

Linseed oil as a model system for surface enhanced Raman spectroscopy detection of degradation products in artworks

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Abstract

Early evidence of materials decay can provide diagnostic insights to conservators and scientists enhancing the overall knowledge on art materials. Limited knowledge is available on the long-term behavior of synthetic and natural polymers used in art. This research poses the foundations for studies on organic materials suffering from autoxidation processes, using nondestructive surface enhanced Raman spectroscopy (SERS) for the detection of commonly present low molecular weight degradation products. Such products are here considered molecular markers for diagnostic investigations, and SERS allows detection limits never reached before. 3D aluminum (Al)-coated SERS substrates are optimized for in situ sampling of artifacts, testing different reference materials, sampling strategies, and instrumental conditions. Linseed oil is an organic material widely used in art, which degradation mechanisms are well-known. Considering that many polymeric compounds follow similar degradation pathways, linseed oil seemed an excellent model material for a wider research on SERS for polymers degradation in artworks.

KEYWORDS

diagnostic markers of degradation, linseed oil, low molecular weight products, photo-ageing, SERS

1 | INTRODUCTION

In the last decades, surface enhanced Raman spectroscopy (SERS) has been established as a technique for the characterization of dyes, organic colorants, inks, and pastels enabling to identify compounds at low concentrations in complex mixtures.^[1–3] Previously, Raman spectroscopy and X-ray fluorescence were widely used to investigate inorganic pigments, especially in their portable versions.^[4] However, SERS has the advantage of quenching the fluorescence and allows reaching incredibly low limits of detection, if compared with traditional Raman

spectroscopy.^[1,2,5] SERS enhances the Raman signal several orders of magnitude and proved to be effective for the discrimination of different coloring media.^[1,2,6–9] It also has emerged as a powerful tool to deal with the inconveniences of sampling in the cultural heritage field.^[1,10] As a matter of fact, microdestructive methods are generally preferred to destructive ones, due to the limited amounts of material required. In conservation science, diagnostic approaches have rapidly evolved towards the determination of degradation markers and preventive measures, and SERS is indeed among the most promising applications in this field.^[2,10] In addition,

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although Raman is reported in studies on binding media and drying oils, to date SERS was not mentioned as a tool for their investigation.^[11]

The most widely reported SERS substrates are silver colloids produced by many different wet chemistry methods, with or without partial aggregation, possibly produced in situ on the studied sample.^[12,10] This paper presents a new method, where a silicone strip sampler is used to transfer fragments of aged organic materials from the artifact surface to a SERS active substrate. To ensure the complete transfer of the chain fragments, solvents with different polarity were tested, and the optimization of the substrates has been presented elsewhere.^[12,13] The research combines the benefits of in-house fabricated highly sensitive aluminum (Al)-coated 3D nanostructured SERS active substrates with the knowledge of oxidative degradation processes of linseed oil, posing new foundations for reliable nondestructive analysis of degradation products of organic materials in art and archaeology.^[14-16] Linseed oil was selected as a model organic material, since its well-known mechanism of autoxidation resemble that of many natural resins and vinyl polymers (e.g., acrylates, polyolefins, and styrenic polymers).^[17-19]

In organic materials, various types of degradation products with a large distribution of molecular weight may form simultaneously. To date, nondestructive detection of low molecular weight (LMW) products has not been reported. On the other hand, volatile organic compounds have been extensively analyzed in museum environments.^[20] As early indicators of degradation, volatile organic compounds are molecular markers of chemical breakdown in polymers degrading mainly due to thermal and hydrolytic processes. Qualitative smell classifications and electrochemical gas detection have been reported in several studies.^[20,21] Until now, the limitations of the available detection methods prevented from valuing the role of LMW products as tools for the early assessment of degradation phenomena in polymers. SERS revealed high potentials in this respect, and linseed oil was considered a meaningful starting material for experimental research.

Linseed oil has been widely used as a binding medium, drying oil, and varnish by many artists and artisans since the antiquity.^[22] It is reported for diverse uses, as wood finish, putty, gilding, linoleum, leather and cloth coating, or nutritional supplement food.^[23] Its main feature is the formation of a thin protective layer on the artwork surface that hardens over time, guaranteeing stability to the painting components, light transparency, and limiting oxygen diffusion into the inner layers. Drying oils are a complex mixture of triglycerides, that is, esters of glycerol with three molecules of both saturated and unsaturated linear fatty acids.^[24] In linseed oil, the linear saturated fatty acids contain 12, 14, 16, or 18

carbon atoms (lauric, myristic, palmitic, and stearic acids, respectively) and unsaturated acids with one, two, or three double bonds (oleic, linoleic, and α -linolenic acids, respectively), being these the main components of the mixture.^[25,26] Initially sticky linseed oil films become touch-dry in few days due to cross-linking promoted by the reactive hydrogen atoms on the allylic positions of the unsaturated acid residues. Such drying reactions continue for many years, and a progressive hardening occurs as the cross-linking proceeds. On the other hand, unchanged glycerides and secondary chain scission products are retained in the mixture and act as plasticizers, lowering the hardening rate. In a diagnostic perspective, several authors proposed the detection of chain scission products, and particularly of the peculiar azelaic acid, as a marker of degradation of linseed oil.^[18] Thermally assisted hydrolysis and methylation pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was used on photo-aged samples of linseed oil, detecting azelaic acid as the most abundant product of oxidative degradation in commercial and artworks samples of linseed oil.^[18,26]

The overall aim of the paper is to build evidence on the application of SERS for the detection of LMW products forming during autoxidative degradation of organic materials, using linseed oil as a model system. Concurrently, the design of the sampling method is presented in detail, discussing the ability of the silicone strip sampler to retain LMW products nondestructively from the artwork, and the influence of different solvents used for microextractions. The analytical results obtained on artificially photo-aged samples are herewith presented. Additionally, reliable analytical methods, namely, Py-GC/MS and size exclusion chromatography (SEC), are backing up SERS findings, while Fourier transformed infrared spectroscopy (FTIR) spectroscopy is completing the data provided.

2 | EXPERIMENTAL

2.1 | Materials and photo-ageing

Purified linseed oil (Titan Oil) films were prepared on microscope glass slides (70 × 25 mm) and on KBr windows to better follow the ageing process by transmission FTIR. The oil was poured and spread uniformly with a paintbrush on the supports, to prepare dry films with a thickness of $50 \pm 10 \mu\text{m}$, as measured by a Mitutoyo Absolute Micrometer. Films for natural ageing were left in laboratory conditions at room temperature, with no light control. Samples prepared for the artificial ageing were left drying for 3 days at room conditions then exposed to a high-speed solar simulator equipped with a Xenon lamp (ATLAS Suntest CPS, Hereaus). The maximum temperature of the samples during irradiation was 45°C, black panel

temperature. Irradiation lasted up to 2,200 hr, corresponding to 65 years of natural ageing according to an estimated accelerating factor of 260 for linseed oil.^[16]

2.2 | Fourier transformed infrared spectroscopy (FTIR)

Analysis were carried out in transmission mode with a Thermo Nicolet NT 6700 spectrometer equipped with Smart Endurance device and DTGS detector with resolution of 4 cm^{-1} in the range of $4,000\text{--}400\text{ cm}^{-1}$ and 32 scans. Data were processed with Omnic 8.1 (Thermo Nicolet).

2.3 | Size exclusion chromatography (SEC)

A PL-GPC 50 Integrated GPC System, equipped with a column Agilent PLgel 5- μm MIXED-C (molecular weight range 200–400,000 Da) and refractive index detector (Agilent Technologies) were used. Tetrahydrofuran stabilized with butylated hydroxytoluene was eluted at a flow rate of 1 ml min^{-1} and 40°C . Calibration was carried out against SEC narrow distribution polystyrene (PS) standards with molecular weight in the range 580–139,400 Da. Retention time relates to molecular weight size, and the software processing provides an approximate molecular weight distribution. In comparison of chromatograms obtained from different samples, the peak areas were always normalized relative to the soluble part.

2.4 | Raman spectroscopy

Raman spectra were recorded with a Renishaw InVia Flex Raman spectrometer, equipped with two continuous wave lasers with emission at 785 and 514 nm, respectively, with gratings of 1,200 and 1,800 lines mm^{-1} . The power range varied between 1% and 5% of the nominal power of the laser, meaning 0.09 mW for the 514-nm laser and 9 mW for the 785-nm laser. The spectrometer slit opening was of 65 μm , using the detector Renishaw CCD 576×400 pix. All the measurements were carried out with a $50\times$ objective (NA = 0.50). The infrared laser works in line focus mode, the focusing spot is a straight line ($2.5 \times 24\ \mu\text{m}$), and the green laser uses a normal mode spot (punctual spot of 4.2 μm diameter). The acquisition time was 10 s.

2.5 | SERS substrates

Substrates were fabricated by ultraviolet nanoimprint lithography using a commercial nanostructured surface (Klarite[®], Renishaw diagnostics) consisting of a square lattice of inverted pyramidal pits as a master mold. Inverted replica were produced through a two-step nanoimprint

lithography protocol where the first liquid polymer material was the two component heat-curing Sylgard 184 (Dow Corning), cured at 80°C for 2 hr. The neat silicone replica was then used without further treatment as a secondary mold to fabricate the direct replica of the master mold and filled with a drop ($<10\ \mu\text{l}$) of a liquid ultraviolet-curable elastomeric tetraurethane acrylate perfluoropolyether derivative.^[16] A mask aligner with an ultraviolet-light source based on light-emitting diodes (Midas System MDA 400LJ) was used as a radiation source (beam wavelength filtered for *i*-line = 365 nm, intensity 20 mW cm^{-2}) with a 6-s exposure time. Polymeric replicas were coated with Al by thermal evaporation. More details on the fabrication procedure are reported elsewhere.^[12]

2.6 | Silicone strip sampler

The indirect sampling method consists in the extraction of surface products through a silicone strip sampler to the 3D SERS substrate for Raman analysis (Video S1). A solvent is used to transfer the small molecular fragments from the silicone sampler to the substrate with a capillary glass tube. Silicone strip samplers were fabricated by casting and thermal curing of a liquid prepolymer (Silgard 184, Dow Corning) under vacuum at 80°C for 2 hr, using a nylon webbing strip as a mold. Preliminary tests by gas chromatography/mass spectrometry confirmed a negligible quantity of siloxanes is being released by the strip during sampling with solvents.

2.7 | Mass spectrometry techniques

A Bruker MALDI-TOF/TOF ULTRAFLEX III mass spectrometer was used for the nanotechnology-assisted laser desorption/ionization time-of-flight and matrix-assisted laser desorption/ionization mass spectrometry experiments. The samples were deposited as diethyl ether or H_2O /acetonitrile (1:1) dissolution (1 μl) on the matrix-assisted laser desorption/ionization or nanotechnology-assisted laser desorption/ionization sample plate, respectively, without matrix nor cationization agent, therefore working with a matrix-free laser desorption ionization procedure. The plates were dried in air at room temperature and inserted into autoflex speed TOF/TOF MS operating in positive reflexion mode, with reflexion voltage of 1,684 kV.

Thermally assisted hydrolysis and methylation-pyrolysis gas chromatography/mass spectrometry analysis were performed on degradation products microextracted with the sampling strip and either polar or apolar solvents on model linseed oil samples. Pyrolysis was performed using a CDS 500 at 400°C for 20 s (10°C ms^{-1} heating rate). For each pyrolysis, a few microliters of a 25% aqueous tetramethylammonium hydroxide solution

(Sigma-Aldrich) were added through a microsyringe to the dry sample in the quartz probe. The probe was inserted in the instrument interface and pyrolysed immediately, in order to reduce at the minimum the evaporation of the tetramethylammonium hydroxide solution. A 6,890 N gas chromatograph (Agilent Technologies) was used to swipe the pyrolysis products. A flow of He at 1 ml min^{-1} and a HP-5MS column (length 30 m; internal diameter 0.25 mm; film thickness $0.25 \mu\text{m}$) were used. Temperature range was from 60°C (3-min dwell time) to 325°C (3-min dwell time), at a rate of $20^\circ\text{C min}^{-1}$. An Agilent 5975 mass spectrometer was used (m/z 50–500, 70 eV). Compound identifications, mass data and retention times, were based on the NIST05 library along with published literature.

3 | RESULTS AND DISCUSSION

The structural changes related to drying and oxidation of linseed oil are traditionally followed by FTIR spectroscopy,^[27–30] as also shown in Figure S1, where the spectra of linseed oil before and after drying is compared with that of a film photo-aged for 2,200 hr. The typical decrease of intensity of peaks due to carbon–carbon double bonds ($3,011$ and $1,656 \text{ cm}^{-1}$, =C–H symmetric stretching vibration, and stretching of *cis* C=C, respectively), the broadening of the carbonyl stretching peak ($1,745 \text{ cm}^{-1}$), and the formation of a broad and intense band assigned to O–H stretching (centered at around $3,470 \text{ cm}^{-1}$) support the auto-oxidation mechanism, schematized in Figure S2 for a linolenic chain.^[17] After the more likely formation of hydroperoxides on linoleic and linolenic components, the alkoxy radicals arising from their decomposition may lead to either alcohols or different carbonyl groups by hydrogen abstraction and β -scission, respectively. An alternative pathway consists in the alkoxy radical addition to C=C double bonds, producing higher molecular weight polymeric triglycerides, which soon become insoluble in common organic solvents. Cross-linking represents the main process taking place during drying, whereas chain scissions become competitive for longer ageing.

Molecular changes related with drying and subsequent oxidation may be monitored in detail by destructive techniques, such as solubility tests and SEC. As an example, the size exclusion chromatogram of linseed oil before drying is compared in Figure S3 with that of the soluble fraction of 2,200 hr photo-aged film extracted with tetrahydrofuran. Insoluble fractions rapidly increase with drying^[18] and reach values up to around 95 wt% for longer artificial ageing, whereas the SEC curve of the corresponding soluble fraction reveals

fragments formed by β -scission. Apart on a huge and narrow peak centered at around 9.5 min associated with the triglyceride component, the fresh oil also shows a shoulder at shorter retention time, possibly due to dimeric fractions already formed by the autoxidation process. In addition, free fatty acids and impurities might be hinted by the appearance of a small peak eluting at longer time. On the other hand, the normalized chromatogram of the soluble fraction of the aged sample shows a low intensity peak with a broader distribution of molecular weights centered at around 9.6 min. The peak has a thin and long tail at retention times smaller than the triglyceride peak of the raw oil, meaning that fragmentation of the cross-linked 3D structure is taking place and brings a continuous distribution of fragments with (number average) molecular weights smaller than that of the original triglycerides, that is, 400 against around 950 Da, respectively.

In principle, Raman spectroscopy offers intrinsically higher sensitivity to double bond vibrations to follow linseed oil drying, but it is only with SERS that all the inherent advantages with respect to FTIR are displayed. It is well known that SERS increases the Raman signal several orders of magnitude due to the increment of the apparent cross-section of the analytes by the strong localization of the electromagnetic field on the hot spots. Within this specific application, on one side, SERS measurements reduce the intense fluorescence emitted from the linseed oil film analyzed, for example, with 514 and 785 nm excitation sources, providing distinctive signals for very low amounts of analyte. On the other, the proposed sampling method and SERS substrates allow to selectively detect a specific fraction of the drying oil.

Raman spectra of fresh linseed oil and touch-dry films were collected from 3D Al-coated SERS substrates immediately after dropping around 20 ng of oil, and 24 hr later (Figure 1a,b, respectively), whereas spectra such as the one shown in Figure 1c could be obtained by microextraction from a silicone strip sampler applied onto photo-aged linseed oil films. In Video S1, the silicone strip is gently pressed onto the film surface. After 30-s application, the physisorbed molecules are dissolved in acetone and transferred to the SERS substrate for Raman signal collection. Spectra are collected after complete evaporation of the solvent. Intuitively, only a fraction of the molecules present at the surface is susceptible to sampling, and in particular nonvolatile LMW compounds formed by chain-scission, as well as possible unpolymerized triglycerides. Actually, the molecular weight threshold of the adsorbed molecules has been evaluated against polymer films produced by evaporation of chloroform solutions of blends of PS or polyethylene glycol (PEG) SEC standards with controlled molecular

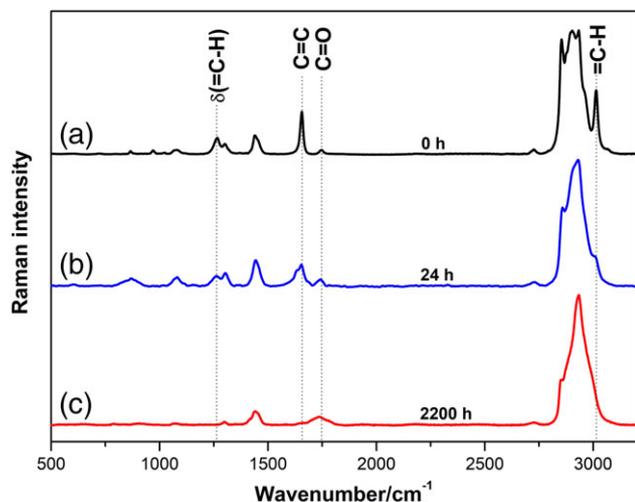


FIGURE 1 Raman spectra of raw linseed oil (a), touch-dry film after 24-hr natural drying (b), and molecules removed with a silicone strip sampler from a 2,200-hr photo-aged film (c) onto an aluminum-coated surface enhanced Raman spectroscopy device, obtained with a 514-nm excitation wavelength

weight and narrow distribution. PS and PEG are considered as representative of the capability of the silicone to interact with apolar and polar structures, respectively. The material sampled by the silicone strip was analyzed by mass spectroscopy techniques (matrix-assisted laser desorption/ionization and nanotechnology-assisted laser desorption/ionization time of flight), and the upper threshold obtained was 2,000–2,500 Da for both polar and apolar structures, as shown in Figure 2. In the case of PEG, macromolecules belonging to the distributions of standards with number average molecular weight around 500 and 1,500 Da may be easily identified, whereas for PS, only the standards with the lowest value, that is, 600 Da, show intense peaks.

In comparison with fresh oil in Figure 1a, the SERS spectrum after 24-hr drying in Figure 1b shows clear decrease of the bands associated to isolated C=C double bonds (a complete band assignment is reported in Table 1). Contrary to FTIR, it is still possible to see traces of double bonds by Raman. For instance, the band at $3,011\text{ cm}^{-1}$, clearly visible in raw oil, becomes a shoulder after 24-hr natural drying, whereas the stretching at $1,654\text{ cm}^{-1}$ loses the majority of its initial intensity. The same behavior can be observed for the band at $1,264\text{ cm}^{-1}$, corresponding to symmetric rock of *cis* double bonds, which inverted its intensity with respect to its neighbor band at $1,302\text{ cm}^{-1}$ belonging to the in-phase methylene twist. Bands associated to carbonyl groups are more difficult to see by Raman than by FTIR, being the small band at $1,747\text{ cm}^{-1}$ (stretching vibration of C=O) the most characteristic. In the raw oil, this signal is due to the esters of the triglyceride, which after drying starts to show changes in

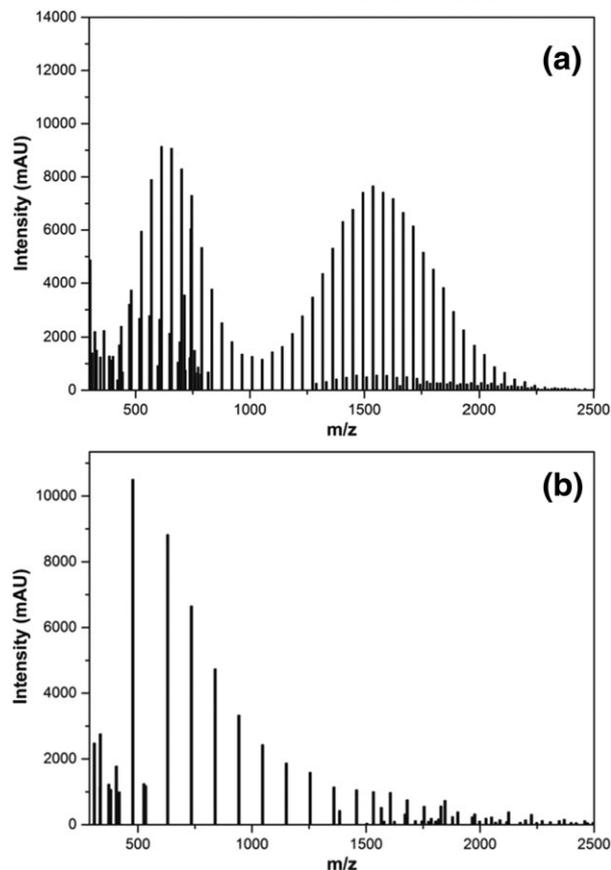


FIGURE 2 Nanotechnology-assisted laser desorption/ionization time-of-flight and matrix-assisted laser desorption/ionization spectra of molecules removed with a silicone strip sampler from polyethylene glycol (a) and polystyrene (b) blend films, respectively

intensity and broadening due to new carboxylic species being formed.

With respect to the spectrum of the molecules sampled from photo-aged films (Figure 1c), degradation phenomena producing LMW products correspond to the almost complete disappearance of the bands at $3,013$, $1,654$, $1,264$, and 721 cm^{-1} , referring to the loss of carbon-carbon double bonds. In fact, only a very weak shoulder can be appreciated at $1,654\text{ cm}^{-1}$ for the C=C stretching. The autoxidation mechanism also predicts the formation of carboxylic species by β -scission of alkoxy radicals. These carbonyl species can remain attached to the cross-linked network or be released as small molecules. This last carbonyl fraction is the responsible for a relevant peak that appears as a broad and intense band centered at $1,740\text{ cm}^{-1}$ (stretching of C=O), slightly displaced with respect to the bands in Figure 1a,b. Broadening implies that a large variety of carbonyl species is being formed. On the other hand, the increase of the carbonyl signal, intrinsically very weak in Raman, suggests a fragmentation process in which small carbonyl functionalized fragments are preferentially released from the cross-linked network. Even though the physisorbed

TABLE 1 Approximate peak position and Raman vibrational assignments of raw linseed oil, touch-dry linseed oil, and degradation markers from photo-aged linseed oil

Raw oil (cm ⁻¹)	Intensity ^a	Touch-dry oil (cm ⁻¹)	Intensity ^a	Degradation markers (cm ⁻¹)	Intensity ^a	Assignment ^b
3,018	s	3,016	sh	-	-	ν (C-H) in C=C-H
2,935	s	2,935	s	2,935	s	ν (C-H) CH ₃
2,904	s	-	-	-	-	ν (C-H) CH ₂
2,856	s	2,860	sh	2,853	sh	ν (C-H) CH ₂
2,731	m	2,730	m	2,730	sh	
1,748	s	1,745	s	1,740	sh	ν (C=O)
1,656	s	1,633–1,658	sh-s	1,653	w	ν (C=C) isolated
1,441	s	1,446	s	1,443	s	δ (CH ₂)
1,308	s	1,308	m	1,302	w	
1,269	s	1,264	m	-	-	γ (CH=CH) <i>cis</i>
1,082	m	1,083	m	1,071	w	ν (O-CH ₂ -C)
1,026	w	-	-	-	-	
975	m	975	w	900	w	ω (CH) in CH=CH
871	sh	873	sh	-	-	
-	-	-	-	783	w	
-	-	604	w	-	-	

^as: strong; m: medium; w: weak; sh: shoulder.

^b ν : stretching; δ : bending; ω : wagging; γ : rocking.

molecular products do not match exactly with the fragments resulting from oil ageing analyzed by SEC, it may be affirmed that the proposed SERS-based methodology have enough sensitivity to enable the detection of these molecules as markers of ageing.

It is worth noting that the higher enhancement of some signals such as the stretching vibrations of C-H bonds is caused by the specificity of the SERS substrates in combination with the laser wavelength used (514 nm). The same bands show a lower intensity when the sample is excited with a laser at 785 nm, so the enhancement could be caused by resonant SERS (surface-enhanced resonance Raman scattering).

Additional information on the chemical nature of the SERS detected LMW products may be provided by pyrolysis of aged linseed oil films through thermally assisted hydrolysis and methylation-pyrolysis gas chromatography/mass spectrometry analysis. Pyrograms of touch-dry oil mostly show peaks due to fatty acid methyl esters belonging to the saturated and unsaturated fatty acids present in the triglycerides: linolenic, linoleic, oleic, palmitic, and stearic acids.^[18] On the other hand, the main components detected after pyrolysis of the aged film, for example, for 2,200-hr photo-ageing as visible in Figure 3, were methyl esters of the saturated fatty acids (palmitic and stearic acids) and traces of unsaturated (di) acids, accompanied by an important peak due to a

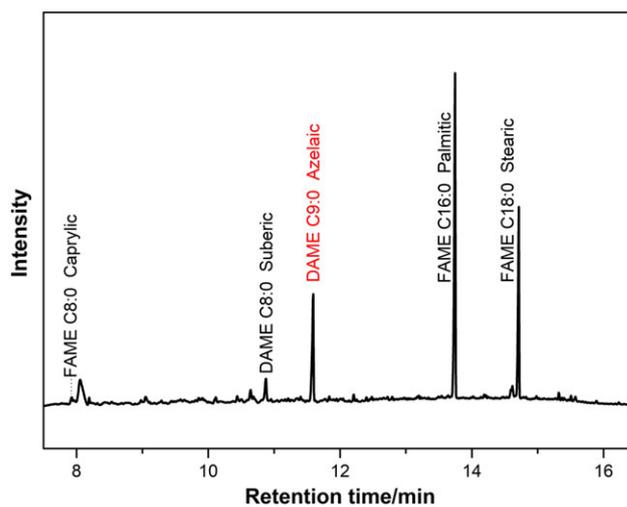


FIGURE 3 Thermally assisted hydrolysis and methylation-pyrolysis gas chromatography/mass spectrometry chromatogram of a 2,200-hr photo-aged linseed oil film. FAMES: fatty acid methyl esters; DAME: diacid methyl ester

diacid methyl ester, related to azelaic acid. Differently from all of the other identified fragments, directly produced by pyrolysis, azelaic acid is considered as the main compound of degradation of linseed oil, formed during oxidation, and released by chain scission at the C9 position of unsaturated acids.^[17,26,31] As a fact, the Raman spectrum in Figure 1c has many common features with

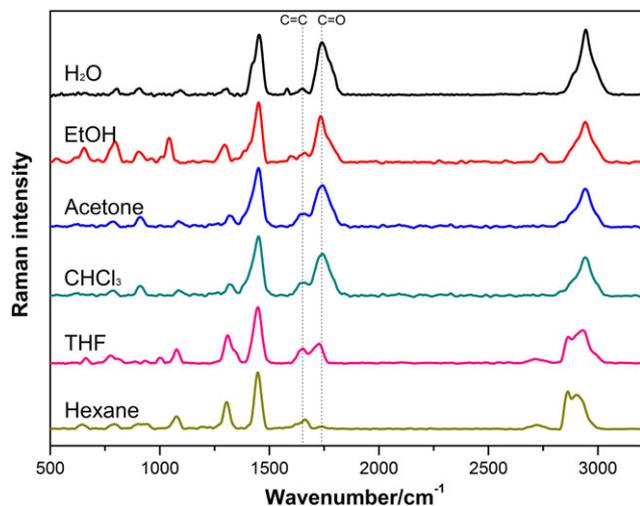


FIGURE 4 Raman spectra of products removed with silicone strip samplers from a 2,200-hr photo-aged linseed oil film and transferred by using different solvents onto 3D aluminum-coated surface enhanced Raman spectroscopy substrates. Excitation wavelength of 785 nm. THF: tetrahydrofuran

the structure of this diacid, thus corroborating the application of the procedure as a diagnostic tool to detect degradation markers.

A further improvement provided by the proposed procedure consists in the possibility of performing a selective sampling of the free molecules from the aged film surface, taking advantage of the features of the solvents used for their transferring. Either polar and apolar molecules stick to the silicone strip samplers by physisorption. Controlling the solvent polarity allows to discriminate the kind of molecules transferred to the SERS substrate for analysis. Photo-aged linseed oil films were sampled with silicone strips and the products transferred to the SERS substrates with different solvents, covering a range of polarity between the most polar water to apolar hexane.^[32] Corresponding Raman spectra are shown in Figure 4, where the main effect of solvent polarity may be deduced by following the relative intensity of the carbonyl band, which is representative of the presence of acids and esters formed during the oxidative process. Polar solvents such as water and ethanol show a good affinity for these compounds and remove most of them from the silicone strip sampler, giving intense carbonyl bands in SERS. On the contrary, as the solvent polarity decreases, less carbonyl compounds are transferred from the silicone strip to the SERS substrate. For instance, the carbonyl band disappeared completely when hexane is used as a transfer solvent.

At the same time, aliphatic bands could bring information about apolar molecules removed by the silicone strip sampler. As an example, the absence of carbonyl related peaks and the only presence of alkyl associated

bands when hexane is used for transferring reveal the nature of such molecules as small hydrocarbon-type compounds. This is the first direct evidence of hydrocarbon formation during linseed oil ageing and provides additional insights on its degradation mechanism, which worth further investigations.

4 | CONCLUSIONS

In summary, SERS proved to be an adequate technique to identify LMW products derived from the degradation of organic materials affected by autooxidation processes. 3D Al-coated SERS active substrates allow to follow structural changes taking place during drying and ageing of linseed oil, as anticipated with FTIR, recording Raman signal from the bulk of the sample. Furthermore, the combination of the silicone strip sampler selectivity with the sensibility of SERS substrates allows using LMW products as diagnostic markers. An additional level of selectivity can be reached by selecting the type of molecules by solvent polarity, during the transfer of the analytes to the SERS active substrate.

Linseed oil revealed to be an excellent model polymer for the optimization of the sampling method. Reliable laboratory techniques, such as SEC and Py-GC/MS, helped to build the evidence and to provide complementary data characterizing the LMW products. In conclusion, the combination of the strip sampler method and the SERS active substrate is the novelty of the work. Negligible amounts of material from oxidized surfaces of artworks are removed, while accurate evidence of LMW products forming with ageing is provided.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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