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# Non-invasive analysis of gilt leather gold varnish and protective layer by infrared reflection-absorption spectroscopy

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## Abstract

As part of a larger research aiming to develop analytical approaches to characterise gilt leather constitutive materials and identify material markers for their attribution, this paper focuses on the organic layers applied on the silver leaves: the gold varnish and the protective layer. Ancient gilt leather varnish recipes were first analysed and compared by ATR-FTIR and Py-GCMS to try to define markers allowing varnish discrimination. The research demonstrates that the two techniques cannot separate varnish recipes based on recipe-specific compounds present in minor concentration, but are sensitive to the variation in the oil-resin ratio. Therefore, quantification of the oil-resin proportion should be considered to help with the decor provenance attribution, as long as the gilt leather has not been lubricated. More importantly, the paper assessed the potential of infrared reflectance spectroscopy as a non-invasive analytical technique to characterise the organic layers applied on the silver leaves. Thanks to the metal leaf that acts as a mirror, infrared reflectance spectroscopy allows collection of high quality reflection-absorption spectra of the gold varnish and the protective layer in gilt leather. In the corpus of historical decors analysed, reflectance FTIR confirmed the presence of an oil-resin varnish in all gilt areas, and revealed, for the first time, the use of a protein compound as a protective layer in the silvered areas, as well as in some gilt areas. In the silvered area, different practices are evidenced, consequently a larger corpus of silvered gilt leather decor should be investigated to determine if these differences can be related to geographical practices.

**6 Keywords:** gilt leather, gold varnish, oil-resin, protective layer, infrared reflection-absorption, Py-GCMS

## 1. Introduction

Gilt leathers are luxurious decorations used all over Europe to embellish the interiors of the richest residences, dating predominantly from the 16<sup>th</sup> to the end of the 18<sup>th</sup> century [1, 2]. Despite the name, they are not defined by the presence of gold. According to a treatise by Fougereux de Bondaroy [3] and other technical sources [4], they were made by applying a silver leaf to the leather, which had a gold-like appearance after being covered with a yellow varnish. On most decors, polychromy was then added on top, but leaving part of the “gold” varnish visible. For aesthetic effects, these decors can combine “gilt” and “silvered” areas. According to historical text, silvered areas were prepared by keeping a very thin varnish layer or by applying a protein-based layer over the leaf. The application of this protein-based layer as a protective layer on the silver surface is also mentioned in historical recipes to prevent corrosion [3]. Figure 1 provides a schematic representation of the different stratigraphies that could be encountered for gilt and silvered areas in gilt leathers. Previous studies on gilt leather fragments revealed the presence of a protein compound in an unprotected or tarnished silver area, however its attribution to the use of a protective layer could not be confirmed [5, 6].

Nowadays it is difficult to date and attribute gilt leathers as they are not signed, and assumptions concerning their provenance are only based on stylistic studies [1, 2]. Identification of the constitutive materials could provide some clues regarding the decor manufacturing process or reveal physical or chemical markers specific of a period, a country or a workshop. For that reason, a large research project has been set up within an interdisciplinary team to characterise the different materials in gilt leather and compare the scientific data with written technical sources and stylistic studies. The aim was to identify markers that could be correlated with the object provenance to help distinguishing the different gilt leathers workshops in Europe. Based on these markers and from the study of historic gilt leather decors, it is hoped to increase the knowledge on manufacturing techniques, classify, and eventually assign artefacts to specific workshops. Additionally, the study of gilt leather materials is essential to better understand the degradations observed and their processes, so to develop suitable conservation techniques.

A multi-technique approach was developed for the analysis of gilt leather combining different elemental and molecular analytical techniques [7]. Initially, ion beam techniques and synchrotron infrared microspectroscopy, two complementary instruments providing high brilliance and chemical sensitivity, were applied to a corpus of gilt leather decors. Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectroscopy (RBS) were implemented to respectively characterise the composition and the thickness of silver leaves on gilt leather [8]. This study revealed the difficulty to use silver leaves for provenance studies, due to the absence of discriminating chemical element in the composition and the thickness variabilities in gilt leather decors, related to the materials, the manufacturing or the life of the objects.

Synchrotron infrared microspectroscopy (SR-FTIR) was used mostly to characterise the organic components. Measurements were carried out on gilt leather thin sections to access the different layers individually, in particular the leather and the varnish layers [7]. For the varnish, the technique identified the presence of an oil-resin mixture that was confirmed by pyrolysis gas chromatography-mass spectrometry (Py-GCMS) with the characterisation of a siccative oil, such as linseed oil, and *Pinaceae* resin. The variation observed in the SR-FTIR spectra was thought to be related to a variation in the oil/resin proportion between different samples. However, similar variation was sometimes also observed within a single sample, suggesting this was also linked to heterogeneities in the thin sections (eg. flatness and thickness). Despite its high spatial resolution, the SR-FTIR was unable to detect the presence of a possible protective layer nor analyse separately the glue layer used to attach the silver to the leather. Additionally, the analytical approach was invasive and complex to

implement as it required to take a sample on the gilt leather artefact, and high skills to prepare thin sections by ultramicrotomy.

A more accessible and non-invasive approach was then sought to analyse the varnish and the protective layers, for that reason reflectance infrared spectroscopy (reflectance FTIR) was investigated. Reflectance FTIR, also called external reflectance FTIR (ER-FTIR) or specular/diffuse reflectance FTIR, is a portable technique that allows non-invasive and contactless analyses, consequently it has largely been applied to investigate cultural heritage objects that cannot be sampled or moved to a laboratory [9, 10, 11]. In this paper, the potential of the technique to analyse non-invasively gilt leather organic layers was assessed. First, ancient gilt leather varnish recipes were analysed and compared by ATR-FTIR and Py-GCMS in order to define markers allowing varnish discrimination. Then, the potential and limitation of reflectance infrared spectroscopy was assessed on gilt leather model samples before applying it on different ancient gilt leather wall-hangings or fragments.

## **2. Materials and methods**

### *2.1 Samples and objects*

Three ancient varnish recipes representative of different countries were prepared in 2007 by Andreas Schulze [4] and analysed in this study: the Italian recipe by Girolamo Ruscelli from 1555 [12], a Dutch recipe from the Mechelse Secretbook dated 1677 [13] and the French recipe by Fougereux de Bondaroy from 1762 [3]. For each recipe, compounds specific to the region or country are found (Table 1). Fougereux de Bondaroy's recipe was also reproduced in our laboratory in 2014 and used for the preparation of the different gilt leather model samples. In order to obtain the desired drying properties described by Fougereux de Bondaroy, we noticed the need to change the ingredients order by introducing the lead-based compounds at the start of the recipe, so to react with the oil. Gilt leather varnish recipes were kept secret, so it was not uncommon at the time to change the ingredients order to preserve know-how. The four varnishes as well as the different raw materials used in these recipes were analysed individually by the Py-GCMS and ATR-FTIR.

Gilt leather model samples were produced following the recipe transposed by Fougereux de Bondaroy [3]. Silver leaves from Manetti (Italy) (95 x 95 mm dimension and around 200 nm thickness) were attached to humidified vegetable tanned leather with skin glue, and then burnished after drying. For half of the samples, the silver leaf was covered with a protective layer made of egg white mixed with water (50/50). Samples with "gilt areas" were then covered with a layer of "gold" varnish, prepared according to the Fougereux's recipe. The "gold" varnish was applied by hand according to the tradition, without control of the thickness, which was evaluated after drying by optical microscopy from a sample section. "Silvered" areas were made by removing the varnish while still liquid on the surface as described in the recipe. The structure of the different model samples are summarised in the stratigraphy presented in Figure 1.

Several historic gilt leather wall-hangings, altar frontals and fragments originally made in France, Italy and Netherlands, were investigated by reflectance infrared spectroscopy:

- 8 gilt leathers produced in the Netherlands from the musée national de la Renaissance in Ecoen (France): "la bataille de Gelboé" wall-hanging, dating from the 17<sup>th</sup> century (2.18 m x 3.28 m), as well as fragments from other decors EC511, EC654, EC733, EC792, EC828, EC1127 and EC1383.
- 11 gilt leathers from a private collection: an altar frontal with a Crucifixion (CBD1) from Italy and dating from the 18<sup>th</sup> century; an isolated panel with the Crucifixion (CBD647) (Italy or Netherlands, 17<sup>th</sup> c.); a border from Boissier's workshop (CBD649) (France, 18<sup>th</sup> c.); fragments from a wall-hanging



with monkeys (CBD629.a.b) (Netherlands, 17<sup>th</sup> c.); a fragment (CBD629c) (Italy, 16<sup>th</sup> c.); fragments from wall-hangings (CBD10, CBD 630, CBD631, CBD632, CBD634, CBD635) (Netherlands, 17<sup>th</sup> c.).

- 2 gilt leathers samples from historic buildings: a fragment from an altar frontal in Golleville church (Netherlands, 17<sup>th</sup> c.); a fragment from a wall-hanging in the l'Isle castle in Switzerland (Netherlands, 17<sup>th</sup> c.).

## 2.2 Analytical techniques

Pyrolysis gas chromatography – mass spectrometry (py-GC/MS) was applied to the raw varnish materials (Venice turpentine, aloes, linseed oil and colophony), the reproduced varnishes recipes as well as the varnish sampled on two historical gilt leathers (“Chateau de l’Isle” and “Golleville”). For the analyses, a small varnish sample (around 10-50 µg) was directly introduced into an eco-cup of 50 µl with 2 µl of a methanolic solution of tetramethylammonium hydroxide TMAH (25 wt%). The sample holder was then inserted into the pyrolyser interface of a Frontier Lab PY-2020iD Pyrolyser, according to the procedure developed for the analysis of reference varnish films [14, 15]. The Py-GC/MS analyses were carried out on a Shimadzu GC2010 gas chromatograph interfaced with a Shimadzu GCMS-QP2010Plus mass spectrometer. Full details of the sample preparation and the analytical conditions of the pyrolysis gas chromatography – mass spectrometry measurements can be found in previous publication [14].

Infrared spectroscopy measurements were obtained with a spectrometer Alpha from Bruker fitted either with a diamond ATR or an external reflectance module. The instrument is equipped with a Global SiC source and a DTGS detector. The measurements in reflectance mode were carried out over an area of around 7 mm, with a working distance of 15 mm. For the analysis of the gilt leather decors, the instrument was placed horizontally on a stand and measurements were collected perpendicularly to the décor (Figure 2). In both modes, the spectra were collected in the 400-4000 cm<sup>-1</sup> spectral range, with a resolution of 4 cm<sup>-1</sup>, and the number of scans was 128 scans in reflectance and 24 scans in ATR. ATR-FTIR spectra were baseline subtracted using linear fragments reduced to a minimum and attached in similar locations. No data post-treatment was applied to reflectance FTIR spectra. For each measurement the microscopic view of the analysed area was recorded by the instrument.

## 3. Results and discussion

### 3.1. Comparison of varnish recipes

The “gold” varnish is central in gilt leather as it gives the gold appearance to the silver leaves. All gilt leather varnish recipes are based on the mixture of a siccative oil, linseed oil, with various pine resin derivatives (colophony, Venice turpentine and sandarac) in different proportion (Table 1). Linseed oil contain mainly triglycerides of saturated and unsaturated fatty acids, whilst pine resin derivatives are complex mixtures of neutral and acidic mono-, sesqui-, di- or triterpenoid compounds. Differences between resins derivatives are related to the presence of specific compounds or changes in the compounds ratios [14, 15]. When mixed, oil and resin react to produce dicarboxylic acids in particular azelaic and suberic acids. Lead based pigments such as massicot (PbO), minium (Pb<sub>3</sub>O<sub>4</sub>) and lead sulphate (PbSO<sub>4</sub>) are introduced in the French and Dutch recipes as siccative to allow rapid drying of the varnish. The remaining compounds in the recipe are added to modify the colour tone of the varnish and create its golden effect. Aloes is a yellow brown colourant that was commonly used in gilt leather recipes. Aloe extract contains mainly anthraquinones (Aloe-emodin) anthranols, anthrones (Aloin), pyrones, and chromones (Aloesin) [16]. Considering the archives, amber (in which succinic acid is the main constituent) [17, 18], asphalt (containing n-alkanes such as stearanes and

hopanes, as well as phenanthrenes and dibenzothiophenes) [19], or saffron (containing mainly  $\alpha$ -isophorone, safranal, eucarvone) [20] are instead country specific compounds, so they could be indicators of the decor provenance.

Infrared spectroscopy and GCMS are common techniques, largely applied in the field to characterise natural substances used in the varnish manufacturing. For each technique, methodologies have been developed to discriminate between these materials that have a complex chemistry. For GCMS analyses, identification is generally based on chemical markers of individual raw compounds [14, 16, 21]: azelaic and suberic acids for linseed oil, dehydroabietic DHA for pine resin (colophony or sandarac), pentacyclic triterpenoides ( $M_w > 400$ ) for Venice turpentine and methylated p-coumaric acid for aloes. For infrared spectroscopies, marker peaks have been identified in the far and the middle range to discriminate between individual resins, sometimes combined with the use of other technique, like Raman spectroscopy, or spectral deconvolution [22, 23, 24].

In the gilt leather model varnishes, mostly the markers of the siccative oil and of the pine resin are identified by both techniques (Figure 3, Figure 4). The marker peak of aloes, p-coumaric acid, was previously observed in very low concentrations in the GCMS chromatogram of the model varnishes by Schulze [4, 16], however in our case it could not be distinguished from the background. The materials specific to each recipe, generally present in minor quantities, such as safran, amber or asphalt could not be detected by either technique. These compounds have likely been altered by the heat or have reacted during the varnish preparation. Nevertheless, differences in the oil-resin ratio are evidenced by both techniques.

The ATR-FTIR spectra of the varnish are very similar but slight variations are observed in the two fingerprint regions around  $2900\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ , associated respectively with the C-H and carbonyl stretching regions (Figure 4). The shift and intensity changes of the FTIR bands can be directly correlated with the difference in oil-resin proportions. Fougeroux's recipe has the highest resin content, which is evidenced in the spectra by the shift of the carbonyl band towards lower frequencies and the intensity decrease of the band at  $2854\text{ cm}^{-1}$ . Considering that its oil/resin proportion is close to 50/50, Fougeroux's varnish spectrum was compared to the spectrum of a simple linseed oil/colophony varnish prepared in proportion 50/50 by Tirat [21, 25]. The two spectra were identical, confirming that the infrared signature originates mostly from the two main components: oil and resin.

In the spectra of the Ruscelli and the Secretbook varnishes, the broad band around  $1600\text{ cm}^{-1}$  is more intense and appears associated with the presence of aloes, present in higher concentration in these varnishes. Nevertheless, it is unlikely that this band could be used to characterise the presence of aloes since this spectral region is strongly affected by the oil-resin content as well as the varnish ageing. Additionally, the marker and unique signal of aloe in GCMS chromatogram, p-coumaric acid, is also encountered in other plants, therefore it was said to be an inconclusive marker for aloe. For that reason, Rizzo investigated other analytical approaches including HPLC and SERS to evidence the use of aloes in varnishes from more specific biomarkers [16].

Considering that the infrared spectra are mostly dependent on the oil-resin ratio, methodologies previously developed by Daher to quantify the oil/resin proportion could possibly be applied here [26, 27]. The methodology involves the application of spectral decomposition calculation from CH stretching massif around  $2900\text{ cm}^{-1}$  and the fingerprint region  $1900\text{--}1330\text{ cm}^{-1}$ . Although this methodology may need to be adapted to aged and degraded varnish, the approach is promising and should be further investigated. Nevertheless, a factor to bear in mind in the case of gilt leather, is the

possible presence of past conservation treatment and its effect on the varnish composition. The analyses of the “Chateau de l’Isle” and “Golleville” gilt leather varnish by Py-GCMS, again showed the markers of the siccative oil and the pine resin, with higher oil content, as well as markers of animal wax including lanolin. Wax and lanolin indicate that a lubricant was applied to the artefact as a conservation treatment in the past. Lubricants were applied either directly on the decor surface or onto the leather, at the back, where it migrated through the different layers up to the varnish. The presence of such lubricant in gilt leather varnish will affect the oil-resin proportion and may cause misinterpretation.

### *3.2. Reflectance infrared spectroscopy of varnishes*

Reflectance infrared spectroscopy is very dependent on the physical and optical properties of the surface and the analysed material. Depending on the surface properties, specular and/or diffuse reflectance signals are collected. These signals are generally weak and the resulting spectra display strong distortions compared to absorption spectra, making their interpretation sometimes complex. Post treatments may be applied, but these are not efficient when different type of reflection signals are collected or when the material is heterogeneous. Another reflectance technique is infrared reflection-absorption spectroscopy (IRRAS). The technique allows the analysis of thin films, from 0.5-20  $\mu\text{m}$ , deposited on shiny mirror-like surface, where the angle of reflection is equal to the angle of incidence [28, 29]. The spectra obtained from this technique are similar to absorption ones, and equivalent to a double-pass transmission experiment, therefore no data treatment are required. In the case of a gilt leather, the silver leaf can act as a mirror, so infrared reflection-absorption spectroscopy measurements can be carried out, and absorption-like spectra of the organic layer applied on top can be collected. For simplicity in the text, the measurements will be referred as reflectance FTIR.

Comparison of the spectra collected on Fougereux’s varnish in ATR and reflection modes gave similar profiles, with only a slight shift of the carbonyl band and the band around  $1200\text{ cm}^{-1}$  in the ATR spectra, likely induced by the ATR mode. The influence of the varnish thickness on the spectra was evaluated by comparing measurements made by reflectance FTIR on silvered areas with varnish thickness around  $1\text{ }\mu\text{m}$  and gilt areas with varnish of various thicknesses (Figure 5). As varnish thickness increases, the  $\nu\text{ C-H}$  band intensity decreases and the carbonyl band broaden and shift towards higher frequencies, together with an increase in the baseline distortion. In these measurements, the best quality reflectance measurement is obtained when the varnish thickness is around  $10\text{-}15\text{ }\mu\text{m}$  (Figure 5). In previous work, the average thickness encountered in historical gilt leather decors was shown to be between  $5$  and  $30\text{ }\mu\text{m}$  [7].

The presence of a protein based layer at the surface of the silver leaf is detected by reflectance FTIR (Figure 6). When the silver leaf is solely covered by a protein layer, the characteristic protein signature is observed in the spectrum with markers peaks observed at  $3295$ ,  $1648$ ,  $1540\text{ cm}^{-1}$ , associated with amide A, amide I and amide II bands respectively. When a thin varnish layer around  $1\text{ }\mu\text{m}$  is applied on top (silvered area), these protein marker peaks are also easily observed. In the presence of a thicker varnish layer of about  $10\text{ }\mu\text{m}$  (gilt area), these marker peaks are very weak but may still be visible (Figure 6). When a thicker varnish layer was present, the marker peaks could not be seen anymore. The use of second derivatives on the spectra was tested but proved unsuccessful to reveal the presence of the protein layer.

### *3.3. Application to historic gilt leather decors*

A corpus of 21 gilt leather wall hangings, altar frontals and fragments was analysed non-invasively by reflectance FTIR. The spectra were collected in different gilt areas free of polychromy, as well as in silvered areas when present.

Under magnification, the surface is non uniform due to the presence of heterogeneities in the varnish application, cracks or corrosion in the silver leaf, or relief in the material, such as punches or embossing. These heterogeneities may affect the signal reflection and cause spectra distortion; nevertheless, in most cases, good quality spectra were obtained (Figure 7). In all gold varnish areas, the spectrum of an oil-resin varnish is identified (Table 2). The variation in the carbonyl peak maxima, observed between 1718 to 1746  $\text{cm}^{-1}$  in gilt areas, may be related to differences in the varnish thickness and/or in oil-resin proportion. The spectrum profile suggests that the “gold” varnish layer thickness in most decors is around 20  $\mu\text{m}$  or greater, due to the slight distortion of the spectrum and the shift of the carbonyl peak to frequencies over 1740  $\text{cm}^{-1}$  (Figure 7, Table 2). The broadening of the carbonyl peak and the loss of the sharp features in the region between 900 and 1500  $\text{cm}^{-1}$  observed in spectra like CBD1, CBD10, and EC654, might be linked to the varnish ageing. In gilt leathers EC654, EC733, Golleville, and Crucifixion, the spectra display the weak protein characteristic peaks in the gold varnish areas, suggesting that a protein protective layer has been applied on the silver leaf before application of the “gold varnish”. Three gilt leathers displayed silvered areas: EC511, CBD1 and Gelboé. Reflectance FTIR proved perfectly suited to analyse silvered areas, as the organic layer was thin and good reflection signal was collected. In these three decors, a protein layer was revealed in the silvered area either on its own or covered by an oil-resin varnish layer (Table 2), thus confirming the existence of this protective layer mentioned in historical texts.

Despite the difficulties to discriminate different varnish recipes, reflectance FTIR analyses can reveal different practices in the decor manufacturing or in the life of the object, as illustrated by the decors discussed below.

Analyses of “la bataille de Gelboé” wall-hanging (Figure 8) were carried out whilst the decoration was under restoration [30]. Within the decor, that displays a historical painted scene, gilt and silvered areas are visible. In the gilt areas, only the oil-resin mixture is visible, whilst in the silvered areas, both a protein-based compound and an oil-resin varnish are detected (Figure 8). The FTIR spectrum profile obtained in the gilt area suggests that the varnish layer thickness is greater than 20  $\mu\text{m}$ . Therefore, if a protein protective layer had been applied before the varnish, it is unlikely to be seen.

The gilt leather CBD1 is an altar frontal with mostly gilt and silvered areas (Figure 9). In the gilt area, the FTIR spectrum indicates the presence of an oil-resin varnish with a broaden carbonyl band. In the silvered area, only a protein compound is detected but the FTIR spectrum is slightly distorted with a change in the amide I / amide II bands ratio, and a derivative peak around 1330  $\text{cm}^{-1}$ , as well as the absence of the amide A band (Figure 9). The origin of these spectral distortions is not yet understood, but could possibly be linked to the heavily cracked silver leaf.

The gilt leather EC511 is a fragment displaying gilt and silvered areas (Figure 10). The silvered area was heavily tarnished, but displays small untarnished zone with a yellow colour. The reflectance FTIR analyses revealed that a protein layer is solely present in the untarnished zone, whilst the gilt area contains only an oil-resin mixture (Figure 10). In the tarnished silver area, a very weak protein signature is also detected, which suggests that a protein layer was originally present but only traces of it remain. From these analyses, it can be hypothesised that the silver corrosion results from the loss of the protein layer, possibly due to over cleaning of the object.

In the Golleville gilt leather fragment, only gilt areas are present, where reflectance FTIR identified an oil-resin varnish with possible protein markers (Figure 11). Some infrared spectra display additional peaks which could be linked to the lubrication treatment revealed by Py-GCMS. Similar peaks could be found in the FTIR spectra of the British Museum Leather dressing (BMLD), a lubricant containing a mixture of lanolin, cedar oil and beeswax, occasionally used in the past to treat this type of leather (Figure 11). Therefore, the infrared analysis further informs that a conservation treatment based on BMLD or similar recipe was applied to the Golleville gilt leather. The possibility to detect past restoration treatments with distinct composition, such as lubricant or modern varnishes, is a very useful information as it could help better understand current degradation or support future conservation treatments. Nevertheless, it should be kept in mind that the sensitivity and specificity of FTIR is limited. Thus, the technique will not be able to distinguish similar compounds, meaning that it cannot identify an exact conservation product or discriminate modern oil treatment from the oil-resin varnish. Additionally, compounds in low concentration are unlikely to be detected, which may explain that the lubricant applied to “Chateau de l’Isle”, and identified by Py-GCMS, was not picked up by reflectance FTIR.

Reflectance FTIR is a very efficient technique for the analysis of organic layer in gilt leather, in particular the analysis of silvered areas. Different practices in the protective layer formulation are revealed from the analysis of the three decors, with either the use of a protein layer on its own or covered with a thin oil-resin varnish layer. Systematic analysis of gilt leather silvered areas by reflectance FTIR would be very valuable to compare techniques between countries or workshops. The technique also evidenced in one decor differences between tarnished and untarnished silver areas. This opens up new perspective of research regarding the understanding of silver tarnishing, thus this approach should be repeated on other gilt leathers with silver tarnish, in order to assess all the potential that could be gained from the technique.

#### **4. Conclusion**

This study is part of a larger research aiming to identify material markers for the attribution of gilt leather decors. In this work, a focus was made on the organic layers applied on the silver leaves: the “gold” varnish and the protective layer mentioned in historical texts. Despite differences in the composition of modern varnish recipes, Py-GCMS and FTIR spectroscopy cannot discriminate these recipes based on recipe-specific compounds. Both techniques mostly display the signature of an oil-resin mixture with only variation in the oil-resin proportion. Quantification of the oil-resin proportion may be a way to compare varnishes recipes, nevertheless this approach would be inefficient to discriminate varnishes with similar oil-resin content or when the decor has been treated by lubricants. Therefore, the need for analytical approaches adapted to the identification of the recipe specific compounds such as safran or asphalt remains necessary.

The paper presents the first application of infrared reflectance spectroscopy to non-invasively analyse the varnish and protective layer of gilt leather decorations. Thanks to the presence of the silver leaf that acts as a mirror, the technique allows the collection of high quality absorbance spectra of organic layer up to 10-15  $\mu\text{m}$  thickness. Thus, reflectance FTIR can be used to characterise the varnish composition in the gilt areas and the protective layer in the silvered areas of gilt leather. In the corpus of historical decors analysed, the reflectance FTIR confirmed the presence of an oil-resin varnish in all gilt areas, and revealed, for the first time, the presence of a protein-based layer in the silvered areas, as well as in some gilt areas. In the silvered area, different practices are evidenced, as the protein layer may be present on its own or covered with an oil-resin layer. This analytical approach should be extended to a larger corpus of gilt leather decors with silvered areas to assess if

the nature of the protective layer could be a possible marker of geographical practice. Additionally, the technique can potentially also detect the presence of past restoration materials with distinct composition, that have been applied on the surface or which have migrated from the leather support. All these information that can be obtained directly in the collection without contact to the object, open up new areas of research in gilt leather analysis, and can bring important knowledge to art historians and conservators.

Further to this work, it would be interesting to carry out complementary analyses or research to provide additional information to the data collected by reflectance FTIR. In the case of silvered areas, the application of proteomic analysis to the protective layer would allow the identification of the nature of the protein layer, to discriminate between egg white and skin glue, or even precise the animal species. In order to select the areas with the optimal varnish thickness, the complementary use of optical coherence tomography (OCT) imaging system, which is also a portable instrument, would be very valuable. Additionally, the technique could also help identify when heterogeneities or several layers are present in the varnish. Lastly, in this study we demonstrated that the band profile and position in the infrared spectra of the varnish were affected by the oil-resin proportion, the ageing and the thickness of the varnish. Further research would be required to better understand the effect of each parameter, in order to possibly extract, in the future, quantitative data from the infrared spectra, and allow better comparison between gilt leather decorations.

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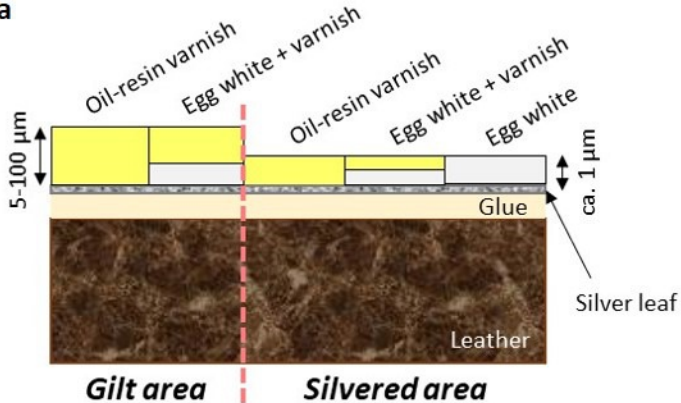
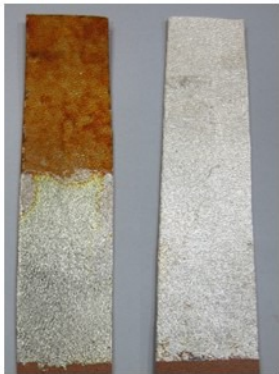
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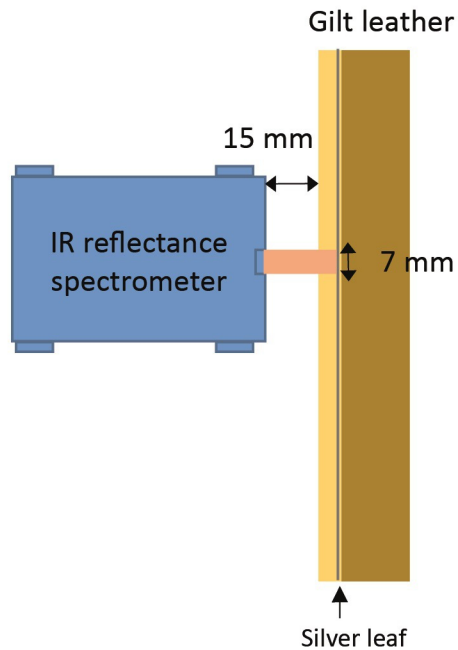
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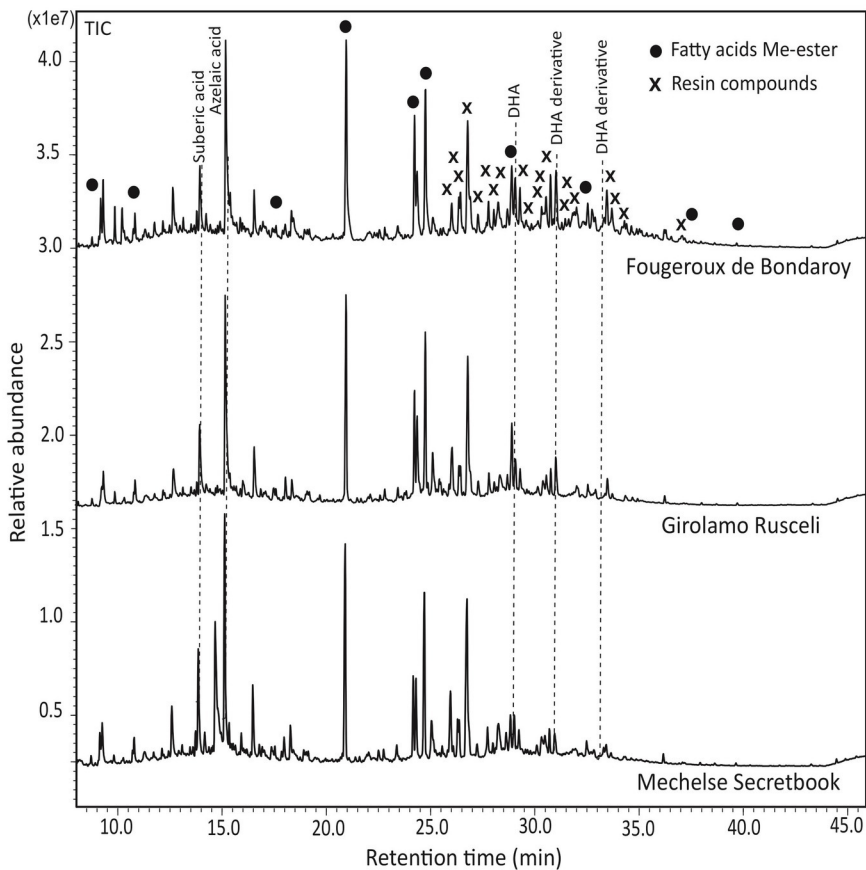
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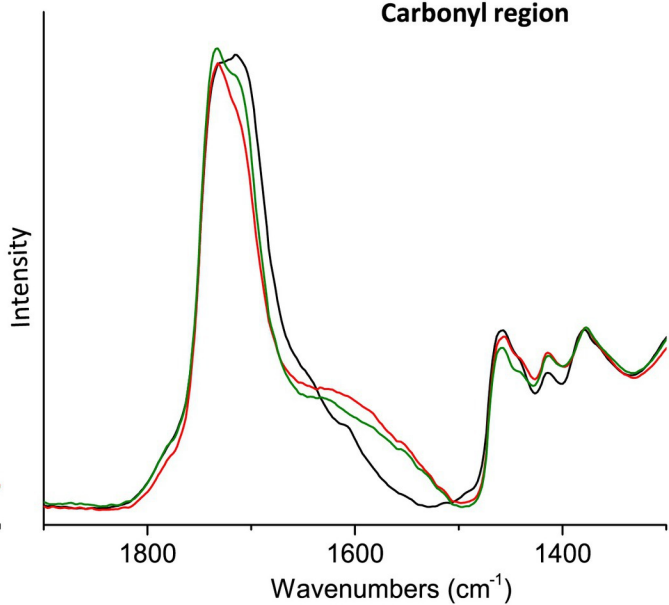
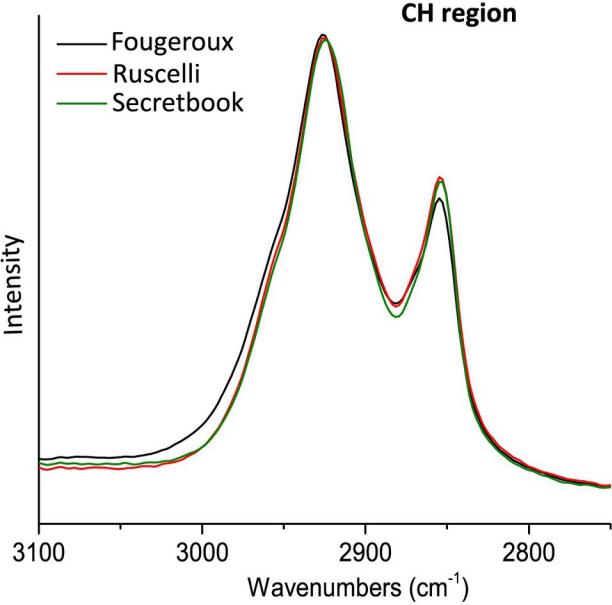


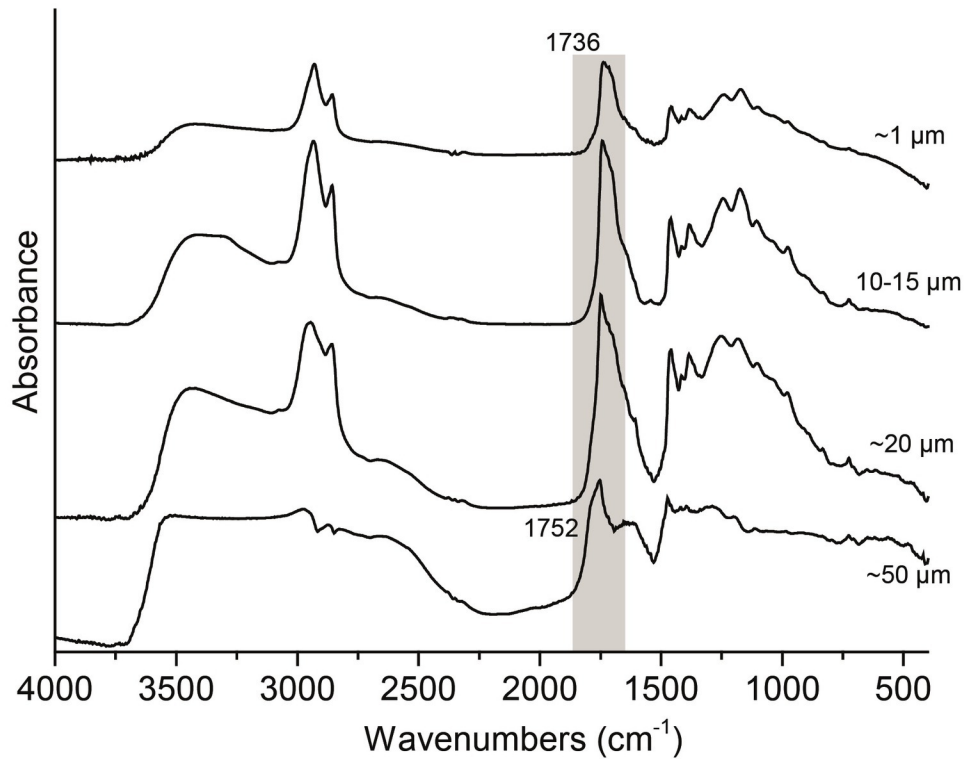
# Gilt area    Silvered area

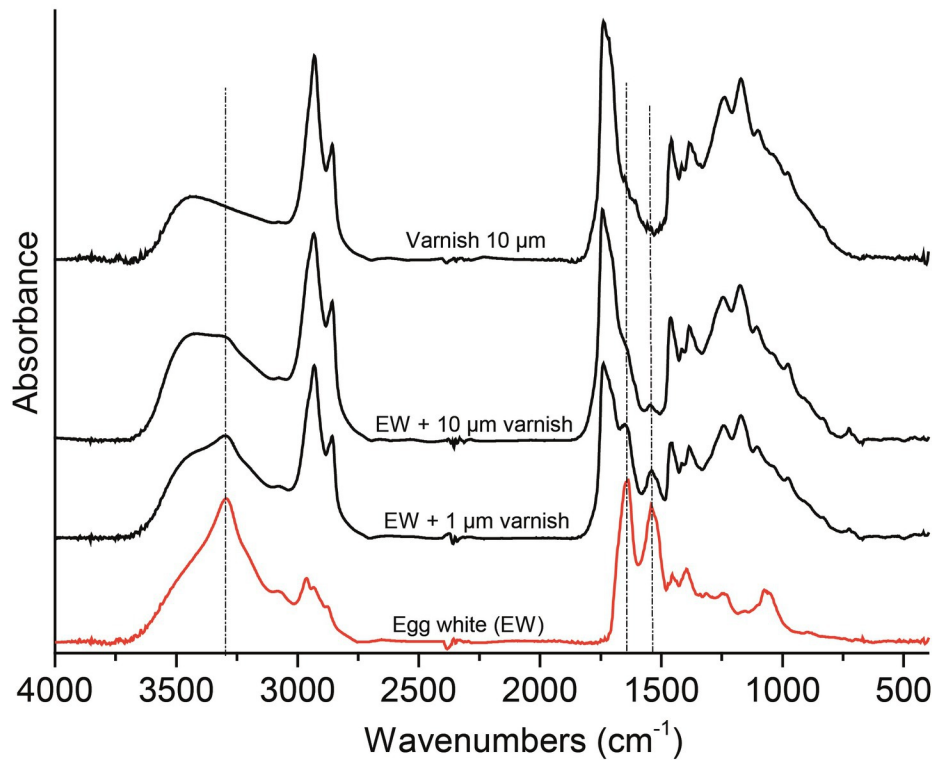


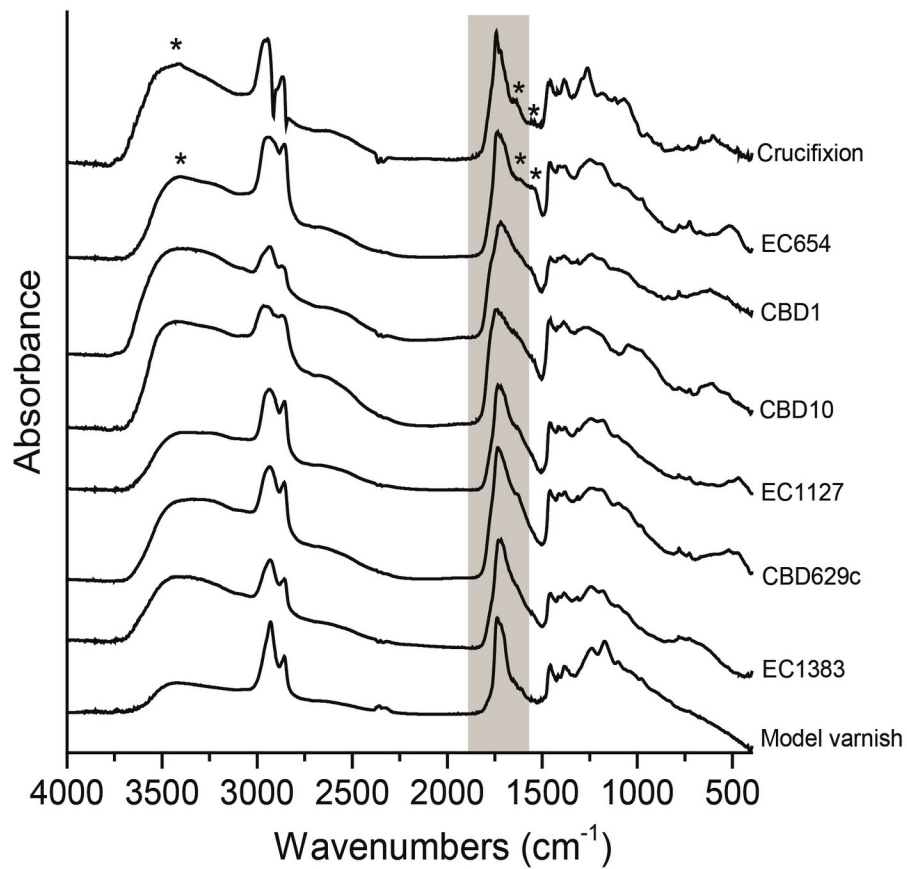


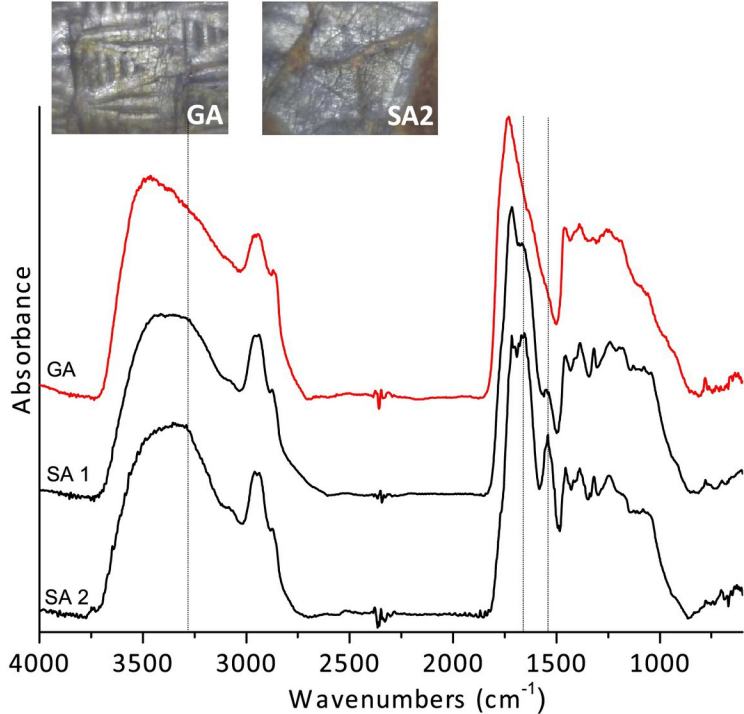




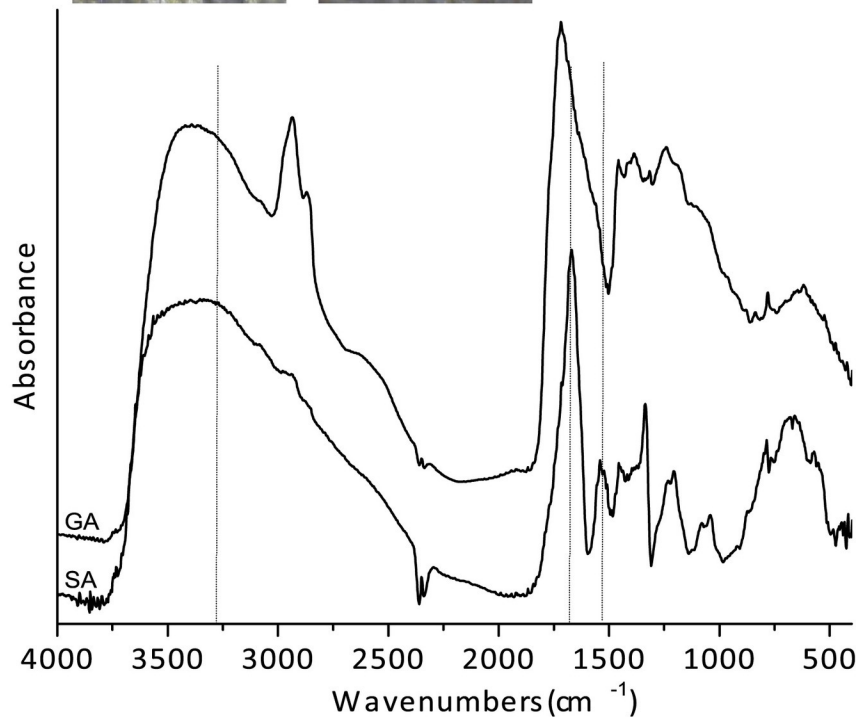
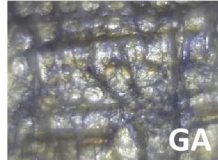


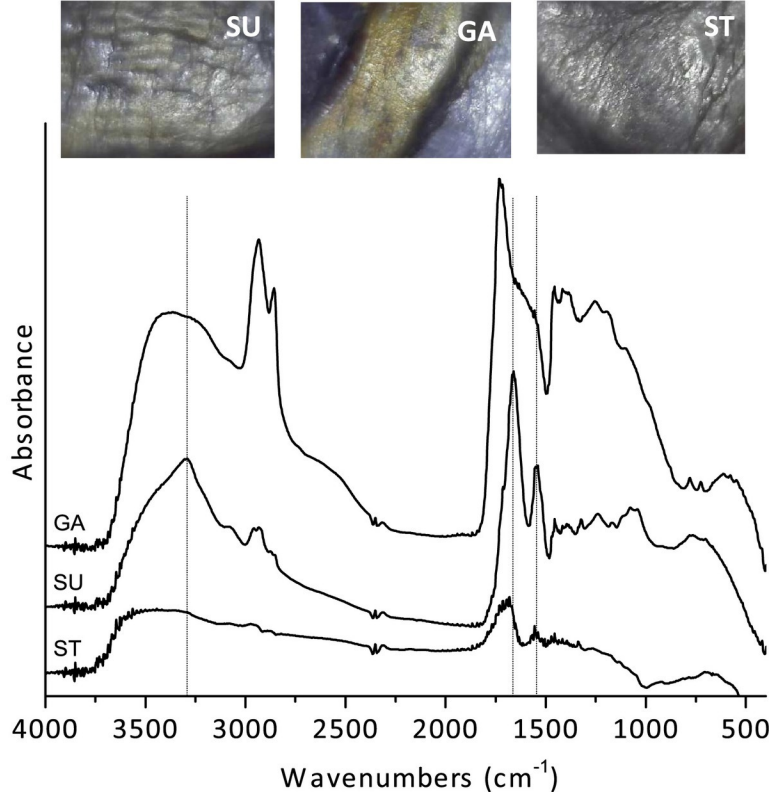


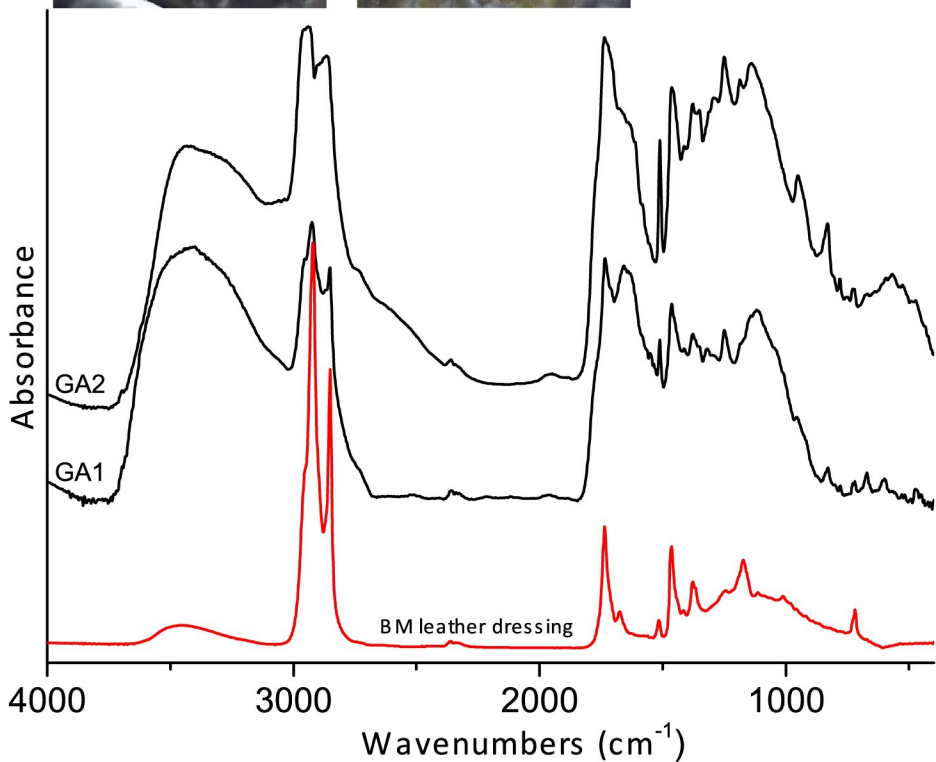












*Table 1: Gilt leather varnish recipes with calculated oil/resin ratios*

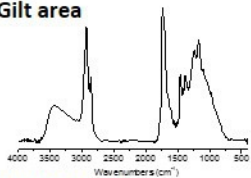
Ingredient	<b>Girolamo Ruscelli</b>	<b>Mechelse Secretbook</b>	<b>Fougeroux de Bondaroy</b>
	Italy - 1555	The Netherlands - 1677	France - 1762
Linseed oil	531 ml	536 ml	514 ml
Colophony/pine resin	166 g	37.5 g	173 g
Venice turpentine		15 g	173 g
Sandarac	166 g	166 g	96 g
Aloes	165.6 g	150 g	76 g
Amber		150 g	
Safran	6.9 g		
Asphalt		7.5 g	
Massicot		1.7 g	1.2 g
Minium			1.2 g
Lead sulphate		0.5 g	
<b>Ratio oil/resin</b>	<b>60/40</b>	<b>57/43</b>	<b>52/48</b>

Table 2: Identification of gilt and silvered areas in historic gilt leathers from reflectance FTIR

Reference	Attribution	CO peak (cm <sup>-1</sup> )	Gilt area	Silvered area
EC511	Netherlands	1722	oil-resin + protein ?	protein
EC654	Netherlands	1736	oil-resin + protein	-
EC733	Netherlands	1718	oil-resin + protein	-
EC792	Netherlands	1740	oil-resin	-
EC828	Netherlands	1740	oil-resin	-
EC1127	Netherlands	1731	oil-resin + protein ?	-
EC1383	Netherlands	1722	oil-resin	-
CBD10	Netherlands, 17 <sup>th</sup>	1740	oil-resin	-
CBD629a.b	Netherlands, 17 <sup>th</sup>	1736	oil-resin	-
CBD629c	Italy, 16 <sup>th</sup>	1727	oil-resin	-
CBD630	Netherlands, 17 <sup>th</sup>	1718	oil-resin	-
CBD631	Netherlands, 17 <sup>th</sup>	1746	oil-resin	-
CBD632	Netherlands ? 18 <sup>th</sup>	1737	oil-resin	-
CBD634	Netherlands, 17 <sup>th</sup>	1738	oil-resin	-
CBD635	Netherlands, 17 <sup>th</sup>	1726	oil-resin	-
CBD649	France, 18 <sup>th</sup>	1745	oil-resin	-
Isle	Netherlands, 17 <sup>th</sup>	1742	oil-resin	-
Golleville	Netherlands, 17 <sup>th</sup>	1731	oil-resin + protein + wax	-
Gelboe	Netherlands, 17 <sup>th</sup>	1730	oil-resin	protein + oil-resin
Crucifixion	Italy or Netherlands, 17 <sup>th</sup>	1743	oil-resin + protein	-
CBD1	Italy, 18 <sup>th</sup>	1718	oil-resin	protein



**Gilt area**



**Silvered area**

