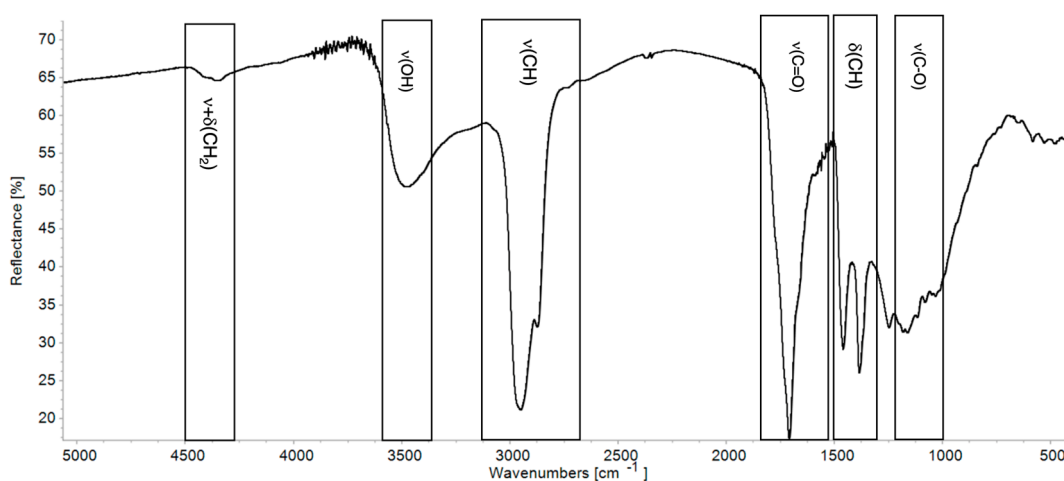


Figure 3. Mastic resin stoved on metal coupon ER-FTIR spectrum with assigned bands.

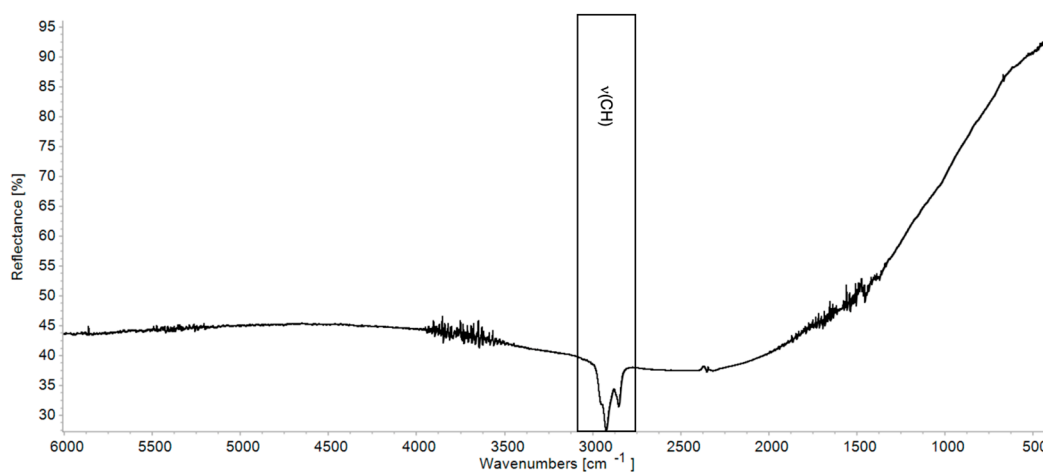


Figure 4. Bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands.

ER-FTIR spectra of pure standards shared absorptions, with only small, but noticeable shifts observed. For example, the doublet attributed to the symmetric and asymmetric stretching of C–H is broader for mastic resin than for linseed oil: 74 cm^{-1} separates the two absorptions of linseed oil, while 80 cm^{-1} separates those for mastic resin, as illustrated in Figure 5. This broadening and shifting, also evident in the $\nu\text{C}=\text{O}$ absorptions at 1743

cm^{-1} for linseed oil and 1707 cm^{-1} for mastic, provides distinct visual, and numerical markers for two kinds of organic materials common to SOC.

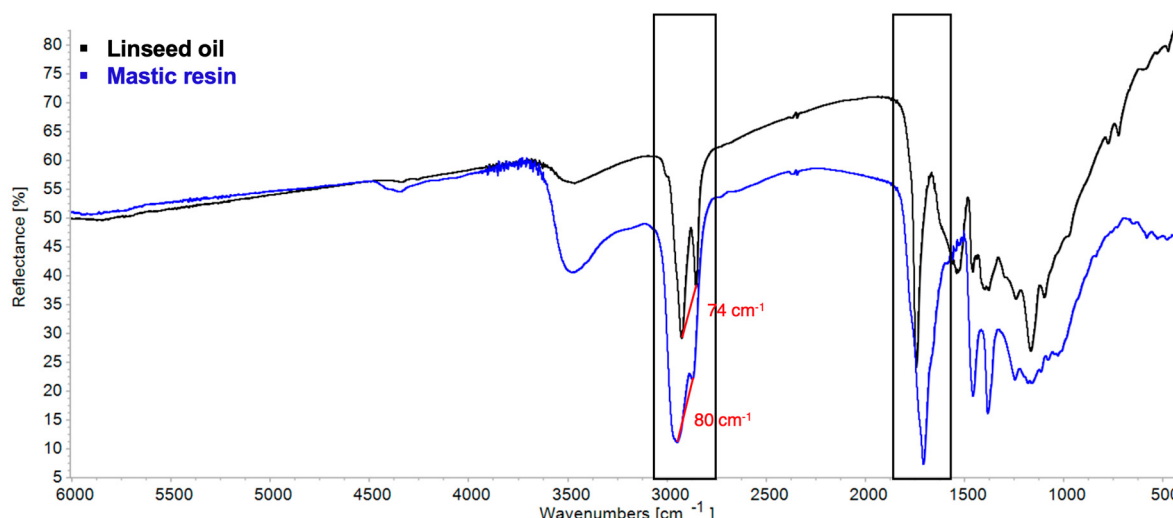


Figure 5. Comparison of linseed oil and mastic resin stoved on metal coupon ER-FTIR spectra highlighting areas of peak shifts and broadening.

ER-FTIR analysis of bitumen was not informative as noise due to variation in humidity during readings interfered with absorptions in the $1800\text{--}1600\text{ cm}^{-1}$ region where characteristic ester, carboxylic acid, and ketone vibrations occur [43]. This part of the fingerprint region has been used to discriminate aging and to characterize physical and rheological properties [45] (p. 5507). Crude source and aging state significantly vary the composition of bitumen. ATR-ER-FTIR, combined with chemometric approaches such as principal component analysis, hierarchical cluster analysis, and linear discriminant analysis, has shown greater success [43,45].

Instead, in the Renaissance, oil- or oil-resin-based varnishes were favored for producing hard, solvent-resistant coatings [2]. Despite the historical prevalence of oleoresinous mixtures, no previously published spectral data for such blends could be identified. This study demonstrates that mixture identification can be approached through characteristic peak addition and shifts in spectra. For example, the $\nu\text{C=O}$ absorptions for linseed oil and mastic resin appear as single peaks at 1743 cm^{-1} and 1707 cm^{-1} , respectively, but in the linseed–mastic blend, they appear as a broadened doublet at 1739 cm^{-1} and 1711 cm^{-1} (Figure 6). Additional peak changes for the linseed–mastic blend are summarized in Table 6. This additive behaviour, combined with shifts and changes in peak intensity or width, can indicate the presence of multiple components.

However, distinguishing blends is not always straightforward. Many organic materials, particularly drying oils and natural resins, share functional groups and produce overlapping spectral features depending on composition, degree of aging, or molecular environment. In blended spectra, this can result in band broadening, shoulders, or minor shifts rather than discrete new peaks. For this reason, interpretation relies heavily on well-characterized reference spectra and direct comparison of expected features. Ultimately, a pattern-recognition approach, guided by spectral comparison and contextual knowledge of historically plausible materials, must be taken. While it may not be possible to discriminate the exact composition of the SOC, general classification is plausible, especially when supported by complementary techniques such as FORS, discussed in the next subsection.

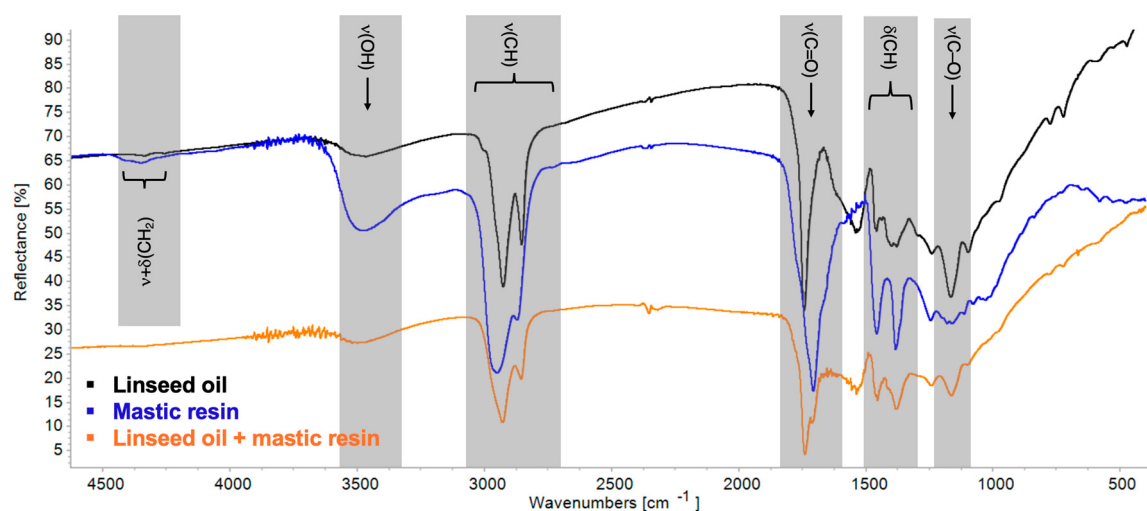


Figure 6. Comparison of linseed oil (black), mastic resin (blue), and linseed oil–mastic resin blend (orange) stoved on metal coupon ER-FTIR spectra with assigned bands.

Table 6. ER-FTIR band assignment (cm^{-1} , with an error margin of $\pm 10 \text{ cm}^{-1}$) for linseed oil, mastic resin, and linseed and mastic blend, stoved on metal coupons, including description of observed shifts. (sh: shoulder.)

	Linseed Oil	Mastic Resin	Blend	Observed Change
$\nu_a(\text{CH}_2) + \delta(\text{CH}_2)$	4339	4412	4338	Weakening
$\nu_s(\text{CH}_2) + \delta(\text{CH}_2)$	4259	4347	4251	Weakening
νOH	3468	3473	3500	Increased absorbance
$\nu_a\text{CH}$	3011 sh, 2926	3079 sh, 2943	2928	Shift and broadening
$\nu_s\text{CH}$	2852	2870	2855	Shift and broadening
$\nu\text{C}=\text{O}$	1743	2638 sh, 2529 sh, 1717, 1696	1739, 1711	Splitting, shift, and broadening
δCH	1532–1387	1460–1387	1453, 1378	Shift, appearance of shoulders
$\nu\text{C}-\text{O}$	1166	1247–1032	1162	Increased absorbance

3.2. FORS

FORS analysis successfully classified oils, resins, and bitumen. Band assignments of pure standards are presented in Table 7. Spectra for linseed oil, mastic resin, and bitumen are shown in Figure 7, Figure 8, and Figure 9, respectively. Given the broad and overlapping nature of overtone and combination bands in the SWIR, traditional interpretation of raw reflectance spectra can be challenging. To address this, the first derivative with respect to the wavelength of the FORS spectra was calculated. Derivative analysis minimizes baseline shifts and intensity variations, enhances the resolution of sharper spectral features, and helps differentiate subtle changes that would otherwise be obscured.

Table 7. FORS band assignment (nm) for stoved reference material on metal coupons prior to artificial aging [20,22,25,46,47]. (Underlined assignment indicates strong absorption; v: stretching; δ: bending; a: asymmetric; s: symmetric; sh: shoulder.)

	$2\nu(\text{CH}_3) + \delta(\text{CH})$		$2\nu(\text{CH}_2) + \delta(\text{CH}_2)$	$2\nu(\text{Ar.CH})$	$2\nu_{a+s}(\text{CH}_2)$	$3\nu(\text{C=O})$	$\nu(\text{OH}) + \delta(\text{OH})$	$\nu(\text{C=O}) + \delta(\text{CH}_2)$	$\nu(\text{Ar.CH}) + \nu(\text{Ar.C=C})$	$\nu_a(\text{CH}_2) + \delta(\text{CH}_2)$	$\nu_s(\text{CH}_2) + \delta(\text{CH}_2)$	$4\delta(\text{CC})$	$\nu(\text{CH}_2) + \nu(\text{C-CO-O})_{\text{aliphatic/aromatic}}$
Linseed oil					1717	1929		2120–2165		<u>2306</u>	<u>2347</u>		2460–2480
Walnut oil					1716			2118–2169		<u>2308</u>	<u>2355</u>		2460–2486
Mastic resin	1371	1426	~1615 sh		<u>1706–1738</u>	~1940	2175, 2265 sh		<u>2299</u>	<u>2401</u>			2463
Pine resin			1600–1623 sh		1717–1774		2180		<u>2305</u>	<u>2354</u>			2493
Bitumen									<u>2311</u>	2359–2408			

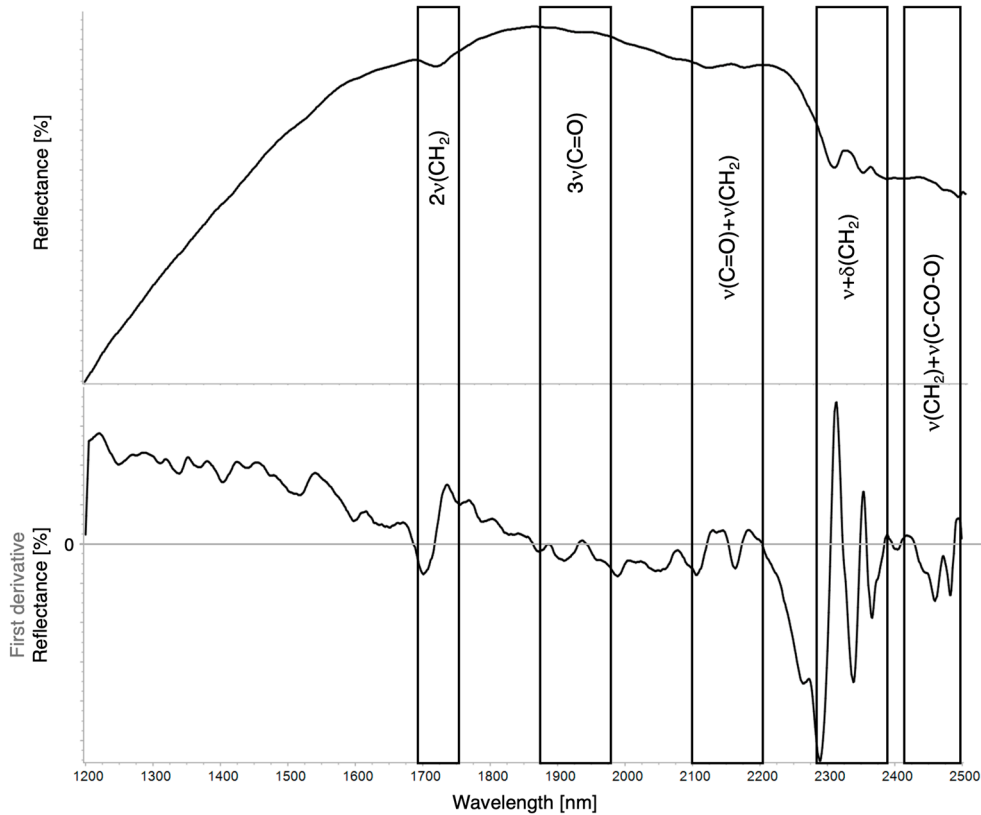


Figure 7. Linseed oil stoved on metal coupon FORS spectrum with assigned bands.

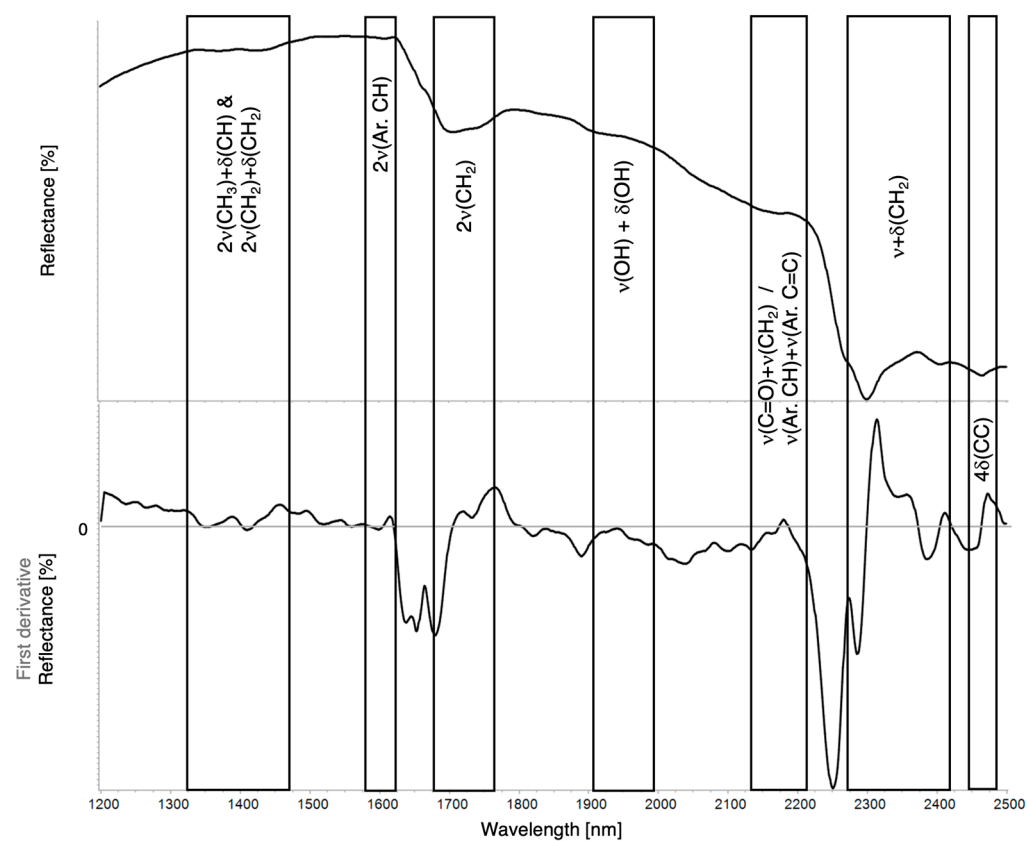


Figure 8. Mastic resin stoved on metal coupon FORS spectrum with assigned bands.

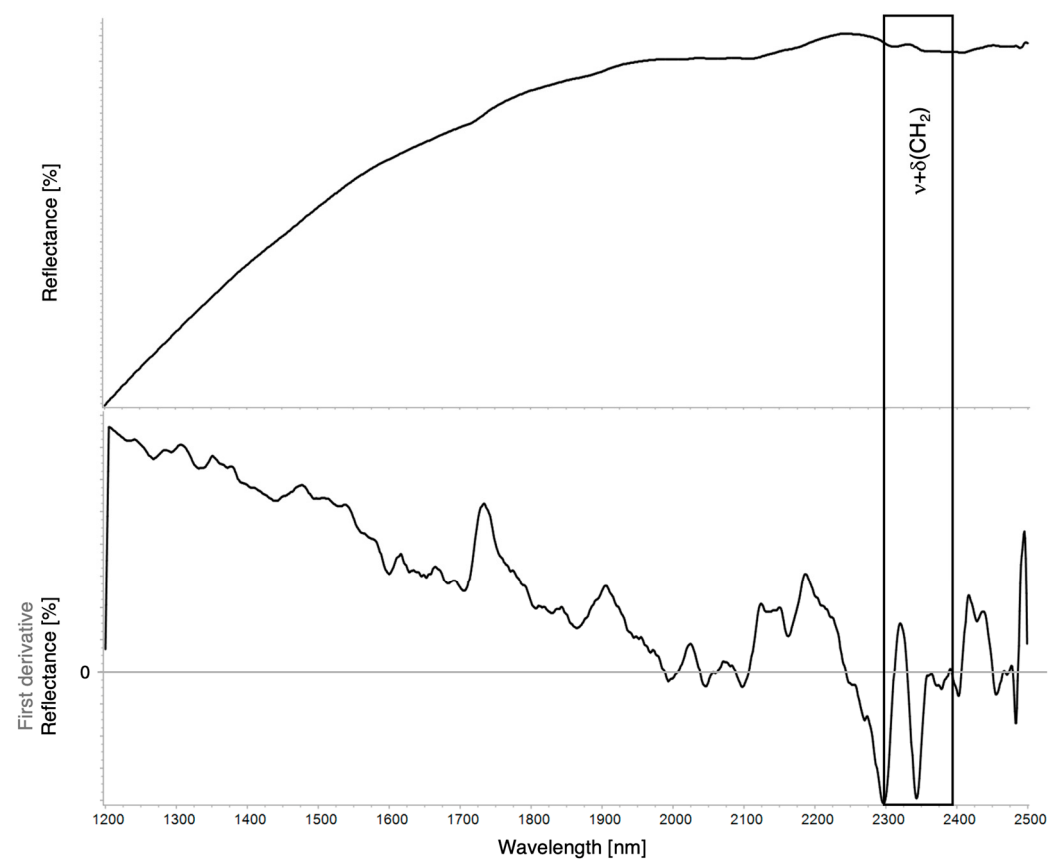


Figure 9. Bitumen stoved on metal coupon FORS spectrum with assigned bands.

Characteristic methylenic C–H stretching and bending combination bands ($\nu_{a+s}(\text{CH}_2) + \delta(\text{CH}_2)$) appear as doublets around 2300 nm for all organic reference materials. First overtone bands (2ν) of CH_2 were also identified for all materials except bitumen, while second overtone (3ν) bands, expected around 1200 nm, were not detected due to limited spectral resolution in this range. Although minor shifts were observed between linseed and walnut oils, their reflectance spectra were too similar to distinguish. By contrast, Amato et al. (2020) differentiated linseed and poppy seed oils using statistical analysis of FORS and diffuse reflectance imaging spectroscopy in the SWIR, particularly at the first overtone of CH_2 groups (~ 1700 nm) [48].

The distinction between mastic and pine resin in this study follows Vagnini et al. (2009), who grouped natural resins in the NIR into two classes based on terpenoid composition [25]. Diterpenoid resins (pine, turpentine, colophony, sandarac, copal) show a resolved doublet in the methylenic stretching and bending overtone region ($5600\text{--}6000\text{ cm}^{-1}$; $1786\text{--}1667\text{ nm}$), while triterpenoid resins (mastic, dammar) display a single broad, unresolved band [25] (pp. 2111–2112). In this analysis, pine resin presented only a subtle doublet rather than a strongly resolved one, whereas mastic showed a broad, convoluted shoulder (Figure 10). Though subtle, these spectral differences provide a reproducible way to distinguish mastic from pine in the SWIR range.

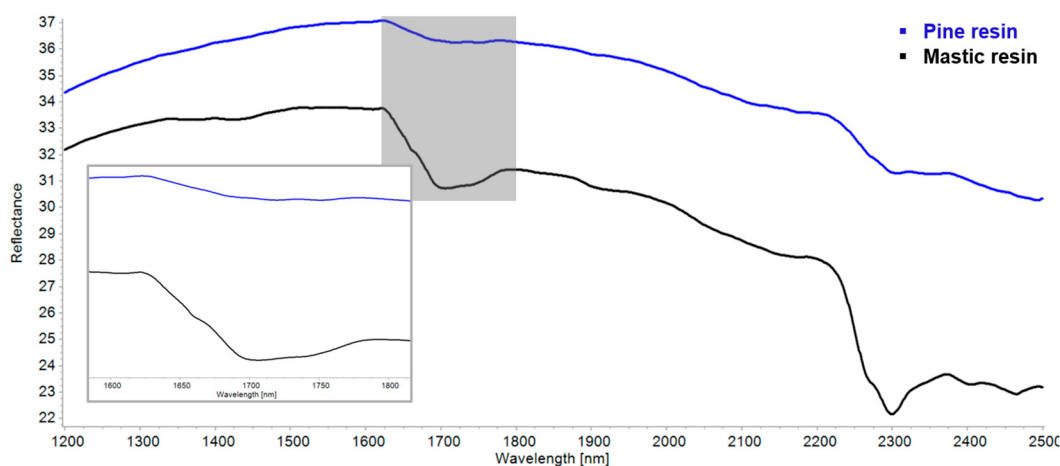


Figure 10. FORS spectra of mastic resin (black) and pine resin (blue) stoved on metal coupons, highlighting different absorption character between 1786 and 1667 nm. Highlighted region demonstrates the convoluted band observed in mastic resin and the subtle doublet in pine resin.

Like ER-FTIR results, band assignment for bitumen was limited. Although some major features associated with aromatic C–H stretching and C–O carbonyl vibrations were identified in the literature [49,50], only the strong doublet near 2311 and ~ 2350 nm could be assigned. Additional absorptions near 2000–2100 nm could not be conclusively attributed.

Regarding the spectra of blended SOCs, changes in peak width, position, and the appearance of combination features in the FORS spectra can indicate the presence of multi-component SOCs. For example, the methylenic C–H combination bands at 2306 nm and 2347 nm in linseed oil (41 nm wide) and at 2299 nm and 2401 nm in mastic resin (102 nm wide) combine in the linseed–mastic mixture to appear at 2300 nm and 2349 nm (49 nm wide), with additional shoulders preserved from the resin (Figure 11). A similar effect was discussed for ER-FTIR previously.

However, in even more complex mixtures, such as walnut–mastic–pine–bitumen (Figure 12), spectral specificity decreases significantly. Individual components become practically impossible to distinguish. This is primarily due to spectral congestion and overlap interference, where overlapping absorptions from multiple organic constituents

cause broad, merged bands that obscure distinct features. Band broadening and weakening is observed, as the additive effects of small shifts and variations in peak position from each component accumulate. Moreover, chemical interactions between components, such as hydrogen bonding or physical blending, may contribute to additional band shifts and increased spectral congestion. While discrete identification of each material is not feasible in these mixtures, the presence of broad features, shoulders, and increased spectral complexity itself serves as an important diagnostic indicator of a multi-component SOC. Recognizing such complexity is essential when interpreting historical coatings, where layered or blended recipes were often employed to achieve specific visual and functional properties.

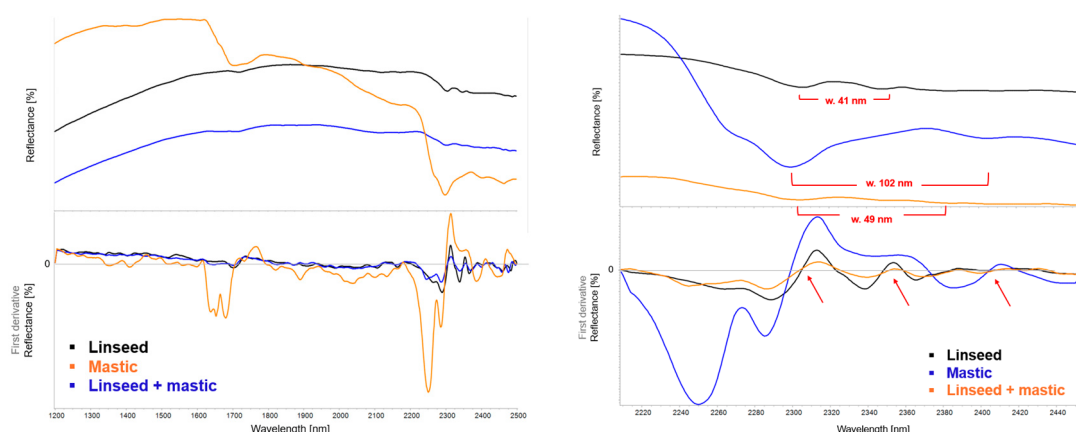


Figure 11. (Left) Overall overlapped FORS spectra of linseed oil (black), mastic resin (orange), and linseed and mastic blend (blue) stoved on metal coupons. (Right) Zoomed area of C–H methylenic combination band near 2300 nm, with shifts/widening highlighted.

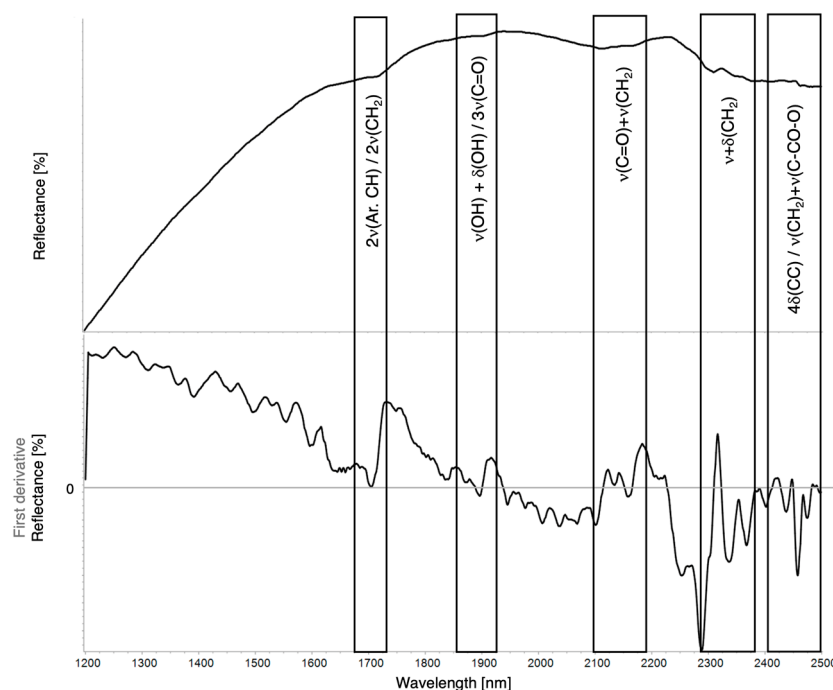


Figure 12. Walnut–mastic–pine–bitumen stoved on metal coupon FORS spectrum with assigned bands.

3.3. Re-Coating/Overcoating

Small Renaissance bronzes, especially those made for domestic settings, were routinely waxed or polished, often in response to changing collector preferences. Once bronzes

entered museum collections, they could be subjected to conservation treatments, with wax and shellac being the most frequently applied materials, used to even out visible damage and wear.

ER-FTIR and FORS analysis successfully identified wax and shellac on metal. ER-FTIR and FORS band assignments are presented in Table 8 and Table 9, respectively. ER-FTIR and FORS spectra are presented in Figure 13 and Figure 14, respectively. Both materials can also be removed using appropriate solvents, revealing the underlying coated surface. The ability to identify wax and shellac non-destructively is essential for conservation, as it enables discrimination between original and non-original coatings, thereby informing treatment strategies and safe methods for removal or reintegration. This is critical, as non-original materials may obscure the artist's intended finish, alter surface chemistry, or mislead historical interpretations regarding the object's condition and appearance.

Table 8. ER-FTIR band assignments (cm^{-1} , with an error margin of $\pm 10 \text{ cm}^{-1}$) for spectral features, including overtones and combination bands for wax on metal [19,50] and shellac [50] on metal. (Underlined assignment indicates strong absorption; ν : stretching; δ : bending; ρ : rocking; a : asymmetric; s : symmetric; sh: shoulder.)

	$\nu_a(\text{CH}_2) + \delta(\text{CH}_2)$	$\nu_s(\text{CH}_2) + \delta(\text{CH}_2)$	νOH	$\nu_a\text{CH}$	$\nu_s\text{CH}$	$\nu\text{C=O}$	$\delta_a\text{CH}$	$\delta_s\text{CH}$	δOH	$\nu\text{C-O}$	ρCH^2
Wax	<u>4320</u>	<u>4250</u>	<u>3539</u>	2952 sh, <u>2920</u>	<u>2849</u>	~1719	<u>1472</u>	<u>1462</u> , <u>1383</u>			<u>729</u> , <u>718</u>
Shellac	~4338		<u>3406</u>	<u>2927</u>	<u>2856</u>	1732 sh, <u>1715</u> , <u>1634</u> sh	1463	1455, <u>1377</u>	<u>1291</u> , <u>1252</u> , <u>1157</u>	1038	<u>725</u>

Table 9. FORS band assignments (nm) for spectral features, including overtones and combination bands for wax on metal [21,50] and shellac [50] on metal. (Underlined assignment indicates strong absorption; ν : stretching; δ : bending; a : asymmetric; s : symmetric; sh: shoulder.)

	$2\nu_a(\text{CH}_2)$	$2\nu_s(\text{CH}_2)$	$\nu(\text{C=O}) + \nu(\text{CH}_2)$	$\nu_a(\text{CH}_2) + \delta(\text{CH}_2)$	$\nu_s(\text{CH}_2) + \delta(\text{CH}_2)$	?	$\nu(\text{CH}) + \nu(\text{CO})/\text{OH vib.}$
Wax	<u>1730</u>	<u>1764</u>		<u>2312</u>	<u>1251</u>	<u>2386</u>	
Shellac		<u>1710</u>	~2135–2172	<u>2305</u>			2434, 2488

ER-FTIR analysis of wax on the linseed oil-coated mock-up isolated a spectral response attributable to the wax. Two sharp bands at 730 cm^{-1} and 719 cm^{-1} , illustrated in Figure 15, correspond to CH_2 rocking vibrations (ρ): the 730 cm^{-1} band reflects the crystalline phase, while the 719 cm^{-1} band reflects both amorphous and crystalline phases [50] (p. 1165). These bands are characteristic of both microcrystalline and natural waxes, including car-

nauba and beeswax [51–55]. Following treatment with odourless mineral spirits, these bands were no longer present in the spectrum, confirming the successful removal of the wax layer. The appearance and subsequent loss of this diagnostic CH₂ rocking doublet can serve as a reliable spectral marker for detecting and monitoring wax presence and removal during conservation treatments.

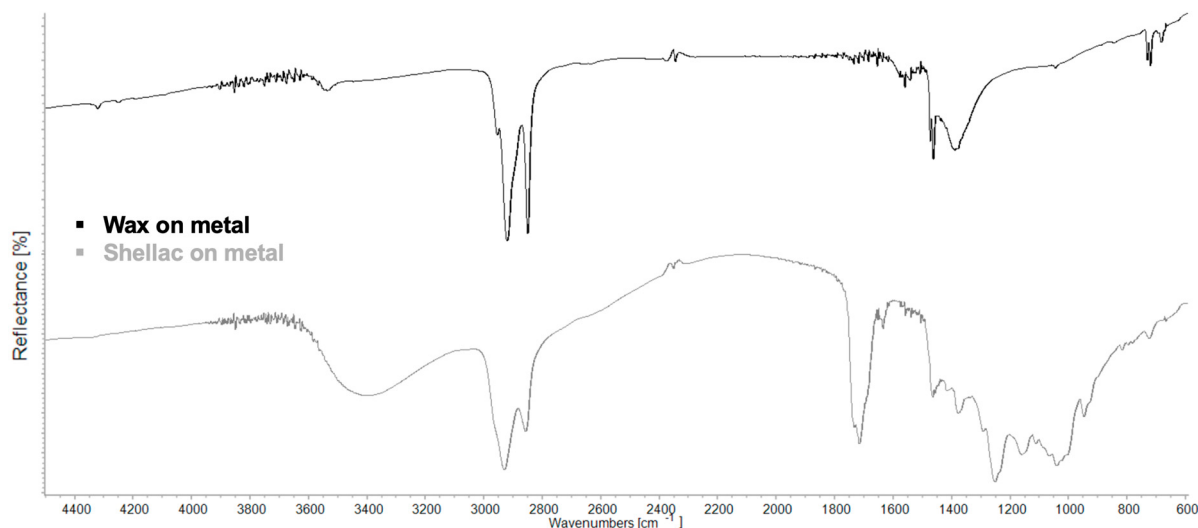


Figure 13. ER-FTIR spectra of wax (black) and shellac (gray) on metal.

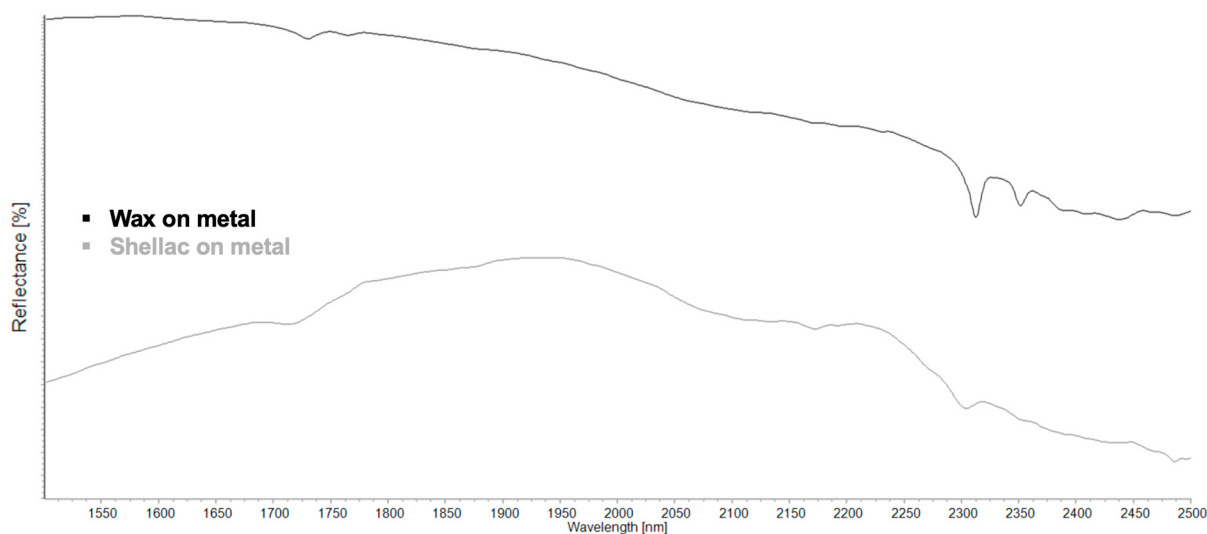


Figure 14. FORS spectra of wax (black) and shellac (gray) on metal.

FORS analysis of wax on the linseed oil-coated mock-up was less definitive (Figure 16). Although spectral changes were observed, no new bands could be confidently assigned. Notable shifts include a change in the second CH₂ overtone from 1717 nm to two separate absorptions at 1726 and 1758 nm. Also observed was the appearance of broad, uncharacterized bands at 1758 nm and 1808 nm. The methylenic C–H stretching and bending combination bands ($\nu_{a+s}(\text{CH}_2) + \delta(\text{CH}_2)$) shifted from 2306 nm and 2347 nm in the linseed oil-coated mock-up to 2312 nm and 2350 nm after wax application, consistent with the literature values for wax in the SWIR [19,21,50]. After removal, these bands returned to their original positions at 2305 nm and 2347 nm.

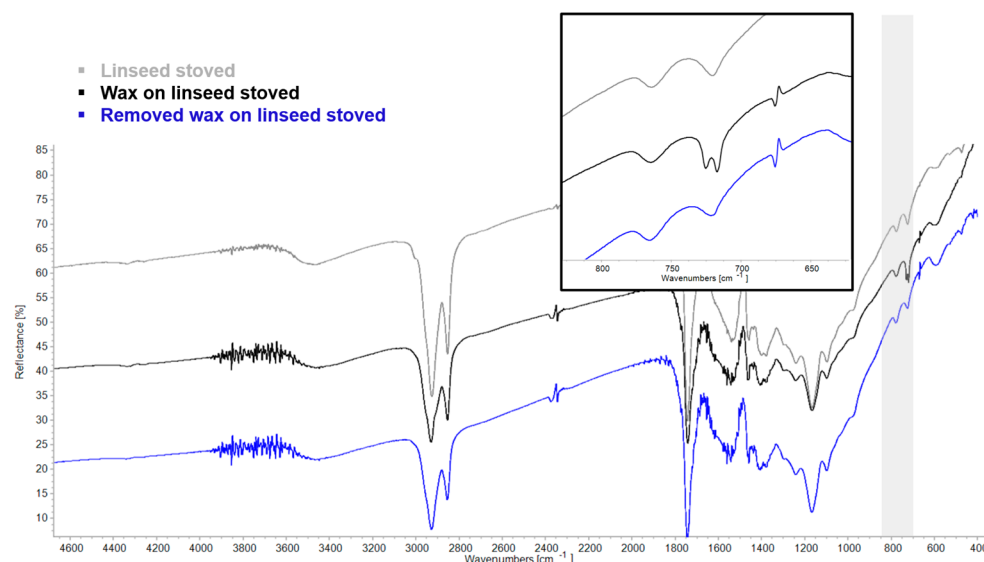


Figure 15. ER-FTIR spectrum tracking application and removal of wax on linseed oil-stoved mock-up (gray: linseed stoved on metal; black: wax on linseed stoved on metal; blue: linseed stoved on metal following removal of wax). Gray highlighted and zoomed band, corresponding to CH_2 rocking vibrations (r), used to monitor application of wax.

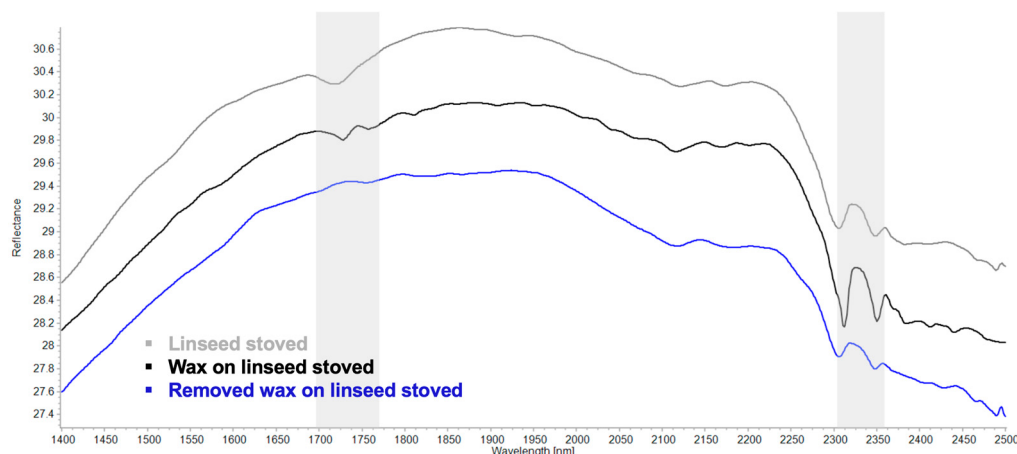


Figure 16. FORS spectrum tracking application and removal of wax on linseed oil-stoved mock-up (gray: linseed stoved on metal; black: wax on linseed stoved on metal; blue: linseed stoved on metal following removal of wax). Gray highlighted bands used to monitor application of wax.

ER-FTIR analysis of shellac on the walnut oil-coated mock-up (Figure 17) revealed a strong absorption at $\sim 1750 \text{ cm}^{-1}$, attributed to the stretching of the carboxyl group (νOH). Although this band is also present in walnut oil, it is more intense in shellac due to the material's high concentration of free carboxylic acid groups [44,55]. Three additional shellac-associated bands were identified. The first two, near 1247 cm^{-1} (C–O stretching) and near 1039 cm^{-1} (C–O stretching), were less clearly defined than the wax-associated bands [50,56] (p. 1167, p. 12). Third, the same CH_2 rocking vibration (ρ) band that appears in wax as a doublet was also observed in the shellac-coated mock-up at 720 cm^{-1} as a singlet. However, it is not as distinct as it is for wax and overlaps with absorptions present in the oil-coated mock-up. All three bands were absent following removal with isopropanol.

The FORS spectrum of shellac on the walnut oil-coated mock-up was ambiguous (Figure 18). The limited availability of published SWIR data for shellac hinders interpretation. Some spectral variation was observed between 1600–1800 nm and 2200–2400 nm, but only one absorption at 2480 nm could be assigned to shellac. This band is a combination

of νCH and νCO , and an overtone of acidic OH vibrations [50] (p. 1167). However, it also overlaps with the $\nu(\text{CH}_2) + \nu(\text{C-CO-O})_{\text{aliphatic}}$ combination band of walnut, complicating interpretation.

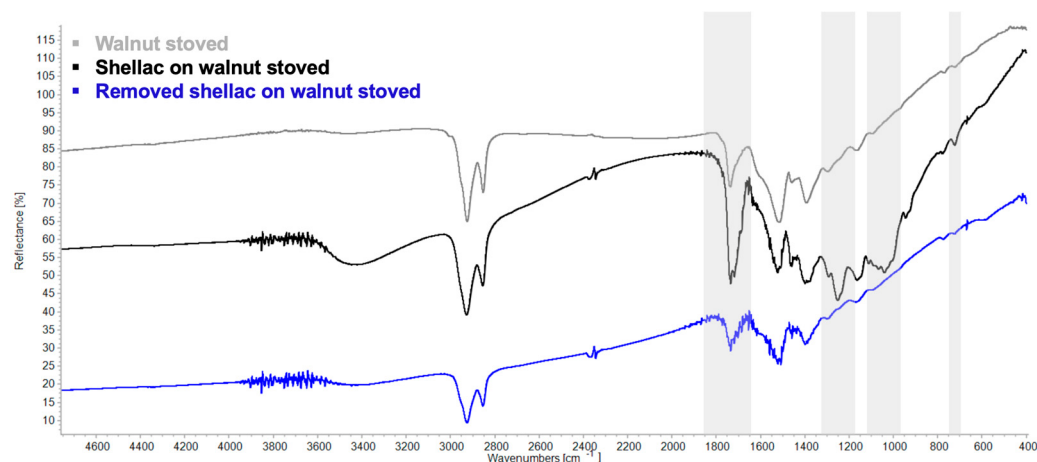


Figure 17. ER-FTIR spectrum tracking application and removal of shellac on walnut oil-stoved mock-up (gray: walnut stoved on metal; black: shellac on walnut stoved on metal; blue: walnut stoved on metal following removal of shellac). Gray highlighted areas correspond to areas of shifts used to monitor application of shellac.

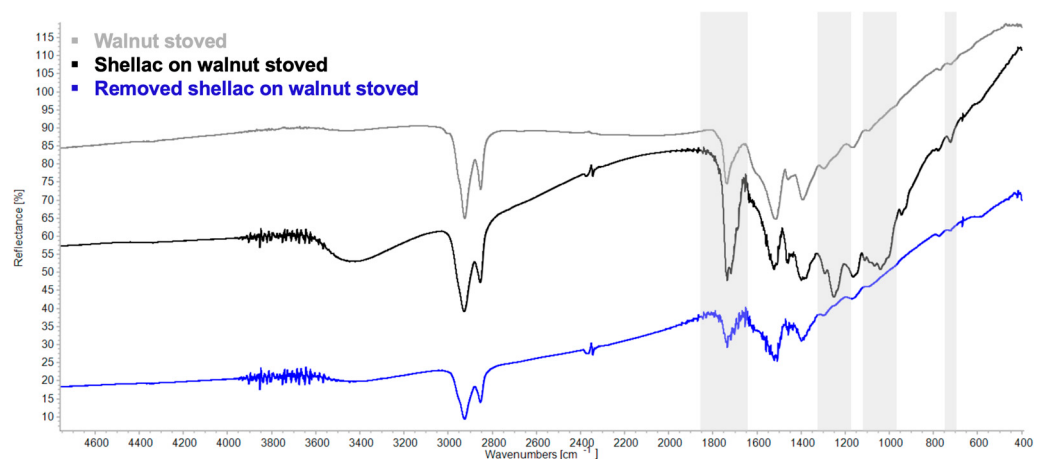


Figure 18. FORS spectrum tracking application and removal of shellac on walnut oil-stoved mock-up (gray: walnut stoved on metal; black: shellac on walnut stoved on metal; blue: walnut stoved on metal following removal of shellac). Gray highlighted bands monitor application of shellac.

4. Discussion

The combined use of ER-FTIR and FORS provides a complementary framework for the non-invasive analysis of SOC on metal substrates. Each technique offers distinct advantages that, when integrated, enable a more complete characterization of drying oils, natural resins, bitumen, wax, and shellac.

ER-FTIR is particularly effective for identifying characteristic functional groups and assessing chemical changes associated with aging in the MIR [41]. However, ER-FTIR faces limitations in discriminating between materials with similar chemical compositions due to overlapping spectral features. FORS, by contrast, operates in the NIR and SWIR regions, providing access to overtone and combination bands that are not captured by MIR spectroscopy. It is well-suited for identifying broader material classes based on methylenic and aromatic overtone features and is sensitive to subtle differences in peak position and

width resulting from blended organic materials, particularly when derivative analysis is applied.

However, FORS spectra exhibit weaker and less specific features, that can be difficult to discriminate, especially in complex mixtures. Machine learning, peak deconvolution, and multivariate statistical methods such as principal component analysis (PCA) demonstrate considerable potential for improving material discrimination of the chemically similar components of SOCs. Studies such as Carlesi et al. (2015) have integrated PCA with FT-NIR and Raman datasets to discriminate compounds from the same organic class in different fresh drying oil films (linseed, stand oil, poppy seed, and walnut) by differentiating functional groups [57].

5. Conclusions

In conclusion, while using ER-FTIR and FORS together clearly offers significant analytical advantages, it should be recognized that material identification remains partly inferential. In practice, it is necessary to look for additive effects—such as peak broadening, shifts, or emerging shoulders—and combine this spectral evidence with visual observations and historical knowledge to make informed interpretations. Although complete separation of every material component may not always be possible, the most significant and relevant features of SOCs, including the primary base material and the presence of resinous additives, can be reliably identified using this complementary approach and the spectral library provided in the Supplementary Materials. This method has been used to successfully identify SOCs on Renaissance bronzes in the collection of the Royal Ontario Museum, Toronto, Canada [58].

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings15101226/s1>, Table S1. Mastic resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S1. Mastic resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S2. Mastic resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S2. Pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S3. Pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S4. Pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S3. Bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S5. Bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S6. Bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S4. Linseed oil stoved on metal coupon ER-FTIR and FORS band assignments; Figure S7. Linseed oil stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S8. Linseed oil stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S5. Linseed oil–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S9. Linseed oil–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S10. Linseed oil–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S6. Linseed oil–mastic resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S11. Linseed oil–mastic resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S12. Linseed oil–mastic resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S7. Linseed oil–mastic resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S13. Linseed oil–mastic resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S14. Linseed oil–mastic resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S8. Linseed oil–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S15. Linseed oil–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S16. Linseed oil–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S9. Linseed oil–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S17. Linseed oil–pine resin–bitumen stoved on metal coupon ER-FTIR

spectrum with assigned bands; Figure S18. Linseed oil–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S10. Linseed oil–mastic resin–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S19. Linseed oil–mastic resin–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S20. Linseed oil–mastic resin–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S11. Linseed oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S21. Linseed oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S22. Linseed oil–mastic resin–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S12. Walnut oil stoved on metal coupon ER-FTIR and FORS band assignments; Figure S23. Walnut oil stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S24. Walnut oil stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S13. Walnut oil–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S25. Walnut oil–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S26. Walnut oil–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S14. Walnut oil–mastic resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S27. Walnut oil–mastic resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S28. Walnut oil–mastic resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S15. Walnut oil–mastic resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S29. Walnut oil–mastic resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S30. Walnut oil–mastic resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S16. Walnut oil–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S31. Walnut oil–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S32. Walnut oil–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S17. Walnut oil–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S33. Walnut oil–pine resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S34. Walnut oil–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S18. Walnut oil–mastic resin–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S35. Walnut oil–mastic resin–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S36. Walnut oil–mastic resin–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S19. Walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S37. Walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S38. Walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S20. Linseed oil–walnut oil stoved on metal coupon ER-FTIR and FORS band assignments; Figure S39. Linseed oil–walnut oil stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S40. Linseed oil–walnut oil stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S21. Linseed oil–walnut oil–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S41. Linseed oil–walnut oil–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S42. Linseed oil–walnut oil–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S22. Linseed oil–walnut oil–mastic resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S43. Linseed oil–walnut oil–mastic resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S44. Linseed oil–walnut oil–mastic resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S23. Linseed oil–walnut oil–mastic resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S45. Linseed oil–walnut oil–mastic resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S46. Linseed oil–walnut oil–mastic resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S24. Linseed oil–walnut oil–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S47. Linseed oil–walnut oil–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S48.

Linseed oil–walnut oil–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S25. Linseed oil–walnut oil–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S49. Linseed oil–walnut oil–pine resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S50. Linseed oil–walnut oil–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S26. Linseed oil–walnut oil–mastic resin–pine resin stoved on metal coupon ER-FTIR and FORS band assignments; Figure S51. Linseed oil–walnut oil–mastic resin–pine resin stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S52. Linseed oil–walnut oil–mastic resin–pine resin stoved on metal coupon FORS spectrum and first derivative with assigned bands; Table S27. Linseed oil–walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR and FORS band assignments; Figure S53. Linseed oil–walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon ER-FTIR spectrum with assigned bands; Figure S54. Linseed oil–walnut oil–mastic resin–pine resin–bitumen stoved on metal coupon FORS spectrum and first derivative with assigned bands.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ER-FTIR	External reflectance Fourier transfer infrared spectroscopy
FORS	Fiber optic reflectance spectroscopy
GC-MS	Gas chromatography–mass spectroscopy
MIR	Mid-infrared
NIR	Near-infrared
PCA	Principle component analysis
SOC	Surface organic coating
SWIR	Short-wave infrared

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