

## Article

# Development of a Thermal Separation Probe Gas Chromatography–Mass Spectrometry Method for Evaluating Wax–Resin Removal by Evolon<sup>®</sup> CR

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**Abstract:** Historically, many canvas paintings were infused with wax–resin mixtures that have discolored over time, distorting the aesthetics of the work, limiting treatment options, and introducing unstable materials into the object. Removal of the wax–resin is often desirable, but before works of art can be treated, a protocol to evaluate the efficacy of the treatment must be established. A mock-up painting was infused with a known amount of a wax–resin mixture made from beeswax and dammar; this material was then extracted through six intervals of exposure to solvent-loaded and dry sheets of Evolon<sup>®</sup> CR, a non-woven textile with a high sorbent capacity. Samples from the Evolon<sup>®</sup> CR sheets from each extraction round were analyzed using thermal separation probe gas chromatography–mass spectrometry (TSP-GC/MS). Normalization of peak areas related to beeswax and dammar to those of Evolon<sup>®</sup> CR revealed the relative amount of wax and resin removed throughout the extraction. The data show that, under these test conditions, the beeswax and dammar appear to be extracted with the same relative efficiency, information that cannot be provided through UV-induced visible fluorescence imaging of the Evolon<sup>®</sup> CR sheets or weight data alone, but which is critical to capture as it has implications for treatment success and the long-term stability of an artwork.



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**Keywords:** wax–resin; lining; reversal; Evolon; gas chromatography–mass spectroscopy; thermal separation probe; UV-induced visible fluorescence

## 1. Introduction

Evolon<sup>®</sup> CR (hereafter Evolon) is a non-woven microfilament textile invented by Freudenberg Performance Materials and consists of 70% polyester and 30% polyamide [1]. It has a smooth, soft surface and is isotropic, lint-free, and capable of absorbing up to 400% of its own weight in liquid [2]. The high sorbent capacity has led to the increasing use of Evolon for varnish removal from paintings. In most applications, the solvent-loaded sheets of Evolon are placed in contact with the surface of the artwork whereupon the solvent solubilizes the varnish, and the dissolved material is then resorbed into the Evolon sheet [1,3,4]. As this treatment often requires less mechanical action, it is seen as a preferable technique that minimizes potentially abrasive interactions with the paint layers.

The utility of Evolon in varnish removal has led to interest in other applications in painting conservation. Two treatments commonly performed on canvas paintings in the past were wax–resin infusion and wax–resin lining [5]. For infusion, the canvas painting is infused with a mixture of wax and resin; for lining, a secondary canvas support is adhered to the original canvas using the wax–resin mixture. These treatments were sometimes performed preventively as an attempt to reduce the deleterious impacts of changes in relative humidity to the canvas and paint layers. In other instances, they were performed to set down and re-adhere lifting paint or to provide support to a weakened or torn

original canvas. The exact recipes for the wax–resin mixtures varied depending upon practitioner but often included combinations of beeswax, mineral wax, colophony, dammar, and/or gum elemi [5,6]. Unfortunately, the saturation of the canvas fibers by the wax–resin adhesive can alter the colors, ground layer, and internal contrast within a painted image [7,8]. Additionally, the resinous materials discolor over time as they oxidize, altering the color of the canvas and ground layer of the painting. In addition to color changes to the ground, paintings subjected to wax–resin infusion or lining may also exhibit changes in solvent sensitivity, alterations in gloss, or become significantly stiffer, losing their drape and flexibility [7]. They are also not able to be effectively treated with many waterborne adhesives, limiting future options. As the wax–resin mixture ages, it becomes increasingly less soluble, establishing a temporal window within which the material may be safely removed.

The high sorbent capacity of Evolon has led to experiments in its use to aid in wax–resin removal. Ly and coworkers tested the efficacy of Evolon poultices on the removal of a mixture of microcrystalline wax and Piccolyte resin (a polyterpenic low-molecular-weight resin) [8]. They noted that none of their tested conditions resulted in the complete removal of the wax–resin mixture and that solvent choice was a critical factor to ensure the solubilization of both the wax and the resin component. Dijkema and Epley developed a wax–resin removal method to treat a still life painting by Georges Braque, *Pitcher, Candlestick, and Black Fish* (1943), that had been lined with wax–resin [9]. The final treatment method, which was developed after 48 preliminary trials, utilized solvent-loaded Evolon to help dissolve and mobilize the wax–resin, dry Evolon to help wick materials away from the painting, and heat and suction from a Willard vacuum table. The heat helped increase the solubility and mobility of the wax–resin mixture, and the vacuum suction encouraged the removal of solubilized material by ensuring a close contact between the back of the painting and the layers of Evolon below. The treatment consisted of three stages, which were performed twice. Briefly, in the first stage, the painting was placed face up over a pair of Evolon sheets, directly underneath the painting was a sheet loaded with xylenes, underneath which was placed a dry, wicking layer sheet; this stack was then heated under a low pressure for 15 min.. In the second stage, a sheet of Evolon loaded with odorless mineral spirits (OMS) was placed on the face of the painting. After 20 min, the wicking layer Evolon was replaced. In the third stage, the OMS-loaded Evolon was removed from the face of the painting, and the painting was allowed to cool under suction. They documented a 14% reduction in weight of the painting due to wax–resin removal and a perceptible color change of the ground, with a measured  $\Delta E_{76} = 4.1 \pm 0.4$ .

Although the Braque painting was successfully treated, many questions remained unanswered and unanswerable; in particular, the amount of wax–resin present in the painting was unknown, so while it was possible to measure the weight of material removed, it was impossible to determine the amount of wax–resin remaining in the artwork. Would further iterations of treatment have removed more wax–resin? It was also unclear if all components of the wax–resin mixture were removed with equal efficacy. It would be undesirable to have the more oxidized and acidic resinous materials remain in the painting. It was clear that the development of an analytical protocol capable of addressing these questions was necessary.

One of the most commonly available techniques used to identify oils, waxes, and resins is gas chromatography–mass spectrometry [10,11]. Pyrolysis is a commonly used sample introduction method used to overcome issues of solubility, cross-linking, and polymerization that many cultural heritage materials are prone to, particularly resins [10,12,13]. Thermal separation probe gas chromatography–mass spectrometry (TSP-GC/MS) is a relatively new technique that is similar to pyrolysis in that it promotes the anoxic thermal breakdown of materials and is proving to be of great use in the analysis of cultural heritage due to the small sample size required [14–17]. Because TSP-GC/MS is capable of identifying materials in wax–resin mixtures, it seemed an ideal technique to develop an analytical methodology around, and the small sample size means that it is feasible to analyze samples taken from

artworks before and after treatment. To establish the ability of TSP-GC/MS to document the removal of wax–resin, a mock-up painting, *Radishes* (Figure 1), was infused with a known amount of a dammar and beeswax mixture, and then the mixture was extracted through a modification of the approach used on *Pitcher*, *Candlestick*, and *Black Fish*. Samples of the used Evolon sheets were analyzed by TSP-GC/MS to identify the materials extracted. By using the amounts of pyrolysis products of Evolon as an internal standard to account for variations in sample size, the relative removal of beeswax and dammar could be followed to determine whether these two very different materials were extracted or if one was preferentially retained in the mock-up. In addition to TSP-GC/MS analysis, the Evolon sheets were weighed before and after use and documented through UV-induced visible fluorescence imaging. These low-tech approaches are more accessible to many conservators although they cannot determine the relative ability of a process to remove both beeswax and dammar.



**Figure 1.** *Radishes* (1993), before treatment image. The scale bar is an RMI Conservation Target (Robin Myers Imaging, Pleasanton, CA USA). The yellow oval in the bottom left of the work denotes the area in the mock-up where samples discussed in the text were taken from.

## 2. Materials and Methods

*Radishes* is a still life painting made in 1993 by B. Epley using oil paints over an acrylic ground on a cotton duck support. It would be unethical to develop a protocol using an actual artwork, and although acrylic paints are often xylene-sensitive, this available work that could be freely experimented on was chosen for the development of the TSP-GC/MS methodology. This treatment approach would not be appropriate on an authentic work of art that had an acrylic ground or paint layers but was appropriate for TSP-GC/MS method development.

**Wax–resin mixture:** As noted previously, there are a large number of historic recipes, and for this protocol development, a 3:1 (*w/w*) mixture of two historically relevant materials, beeswax and dammar, was chosen to simplify the interpretation of the TSP-GC/MS data. The beeswax (Plaza Art, Nashville, TN, USA) was heated in a double boiler until it melted, and then, the dammar (Kremer Pigments, New York, NY, USA) was added, and the mixture was allowed to continue heating with occasional stirring for approximately three hours

until the dammar dissolved. The mixture was then strained twice: first, through two conical medium mesh sleeves, and second, through cheesecloth folded into six thicknesses that had been sandwiched between two conical medium mesh sleeves.

*Radishes:* the unstretched mock-up was first weighed and then molten wax–resin mixture at approximately 50 °C was applied to the verso with a paint roller.

To remove the wax–resin mixture, a modification of the treatment protocol used on the Braque painting by Dijkema and Epley was chosen [9]. A manuscript describing the full development of this protocol is under preparation. It must be emphasized that the method described here was performed on a mock-up, and that before any work of art is treated with this or any other methodology, it is necessary to carefully evaluate its solvent and heat sensitivity to minimize the risk of damage; this protocol should not be universally applied.

Evolon (Deffner & Johann, Röthlein, Germany), Dartek (nylon 6,6, 0.75 mil thick, TC Transcontinental, Montreal, QC, Canada), solvents, heat, and suction were utilized. All Evolon sheets used in this trial protocol were weighed prior to use to enable the calculation both of mass of materials removed during the protocol and to calculate the mass of solvents needed for the solvent loaded, described herein. The mock-up was set face up atop a pair of Evolon sheets; the sheet directly under the mock-up was the solvent delivery sheet (X) that was pre-loaded with twice its weight in xylene (Sigma-Aldrich, St. Louis, MO, USA), and underneath the solvent delivery sheet was the wicking layer sheet (W). The face of the mock-up was then covered in Dartek to slow the evaporation of the solvents and ensure good contact between the back of the mock-up and the Evolon sheets. This orientation is critical to draw the wax–resin present on the back of the mock-up into the Evolon sheets. After 10 min, the first set of X and W sheets was exchanged for a new pair of sheets. Also, at this point, a sheet of Evolon pre-loaded with twice its weight of Shellsol odorless mineral spirits (OMS) (Shell Chemicals, Houston, TX, USA) was placed on the face of the mock-up and the stack of materials was re-covered with Dartek. An OMS-loaded sheet had proved effective in the treatment of the Braque, and thus, it was included here [9]. After 10 min the X and W sheets were again exchanged, while the OMS-loaded sheet remained in place. An additional three exchanges of X and W sheets were made at 10 min intervals. Thus, over the course of one hour, the mock-up was exposed to six X and W sheets, which were changed every 10 min. The OMS-loaded sheet remained in contact with the painting for 50 min. At the end of the six intervals, the Dartek and layer of Evolon on the face were removed, and the table and mock-up were allowed to reach room temperature gradually.

The extraction was performed atop a Willard heat and suction table (Willard Conservation Equipment Engineers, Chinchester, UK). To keep the table free of molten wax–resin, the table was covered with a sheet of Hollytex (a spunbonded polyester, Ahlstrom Paper Group, Amsterdam, The Netherlands) prior to treatment. Prior studies undertaken before the treatment of the Braque painting suggested that the ideal temperature of the painting that would both mobilize wax–resin yet avoid damage to the work was around 50 °C [9]. Additionally, in a currently unpublished work, the melting temperatures of samples of wax–resin mixtures from several other paintings in the Menil Collection were determined to vary between 53 and 61 °C. To achieve this range on the Willard table, the target temperature was set to 78 °C, and the safety reset was set to 80 °C, which caused the table to heat up to 80 °C, after which the heating element would turn off, thus ensuring that the mock-up could not be over-heated. Resetting the table turned the heating element back on. During the extraction trial, the table had to be reset multiple times to prevent the table from cooling too much and to keep the temperature close to the target temperature of 78 °C. While the target temperature of the table was 78 °C, the temperature measured at the Dartek surface atop the mock-up ranged between 55 °C and 60 °C throughout treatment, due to the insulating effect of the underlying layers. The suction pressure of the table was kept at 7 mbar throughout the treatment to encourage good contact between the mock-up and Evolon sheets and help pull extracted material away from the mock-up into the underlying solvent-loaded and wicking layer sheets.



After the extraction process, the solvents present in the mock-up and in the Evolon sheets were allowed to evaporate over the course of several weeks. The mock-up and Evolon sheets were then re-weighed to calculate after-extraction weights.

*Samples:* Samples of the bare canvas, of the canvas and ground, and of the canvas, ground, and paint layers were taken from *Radishes* before infusion and after wax–resin extraction. Samples were also taken from the six xylene-loaded layers (X–X5) and six wicking layers (W–W5), from the same location to ensure variations in the painting did not influence results. A portion of the before- and after-extraction samples of *Radishes* were embedded in Bio-plastic (Ward’s Science, Rochester, NY, USA) and polished to reveal the stratigraphy using Micro Mesh sheets (1500–12,000 grit) (Scientific Instrument Services, Palmer, MA, USA).

*Optical microscopy:* Images of the embedded cross-section samples under both normal oblique and UV illumination using B-2A filter cube were obtained using a Zeiss Axio-CamMRc5 camera controlled by Zeiss Axiovision AC software release 4.5 (White Plains, NY, USA). The camera was mounted onto a Nikon Labophot-Pol optical microscope, and the samples were imaged using the 10× objective (Melville, NY, USA).

*Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDX):* Backscatter electron images of the uncoated cross-section samples were taken with a JEOL JSM-IT100 SEM (JEOL Ltd., Peabody, MA, USA) in low vacuum mode at a pressure of 50Pa, at an accelerating voltage of 20 kV, a probe current of 40 (unitless), and a 10 mm working distance. EDX analysis using the integrated detector was performed under the same working distance and pressure conditions, but with higher probe currents of 65 to increase the counts.

*Thermal Separation Probe-GC/MS (TSP-GC/MS):* Samples were analyzed using a TSP (Agilent Technologies, Inc., Palo Alto, CA, USA), installed in a multimode inlet on an Agilent 8890 gas chromatograph. The multimode injector with TSP was operated in a 25:1 split mode, and the temperature was ramped from 50 to 450 °C at a rate of 900 °C/min. The final temperature was held constant for 3 min, and then decreased to 250 °C at a rate of 50 °C/min and held at 250 °C for the remainder of the run. For the gas chromatographic separation, two Agilent HP-5MS ultra-inert fused silica columns (15 m × 0.25 mm i.d., 0.25 µm film thickness) separated by a midpoint backflush assembly were used. Ultra-high purity helium carrier gas was used with a constant flow of 1.2 mL/min on the front column (inlet to midpoint backflush assembly) and 1.3 mL/min on second column (midpoint backflush assembly to the MS transfer line). The GC oven was programmed to ramp from 40 °C to 200 °C at 10 °C/min and 200 °C to 310 °C at 6 °C/min, with a hold time of 20 min (54.33 min of total run time). The GC was interfaced to an Agilent 5977B single quadrupole mass selective detector. The MS transfer line temperature was 280 °C; the MS ion source was held at 280 °C and the MS quadrupole at 150 °C. The MS was operated in E.I. positive mode (70 eV) and set to scan from 45 to 550 amu (5–25 min), 50–750 amu (25–30 min), and 50–800 amu (30 min–end run). Methyl derivatives of the samples were formed in situ in the TSP using tetramethylammonium hydroxide (TMAH, 2.5% in methanol, Sigma-Aldrich, St. Louis, MO, USA).

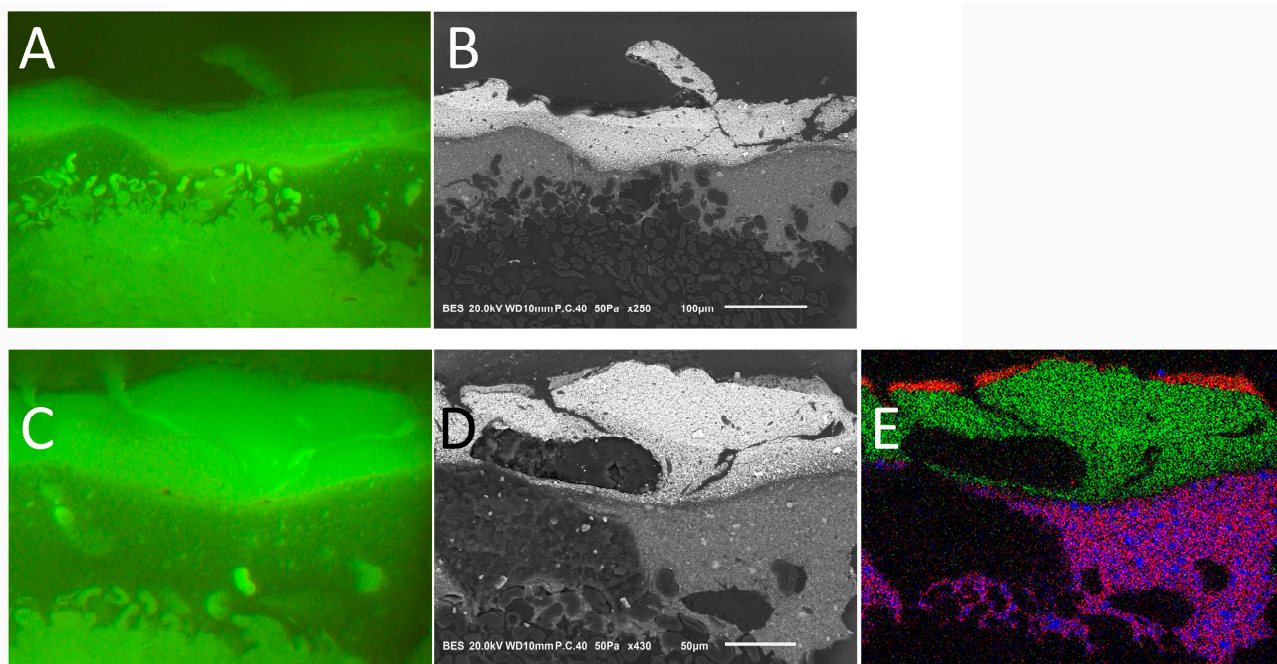
All GC/MS data were analyzed using a version of ESCAPE (Expert System for Characterization using AMDIS Plus Excel) developed specifically for Py-GC/MS of synthetic paint media [18,19]. Briefly, the total ion chromatogram (TIC) for a sample was analyzed by AMDIS (Automated Mass spectral Deconvolution and Identification System, version 2.73, NIST, Gaithersburg, MD, USA) to identify synthetic paint media marker compounds based on both mass spectral library matching and retention index. This information was output as an AMDIS report, which was then pasted into the Synthetic ESCAPE Excel report template (Excel version 2402). The template uses formulas to automatically sort and sum areas of the marker compounds and produce graphs and tables associated with the major classes of synthetic paint media: oil/alkyd, acrylics, epoxy, urethane, and vinyl. A manuscript providing the full description of Synthetic ESCAPE and its application to the analysis of synthetic paint media is in preparation for publication.

Images of the ultraviolet-light-induced visible fluorescence of the used Evolon sheets were taken using a PhaseOne XF, equipped with a IQ3 100 mega-pixel digital back (PhaseOne, Copenhagen, Denmark) and a Schneider Kreuznach 80 mm LS Blue Ring f/2.8 AF lens (Bad Kreuznach, Germany). The lens was fitted with a B + W 484 (Schneider Kreuznach, Bad Kreuznach, Germany) and a Tiffen 2E filter (Hauppauge, NY, USA) to ensure only light of 420–700 nm is captured. The camera was set to ISO 100 with a f/12 aperture. UV illumination was provided by two UV Systems (Renton, WA, USA) having TripleBright II lamps with over-lamp Hoya U-325C filters (Milpitas, CA, USA) to block visible light above 420 nm. RAW image captures included the UV Innovations™ Target-UV™ (UV Innovations™, <https://www.uvinnovations.com/>, Fremont, CA, USA); the images were white-balanced following the published UV Innovations™ standards for the processing of 'low' fluorescent materials [20] and then saved as Tiff files. To extract Lab values, the white-balanced Tiffs were opened in Photoshop, and the color picking tool, set at a  $101 \times 101$  pixel average (equivalent to  $0.42 \text{ cm} \times 0.42 \text{ cm}$ ), was used to measure the Lab values of the Evolon sheets in 5 locations on the sheet that were underneath the pictorial area of *Radishes* (upper right, upper left, lower left, and lower right quadrants, and the center of the sheet). These five measurements were averaged, and the standard deviations were calculated.

### 3. Results

#### 3.1. Characterization of Radishes

Although the focus of this investigation was on the development of the TSP-GC/MS analysis protocol, the authors felt that an understanding of the materiality of the mock-up would be beneficial when interpreting those results. Visible (not shown) and UV light microscopy of cross-section samples taken from the mock-up before and after extraction (location indicated in Figure 1) showed the presence of a dull fluorescent white ground of uneven thickness containing canvas fibers that are more highly fluorescent. The careful visual inspection of the brightly fluorescent white surface layers suggested that additional three paint layers were present (Figure 2). This was confirmed by SEM-EDX, which revealed the presence of three distinct layers on top of the white ground. Elemental mapping of the after-extraction sample indicates that the thick, uneven ground likely contains titanium white and calcium carbonate. Over this are two paint layers of variable thickness, both containing zinc white, and the upper one is more pigment rich and thus appears brighter in the backscatter image. The thin, interrupted surface layer is likely pigmented with titanium white. Both pre-infusion and post-extraction samples show cracking of the surface paints, likely caused by the sampling procedure. In the after-extraction sample, the ground layer shows a patch that appears darker in the backscatter image and is depleted of pigments in the EDX map. This phenomenon has been seen before in other samples made from soft acrylic paints where the manual polishing of the sample can cause the thick areas of the media to 'fuzz' and stand slightly proud of the surface rather than be smoothly polished. The lowest zinc-containing paint layer of this sample has a void that appears to have partially been filled with embedding medium. As this occurs in the center of a paint layer rather than at an interface between paint layers, it may be a result of paint application technique rather than an indication that the extraction has caused physical damage to the sample. Further samples would be necessary to confirm this.

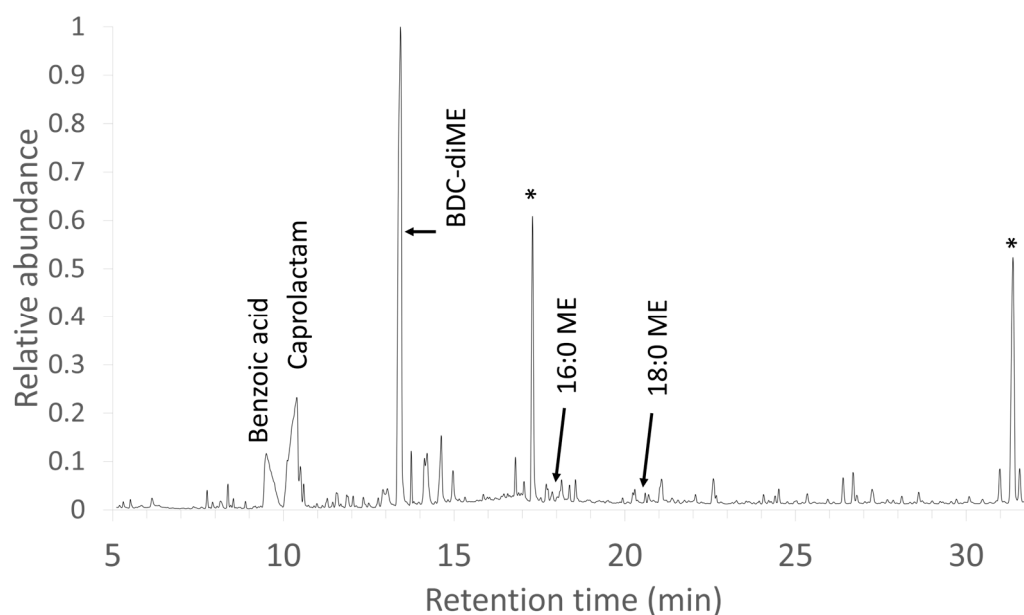


**Figure 2.** Cross-section sample of Radishes: (A) before wax–resin infusion under UV illumination and a B-2A filter cube; (B) before wax–resin infusion backscatter electron image; (C) after extraction under UV illumination and a B-2A filter cube; (D) after extraction backscatter electron image of the sample; and (E) elemental map of the after extraction sample, showing titanium in red, calcium in blue, and zinc in green.

TSP-GC/MS analysis of the ground layer revealed peaks characteristic of a poly(*n*-butyl acrylate-methyl methacrylate) (p(*n*BA-MMA)) acrylic paint, with peaks attributable to *n*BA, and *n*BA-MMA sesquimers, dimers, and trimers (some butylmethacrylate was also detected); the MMA peak eluted during the solvent delay [21]. The sample containing the surface paints revealed the methyl esters of fatty acids including hexadecanoic acid (16:0 ME) and octadecanoic acid (18:0 ME) and dicarboxylic acid peaks indicative of drying oils. Methyl esters of both nonanedioic acid and oleic acid (18:1 ME) were present, indicating that although the relatively young paint film has undergone oxidation, it is not fully oxidized (nonanedioic acid/18:0 ME = 0.63; 18:1 ME/18:0 ME = 0.51) [22–24].

### 3.2. TSP-GC/MS Characterization of New, Unused Evolon

Prior studies on the pyrolysis GC/MS of Evolon at 660 °C have shown the primary pyrolytic products to be caprolactam and 1,4-benzenedicarboxylic acid (BDC), with some benzoic acid also present as a further breakdown product of BDC [1]. The thermal separation probe used in this work has a lower maximum working temperature of 450 °C, and although benzoic acid, caprolactam, and the dimethyl ester of 1,4-benzenedicarboxylic acid (BDC-diMe) are the most intense peaks, additional peaks at higher retention times were also present in the TIC (Figure 3). These peaks, indicated with an asterisk in Figure 3, have major fragmentation ions at *m/z* 135 and 163, indicating they are likely higher order multimer units of polyethyleneterephthalate that contain BDC. The presence of these species may be a result of the lower achievable maximum temperature of the TSP unit, resulting in less complete pyrolysis. Baij et al. reported that small amounts of 16:0 ME and 18:0 ME were detected in their analysis [1], and small amounts of these species were also detected here.



**Figure 3.** Total ion chromatogram (TIC) of a sample of Evolon obtained by TSP-GC/MS. Major pyrolytic products are labeled, and the peaks marked with an (\*) are multimers of the polyester portion of the material.

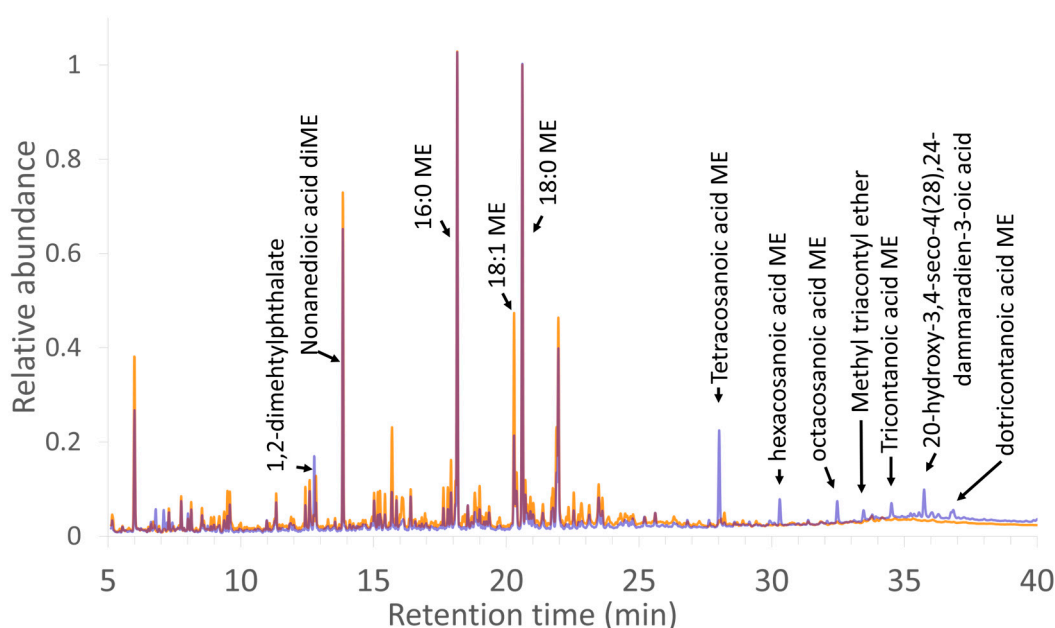
### 3.3. Documentation of Wax–Resin Removal by TSP-GC/MS

The untreated mock-up weighed  $0.058 \text{ g/cm}^2$ ; after infusion with the wax–resin mixture, the weight increased to  $0.092 \text{ g/cm}^2$ . After the wax–resin extraction and solvent evaporation, the mock-up weighed  $0.060 \text{ g/cm}^2$ , indicating that approximately 94% of the wax–resin mixture had been extracted by the process. Comparison of the TICs of samples from *Radishes* before wax–resin infusion and after extraction confirms that some wax–resin material remains detectable in an after-extraction sample (Figure 4). In particular, peaks attributable to long chain fatty acids (tetracosanoic acid ME to dotriacontanoic acid ME) and one peak related to dammar (20-hydroxy-3,4-seco-4(28),24-dammaradien-3-oic acid) are detected in the after-treatment sample [25–27]. The majority of peaks that show a decreased intensity in the after-extraction sample are derived from the acrylic ground, indicating that unequal ratios of ground and surface paints were present in the two samples. The cross-section samples seen in Figure 2 show that the ground and paint layers are variable in thickness, so variability in ground-to-surface paint ratios between any two samples can be expected. The peak area for the methyl ester 18:1 is noticeably lower in the after-treatment sample compared to the peak for 18:0 ME, as is that of nonanedioic acid (although to a much lesser extent), suggesting that some of the original components of the paint film may have been extracted along with the wax–resin material. However, care must be taken in this interpretation, as the cross-section samples in Figure 2 show that there is significant variation in the thickness of paint layers and pigments, including zinc white, which can have a significant impact on the oxidation and polymerization of drying oils [28–31]. The seemingly higher levels of 18:1 in the pre-extraction sample could arise from the sample having relatively more zinc white, a pigment known to prevent oxidation of 18:1 through the formation of zinc soaps [28,29].

In order to better understand the relative removal of dammar and beeswax through the extraction process, samples of the xylene-loaded and wicking layer Evolon sheets used in each interval were analyzed by TSP-GC/MS. No materials deriving from the acrylic ground were seen in the TICs of the Evolon sheets. To account for variances in sample sizes and pyrolytic efficiency, we investigated the use of the two major pyrolysis products of Evolon, caprolactam, and BDC-diME as internal standards. First, AMDIS was used to generate the integrated signal area for all peaks in the TICs, and then, the peak areas were



normalized so that either the caprolactam or the BDC-diME peak areas were set to a value of one; there were no significant differences in the data standardized to either species, so either caprolactam or BDC-diME can be used as an internal standard.

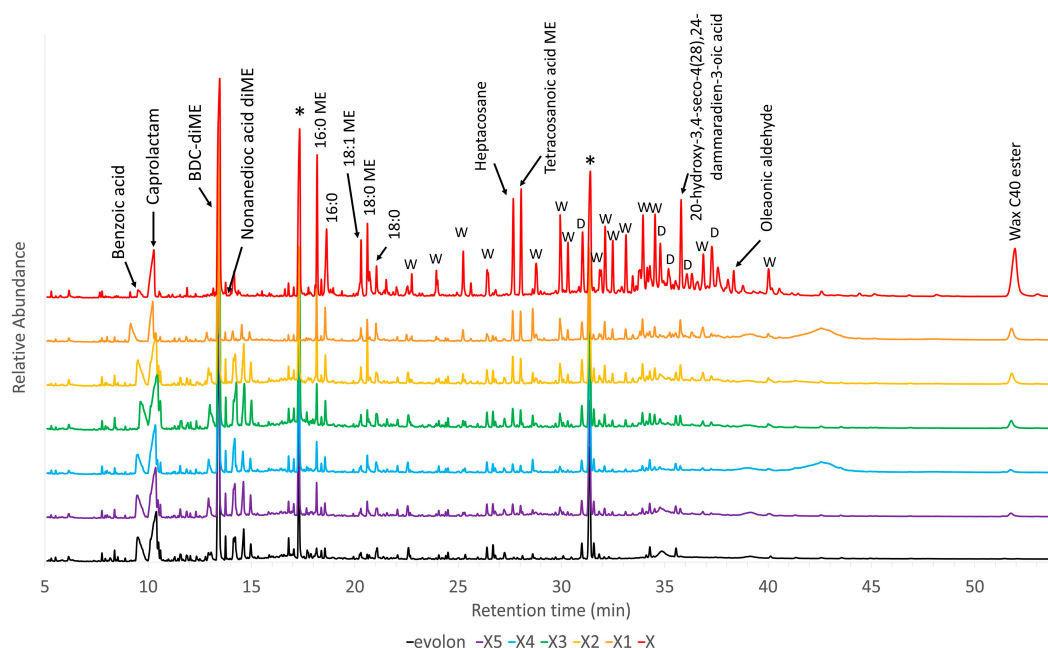


**Figure 4.** Comparison of the TICs taken from paint samples of *Radishes* before (orange) and after (purple) treatment. The TICs were normalized to the height of the 18:0 ME peak. The 18:0 ME peak was chosen as it is a relatively minor component in beeswax (2.6% of the acid component) unlike palmitic acid (59.8% of the acid component) [32] and so derives primarily from the surface paint.

Figure 5 shows the TICs of the xylene-loaded Evolon sheets from each round normalized to the BDC-diME peak (note that the TICs are vertically offset to improve legibility). The peaks of species associated with wax and dammar are most intense in the X sheet, the one that was first placed in contact with the mock-up. The relative amounts of wax–resin species decrease with each change-out of sheets, with very little wax–resin seen in the X5 sheet. The TICs from the wicking layer Evolon sheets are not shown, but follow the same trend, with W having the highest amount of wax–resin material and W5 having barely detectable amounts. In their treatment of the Braque painting, Dijkema and Epley had noted that the capillary action of the wicking layer Evolon was more effective than the suction from the vacuum table in the removal process [9]. The detection of wax–resin material in both the xylene-loaded and wicking layer sheets used in this experiment shows the extracted material was successfully pulled away from the mock-up into the xylene-loaded sheets and then subsequently the wicking layer sheets during the extraction, confirming their findings.

Figure 6 better illustrates the decreasing amounts of material extracted in each interval. Select species were chosen to include those that may relate to the wax (heptacosane, tetracosanoic acid ME, and the wax C40 ester), dammar (20-hydroxy-3,4-seco-4(28),24-dammaradien-3-oic acid, oleanolic anhydride), or both the beeswax and paint layer (16:0, 16:0 ME, 18:0 ME, 18:1 ME). The integrated signal areas of these materials when the signal of BDC-diME peak is normalized to one are shown (the results when caprolactam is used as an internal standard are equivalent and not shown). Although BDC-diME and caprolactam are both pyrolysis products of Evolon, there is some variability in the relative amounts of these species. In all samples of Evolon analyzed in this study, the integrated signal of caprolactam relative to that of BDC-diME was  $0.37 \pm 0.03$ , suggesting that although the internal standardization method has some variability, overall trends can be captured. In both the xylene-loaded and wicking layer sheets, approximately 75–97% of the wax–resin

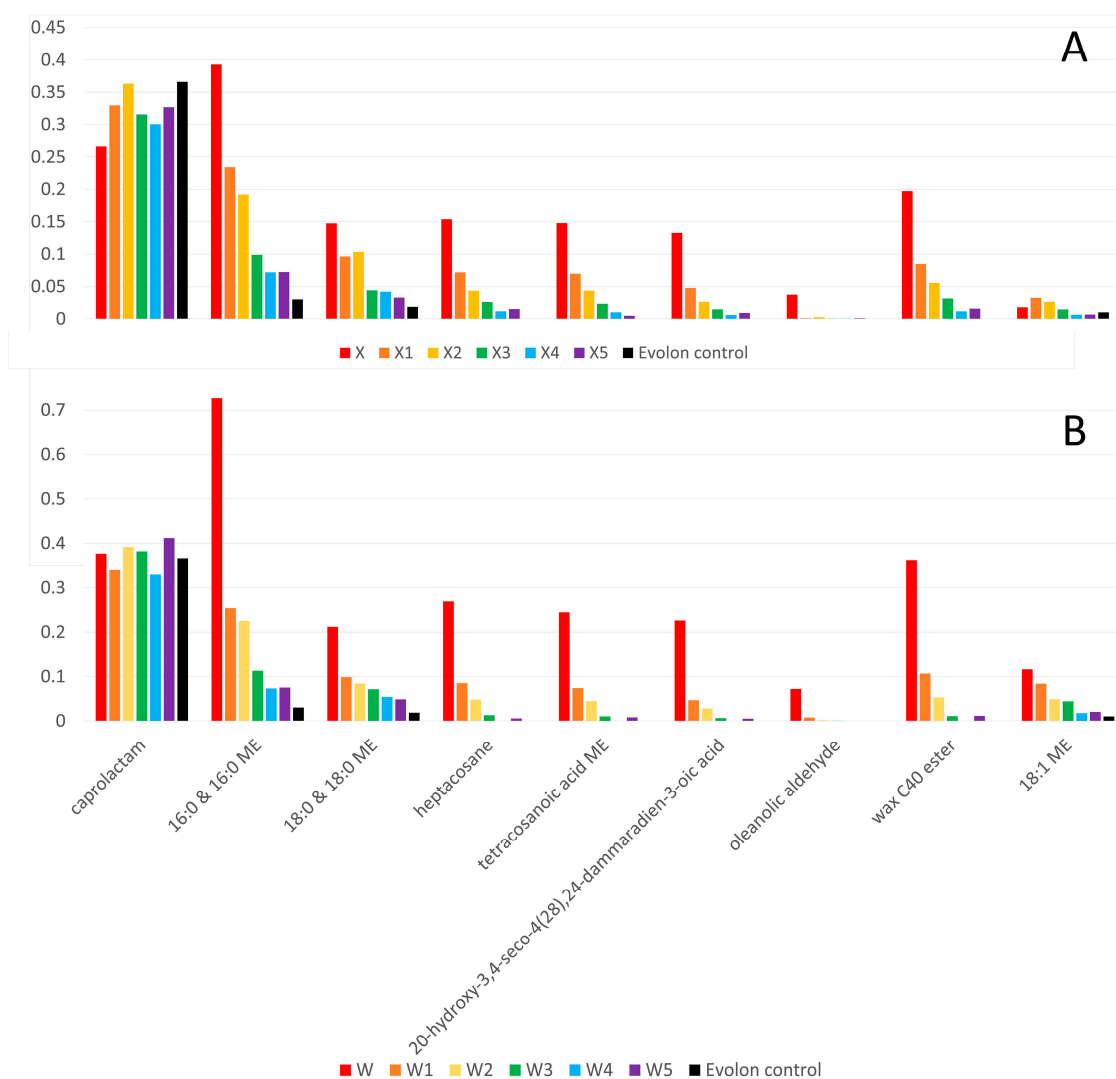
species removed are performed within the X–X2 and W–W2 rounds, and both wax and dammar appear to be removed with equal efficacy.



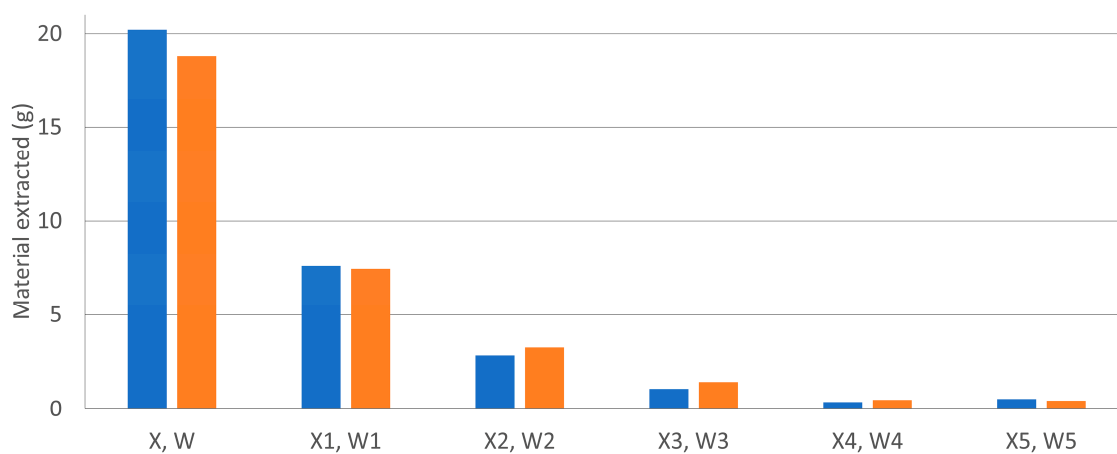
**Figure 5.** TICs of the used xylene-loaded Evolon sheets and unused Evolon normalized to the BDC-diME peak and vertically offset for legibility. Peaks discussed in the text are explicitly labeled, other peaks associated with wax are labeled ‘W’, those with dammar are labeled ‘D’, and higher order multimers of polyester are labeled with an asterisk.

Although the analysis of paint samples from the mock-up suggested that 18:1 and a small amount of nonanedioic acid may have been extracted from the mock-up during treatment (Figure 4), the Evolon sheets showed barely any detectable amounts of nonanedioic acid. In Figure 5 the peak for nonanedioic acid is within the baseline of the TICs, indicating that this material was not mobilized by the extraction process. The difference in peak areas seen in Figure 4 is thus likely a sign of variability in the surface paints of the mock-up. Figure 5 reveals that 18:1 is mobilized during the extraction process as is 18:0. Both of these species occur in oil paint films and in beeswax; the latter has 2.5% 18:0 and 4.1% 18:1 [32]. Therefore, it is unclear whether these fatty acids detected in the Evolon are derived from the mock-up or the beeswax or both. In the absence of isotopic labelling—a difficult undertaking—TSP-GC/MS will not be able to determine if the extracted 18:0 and 18:1 are derived from the beeswax or the oil paints on the mock-up.

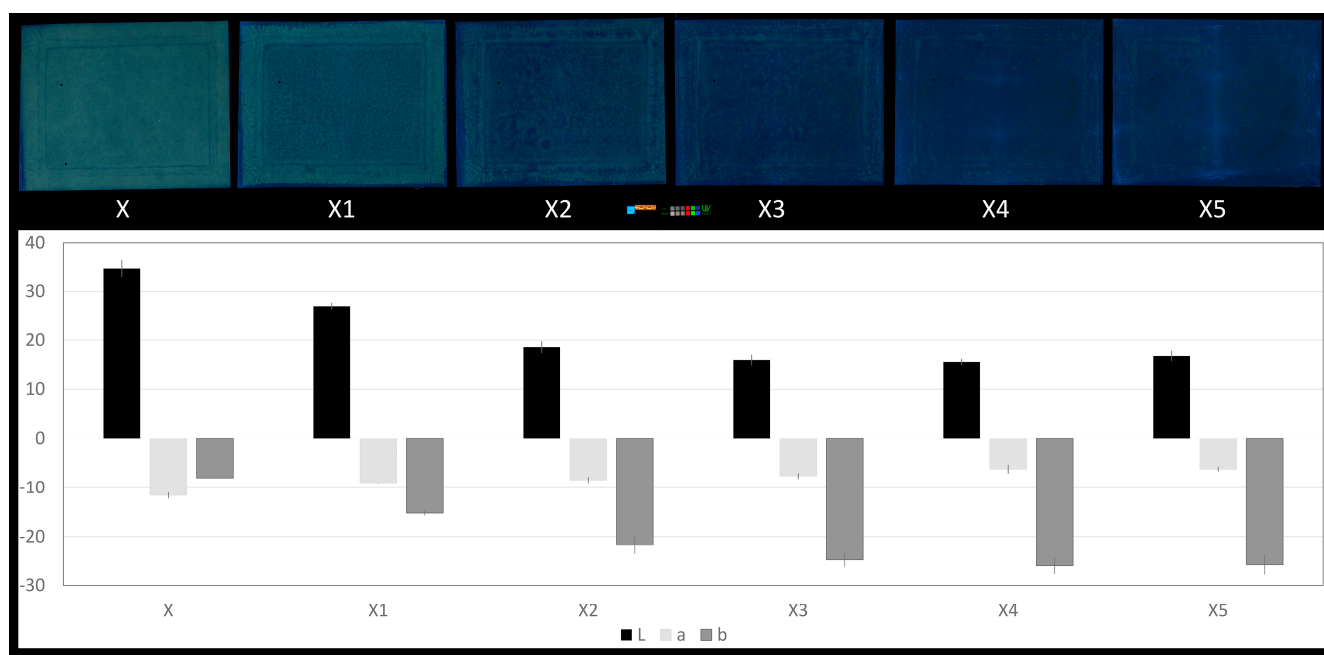
The trends seen in the TSP-GC/MS data are also captured in the amount of material sorbed into the Evolon sheets (Figure 7) and images of the used Evolon sheets taken under UV illumination (Figure 8). Resin and wax both exhibit UV-induced visible fluorescence that can be documented through imaging. The Evolon sheets used earlier in the extraction process exhibit a brighter, yellower fluorescence that decreases over the first three intervals of extraction.



**Figure 6.** Relative amounts of different species extracted when the data are normalized to the signal of BDC-diME. Panel (A) shows results from the xylene-loaded Evolon sheets and panel (B) from the wicking layer Evolon sheets.



**Figure 7.** Weights of extracted materials taken up by the xylene-loaded (X) and wicking (W) Evolon sheets during the different extraction processes.



**Figure 8.** UV-induced visible fluorescence images of the used xylene-loaded Evolon sheets and Photoshop-derived Lab values for the sheets. The scale bar is an RMI Conservation Target.

#### 4. Discussion

Conservation practices are constantly evolving, and the ethics of the field require that new treatment protocols be carefully evaluated so that their efficacy and impacts on the works of art are understood. To design the protocol for their treatment of the Braque painting, Dijkema and Epley first removed the lining canvas and conducted extraction trials by immersing weighed sections of the lining canvas in different solvents and used the pre- and post-extraction weight difference to determine which solvents were most effective in removing the wax–resin mixture, which was of an unknown composition [9]. They found that xylene and OMS were the most successful but were unable to determine what percentage of the wax–resin present was being removed, what components were being removed, and what was being left behind. As there were many different historical recipes for wax–resin mixtures, assessing the solubility of the wax–resin is an important first step; however, many resins oxidize and polymerize as they age, thus becoming more difficult to solubilize [25,33–39]. The ability of TSP-GC/MS to identify resinous components would permit the analysis of pre- and post-extraction lining canvas fragments, thus revealing the efficacy of extraction of the different materials. Although not to be undertaken without sufficient reason, the small sample size required by this technique would also permit the analysis of the actual work of art itself.

In an extraction process such as that used on the Braque [9], it is very valuable to be able to track what is being removed at different stages of the treatment process. Although quantitative pyrolysis GC/MS is difficult, the TSP-GC/MS analysis of the used Evolon sheets and the normalization of peak areas to a pyrolysis product of Evolon provided a facile means to account for variations in sample size and thus assess the relative removal of beeswax and dammar from the mock-up at different intervals in the extraction process. This approach also avoids the variability induced by the solubilization of materials from the Evolon sheets, an approach previously used to evaluate the extraction of oil paint components into Evolon [40]. In this experiment, the TSP-GC/MS results indicate that the beeswax and dammar were removed with relatively equivalent efficacy and that the majority of the wax–resin mixture was removed in the first three intervals. These findings were mirrored by colorimetry of the UV-induced visible fluorescence images, suggesting that this lower tech, more accessible approach can also be used to document the relative



efficiency of different treatment intervals if the more complicated mass spectroscopic approach is not available; however, these approaches cannot track the differential removal of wax and resinous components in a mixture. These approaches are also incapable of measuring the small but detectable amounts of both beeswax and dammar that remained behind in the mock-up after the full process. As previously noted, aging and oxidative processes alter the solubilities of materials, including beeswax and dammar [25,33,41,42]. The wax–resin mixture used on the mock-up was unaged, so the results seen for the protocol used in this test case may not be applicable to naturally aged mixtures containing the same components.

Laser speckling imaging has shown that when the solvent-loaded Evolon is used to remove varnish layers, the varnish layer initially retards the interaction of the solvent with the paint layer [43]. As exposure times lengthen and the varnish is solubilized, the solvent migrates into the paint and increases the dynamics of that layer. If the wax–resin had a similar protective effect, one could hypothesize that, as it is removed, the increasing interaction of solvent with the canvas and then the ground and oil paint layers might result in the greater mobilization of species related to the oil paint. 18:0 and 18:1 may be associated with the oil paint in the mock-up, the beeswax [44], or both. If derived mainly from the paint of the mock-up, these species might exhibit a delay in sorption into Evolon, with relatively less material being extracted in the first treatment interval and relatively more in later intervals. Examination of Figure 6 shows no clear evidence for this. This may be because the mobilized species are derived primarily from beeswax. If a portion is derived from the paint layer, the lack of apparent delay could be due to the use of the OMS-loaded Evolon sheet applied to the surface of the mock-up that helped ensure a relatively even exposure of all layers, wax–resin, canvas, ground, and paint, to solvents throughout the extraction process. It may also be an indication that the wax–resin in the canvas of the mock-up may be more permeable to solvents than an intact varnish layer, so solvents moving from the solvent-loaded Evolon sheet below the mock-up may have migrated into the wax–resin, canvas, ground, and paint layers with relatively similar speeds.

Any intervention into artworks is fraught, and ‘cleaning controversies’ have been documented from antiquity [45]. With the advent of scientific methods, the impact of solvents on paintings is better understood [46–52]. Solvent leachable materials in oil paints include glycerides, free fatty acids, oxidized fatty acids, and the products of their further oxidation such as diacids. Mobility of these components in paint films is dependent upon complex factors including levels of oxidation, hydrolysis, and chelation to pigment metal ions [43,48,51,53,54]. The removal of original materials is always a consideration when a possible treatment is being considered. Small molecules can act as plasticizers for a paint film, and their loss could lead to embrittlement [46,47,50,54,55]. However, the majority of old master paintings in museums have been exposed to solvents multiple times over the course of their existence. Some paintings, even under extreme solvent exposure conditions, display little extraction of materials, suggesting that most material may have been removed in past treatments [49,50]. Balancing the possible removal of original materials with the benefits gained from the removal of non-original wax–resin materials is a complicated decision. The approach described here offers scientific tools to better document and understand what occurs during an extraction protocol, which the authors hope will aid those considering wax–resin removal by providing a way to make more informed decisions.

## 5. Conclusions

The high sorbancy of Evolon has made it an attractive material for painting conservation treatments, but little work has been performed to date on determining its effectiveness for treatments other than those involving varnish removal. Although weight data and UV-induced visible fluorescence were able to parse the relative efficacy of the wax–resin removal at different extraction intervals, they cannot determine what material is being removed. TSP-GC/MS analysis of used Evolon sheets using the pyrolytic products of Evolon

as an internal standard proved to be a means to circumvent the traditional difficulties associated with quantitative pyrolysis and allowed the removal of beeswax and dammar to be individually followed. This approach offers a relatively facile way to evaluate the efficacy of reversals of historic paintings that have been wax–resin lined or infused when the amount of wax–resin present in the artwork is unknown.

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