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A Preliminary Spectroscopic Approach to Evaluate the Effectiveness of Water- and Silicone-Based Cleaning Methods on Historical Varnished Brass

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Abstract: Soiling deposition and wrong conservation practices are among the causes of the decay process that can affect the morphological, mechanical, and compositional features of the varnish, the most exposed layer of an artefact. In this perspective, the identification of the best cleaning practices is a priority. During the 18th century, scientific instruments of the highest quality were built, and peculiar varnishes were produced to confer protection and elegance to their metal elements. For this study, based on a historical recipe, we have reproduced a peculiar spirit varnish, enriched with natural resins and colorants, and we have applied on it a synthetic soiling mixture to simulate the aging conditions. We have then performed a non-invasive multi-analytical study to monitor the effectiveness of two water-based and a silicone-based, cleaning methods, namely, water in agarose, Tween 20 (3%) in agarose, and Velvesil™ Plus. The study includes colorimetry, Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF) mapping, coupled with chemometrics. Principal component analysis applied to FTIR spectral data has been demonstrated to be a powerful tool to enhance weak variations in the IR spectra, empowering the interpretation of cleaning effect versus the application time of each cleaning test.

Keywords: FTIR spectroscopy; XRF mapping; colorimetry; PCA; varnished brass

1. Introduction

Historically, brass has always been employed for the metal components of scientific instruments due to its malleability and ductility, and to its golden aspect aimed to confer their elegance. Such a surface, in many artefacts, was protected and enriched by varnishes. The role of these varnish layers is crucial, representing part of the technological value of these objects. In fact, varnishes preserve the

metal from the triggering of the corrosion in the alloy caused by environmental moisture, pollutants, and other decaying factors [1]. During the 18th century, the manufacturing of scientific instruments reached its apogee bearing to the use of peculiar materials and procedures that today make these objects a unique portion of the cultural heritage.

Varnish recipes are described in historical treatises and dictionaries [2]. Within the literature, the Swedish chemist Jons Jacob Berzelius (1779–1848) [3] was the first to recommend the protection of scientific instruments by an organic coating. Some recipes from his volume refer to a varnish made of natural resins and colorants, able to preserve and confer a shiny golden aspect to the surface. This varnish is described to have outstanding properties, very close to those of the precious Chinese lacquer made of the sap of the Rhus Verniciflua tree (*Toxicodendron vernicifluum*), brought to fame in Europe during the 18th century thanks to the Jesuit pilgrims' writings [4].

Nowadays, historical scientific instruments are preserved as cultural heritage objects, but in the past centuries they were used in the laboratories and their surfaces were exposed to soiling, aggressive cleaning, and hands sweat deposition. The preservation of this class of objects and their consideration as cultural heritage artifacts is recent and protocols are still not available neither for the restoration nor for the cleaning procedures.

To fill this gap of knowledge and to lead toward an aware preservation practice of these objects, it is necessary to perform experimental studies focused on the specific constituent materials of historical scientific instruments. While several publications deal with cleaning methods for polychrome surfaces [5–7], only a few of them regard the interaction between natural resins and cleaning methods [8].

As concerns the cleaning procedures, a first approach in the cultural heritage field started with a systematic development of aqueous methods carried out by Richard Wolbers in the 1980s of the 20th century [9,10]. As known, water can solubilize ionic compounds and some hydrophilic films, but its solvent power can be extended also to non-polar fractions. The water solvent power, in fact, can be modulated by adding, for instance, acids and bases, surfactants, or enzymes. Moreover, the addition of agarose increases the solution viscosity, producing the so-called rigid gels, which ensure a safe and controlled action on delimited areas [11]. The incessant improvement of this highly flexible method allows it to be the most powerful, safe, and adjustable tool [12,13]. It is widely employed, notwithstanding the huge variety of available methods and cleaning products [14–18].

Over recent decades, with the development of the ready-to-use industrial products, numerous cleaning procedures have been getting popular among the restorers. Above all, the silicone-based solvent ones [19]. They are known to be non-toxic, in a gel shape, and mainly suitable for water-sensitive surfaces and acrylic paint [20–22].

In this study, a non-invasive methodology, which includes colorimetry, and Fourier transform infrared (FTIR) and X-ray fluorescence (XRF) spectroscopies, was accomplished to investigate the effect of three cleaning methods widely used in the restoration practice. In the field of cultural heritage, colorimetric measurements are customarily used to evaluate the cleaning effectiveness [23,24] by checking the modification in chromatic feature of the surfaces; XRF spectroscopy proved to be powerful in disclosing the distribution of elements in low concentration [25]; and FTIR spectroscopy is often employed in all its different configurations mainly to monitor the molecular changes in the varnish caused by aging or interaction with the cleaning agents [26–30]. In this framework, the present paper aims to show and discuss the new insights obtained from the development of a previous preparatory study [31]. To this aim, deionized water in agarose gel, Tween 20 in 3% deionized water solution supported in agarose gel, and the Velvesil™ Plus were selected as cleaning methods to be tested, for their different polarity and surfactant action. They were applied to soiled brass mock-ups coated by traditional protective materials.

Univariate and multivariate data analysis approaches were investigated to study the cleaning dynamics. With the goal of interpreting FTIR and colorimetric results with a multivariate perspective, principal component analysis (PCA) was considered to explore the cleaning dynamics and confirm—

as well as clarify—the findings based on the univariate approach. Different studies witness the use of this unsupervised procedure to explore multivariate data in the cultural heritage field [32–36].

In Section 2, we will describe the materials and the procedures used to build up the mock-ups and the employed analytical approach. In the following Section 3, we will present and discuss the results achieved through the analytical approach. Finally, in the concluding section, we will summarize the main results about the cleaning test effectiveness and the applied methodology.

2. Materials and Methods

2.1. Mock-Up and Varnish Preparation

The mock-ups were obtained by applying a spirit-based varnish layer on a lamina of brass OT 63 UNI 4892 Cu63%-Zn37% ($10 \times 5 \times 0.1$ cm). The varnish was formulated according to a historical recipe [3]: shellac (Bresciani. Milan, Italy, Art.55881 28.35 g), sandarac (Bresciani., Milan, Italy, Art.56143, 56.70 g), mastic (Bresciani., Milan, Italy, Art.56111, 28.35 g), elemi gum (Bresciani., Milan, Italy, Art.55812, 56.70 g), dragon's blood (Bresciani., Milan, Italy, Art.57491, 28.35g), gummi-gutta (Bresciani., Milan, Italy, Art.55851, 21.26 g), curcuma (21.26 g), saffron (12 grains), crushed glass (85.10 g), and ethanol 85% (Girelli Alcool, Milan, Italy, 57.00 g). The varnish was applied to the specimens using a soft brush. A specimen named Tq—made up of metal and varnish—was kept as a benchmark. Three other specimens underwent a procedure to simulate the usage condition and the soiling deposition.

2.2. Artificial Soiling and Sweat Deposition

A soiling mixture made of two phases, dry and wet, was prepared according to existing protocols and experimentations [37]. The dry portion of the soiling mixture was composed of (i) sphagnum peat moss (20.82% *w/w*), (ii) carbon black (Bresciani. Milan, Italy, Art.60609, 1.92% *w/w*), (iii) iron oxide (Bresciani. Milan, Italy, burnt sienna pigment, Art.60603, 0.55% *w/w*), (iv) gelatin (10.41% *w/w*), (v) soluble starch (Bresciani. Milan, Italy, Art.51761, 10.41% *w/w*), (vi) Portland type I cement (18.63% *w/w*), (vii) silica gel (Bresciani. Milan, Italy, Art.57592, 1.92% *w/w*), (viii) lime (Bresciani. Milan, Italy, Art.52791, 16.71% *w/w*), and (ix) kaolin (Bresciani. Milan, Italy, Art.52861, 18.63%*w/w*). The wet portion of the mixture consisted of (i) high-grade mineral paraffinic oil (0.8 mL) and (ii) chloroform (99% pure CHCl_3 , Sigma-Aldrich St. Louis, Missouri, USA, 19.1 mL). Accordingly, 1.1g of the dry mixture was mixed with 20 mL solution of oil in chloroform (4.5% *v/v*); thus, forming a 3% *w/v* heterogeneous 2-phase suspension [8]. The mixture was applied by a soft brush on the specimen surfaces, covering at least half of the surface. A second coat was applied after ca. 30 min.

Synthetic sweat was sprayed on samples to simulate the contact with the instrument user. The synthetic sweat was chosen according to DIN ISO 9022-12 to imitate human hand sweat with a pH of 2.3 (Synthetic Urine e.K., Eberdingen, Germany).

Each specimen displayed different treatments on their surface, as shown in Figure 1a–c: the soiled area (S), the sweaty one (Sw), the area where both soiling and sweat were present (SSw), and the area where the only varnish was applied (V).

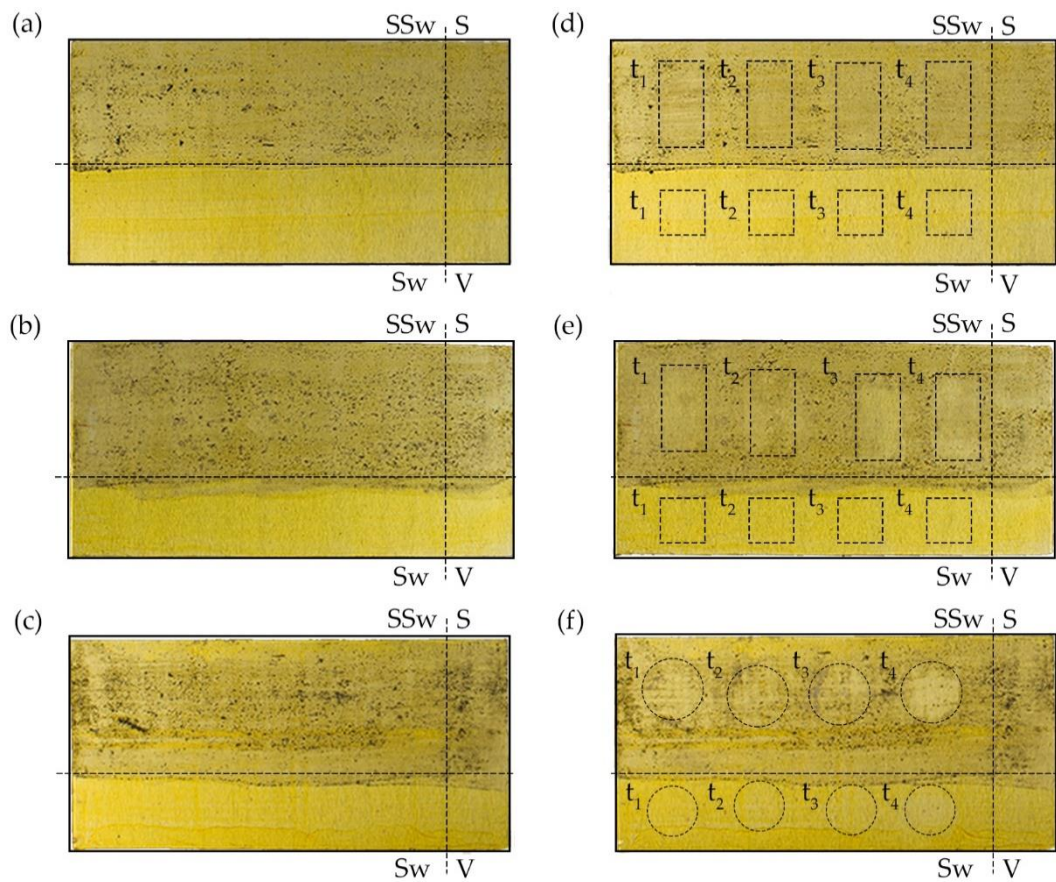


Figure 1. Photographic documentation of clean-ups, before (left) and after (right) the cleaning tests, respectively: water in agarose (a,d), Tween 20 (b,e), and Velvesil™ Plus (c,f). Treated areas and test distribution for each application time are schematically highlighted.

2.3. Cleaning Tests

Three cleaning tests were carried out on the SSw and Sw areas. They were selected among the most used agarose-based rigid gels and silicone-based methods: (i) deionized water in agarose gel (agarose: 0.75 g, H₂O 48 mL [38]), (ii) Tween 20 (Honeywell Fluka™ Fisher Scientific Italia, Rodano Milan, Italy) 3% deionized water solution supported in agarose gel (agarose: 0.75 g, Tween 20 1.5 mL, H₂O 48 mL [38]), and (iii) Velvesil™ Plus added with its solvent Cyclomethicone D5. Velvesil™ Plus (Momentive Performance Materials, Inc., Waterford, NY, USA) consists of a silicone copolymer gel and a silicone-based surfactant in a silicone-based solvent [19]. For each cleaning method four application times were considered according to the recommended cleaning practice. The following application times were selected: $t_1 = 30$, $t_2 = 60$, $t_3 = 90$, $t_4 = 180$ min for the water in agarose; $t_1 = 45$, $t_2 = 60$, $t_3 = 90$, $t_4 = 180$ min for the Tween 20 (3%); and $t_1 = 5$, $t_2 = 15$, $t_3 = 25$, $t_4 = 45$ min for the Velvesil™ Plus. The Velvesil™ Plus was applied for shorter times due to its faster action compared to the other considered procedures. When t_0 is reported in the text, it is referred to the surface condition before the tests, namely the sweaty (Sw), and sweaty and soiled (SSw).

The cleaning tests were applied along a line from the left to the right with an ascending order of application time, respectively for the SSw and the Sw areas. The shape of the test areas depended on the viscosity of the cleaning product: the agarose gels were applied in a rectangular shape 2×1 cm sized in the SSw area and in a square shape 1×1 cm sized in the Sw area, whereas the Velvesil™ Plus was spread in a round of 1.5 cm of diameter or less. In order to facilitate the reading of the results, the test areas are highlighted for each specimen in Figure 1d–f in which a change is recognizable in the delimited cleaned areas with respect to the surfaces represented on Figure 1a–c.

2.4. Non-Invasive Analytical Investigation and Data Analysis

A multi-analytical non-invasive approach was used to estimate the efficiency of each cleaning test in the removal of the artificial soiling.

Photographic documentation under visible light was acquired with a Nikon D4 full-frame digital camera equipped with a 50 mm f.1.4 Nikkor objective using a Softbox LED lamp. Colorimetric measurements were accomplished using a portable Konica Minolta CM-2600d spectrophotometer (Chiyoda, Tokyo, Japan). The average of the SCE values was considered (10 repetitions in the SSw and Sw area before and after the application of the treatments, and 3 repetitions after cleaning in the tested area for each time of application), and the dataset was processed in the CIE Lab space (CIELAB 1976). The chromatic difference (expressed as ΔE^*) between the SSw and the Sw surfaces, and the corresponding cleaned ones, were considered. Moreover, L^* difference (ΔL^*) values were used to evaluate the darkening and the bleaching of the surface due to the removal of black particles in the soiling mixture. Furthermore, the colorimetric parameters (L^* , a^* , and b^*) were auto scaled and the dataset 3×192 (variables \times objects) was explored by PCA. A differential value ($\Delta PC1$ and $\Delta PC2$ scores) was calculated subtracting the score values of the cleaned areas during the time from the respective soiled area or soiled and sweaty one. Those differential values were used to study the behavior of the chromatic features depending on the application time of each cleaning method.

The portable ELIO XRF spectrometer produced by XGLab (Milano, Italy) with Rh anode was employed to collect XRF maps on the specimen surface (40 kV, 15 μ A, 3 s per spectrum). The elemental distribution was pointed out by heat maps before and after the cleaning procedure. Ca, as part of the dry fraction of the soiling mixture, was considered a marker for the soiling presence/removal, and Si distribution was also taken into account to determine any residue of Velvesil™ Plus. No marker elements were detected in the sweaty area; in this case, in fact, the technique was slightly informative.

Transflection mode FTIR spectra were recorded with the Alpha portable spectrometer (Billerica, MA, USA) equipped with R-Alpha module. Spectra were collected between 7500 cm^{-1} and 400 cm^{-1} at the resolution of 4 cm^{-1} with an acquisition time of 1 min. The beam diameter measured 5 mm. Each spectrum resulted from the average of the three measurements in the same area, in order to assess the analytical reproducibility. The selected dataset employed for the processing consisted of 36 spectra collected in the central point of the areas previously described and corresponding to the different treatments: two points in V, one in SSw and one in Sw; four points in SSw; and four in Sw, respectively for each cleaning application time. Data were processed in OPUS 7.2 software (Billerica, MA, USA). In this study, diagnostic bands were identified for the inorganic fraction of the soiling mixture, mainly ascribable to the Portland cement (CaO 61–67%, SiO₂ 19–23%, Al₂O₃ 2.5–6%, Fe₂O₃ 0–6%, and SO₃ 1.5–4.5%) and the mineral kaolin. Variation in the absorbance intensity of the inorganic fraction bands was considered to evaluate the soiling removal. Moreover, diagnostic bands of the Velvesil™ Plus were identified and considered for the detection of the cleaning residues. FTIR spectra were reduced in the range $1800\text{--}490\text{ cm}^{-1}$ (36 objects \times 702 variables) and transformed by smoothing (Savitzky–Golay, 3 wavelengths gap size) and mean center to be explored by PCA. Each cleaning method was investigated by independent scores plot to enable a clear understanding of each trajectory or behavior. Starting from the diagnostic bands, the loadings allowed us to explain what affects the distribution of the data had along the considered PC, hence suggesting hypothesis about the factors responsible for the cleaning tests effectiveness. All the multivariate data analysis was performed in Matlab environment (v. 2016a, Mathworks, Inc., Natick, MA, USA) using the PLS toolbox (ver. 8.5, Eigenvector Research, Inc., Manson, WA, USA) software package.

The whole analytical campaign was carried out for each step of the mock-up preparation respectively, before and after the varnishing, the soiling, and the sweat application, and after the cleaning tests.

3. Results and Discussion

In this paper, the main results are discussed and organized by analytical techniques in three subsections: (Section 3.1) colorimetric investigation, (Section 3.2) XRF spectroscopy, and (Section 3.3) FTIR spectroscopy.

3.1. Colorimetric Investigation

As concerns the SSw area, the ΔE values smoothly decreased ($\Delta E^*_{t_1} = 4.17$) for the water in agarose cleaning test till approaching a value close to zero (t_3). The values of the total color variation ΔE^* are shown in Table 1. After 180 min, no differences with the soiled surface were detected. The poor effectiveness of the cleaning method inferred by the drop of L^* value at t_1 , confirmed a darkening of the surface, and also by the slight variation of a^* and b^* (Table 2).

Table 1. Total color variation (ΔE^*) between the area where both soiling and sweat were present (SSw)/the sweaty area (Sw) surfaces, and the corresponding cleaned surfaces at different application times (t_1, t_2, t_3 , and t_4).

		Water in Agarose	Tween 20	Velvessil™ Plus
SSw	t_1	4.17	3.05	4.70
	t_2	1.55	2.30	2.37
	t_3	0.61	3.26	4.56
	t_4	1.12	3.82	5.29
Sw	t_1	3.97	4.94	8.41
	t_2	3.83	5.47	10.30
	t_3	3.67	5.54	12.63
	t_4	4.81	6.55	16.95

Table 2. Color coordinates L^*, a^* , and b^* measured before (t_0), and after the cleaning tests (t_1, t_2, t_3 , and t_4).

		Water in Agarose			Tween 20 in Agarose			Velvessil™ Plus			
		L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*	
SSw	t_0	65.04 ± 1.18	2.22 ± 0.14	40.65 ± 1.30	61.54 ± 1.55	2.43 ± 0.19	41.70 ± 1.58	61.55 ± 2.37	3.14 ± 0.36	42.82 ± 3.04	
		62.48 ± 0.65	2.52 ± 0.12	37.37 ± 0.17	63.87 ± 0.25	2.62 ± 0.16	39.74 ± 0.79	64.20 ± 0.25	2.93 ± 0.07	38.94 ± 0.24	
	t_1	63.79 ± 0.36	2.60 ± 0.05	41.49 ± 0.18	63.52 ± 0.40	2.68 ± 0.06	40.56 ± 0.21	62.28 ± 0.13	3.05 ± 0.02	40.57 ± 1.26	
		64.85 ± 0.35	2.45 ± 0.023	40.11 ± 0.13	64.64 ± 0.06	1.92 ± 0.10	40.84 ± 0.52	64.02 ± 1.17	2.99 ± 0.25	38.99 ± 0.63	
	t_2	65.40 ± 0.43	2.64 ± 0.04	39.67 ± 0.46	64.35 ± 0.97	2.46 ± 0.17	39.11 ± 0.34	64.79 ± 1.02	2.44 ± 0.20	38.69 ± 0.05	
		64.81 ± 0.58	1.56 ± 0.18	50.78 ± 2.75	65.15 ± 0.34	1.56 ± 0.15	58.32 ± 0.98	64.21 ± 0.40	2.99 ± 0.50	58.15 ± 2.82	
	Sw	t_0	61.44 ± 0.06	1.44 ± 0.15	48.70 ± 0.93	62.25 ± 0.29	1.60 ± 0.16	54.33 ± 1.04	64.40 ± 0.20	2.05 ± 0.06	49.80 ± 0.95
		t_1	61.10 ± 0.42	1.64 ± 0.14	49.86 ± 0.47	61.80 ± 0.29	1.33 ± 0.02	54.01 ± 0.04	64.32 ± 1.26	2.12 ± 0.20	47.89 ± 3.25
t_2		61.86 ± 0.40	1.56 ± 0.10	48.61 ± 0.93	61.73 ± 0.22	1.23 ± 0.12	53.97 ± 0.56	63.78 ± 0.60	2.25 ± 0.02	45.55 ± 0.46	
t_3		61.40 ± 0.05	1.72 ± 0.03	47.40 ± 1.17	62.64 ± 0.39	1.16 ± 0.03	52.29 ± 0.40	63.17 ± 1.33	2.77 ± 0.03	41.24 ± 0.08	

* Each value is accompanied by its standard deviation.

This behavior could be due to the interaction between the water and the polar portion of the soiling mixture: the gel showed mild efficiency in drawing the particles that were widely spread instead of removed. The PCA results, expressed in differential PC scores vs. cleaning time (explaining

48.12% and 33.84% of the variance, respectively for the PC1 and the PC2) are displayed in Figure 2a. Similar behavior was observed for the Δ PCs referred to in the Sw area, except for 30 min of exposure, where an increase of the Δ PC was observed (Figure 2b).

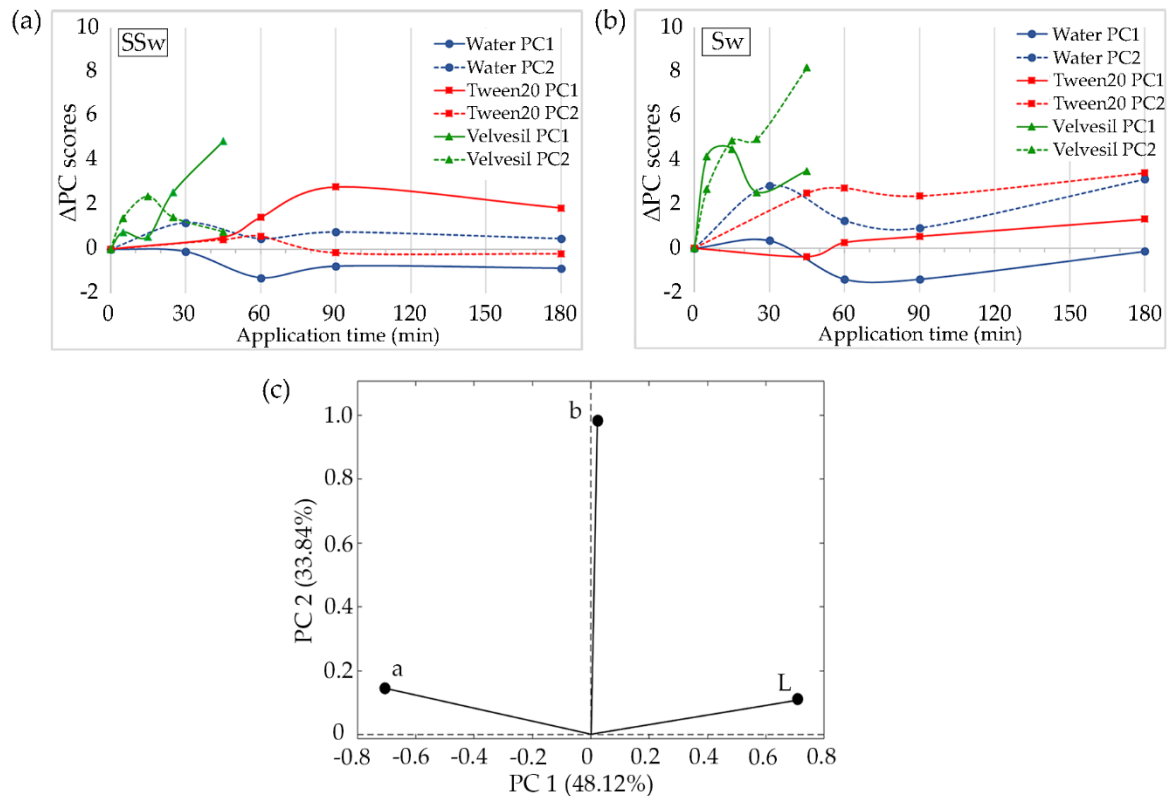


Figure 2. Principal component analysis (PCA) results on the colorimetric dataset expressed in differential PC scores vs. cleaning time for the three methods in the SSw (a) and Sw (b) area; in (c) the loadings are displayed.

An accurate reading of the loadings (Figure 2c) allowed us to explain these results: Δ PC1 behavior was mainly driven by the L^* variability, whereas the Δ PC2 was influenced by the a^* and b^* variability, with a higher influence by the latter. The hypothesis about the effect of the water in the agarose test was strengthened. In fact, Δ PC1 and Δ PC2 were characterized by a drop of around 60 min, related to L^* and b^* , confirming what was observed by ΔE^* trends. There were no cases demonstrating the water in agarose cleaning effect. Indeed, the blue and light blue lines (Δ PC1 and Δ PC2 of the water in agarose test) did not rise back and exceed the starting point of the soiled dark surface.

As regards the Tween 20 (3%) in agarose, it seemed to be more effective than the water in agarose in removing the dark matter: after cleaning, ΔE^* in SSw area varied from 2.30 (t_1) up to 3.82 (t_4) and L^* grew ($\Delta L^*_{\max} = 3.11$ after 90 min), signifying bleaching due to the removal of black particles, facilitated by the surfactant action of the solvent.

Observing the Δ PC scores trend in Figure 2a, three phases are recognizable: in the first phase, i.e., within 45 min, both Δ PC1 and Δ PC2 rose constantly; in the second phase, i.e., between 45 and 90 min, a drop of Δ PC2 was followed by a third phase described by a plateau. As a matter of fact, the second phase was the most effective one: L^* kept rising, showing a removal of the dark matter but a different action was observed for b^* suggesting a change in the yellow tone.

This was confirmed by the loading investigation (Figure 2c) in which Δ PC1 described L^* variability, whereas the Δ PC2 was influenced by a^* and b^* coordinates. In the Sw area, ΔE^* values varied from 4.94 (t_1) up to 6.55 (t_4) (Table 1): the variation was supported by the decreasing trend of L^* and b^* , ascribable to an unexpected darkening and to a yellow component variation of the surface feature after

the cleaning. ΔPC score supported this variability suggesting also, in this case, that the major action was carried out between 45 and 60 min of application time (Figure 2b).

Concerning the Velvesil™ Plus cleaning test for the SSw area, ΔE^* varied from 2.37 to 5.29 with an increasing trend since t_2 . As in the Tween 20 test, L^* resulted to be the parameter that most affected this variation (ΔL^*_{\max} up to 3.24 after 45 min) due to the dark layer removal and to the consequent surface bleaching. About a^* and b^* , the variation of the latter was not negligible (Table 2) suggesting a modification of the yellow component. Additionally, in this case, the ΔPC s scores endorsed these observations by displaying the presence of three different phenomena occurring in three different moments: in 5, in 15, and after 15 min. In the first 5 min, ΔPC s described a rising of L^* that seemed to represent the best conditions for the dark matter removal. After 5 min a rise of $\Delta PC1$, respectively linked to a drop of $\Delta PC2$, could raise some doubts about the advantage of using a long application time of Velvesil™ Plus from the chromatic feature point of view.

The results obtained for Sw are as unexpected as those obtained for the Tween 20: the value of ΔE^* varied from 8.41 up to 16.95. If combined with a substantial reduction in the b^* value ($\Delta b^*_{\max} = 16.91$ after 45 min) that seemed to drag this trend, it could point to a change in the yellow component. This behavior is well described by the ΔPC s scores (Figure 2b). The results of the Velvesil™ Plus test highlighted the strongest action. In fact, this highly non-polar and surfactant product seemed to interact also with the hydrophobic components of the sweat, probably inducing a transformation in the aesthetic properties of the surface.

3.2. XRF Spectroscopy

The spatial distribution of Ca, obtained through XRF mapping, was used as the marker for the presence of the soiling layer and for its spatial distribution. The analysis showed that the three cleaning methods displayed a different degree of effectiveness in removing the soiling layer (Figure 3a–c). In detail, the use of water in agarose (Figure 3a) appeared not to be effective in Ca removal after 180 min: the slight differences in Ca amounts among the application times confirm the mild action carried out on the soiling.

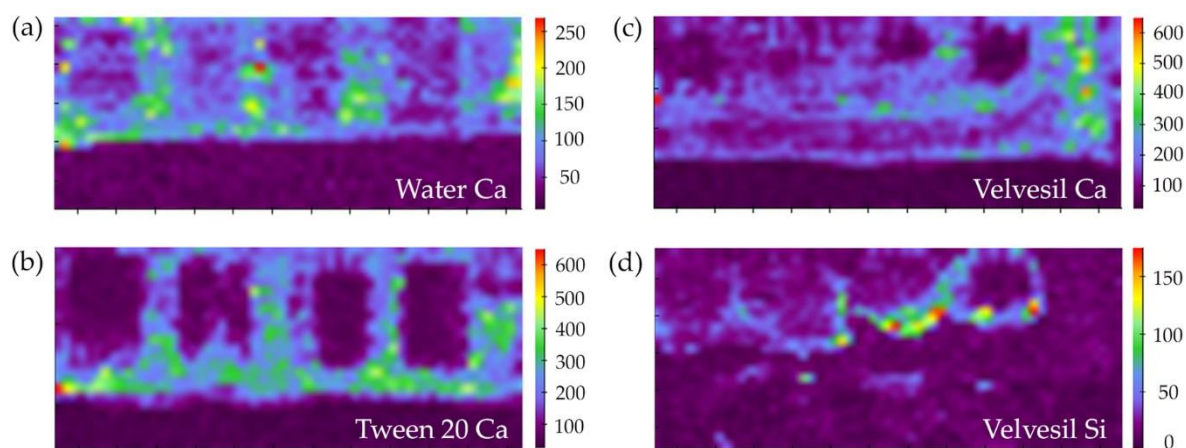


Figure 3. X-ray fluorescence (XRF) maps of the SSw area after the cleaning tests, respectively for water in agarose (a); Tween 20 (b); Velvesil™ Plus where Ca distribution highlights the cleaned area (from t_1 to t_4 , from the left to the right) (c); and Si distribution revealed Velvesil™ Plus residues (d). The heat map colors represent the minimum (blue-violet) and the maximum (red) values.

Instead, when observing the XRF maps of the mock-ups cleaned by Tween 20 (3%) (Figure 3b) and Velvesil™ Plus (Figure 3c), we note that Ca is never detected in the areas of the cleaning tests. In particular, for what concerns the Velvesil™ Plus (Figure 3c), the edges of the cleaning test areas are less defined than those of the Tween 20 tests. The removal of soiling is observed at t_1 and no trend during the time was noticed.

As regards exclusively the Velvesil™ Plus method, a not negligible quantity of Si was detected on the cleaned surface: its distribution allowed us to monitor the cleaning residue, as shown in Figure 3d. These results confirm what was previously supposed based on colorimetric observations: water in agarose seemed to interact with the soiling, but with a low removal power, whereas Tween 20 and Velvesil™ Plus were able to remove almost completely the soiling through their surfactant action. Moreover, by the XRF mapping, it was possible to highlight that the changes which occurred, were observed only in the area of the application of the cleaning test. It demonstrated that the interaction was limited to the areas where there was an effective contact between the cleaning products and the surface, and where the phenomena of absorption or binding were not detected. Nonetheless, it is worth noting that the selection of the cleaned area was more accurate in the case of the rigid gels (agar as support) with results more suitable for tiny and well-defined areas due to its stiffness. Contrarily, the silicone-based product seems to be unlikely to be accurately spread into the edges.

3.3. FTIR Spectroscopy

The high complexity of both soiling mixture and historical varnish, in terms of number and variety of constituents, makes the interpretation of the spectra complex. Nonetheless, thanks to the direct observations of the spectral signals and the PCA, relevant results were achieved, and some decisive information was gained, mainly about the Velvesil™ Plus test.

The two bands of the Portland cement and kaolin inorganic fractions, with the absorbance maxima falling respectively at 533 cm^{-1} and 468 cm^{-1} (Figure 4), were identified as diagnostics of the cleaning effectiveness.

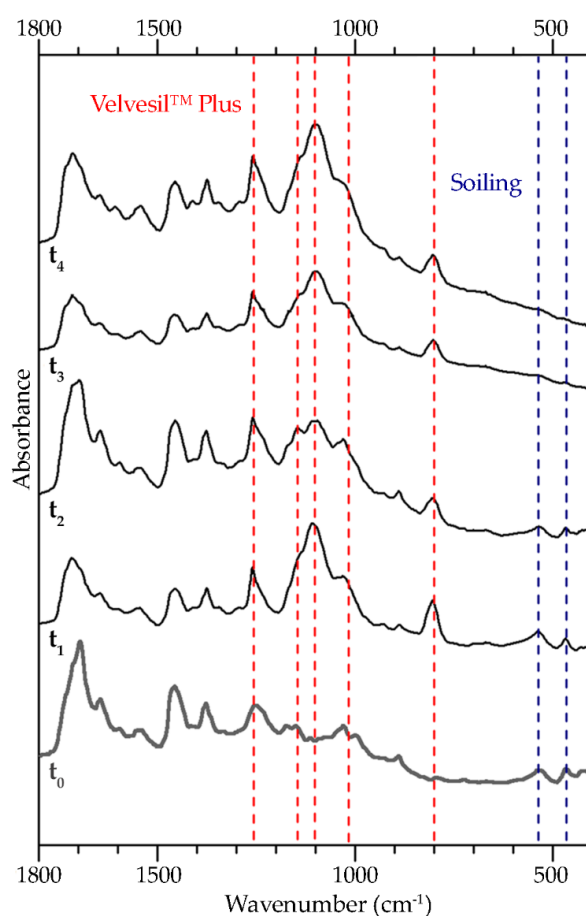


Figure 4. Fourier transform infrared (FTIR) spectra of the Velvesil™ Plus test from t_0 (bottom grey line) to t_4 (top)—Velvesil™ Plus (red) and soiling mixture (blue) diagnostics bands are highlighted.

The intensity reduction of these spectral features were able to provide quality information about the capability of the employed products to remove the soiling from the varnished surfaces. This reduction was clearly observed in the spectra collected in the Velvesil™ Plus test areas. They evidently showed a significant drop in the intensity, until disappearing, from t_0 to t_4 , proving the positive cleaning effect of this cleaning procedure (Figure 4). However, FTIR spectroscopy analysis showed that the use of Velvesil™ Plus has some disadvantages to be taken into consideration in the art conservation field: after cleaning, residues of the product were detected on the surface, proved by the persistence of the silicone bands in the $1500\text{--}1000\text{ cm}^{-1}$ range and 800 cm^{-1} . These hypotheses were corroborated by the results of the PCA shown in Figure 5a. The analysis explains a total of 88.73% variance by the first two components: 73.23% and 17.50% of the total variance, respectively for the PC1 and the PC2.

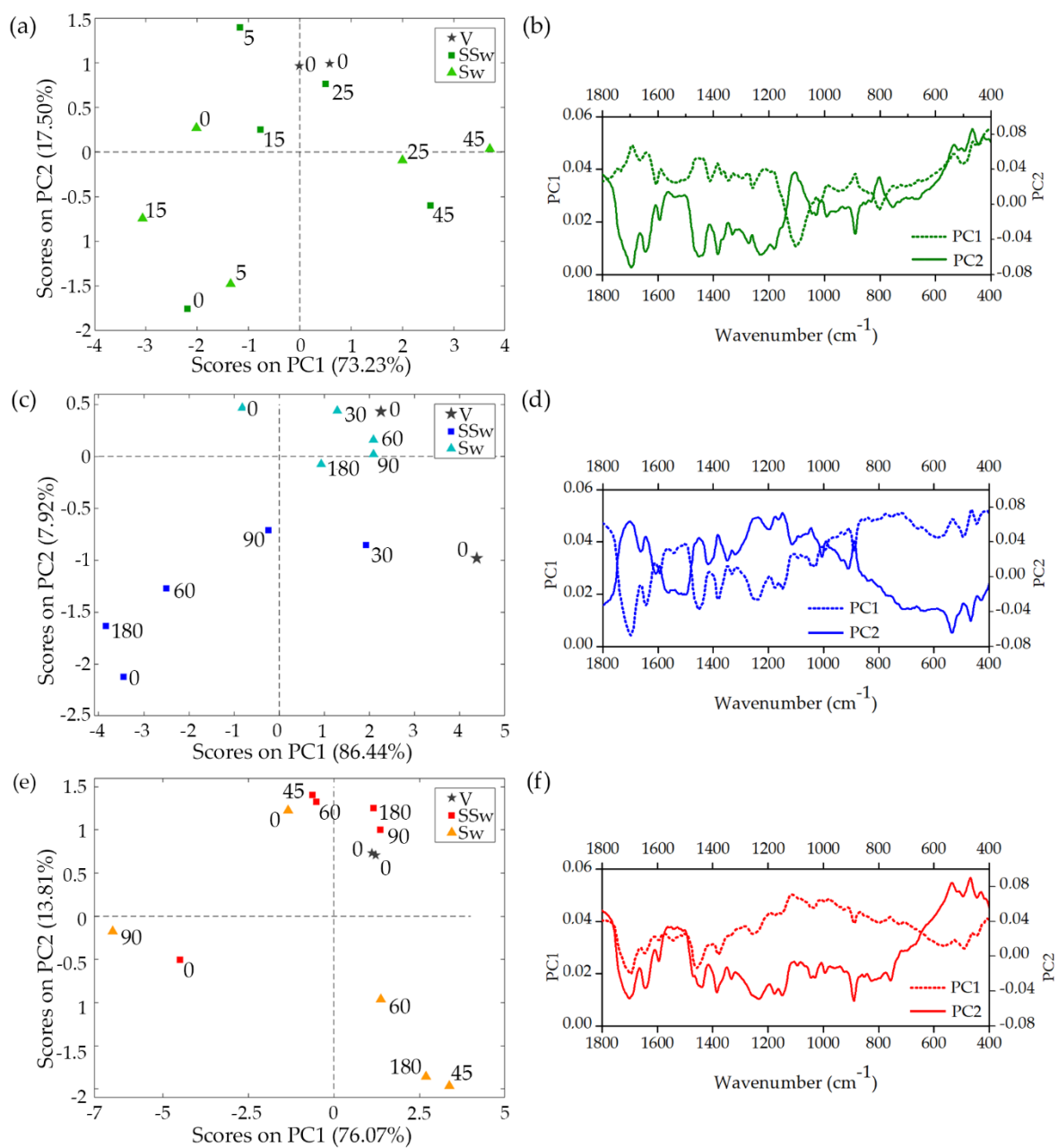


Figure 5. Score plots and loadings of the test with Velvesil™ Plus (a,b), water in agarose (c,d), and Tween 20 (e,f) are displayed. In the score plots, the application time is expressed in minutes by the labels.

In the scores plot, four areas were recognizable, corresponding to the four quadrants. Spectra of the original varnished surface (grey stars) were placed in the first quadrant (I), where both PCs assume positive values. This resulted in being the quadrant in which the spectra of well-cleaned surfaces were better described. In this portion, the clean areas were supposed to be represented. On the opposite quadrant (III), where the PCs were both negative, the spectra corresponding to the soiled condition (the green square) were grouped. The II quadrant (PC1 negative–PC2 positive) assembled the spectra corresponding to a mild effect of the cleaning and a presumed presence of sweat. Finally, in the IV quadrant (PC1 positive–PC2 negative) of the scores plot, the spectra characterized by the presence of the residues of the Velvesil™ Plus were positioned, as already shown by the direct observation of the spectra. The distribution in the scores plot was supported by the loadings plot (Figure 5b); the range portions, where the PC1 showed high variability and assumed lower values, included the diagnostic bands of the soiling and the silicone residues. The presence of such a residue that could affect the distribution of the green squares and triangles in the second quadrant, could cover the effect of the cleaning. Under this scenario, the cleaning at 45 and 25 min could also be suitable.

As concerns the water in agarose and the Tween 20 cleaning tests, the PCA approach turned out to be powerful and fundamental to visualize the difference among the spectra that, by a preliminary visual approach, were all very similar to each other and little descriptive. In the new space described by PC1 and PC2, the variability of the spectra was well displayed and the discussion of the scores plot by the loadings could guide to a hypothesis very similar to those introduced by the colorimetric data analysis. In Figure 5c, which shows the scores plot of PCA (PC1 explaining 86.44% and PC2 explaining 7.92% of the total variance) for the water in agarose test, both varnished and cleaned samples were characterized by a positive value of PC2, whereas soiled surfaces assumed negative values. Along the PC1, it was expected to distinguish spectra by the effect of the cleaning. However, due to the high but unavoidable variability of the surfaces, remarked by the position of the varnish cleaned surface (grey stars), circumspect considerations must be applied. Nonetheless, it is quite clear that cleaning effectiveness did not seem to depend on the application time. In particular, for the SSw area, the longest application times were close to the soiled reference (the blue square at time zero). A first mild effect could be recognized in 30 min exposure, whereas longer time seemed to spread the soiling without removing it. This is shown by the PC2 loadings (Figure 5d), characterized by a high contribution of soiling diagnostic bands around 500 cm^{-1} . It means that for those spectra identified with a negative PC2, it was likely to strengthen the hypothesis that the soiling was not removed. In the case of the water in agarose, it was true for all the application times, suggesting the inadequacy of this method for both the chromatic and compositional features.

Tween 20 in agarose seemed to have a good effect in removing the soiling from the SSw area since the first application time; all the red squares in Figure 5e were very close to the grey stars, which represented the original varnished surface, and very far from the red square at zero time that described SSw. Despite the peculiar behavior being shown by the scores and the loadings plot for the spectra collected in the Sw, respectively in Figure 5e,f, they were grouped in a very positive PC1 (76.07% explained variance) and in negative PC2 (13.81% explained variance) area, except for the 90 min application time that could be considered an outlier. No relevant explanations drive this distribution, calling the need for further pre-processing approaches and variable selection strategies.

4. Conclusions

In this study, we investigated the removal of soiling from varnished surfaces using aqueous methods in gel and a silicone-based material. We demonstrated that the effectiveness of the cleaning procedures can be evaluated through the analysis of specific IR absorbance bands, related to the inorganic fraction of the soiling mixture, and through the Ca spatial distribution, detected by XRF mapping. We also highlighted the benefits of treating colorimetric and IR spectral datasets with a chemometric approach, i.e., PCA, demonstrating how the multivariate method allows a better explanation of the dynamics of the soiling removal. Variations in the intensity of the selected IR bands

and in the Ca spatial distribution inferred that deionized water in agarose has a weak action in the soiling removal, whereas Tween 20 (3%) in agarose and Velvesil™ Plus produced more remarkable effects.

For what concerns the use of deionized water in agarose, it is worth noting that its removal action was mild. Further, we did not observe an improvement of the chromatic features, probably due to the weak capability of the gel to remove dark matter particles. This issue let us infer that such a method is not suggested in the presence of a dark soiled surface. Better results could be expected with longer application times and this will be the object of further experimentation.

Regarding the Tween 20 (3%) in agarose, we demonstrated that it was the most effective in removing the dark matter in the shortest time employed in this research (45 min). Nonetheless, we also observed that not all the soiling matter was removed even at the longest time (180 min). In this case, the polar affinity coupled with the surfactant property of the solvent could be responsible for the removal action, revealing also the nature of the mixture soiling–sweat.

As regards the Velvesil™ Plus, its effectiveness was proved within the first 5 min. A longer application time, 25 and 45 min, could compromise the varnish and its properties. Nonetheless, PCA results warn about the reading of these data since the presence of the product residues could cover the information about the cleaning effect. Moreover, it was shown that its non-polar and surfactant nature could also probably play a role in sweat removal. Despite this first observation, the study of the interaction between the Tween 20 or the Velvesil™ Plus and the sweaty surface is still an open challenge that requires further investigation.

An outstanding result was represented by the PC1 loading being always positive for the spectral data. It is highly informative of the fact that is essential to go on with further data processing and manipulation, including, for instance, the reduction of the spectral range in specific areas of interest and a different pre-processing strategy, in order to enhance the tiny features that at the moment are hidden by the high similarity between the collected spectra. Above all, it is necessary to disclose the dynamics of the sweaty surface that was not possible to be deeply explained until now. In this perspective, further data processing is ongoing.

To conclude, for what concerns this step of the study, some practical outstanding results for the conservators and the restorers were gained mainly concerning the Velvesil™ Plus test: the presence of post-cleaning residues was demonstrated by the FTIR spectroscopy, the interaction with the resins of the historical varnish could be supposed in the case in which the soiling coat is missing; and the XRF maps showed a low accuracy in the selection of the area to be cleaned.

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