Application of coatings on silver studied with punctual and imaging techniques: from specimens to real cases

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Abstract. The protection of silver artifacts with a coating of organic material isolating the surface from oxygen and S-bearing gases is still one of the most used techniques for the preservation of silver surfaces. A variety of materials suitable to this purpose are being used in the conservation practice. Among them there are acrylic polymers, nitrocellulose lacquer, microcrystalline wax and combination of them in superimposing layers. They are applied either by brush or, in some cases, by spraying. The first stage in a conservation project is often the cleaning of residuals of old protectives, aimed at making the silver surface free from remnants of yellowish materials and enabling the application of new coatings. Unfortunately, removing aged coatings and applying new ones are “blind” processes, since the techniques available for not invasively monitoring the surface of silver artifacts are punctual and do not allow an overall overview of the surface. This is the case of reflectance FTIR and thickness measurement with the Eddy Current technique, which, apart from being punctual, are tricky to apply to uneven surfaces. In this paper, we aim to show the benefits of using an imaging technique, UV induced VIS luminescence, for monitoring the presence and the distribution of protective coatings on silver surfaces and of combining it with reflectance FTIR and thickness gauge. At first, our study was focused on specimens treated with nitrocellulose, acrylic emulsion and microcrystalline wax. The application of the treatments was studied with UV-induced VIS luminescence as well as with the abovementioned punctual techniques to cross-validate the outcome of each method and to assess their suitability for application on organic protective layers on silver artifacts. In a further stage, UV induced VIS luminescence was applied to a real case, a silver chalice that was treated with nitrocellulose lacquer after cleaning.

1. Introduction

In the field of the conservation of historical silver artworks, the very first step to properly plan a preservation project is the identification of varnishes and their remains from previous restoration treatments. Indeed, it is not easy to detect the presence of such varnishes and to characterize their spatial distribution, not even by means of optical microscopy, except for those made up of materials that have turned yellow over time. Applying the coating after the cleaning treatment is another stage of the silver conservation process in which checking the homogeneity in the spatial distribution of organic layers plays a key role. This is particularly true in the cases of more complex shaped artwork or when reliefs, folds and curves are present, as there is no possibility for the conservator to visually control the process and to prevent the development of thickness inhomogeneity or even gap in the varnish layers. Therefore, there is a clear need to have an available method for monitoring the varnish layer even when applying the coating after the cleaning treatment

To this aim, further analyses, in addition to the visual examination of the surface, are recommended either by microinvasive methods (namely by sampling a minimal amount of varnish) or through noninvasive ones, using anyhow FTIR spectroscopy for the molecular characterization of old
materials [1]. Although these materials in most cases will be removed during the cleaning treatment, it is important to keep the sample amount for analysis as much as limited as possible in order not to remove old patinas or not to damage the metal surface. For this reason, there is an increased preference towards a non-invasive approach by means of reflectance FTIR spectroscopy. This method proves particularly effective for the molecular characterization of thin layers of organic materials on surfaces that do not adsorb the mid IR wavelengths, such as metals [2, 3]. Thanks to its noninvasiveness, reflectance FTIR allows analysis in different areas of the artwork to gain information on the presence and the relative amount of a coating. Nevertheless, it has to be taken into account that the methodology is based on a punctual probe and, owing to constraints in the acquisition setup of the currently available tools, is not suitable to effectively map materials over a surface with a complex shape and with either embossed or chiseled details.

Homogeneities in the coating can be monitored by means of thickness measurements with the Eddy Currents technique [4, 5]. This method allows the measuring of the thickness of non-conductive films, such as organic films, on conductive substrates, such as silver: even in this case, however, the measurement provides point-wise data rather than an image. Further limitations of the Eddy Currents technique are that, although sampling is not required, a contact between the probe and the surface under measurement is necessary and, in some cases, unacceptable indentations or impressions are left on the surface, if the film itself is not interrupted. Besides that, the Eddy Current technique is sensitive to surface roughness, curvature, and distance from an edge. Most recently implemented imaging techniques such as terahertz [6] and ultrasound [7,8] have provided promising results regarding the investigation of coatings on metal, although the difficulty in their employment, transportability, and data interpretation may result in a limitation for a widespread use in conservation practice. Indeed, in a conservation project it is often necessary to carry out quick checks, even to the detriment of the completeness of information that could be gathered by means of more complex methods. For this reason, in recent years, several attempts have been made to employ imaging techniques for the analysis of metal artworks, in order to investigate both alteration products and transparent varnishes [9].

This work is focused on the optimization of the acquisition setup for the photographic technique in order to obtain high-quality reflectance and photo-induced luminescence imaging of silver artifacts in the UVA-VIS regions. We propose an approach for the investigation of varnishes on silver artworks that combines UV-induced VIS luminescence imaging with the Eddy Current thickness measurement and reflectance FTIR spectroscopy to relate differences in luminescence intensity to both thickness and IR band intensity and shape.

2. Materials and methods

2.1 Samples preparation.

Some 7 cm x 2.5 cm x 0.1 cm sterling silver alloy plate specimens (95% Cu-5% Ag) have been prepared with smooth and with chiseled surfaces. On the smooth specimens, an incision with the sharp point of a compass was made with the aim of creating a discontinuity on the surface similar to the ones found on objects with various decorations. The specimens were polished with sandpaper and finished with abrasive pastes with different grain sizes. In the end, surfaces were degreased with acetone. As a coating, three varnishes commonly used in the conservative practice were chosen:

- Zapon (a nitrocellulose lacquer supplied by Lechler) 70% in a mixture of 20% isopropyl alcohol - 40% isothane - 40% acetone;
- Incral44 (an ethyl methacrylate and methyl acrylate based blend, supplied by CTS Europe) 70% in butyl acetate;
- R21 (microcrystalline wax supplied by CTS) 2% in cyclohexane.

The coatings were applied by brush. A strip on the short side of the sample was left uncoated as a reference area. The wax applied hot and later polished with a cloth. Table 1 sums-up the treatments applied on the specimens (smooth and chiseled).
2.2 **UV-induced VIS luminescence imaging.**

UV-induced VIS luminescence was collected employing xenon-based sources. The UV component was selected using optical glass band-pass excitation filters with 65.8% transmittance at 360 nm and very low transmittance in the violet (0.22% at 390 nm). A red component reflected by metal surfaces, clearly visible in the images shown below, was due to the very low transmittance in the VIS region between 690 and 750 nm (with a 2.2% peak at 710 nm) of the excitation filters employed. It was not deemed necessary to subtract the red component, neither in the acquisition nor in post-processing phases, because it was not considered a disturbing element for the data interpretation. The UV component in outgoing was blocked with a long-pass filter with almost no transmittance (10-5%) at 400 nm and 50% at 418 nm. The low luminescence signal was amplified during both the data collection and post-processing ensuring an optimal signal-to-noise ratio thanks to the employment of a high performance CMOS sensor. More specifically, we used a commercial camera for astronomical photography equipped with a CMOS Full Frame sensor (35.9x24.0 mm, pixel pitch of 4.9 μm, 14 bit dynamics).

2.3 **Thickness measurements.**

A Karl Deutsch Thickness Gauge, based on the Eddy Currents method, was used to non-destructively evaluate the coating thickness; the measurement area is 1mm diameter and the zero calibration procedure was adopted on uncoated silver surface. Measurements were checked on the same surface used for calibration with thickness standards. On each area, a number of 20 evenly distributed measurements were repeated.

2.4 **Reflectance FTIR spectroscopy.**

The composition and amount of the coating material were characterized with a portable FTIR spectrometer (Alpha Bruker) operating in total reflection mode. The instrument is equipped with a camera shooting the region around the measuring spot, which is 3 mm diameter Spectra were acquired with resolution of 4 cm\(^{-1}\) in the 7500-375 cm\(^{-1}\) range, collecting 100 scans.

| Sample | Surface finishing          | Surface coating                     |
|--------|----------------------------|-------------------------------------|
| 13     | Smooth with engraving      | 1 layer of Zapon+ 1 layer of R21    |
| 15     | Smooth with engraving      | 1 layer of Incral44+ 1 layer of R21 |
| 18     | Chiseled                   | 1 layer of Zapon                    |
| 22     | Chiseled                   | Half sample with one layer of Zapon, half sample with two layers of Zapon |

Table 1

3. **Results and discussion**

Figure 1 shows the visible photo and the UV-induced VIS luminescence image of four flat samples. Samples 13 and 15 are smooth and were respectively coated with a layer of Zapon (13) and Incral (15) with a further layer of wax on top. Although the photo in visible light shows some inhomogeneity in the coating, with accumulations distributed at the end of the samples (short sides), the UV-induced VIS luminescence image clearly highlights the brush strokes and the filling of small holes of the surface.

Thickness measurements show that the average thickness of the two types of coating is very similar (around 8 μm for the specimen with Incral+ wax and around 9 μm for the specimen with Zapon+ wax). In the sample 13, three zones are differentiated according to the thickness: one near the engraving (average thickness 5.9 μm with 13% standard deviation), one central (average thickness 7.8 μm with 17% standard deviation) and one close to the untreated strip (average thickness 14 μm with 14% standard deviation).
Reflectance FTIR spectra show different features in correspondence of different thickness and different luminescence response. Near the untreated strip, where the thickness is higher, the spectrum of Zapon (not shown here) exhibits both derivative-like bands and not distorted bands, while near the incision, where both luminescence response and thickness are lower, the spectrum features no distortions at all, being the coating so thin that the Fresnel component of the reflected beam is negligible. Sample 15 shows an overall less intense luminescence response. Thickness measurements give an area near the untreated strip with a smaller thickness (3.6 μm with 30% standard deviation), an area in the center with a greater thickness (15 μm with 17% standard deviation) and an area near the engraving with thickness of 6 μm (23% standard deviation), all in agreement with luminescence distribution shown in the image. The probe sensing small width (about 2 mm in diameter) accounts for the observed pretty high values of standard deviation, being the film thickness very variable on a extremely short scale, as observed when luminescence images are magnified. Samples 18 and 22 are instead chiseled and have been coated with Zapon alone. In Figure 2, we show the reflectance FTIR spectra of three areas of sample 18. Area 1 is close to the untreated strip, where more luminescence is detected, Area 2 refers to the central portion of the coupon with a luminescence of medium intensity,
while Area 3 is near the edge, where little luminescence is shown. The area of the bands that do not show distortions (like the signal due to C-H stretching in the 2830-3030 cm\(^{-1}\) region) increases from Area 3 to Area 1. Other bands (like the one at 1286 cm\(^{-1}\) associated to nitrate group [10]) show changes from a derivative-like shape to mixed character for Area 2 and 3, when luminescence decreases. One half of specimen 22 was coated with a second layer of the same nitrocellulose varnish.

Figure 2: Reflectance FTIR spectra of three areas of sample 18 (Area 1 corresponds to high luminescence, Area 2 to luminescence of medium intensity and Area 3 to scarce luminescence).

Figure 3: Reflectance FTIR spectra of sample 22, spectrum A: area coated with one layer of Zapon, spectrum B: area coated with two layers of Zapon. Transmittance spectrum of Zapon is shown as reference.

The luminescence image clearly shows the difference in response of the two parts. Thickness measurements provide a value of 11.6 µm on the single layer side and of about 23 µm on the double
layer side. In both cases, the poor planarity of the surface has an influence on the accuracy of the measurement and accounts for the high standard deviation, around 30%. Changes of bands shape and intensity are observed in reflectance FTIR spectra, as reported in Figure 3, where spectra of the two half of sample 22 are shown, together with reference transmittance spectrum of Zapon. The overall intensity of bands of spectrum B (two coatings of Zapon) is higher than those of spectrum A and, in particular, the peak area for the 2830-3030 cm\(^{-1}\) bands (not distorted in both spectra) is 67.5 in spectrum B, nearly twice than for the same bands of spectrum A (peak area 34). Less intense peaks (1380, 1071 and 840 cm\(^{-1}\)) are not distorted in A, while exhibit a derivative-shape for B. Intense, distorted bands for both spectra, on the other hand, are distorted also for the one layer half but show a change from a derivative-like to a mixed aspect when the thickness increases, owing to the increasing contribution of the Restrahlen character [11]. Thus, the behavior of IR reflectance signals is in agreement with the changes of the luminescence response and with the measured thickness.

The effectiveness of the UV-induced VIS luminescence technique in characterizing the spatial distribution of the protective was tested, as a significant case study, on a tarnished silver chalice with engravings, chiseled and embossed parts, dated back to the first half of the 18th century (a detail is shown in Figure 4). The Tuscan manufactured chalice comes from the Museo di Arte Sacra di Incisa val d’Arno (Italy), has a height of 22.5 cm and a base diameter of 11.5 cm. The chalice was coated a few years ago with Zapon by students during a conservation class. In the case of a real case study, the distribution of the coating, partly observed even with visible light, is less evident to the naked eye than in the case of the samples shown above, partially due to differences in the color of the metal between zone and zone (such as the yellowish tone of the upper edge). The UV-induced VIS luminescence (Figure 4), instead, documents a quite uneven application with crossed brushstrokes in the upper part. The lower part, exhibiting an elaborate decoration, shows areas with a more intense UV-induced VIS luminescence and areas where the response is nearly absent. Thickness values were measured on the cup of the chalice (Figure 5). The thickness data shown in the figure are consistent with the intensity of fluorescence: thickness on the central and left areas above the embossed decoration is higher than on the right. The upper, less luminescent, portion of the cup, visible in figure 4, shows a thinner layer of varnish of about 13 μm. The average standard deviation of thickness on the whole upper part is quite high (30%), confirming the dispersion of thickness values. In the lower part of the chalice, owing to the complex shape of the worked details, only the UV-induced VIS luminescence was able to provide information on the presence and homogeneity of the organic film.

![Figure 4. Tarnished silver chalice, with engravings, chiseled and embossed decorations, first half of the 18th century, detail. The chalice in reflected VIS light (left) and UV-induced VIS luminescence (right).](image-url)
Figure 5. Detail of the cup of the chalice with average thickness (in μm) measured on areas with different luminescence intensity. Standard deviation in % is also shown.

4. Conclusions
This work has explored the possibility of using UV-induced VIS luminescence imaging for monitoring the application of protective organic coatings on silver artworks. The method was tested on Sterling silver samples with different features that mimic some of the working techniques usually encountered on historical silver objects, like engravings and chiseled surfaces. The coating materials include the most widespread used protectives for historical silver, i.e. acrylic resin, nitrocellulose lacquer, wax and combination of them.

The particular set-up used in this work enabled us to get an enhanced UV-induced VIS luminescence response and to reveal different evenness of the protective coatings. Measurements of coating thickness made with the Eddy Current methods show a good agreement with the intensity of luminescence of the different areas. Intensity differences in each sample match also the trend of reflectance FTIR spectra, since those collected in areas with greater luminescence intensity exhibit distorted signals and higher peaks respect to those from less bright areas.

After validation trials on samples, the method was tested on a silver chalice treated with nitrocellulose lacquer. Notwithstanding the difficulties of imaging an object with such a complex shape, UV-induced VIS luminescence provided evidences of not uniform coverage of the surface, in particular on areas with embossed details, like in the chalice foot. Again, thickness variability is in agreement with luminescence differences. Therefore, the imaging of UV-induced VIS luminescence is recommended as a hands-on and powerful method to check the application of the most common protective coatings on historical silver objects. Another point is that the combination of three techniques offered the possibility of an interesting cross-validation on very thin layers of organic materials on metal. Despite their substantial different physical principles and their different acquisition approaches (imaging, punctual, with contact and contactless), the achievements are basically consistent and let us use each of them in a more confident way as tools to support conservation projects on silver artworks. Further work is planned to test the sensitivity of UV-induced VIS luminescence, together with that of reflectance FTIR and Eddy Current gauge, to very small amount of protective materials and to check the suitability of this approach to follow the phase of the removal of old protective films on silver and to detect even tiny residuals of films upon cleaning.

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