Cleaning of historical scientific instruments: first analytical studies

Michela Albano [1,2], Giacomo Fiocco [1,3], Claudia Invernizzi [1,4], Maurizio Licchelli [1,5], Marco Malagodi [1,6], Raffaella Marotti [7], Curzio Merlo [1,8], Tommaso Rovetta [1], Daniela Comelli [2]

[1] *Arvedi Laboratory of non-Invasive Diagnostics, CISRiC, Università degli Studi di Pavia, Via Bell'Aspa 3, 26100 Cremona, Italy, michela.albano@unipv.it, giacomo.fiocco@unipv.it, claudia.invernizzi@unipv.it, maurizio.licchelli@unipv.it, tommaso.rovetta@unipv.it, curzio.merlo@unipv.it*

[2] *Department of Physics, Polytechnic of Milan, Piazza Leonardo da Vinci 32, 20133, Milano, Italy, daniela.comelli@polimi.it*

[3] *Department of Chemistry, Università di Torino, Via Pietro Giuria 5, 10125, Torino, Italy*

[4] *Department of Mathematical, Physical and Computer Sciences, Università degli Studi di Parma, Parco Area delle Scienze, 7/A, 43124 Parma, Italy*

[5] *Department of Chemistry, Università degli Studi di Pavia, via Torquato Taramelli, 12, 27100, Pavia, Italy*

[6] *Department of Musicology and Cultural Heritage, Università degli Studi di Pavia, Corso Garibaldi 178, 26100 Cremona, Italy, marco.malagodi@unipv.it*

[7] *Department of Pure and Applied Sciences (DiSPeA), Università degli Studi di Urbino "Carlo Bo", piazza della Repubblica, 13, Urbino, Italy, raffaella.marotti@uniurb.it*

[8] *Laboratorio di Diagnostica applicata ai Beni Culturali di Cr.Forma, Corso Giacomo Matteotti 17, 26100 Cremona, Italy, laboratorio.diagnostica@crforma.it*

Abstract – **Over the recent decades, the identification of scientific instruments as cultural heritage has drawn attention to their preservation, and today a lack of knowledge about this topic is drastically evident. Varnishes used during the 18th century in Europe and applied as a protective layer on brass components were known as imitation of Chinese lacquer coming from the oriental tradition. These varnishes were well considered for aesthetic and mechanical properties at the time which the manufacturing reached its apogee, and today they still protect the surface of a great number of historical masterpieces.**
A non-invasive methodology is employed to characterize the varnish reproduced with a traditional recipe and to monitor the effect of three cleaning methods widely used within the restorers' community.

I. INTRODUCTION

During the 18th century, the manufacturing of scientific instruments reached the apogee and became matter of study also for the experimental sciences. Brass was widely employed as metal components due to its malleability, ductility and golden aspect. Its surface was protected and enriched by varnishes, with a technological and aesthetic value. The scientific and historical relevance of these instruments required new procedures for their preservation and restoration, mainly due to the precious coated surface.

Varnish recipes and application procedures are described in historical treatises and dictionaries. Within the literature, the Swedish chemist Jons Jacob Berzelius (1779-1848) [1] was the first to recommend a protecting procedure of scientific instruments by an organic coating. Some recipes from Jons Jacob Berzelius volume refer to a varnish made by natural resins and colorants, able to preserve and to confer a shiny golden aspect to the surface. This varnish is described to own amazing properties which are very close to those typical of the precious Chinese lacquer made by the sap of the Rhus Vernicilua tree (*Toxicodendron vernicifluum*), brought to fame in Europe during the 18th century thanks to the Jesuit pilgrims' writings [2].

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

Experimental studies are necessary to fill this gap of knowledge and to lead towards an aware preservation practice of these objects.

While several publications deal with cleaning methods for polychrome surfaces [3], only a few of them concern the interaction between natural resins and cleaning methods [4]. Cleaning procedures started in the field of cultural heritage with a systematic development of aqueous methods carried out by Richard Wolbers in the '80s of 20th century [5]. Since that moment a powerful, safe and adjustable tool as the agarose-based rigid gels has been improving and currently using [6]. Nowadays, the cleaning procedures have been getting wider thanks to the ready-to-use products available on the market, such as silicon-based solvents [7].

In this paper, a preliminary study by means of a non-invasive methodology is reported on some cleaning methods widely used in the restoration practice. Three cleaning methods, differing for polarity and surfactant action, have been selected (deionised water in agarose gel, Tween 20 in 3% deionised water solution supported in agarose gel and Velvesil™ Plus) and applied to brass mock-ups treated by traditional protective materials, mimicking the soiled scientific instruments surfaces.

II. MATERIAL AND METHODS

A. Mock-up and varnish preparation

The mock-ups were performed applying a spirit-based varnish layer on a lamina of brass OT 63 UNI 4892 Cu63% - Zn37% (10 x 5 x 0.1 cm). The varnish was formulated according to a historical recipe [1]: shellac (28.35 g), sandarac (56.70 g), mastic (28.35 g), elemi gum (56.70 g), dragon's blood (28,35g), gumma-gutta (21.26 g), curcuma (21.26 g), saffron (12 grains), crushed glass (85.10 g) and ethanol 85% (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.

B. Artificial soiling and sweat deposition

A soiling mixture made by two phases, dry and wet, was prepared according to existing protocols and experimentations [8]. The dry portion of the soiling mixture was made by (i) sphagnum peat moss (20.8% w/w), (ii) carbon black (1.9% w/w), (iii) iron oxide (burnt sienna pigment, 0.5% w/w), (iv) gelatine (10.4% w/w), (v) soluble starch (10.4% w/w), (vi) Portland type I cement (18.6% w/w), (vii) silica gel (1.9% w/w), (viii) lime (16.7% w/w) and (ix) kaolin (18.6% w/w). The wet portion of the mixture consisted of (i) high grade mineral (paraffinic) oil and (ii) chloroform (99% pure $CHCl_3$) [4]. Once blended the two phases, the mixture was applied on

the specimen surfaces, covering at least the half of the surface. A second coat was applied after ca. 30 minutes.

Synthetic sweat has been 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., Germany).

Each specimen displays different treatments, as shown in Fig. 1 (on the left): the soiled area (S), the sweaty one (Sw), the area where both soiling and sweat are present (SSw) and the area where only varnish is applied (V).
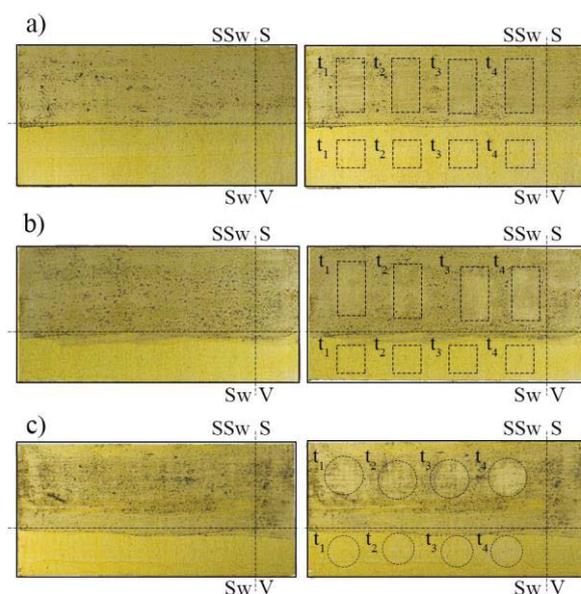

Fig. 1. Photographic documentation in the visible range of the three mock-ups, before (left) and after (right) the cleaning tests, respectively: Water in agarose (a), Tween20 (b) and Velvesil™ Plus (c). Treated areas and test distribution are schematically highlighted.

C. 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 silicon-based methods: (i) deionised water in agarose gel (agarose: 0,75 g, H_2O 48 ml [9]), (ii) Tween 20 (Honeywell Fluka™) 3% deionised water solution supported in agarose gel (agarose: 0.75 g, Tween 20 1.5 ml, H_2O 48 ml [9]) and (iii) Velvesil™ Plus added with its solvent Cyclomethicone D5. Velvesil™ Plus is purchased by Momentive Performance Materials, Inc., and consists of a silicon copolymer gel and a silicon-based surfactant in a silicon-based solvent [7]. Four application times for each cleaning method were considered (minutes): $t_1=30$, $t_2=60$, $t_3=90$, $t_4=180$. 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 in 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 tests depends on the softness: the thicker agarose gels were applied in a rectangular shape 2x1 cm sized in the SSw area and in a square shape 1x1 cm sized in the Sw area, whereas the Velvesil™ Plus in a round of 1.5 cm of diameter or less. In order to facilitate the reading of the results the tests areas are highlighted for each specimen in Fig.1 on the right.

D. Non-invasive analytical investigation

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

A photographic documentation was carried out using visible light. It was acquired with a Nikon D4 full-frame digital camera equipped with a 50mm f.1.4 Nikkor objective using a Softbox LED lamp. Colorimetric measurements were accomplished with a portable Konica Minolta CM-2600d spectrophotometer and the average of the SCE values was considered, and the dataset was processed in the CIELab 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. The portable ELIO XRF spectrometer (XGLab srl, Milano, Italy) with Rh anode was employed to collect XRF maps on the specimen surface (40 kV, 15 µA, 3s per spectrum): the elemental distribution was pointed out by heat maps before and after the cleaning. Ca as part of the dry fraction of the soiling mixture was considered as 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 the technique was indeed slightly informative. Transflection mode FTIR spectra were recorded with the Alpha portable spectrometer (Bruker Optics, Germany/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 minute. Data were processed in OPUS 7.2 software. Diagnostic bands were identified for the inorganic fraction of the soiling mixture, mainly ascribable to the Portland cement (CaO 61-67%, SiO_2 19-23%, Al_2O_3 2.5-6%, Fe_2O_3 0-6%, SO_3 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.

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

III. RESULTS AND DISCUSSION

In this paper, the main results are discussed and organized by analytical techniques in three sections: (A) colorimetric investigation, (B) XRF spectroscopy and (C) FTIR spectroscopy.

A. Colorimetric investigation

The total colour variation ΔE^* is shown in Fig. 2 as a function of the application time of the three cleaning methods in the SSw and Sw areas.
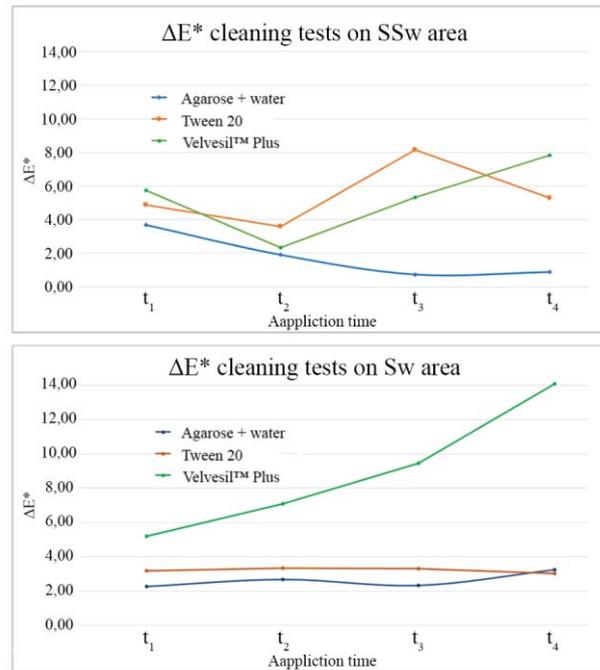

Fig. 2. ΔE* as a function of the application time of the three cleaning tests for both the area SSw (top) and Sw (bottom).

ΔE^* smoothly decreased ($\Delta E^*_{t1}=3.68$) for the water in agarose cleaning test till approaching a value close to zero (t_3). It could display that after 180 minutes there are no differences with the soiled surface. Such an ineffectiveness is supported by the drop of L^* value at t_1 that confirmed a darkening of the surface and by the slight variation of a^* and b^* (Table 1). This behaviour could be due to the interaction between the water and the polar portion of the soiling mixture coupled with a mild efficiency of the gel in drawing the particles that are not removed but widely spread.

As regards the Tween 20 (3%) in agarose, it seemed to be more effective in the dark matter removal: ΔE^* in SSw area after cleaning varied from 3.50 (t_2) up to 8.15 (t_3) and L^* grew after cleaning ($\Delta L^*_{max}=$ 7.81 after 90 minutes), indicating a bleaching mainly due to the black particles removal, in this case facilitated by the surfactant action of the solvent. In the Sw area, a ΔE^* value of 3 was measured constant over time: a variation is

appreciable only in the first 30 minutes of application.

Otherwise, concerning the Velvesil™ Plus cleaning test for the SSw area, ΔE^* varied from 5.74 to 7.84 and an increasing trend could be recognised since t_2. As in the Tween 20 test, L^* resulted to be the parameter which most affect this variation (ΔL^*_{max} up to 7.54 after 180 minutes) and it is due to the dark layer removal and to the consequent surface bleaching. About a^* and b^*, their variation was negligible (Table 1). The data regarding Sw were unexpected: the value of ΔE^* varied from 5.22 up to 14.10, combined to a substantial reduction in the b^* value ($\Delta b^*_{max}=13.23$ after 180 minutes) that seems to drag this trend, signifying a change in the yellow component. The results of the Velvesil™ Plus test, highlight the strongest action of a highly non-polar and surfactant product that seems to interact with the hydrophobic components of the sweat, inducing a transformation in the aesthetic properties of the surface.

Table 1. Colour coordinates L* a* and b* measured before (t₀) and after the cleaning tests (t₁, t₂, t₃, t₄).

Agarose		L*	a*	b*
SSw	t_0	68.94	2.68	42.23
	t_1	66.60	3.09	39.42
	t_2	67.35	3.07	43.22
	t_3	68.34	2.91	41.86
	t_4	69.24	3.14	41.54
Sw	t_0	78.42	1.84	51.6
	t_1	76.41	1.72	50.66
	t_2	75.78	2.00	51.25
	t_3	76.58	1.86	50.27
	t_4	76.48	2.02	49.08

Tween 20		L*	a*	b*
SSw	t_0	65.11	2.87	43.17
	t_1	69.98	3.09	43.26
	t_2	68.59	3.14	43.90
	t_3	72.92	2.59	45.49
	t_4	70.33	3.02	42.33
Sw	t_0	78.05	1.91	58.03
	t_1	75.77	1.97	55.79
	t_2	76.00	1.70	55.39
	t_3	76.61	1.61	55.08
	t_4	76.55	1.65	55.42

Velvesil™ Plus		L*	a*	b*
SSw	t_0	65.30	3.62	44.68
	t_1	70.51	3.39	42.27
	t_2	66.72	3.48	42.84
	t_3	69.99	3.41	42.19
	t_4	72.84	3.04	42.63
Sw	t_0	76.83	3.35	57.60
	t_1	75.54	2.41	52.64
	t_2	75.76	2.54	50.65
	t_3	75.06	2.74	48.33
	t_4	71.95	3.51	44.37

B. XRF spectroscopy

Ca was selected as marker of the soiling layer and its distribution obtained through XRF mapping showed that it was removed by each cleaning method with a different degree of effectiveness (Fig.3a, b and c). Results for the water in agarose tests (Fig.3 a) showed that Ca was not removed after 180 minutes and a slight difference in the intensity among the application times was observed, confirming the mild action carried out on the soiling.
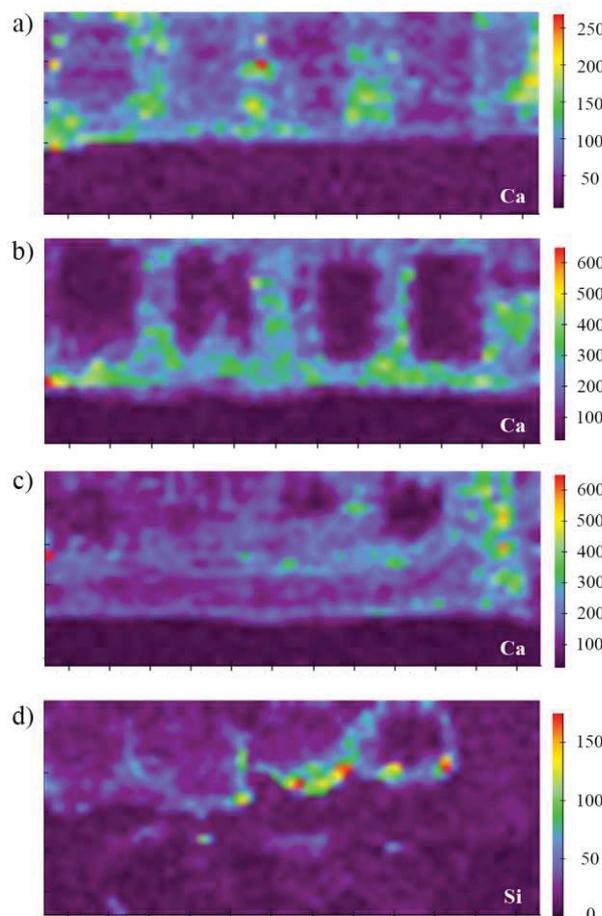

Fig. 3. XRF maps of the SSw area after the cleaning tests, respectively for water in agarose (a), Tween 20 (b) and Velvesil™ Plus (c): Ca distribution highlights the cleaned area (from t₁ to t₄, from the left to the right). Si distribution reveals Velvesil™ Plus residues (d). The heat map colours represent the minimum (blue-violet) and the maximum (red) values.

Observing the XRF maps of the mock-ups cleaned by Tween 20 (3%) (Fig. 3b) and Velvesil™ Plus (Fig. 3c), Ca is never detected in the areas where the cleaning tests were carried out. For what concerns the Velvesil™ Plus (Fig. 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 is Fig. 3d.

Those results would confirm what previously supposed on the bases of colorimetric observation: water in agarose seems to interact with the soiling but with a low removal power, whereas Tween 20 and Velvesil™ Plus can be able to remove almost completely the soiling through their surfactant action. Moreover, by the XRF mapping it was possible to highlight how the selection of the cleaned area is more accurate in the case of the rigid gels that results more suitable for tiny and well-defined areas.

C. FTIR spectroscopy

The high complexity of both soiling mixture and historical varnish in terms of number and variety of constituents, let very complicate the interpretation of the spectra. Nonetheless, some relevant data were collected, and some decisive information were 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} (Fig. 4), were identified as diagnostic of the cleaning effectiveness.
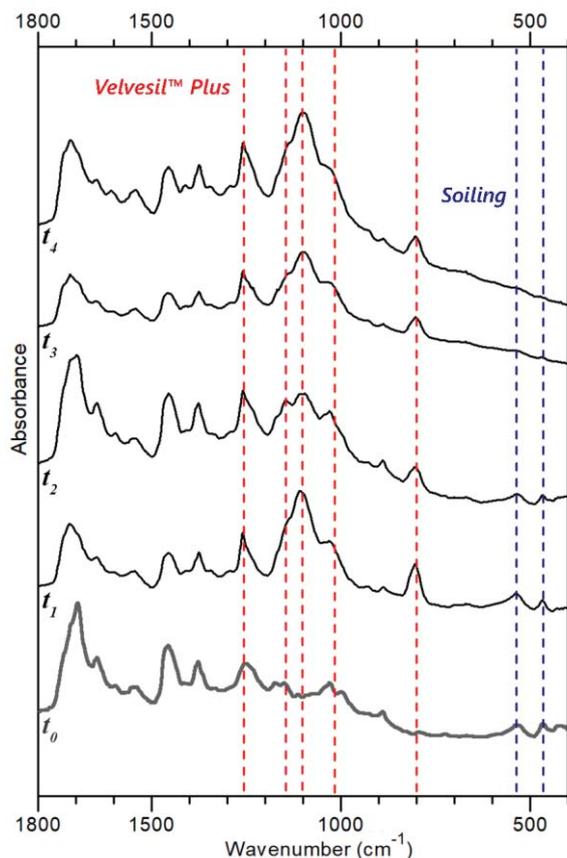

Fig. 4. FTIR spectra of the Velvesil™ Plus test from t_0 (bottom) to t_4 (top) - Velvesil™ Plus (red) and soiling mixture (blue) diagnostics bands are highlighted.

The intensity reduction of these spectral features was able to provide quality information about the capability of the employed products to remove the soiling from the varnished surfaces and it was clearly observed in the spectra collected in the Velvesil™ Plus test areas. They evidently showed a significant drop of the intensity, until disappear, from t_0 to t_4, proving the positive cleaning effect of this application (Fig. 4). Moreover, FTIR spectroscopy analysis showed that the use of Velvesil™ Plus would exhibit some disadvantages to be taken into consideration in the art conservation field: after cleaning, residues of the product were detected on the surface as the persistence of the silicon bands in the 1500-1000 cm^{-1} range and 800 cm^{-1} proved.

IV. CONCLUSION

This study investigated the removal of soiling from varnished surfaces using aqueous methods in gel and a silicon-based material. Their action efficiency was explored by identifying specific IR absorbance bands related to the inorganic fraction of the soiling mixture and outlining Ca as a marker of the same mixture by the XRF spectroscopy distribution maps. Variation in the selected bands intensity and in the elemental distribution reveal that deionized water in agarose had a weak action in the soiling removal, whereas Tween 20 (3%) in agarose and Velvesil™ Plus produced more remarkable responses. For what concerns the deionized water in agarose, it is worth noting that the removal action was mild and that an improving of the chromatic feature was not observed during the application time considered in this study, probably due to the weak capability of the gel to remove the particle. It leads to the hypothesis that the use of such a method is not suggested in case of dark soiled surface. Better results could be expected with longer application times and this will be object of further experimentation.

Regarding the Tween 20 (3%) in Agarose, it resulted effective in removing the dark matter also in the shorter time, even though it was observed that not all the soiling was removed after the extended one. In this case the polar affinity coupled with the surfactant property of the solvent could be the highly responsible of the removal, revealing also the nature of the mixture soiling-sweat. As regard the Velvesil™ Plus, its efficiency depends on the application time: a significant removal was observed starting from 90 minutes of application and it was proved that probably its non-polar and surfactant nature is able to play a role also in the sweat removal, conversely to the other tested methods. Despite of this first observation, the study of the sweaty surface is an open challenge that requires further investigation.

To conclude, 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 varnished could be supposed in the case in which the soiling coat is missing; concluding, the XRF maps showed a low accuracy in the selection of the area to be cleaned.

V.   REFERENCES

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