PRIN2020 *SUPERSTAR - Sustainable Preservation Strategies for Street Art -*

WP6 Deliverable D6.1 Good practices and recommendations for the knowledge, conservation and safeguard of contemporary murals exposed in outdoor conditions

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1. Introduction

From the material point of view, contemporary murals are complex and critical artworks, that deserve special attention and care. The Superstar project undertook three years of advanced research activities to address different conservation challenges related to the knowledge and the preservation of these paintings in outdoor urban conditions. An overview of the challenges related to the preservation of these artworks can be found in the review by Pagnin L. et al.[1].
Prolonging the lifetime of contemporary murals can be attained employing virtual conservation, based on cataloguing activitiers and on the set-up of appropriate digital archives (out of the scope of Superstar project Deliverable D.6.1). However, when material conservation of the artwork in the context where it was created is tackled, active conservation and restoration is needed, aimed at slowing the ageing processes.
The objectives of the investigation and research efforts during Superstar Project target the assessment of the material composition and the state of conservation, and the reduction of the rate of deterioration. In particular, the main outputs of the Superstar project are summarized as follows:
a) set-up of an integrated analytical protocol to investigate and identify mural paint materials and their state of conservation;
b) set-up of cleaning methodologies and procedures for the removal of vandalistic graffiti from outdoor exposed painted surfaces;
c) set-up of protective methods and procedures for painted outdoor exposed surfaces.

This document (Deliverable D6.1) collects the practical outputs of the research: the procedures that have been set-up for the different phases of the intervention (survey, cleaning and protection). These guidelines can be exploited by artists, conservators and restorers, public entities that manage the creation and conservation of commissioned murals, and by professionals and associations involved in the safeguard of contemporary muralism located in urban, polluted, and stressful conditions.
Any conservation procedure starts with a thorough survey activity[2], based on assessed protocols among conservators and restorers: a geometrical survey with VIS photo-

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[1] Pagnin, L., Guarnieri, N., Izzo, F. C., Goidanich, S., & Toniolo, L. (2023). Protecting Street Art from Outdoor Environmental Threats: What Are the Challenges?. Coatings, 13(12), 2044.
[2] Mezzadri, P. Contemporary Murals in the Street and Urban Art Field: Critical Reflections between Preventive Conservation and Restoration of Public Art. *Heritage* 2021, 4, 2515–2525, doi:10.3390/heritage4030142

documentation; a visual survey of the different deterioration patterns[3]; the restitution and mapping activity of the state of conservation, based on a shared accepted glossary of terms, indicating the deterioration patterns and the main decay phenomena. The Italian Istituto Centrale del Restauro and the Fondazione CRC Venaria Reale, collaborating with the Project, shared their experiences and know-how with the researchers involved in the Superstar project, allowing to build up a solid reference framework for the project outputs, to be offered to a wide range of stakeholders.

The main objectives achieved by the Superstar project are as follows:

- ***Recommendations for the safeguard and preventive conservation actions*** (location, support walls, renders and plasters, primer, quality of materials, etc.).
  The Superstar project activities have been based on laboratory and onsite testing including the study of a range of different recent murals in Milan and Turin (see Scientific Report Deliverable 6.2). These case studies allowed us to collect a set of observations and to draw important considerations about:
  - the selected **locations**; the vertical surfaces selected for commissioned and non-commissioned mural and public art are often inappropriate in terms of long term survival of the artwork, as in the case of industrial sites, rampart, embankments, overpasses, with reinforced concrete supports in a poor state of conservation (carbonation, chlorides presence, salt efflorescence, map cracking, etc.);
  - the type of **support**; the support (essentially the renders and plasters) is often inadequate as for quality and state of conservation; the deterioration patterns affecting the support need to be carefully evaluated in preliminary survey phases, and may include: plaster detachments, moist areas, humidity infiltrations, cracks and deformations, bowing, biological colonization. A careful preparation of the support is key requirement for the long term survival of a mural;
  - the application of **primers**; the use of primers before applying the paint has been demonstrated a key good practice to favor a suitable adhesion between the support and the painting materials, preventing the deterioration of the painting layer itself;
  - the quality of **painting materials**; it has been demonstrated that the quality of painting materials (type of varnishes/paints) strongly affects the lifetime and durability of the artworks, especially in the outdoor urban polluted environment. It is preferable to select outdoor resistant varnishes/paints for renders, avoid mixing of paints of different composition, prefer brush to spray application methods, and perform preliminary application tests. After the experimental work carried out in the framework of SuperStar project, the laboratory testing revealed that Styrene-based paints are more stable to solar irradiation and rain washing than Acrylic-based and Alkyd-based paints.
- ***Investigations protocols*** *(non- invasive and micro-invasive diagnostic tools).*

[3] Glossary *CAPuS, Conservation of Art in Public Spaces*. Available online: https://www.capusproject.eu/glossary/ (accessed on 30 March 2025).

The research activity has been devoted to set-up and test an effective protocol for the characterization of painting materials and surfaces, comprising non-invasive and micro-invasive testing/analytical methods (WP3, results summarized and reported in § 2 in this document).

- ***Cleaning** methods for the painted surfaces (advanced cleaning methodologies).*
  Innovative cleaning methods to remove vandalic and undesired graffiti painting have been developed and set-up in the framework of the project (WP4, summarized in § 3 in this document), and precisely:
  - chemical cleaning systems based on nonwoven mats and green solvents, specifically γ-valerolactone and dimethylcarbonate;
  - laser cleaning methods.
- ***Direct protective treatments** (water repellent products; durability and maintenance)*.
  In the framework of the project, protocols for the selection and testing of protective materials have been developed and optimized, both in laboratory and onsite conditions, and precisely:
  - laboratory testing protocol for the assessment of the compatibility and effectiveness of protective treatments;
  - laboratory procedures for artificial ageing;
  - onsite testing protocol for the assessment of the compatibility and effectiveness of protective treatments in natural ageing conditions.

2. Guidelines for a multimodal analytical methodology for material characterization

The study of the paint materials in urban muralism and the understanding of their chemical and physical transformation over time is a difficult challenge. This is due to the continuous changes in the complex formulation and quality of industrially produced paints and their inherent vulnerability when exposed to outdoor and urban environments, including sunlight, temperature fluctuations, relative humidity changes, precipitation, wind, and pollutants. Additionally, the vast expanse of the painted surfaces and their varying exposure to environmental conditions, particularly when applied to walls with different orientations, make it essential to develop an analytical strategy that can provide representative and reliable results. Given these constraints, a multiscale and modular analytical approach, easily adaptable to the specific issues of the object under investigation, is preferable. Investigation protocols must be designed to answer the different questions to support the conservation and protection of urban art: which are the applied materials? Are they subject to chemical and physical changes? Which degradation mechanism is occurring? How fast is the decay? How does it depend on surface exposure? The diagnostic tools available to address these questions vary widely and, considering also recent technological advancements, range from non-invasive in situ spectroscopic methods to advanced micro-destructive analyses with high specificity and include hyperspectral imaging and aerial surveys by drones.

In the following sections, various techniques and approaches are presented based on the information provided, with recommendations on their integrated use to develop a comprehensive understanding of the materials in urban muralism and of their state of conservation in relation to the entire surface. While the list of analytical techniques is obviously not exhaustive, the proposed analytical process provides a clear outline of the workflow to be followed.

2.1 *Analytical approaches for material characterization and control of chemical and physical changes*

Considering the specific requirements for the scientific investigation of materials in urban muralism, a two-level protocol was developed to i) include analyses that minimally impact the original materials while still being representative of the entire surface, and ii) maximize the specificity of the analytical information provided.

Figure 2.1 illustrates the workflow of the proposed analytical protocol, which is structured into three primary steps. The first step involves in situ, non-invasive analytical campaigns using portable instrumentation, providing a rapid and accessible means of data collection representative of all the mural surface. The second step involves studying the paint stratigraphy through complementary microscopy and micro-spectroscopy techniques applied to cross-sections. The third step leverages the high specificity of micro-destructive analyses conducted with advanced laboratory instrumentation to address specific analytical challenges and provide more detailed insights. In the workflow, the initial data from non-invasive analysis guide the selection of subsequent analytical steps, optimizing the entire investigative process. In a circular way, the information obtained by micro-destructive techniques can then be used to better interpret the data acquired in situ.

From a broader perspective, these same analytical techniques are essential for designing strategies to monitor the conservation state of materials and study degradation mechanisms, as illustrated in the diagram of Figure 2.2.

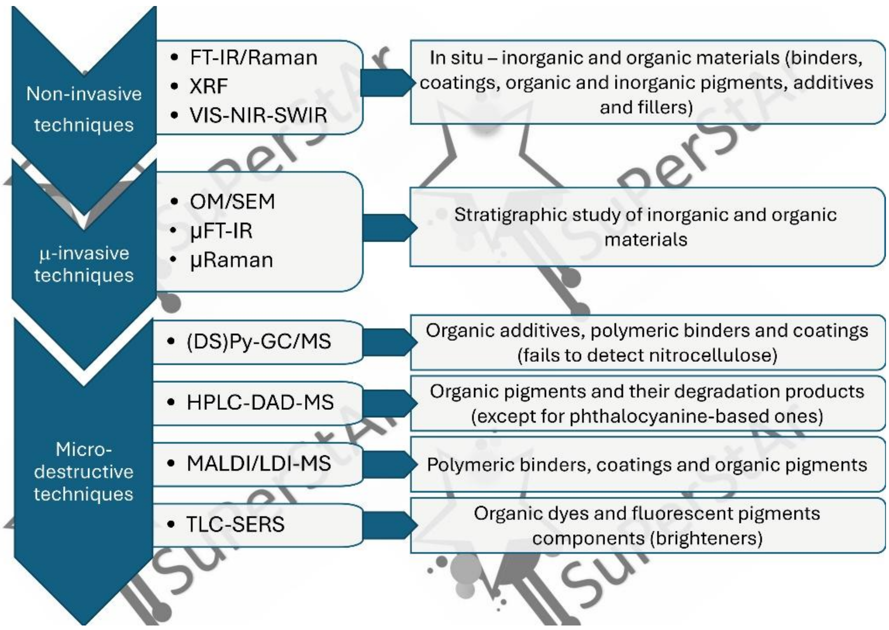

Figure 2.1. Diagram summarizing the workflow of the multiscale, multimodal analytical methodology for material characterization in urban muralism.

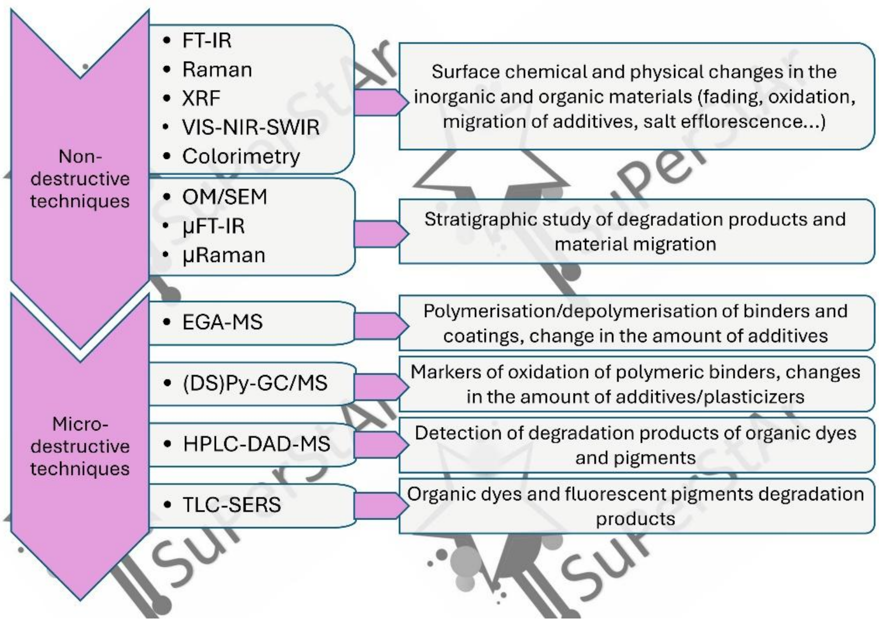

Figure 2.2. Diagram summarizing the analytical information gained by combining complementary analytical information from the integrated analytical protocol to control the state of conservation of paint materials in urban muralism.

2.1.1 *Non-invasive techniques*

In accordance with the established recommendations for the scientific study of works of art, the use of portable analytical instrumentation, primarily **X-ray fluorescence** (**XRF**), **external reflection Fourier Transform Infrared spectroscopy** (**FT-IR**) in the mid-infrared range (7000-400cm^{-1}), **Raman** spectroscopy, and **Visible-Near-ShortWave Infrared** (**VIS-NIR-SWIR**, 400-2500nm) reflectance spectroscopy, enables in situ analysis providing initial material discrimination of paintings in a totally non-invasive way[4]. This approach is especially suited for the study of contemporary outdoor murals, considering the unique requirements of their analysis. Elemental characterization provided by XRF analysis (identification of elements with atomic number Z>12) integrated with the molecular information from vibrational and electronic spectroscopies (VIS-NIR-SWIR, FT-IR, and Raman) enables the identification of pigments, dyes, organic components from the binders and the coatings, and additives[5]. The approach leverages the complementarity of the analytical information, the different sensitivity of the

[4]Brunetti, B., Miliani, C., Rosi, F., Doherty, B., Monico, L., Romani, A., & Sgamellotti, A. (2017). Non-invasive Investigations of Paintings by Portable Instrumentation: The MOLAB Experience. In: Mazzeo, R. (eds) *Analytical Chemistry for Cultural Heritage. Topics in Current Chemistry Collections*. Springer, Cham. https://doi.org/10.1007/978-3-319-52804-5_2

[5]Rosi, F., Grazia, C., Fontana, R., Gabrieli, F., Pensabene Buemi, L., Pampaloni, E., & Miliani, C. (2016). Disclosing Jackson Pollock's palette in Alchemy (1947) by non-invasive spectroscopies. *Heritage Science*, 4, 1-13. doi.org/10.1186/s40494-016-0089-y

techniques to the various components present in industrial paints and also the diverse probed depth as a function of the radiation penetration.
Non-invasive in situ analysis integrated with **colorimetry** is also the first choice for the short- and long-term monitoring of the chemical and physical changes occurring in paint surfaces with ageing. The provided information useful for understanding the degradation mechanisms involved is outlined in the first block of the diagram in Figure 2.2 and encompasses the detection of degradation products from oxidation or hydrolysis, migration of salts or paint additives, fading or discoloration of dyes and pigments, and soiling.

2.1.2 *Micro-invasive techniques*

Traditional cross-sectional studies of paint micro-samples by **Optical Microscopy** (**OM**), **Scanning Electron Microscopy** combined with **Energy Dispersive X-ray Analysis** (**SEM-EDX**), and FTIR and Raman micro-spectroscopies (**μFTIR** and **μRaman)** are well-established approaches for gaining a deeper understanding of paint stratigraphy. This information is crucial not only for reconstructing material distribution but also for understanding degradation processes such as material migration, salt recrystallization, paint photo-oxidation at the air-surface interface, and soiling (see scheme in Figure 2.2).

2.1.3 *Micro-destructive techniques*

Detailed molecular information can be obtained by employing thermoanalytical techniques such as multi- or single-shot analytical **pyrolysis coupled with gas chromatography and mass spectrometry** (**Py-GC/MS**), and **evolved gas analysis-mass spectrometry** (**EGA-MS**)[6,7]. These techniques do not entail any sample pretreatment and require less than 0.1 mg of sample for the characterization of the paint binders and organic additives in the paint formulations. If Py-GC/MS is employed, information on polymeric binders (except for cellulose nitrate), additives like plasticizers, emulsifiers and organic dyes and pigments can be obtained from the same micro-sample. EGA-MS is particularly suited for the study of the degradation of materials, being able to compare the changes in thermal stability of polymers subjected to different ageing conditions. Whenever the characterization of organic pigments and possible degradation products is required, **liquid chromatography interfaced with spectrophotometric detectors** (**HPLC-DAD**) or **tandem mass spectrometry** (**HPLC-MS/MS**) are the techniques of election, due to their extreme sensitivity and ability to identify unknown species[8]. HPLC-based methods require the solubilization of the sample (less than 0.1 mg) prior

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[6] Degano, I., Modugno, F., Bonaduce, I., Ribechini, E., & Colombini, M. P. (2018). Recent advances in analytical pyrolysis to investigate organic materials in heritage science. *Angewandte Chemie*, 57(25), 7313-7323. doi.org/10.1002/anie.201713404

[7] La Nasa, J., Campanella, B., Sabatini, F., Rava, A., Shank, W., Lucero-Gomez, P., Modugno, F. (2021). 60 years of street art: A comparative study of the artists' materials through spectroscopic and mass spectrometric approaches. *Journal of Cultural Heritage*, 48, 129-140. doi.org/10.1016/j.culher.2020.11.016

[8] Tamburini, D., Sabatini, F., Berbers, S., van Bommel, M. R., & Degano, I. (2024). An introduction and recent advances in the analytical study of early synthetic dyes and organic pigments in cultural heritage. *Heritage*, 7(4), 1969-2010. doi.org/10.3390/heritage7040094

to analysis and are thus suited for the study of most organic pigments, with the notable exception of phthalocyanine-based pigments. A versatile alternative strategy entails the application of **matrix-assisted laser desorption mass spectrometry** (**MALDI-MS**) or **laser desorption-ionization mass spectrometry** (**LDI-MS**) to solid samples. This technique is suitable for fast and sensitive detection of both binders and organic pigments without any laborious sample pretreatment[9,10].

Among the vivid and colorful pigments used in urban artworks, fluorescent spray paints deserve particular mention for the unique challenges they present from an analytical point of view. These paints are often based on daylight fluorescent pigments that are solid dye solutions embedded into a resin carrier. They typically feature a formulation containing less than 5% fluorescent dye and 95% resin. Anti-foam agents, UV-stabilizers and optical brighteners can also be added. To study these materials, a conventional Raman approach may not be very effective. It is important to remember that the technique is not selective and tends to reveal the presence of those substances that have a high "*cross section*" to scatter the laser light; furthermore, the specific nature of these materials tends to cause a high level of fluorescence that risks obscuring the analyte signal, even using excitation radiation in the near infrared. A simple and effective approach is to couple a separation technique, such as **thin-layer chromatography** (**TLC**), with **surface enhanced Raman spectroscopy** (**SERS**), a variant of the standard Raman technique that uses noble metal nanostructures to enhance the signal[11]. Separated TLC spots are easily visible under a UV lamp (365 nm). By dropping a few microliters of a silver nano colloid on the spots and focusing a green laser light (λ=532nm), it is possible to identify the mixed dyes and sometimes also the brighteners[12]. The number of fluorescent dyes available and suitable for daylight fluorescent pigment manufacture is, in fact, limited. As a result, the dye solution is usually formulated with multiple fluorescent dyes (in some instances with the inclusion of a non-fluorescent dye), so that a broader range of hues may be achieved.

2.3 *Integrated analytical protocol and scale-up of the information across the whole mural surface*

The workflows schematized in Figures 2.1 and 2.2 well explain how to direct the investigation process by integrating the analytical information provided by complementary techniques used in sequence, from non-invasive analysis to micro-invasive and/or micro-destructive investigations, based on informed decisions driven by specific research questions. However,

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[9] Rigante, E. C., Calvano, C. D., Picca, R. A., Modugno, F., & Cataldi, T. R. (2023). An insight into spray paints for street art: Chemical characterization of two yellow varnishes by spectroscopic and MS-based spectrometric techniques. *Vacuum,* 215, 112350. doi.org/10.1016/j.vacuum.2023.112350

[10] Calvano, C. D., Ventura, G., Cataldi, T. R., & Palmisano, F. (2015). Improvement of chlorophyll identification in foodstuffs by MALDI ToF/ToF mass spectrometry using 1, 5-diaminonaphthalene electron transfer secondary reaction matrix. *Analytical and Bioanalytical Chemistry*, 407, 6369-6379. doi.org/10.1007/s00216-015-8728-9

[11] Ferretti, A., Floris, E., Campanella, B., Degano, I., & Legnaioli, S. (2024). "Welcome to the jungle": TLC-SERS to wade through real complex mixtures of synthetic dyes. *Microchemical Journal,* 206, 111439. doi.org/10.1016/j.microc.2024.111439

[12] Sabatini, F., La Nasa, J., Degano, I., Campanella, B., Legnaioli, S., Saccani, I.; Modugno, F. Fluorescent Paints in Contemporary Murals: A Case Study. *Heritage* 2023, 6, 5689-5699. https://doi.org/10.3390/heritage6080299

the peculiar characteristics of large surface areas with varying exposures, commonly found in urban muralism, pose a significant challenge in obtaining analytical information from spot analyses that is representative of the entire mural. In consideration of this, the advancement of spectroscopic techniques to imaging methods represents one of the most significant achievements in the development of new analytical approaches in heritage science. Specifically, **macroXRF** (**MAXRF**) and **VIS-NIR-SWIR hyperspectral** and **multispectral imaging** have emerged as key techniques in the development of commercial instrumentation for non-invasive imaging diagnostics of cultural heritage objects. They enable the characterization of materials and of their distribution, which is then presented as chemical maps that are easily interpreted, even by non-scientists. The imaging analysis may cover surfaces up to a few square meters in size, with spatial resolution depending on the technique: 0.2-2 mm for MAXRF and from tens of microns to a few mm for VIS-NIR-SWIR hyperspectral/multispectral imaging, depending on the sensor and the camera's working distance. The opportunity to use imaging techniques offers unquestionable advantages both for material characterization and the monitoring of chemical-physical changes in the study of urban muralism. Nevertheless, the surface extension reached by the available instrumentation is still insufficient to cover surfaces that can reach hundreds of square meters. A new outcome of the project is the experimentation of using multispectral and hyperspectral sensors mounted on drones (**Unmanned Aircraft Systems, UAS**) for aerial acquisitions. The coupling with a laser scanner and a GPS system allows for the reconstruction of an orthophoto mosaic of the hyperspectral/multispectral dataset of all the mural surface to be acquired. The integration of coherent data processing for datasets from both 'ground' instrumentation and drones, guided by the highly specific information provided by spot techniques, ensures the accurate upscaling of these data to cover the entire surveyed surface. This process is shown in the scheme of Figure 2.3.

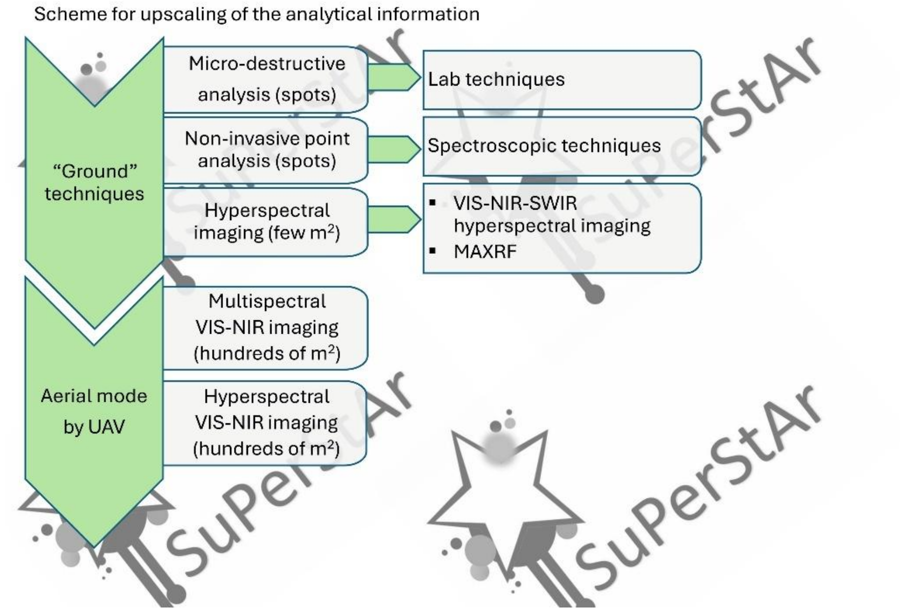

Figure 2.3. Diagram outlining the workflow for scaling up the information derived from the integrated analytical protocol across the entire surface.

3. Guidelines for innovative cleaning procedures

3.1 Chemical cleaning systems production and optimization of the methodology

The cleaning systems proposed in this section are based on nonwoven mats and green solvents, specifically γ-valerolactone and dimethylcarbonate. In this section, we provide the parameters for producing the materials and indications on how to use the prepared materials to remove unwanted overpainting[13,14].

Generally, before selecting the most suitable material, verifying the composition of the unwanted layer and/or its solubility in the selected solvent is recommended.

3.1.1. Production

Two mats can be employed for the removal of unwanted overpainting. The non-photothermal PULL (based only on pullulan) is suitable for removing soluble materials such as acrylic varnishes, and the photothermal PULL_SI (based on pullulan and melanin nanoparticles) is recommended for highly insoluble varnishes such as alkyd spray paints.

Extraction of melanin nanoparticles

Melanin nanoparticles (NPs) were obtained through a centrifugation-based method. Cuttlefish ink was extracted from the ink sac and diluted with Milli-Q water. The resulting ink dispersion underwent centrifugation at 3,000 rpm for 10 minutes to eliminate residual impurities such as sand or ink sac fragments. The supernatant was then collected, diluted with Milli-Q water, and subjected to an additional centrifugation step at 6,500 rpm for 10 minutes. The supernatant was discarded, and the pellets were washed three times with Milli-Q water via centrifugation. Finally, the obtained melanin dispersion was dried in an oven at 60 °C.

Production of electrospun mats

The mats were produced with a laboratory electrospinning machine. Table 3.1 summarizes the parameters for the production.

Table 3.1. Production parameters for the proposed electrospun mats*,**.

Mat name	Polymer	Solvent	Concentration	Solution preparation	Rate	Voltage	Distance needle-collector	Needle inner diameter
PULL	Pullulan	H_2O	19% g/mL	stirring	0.8 mL/h	21-22 kV	18 cm	0.51 mm

[13] A. Menichetti *et al.*, 'Nanofibrous Photothermal Materials from Natural Resources: A Green Approach for Artwork Restoration', *ACS Applied Materials and Interfaces*, vol. 16, no. 50, pp. 69829–69838, 2024, doi: 10.1021/acsami.4c14532.

[14] F. Ramacciotti *et al.*, 'Microporous electrospun nonwovens combined with green solvents for the selective peel-off of thin coatings from painting surfaces', *Journal of Colloid and Interface Science*, vol. 663, pp. 869–879, Jun. 2024, doi: 10.1016/j.jcis.2024.03.006.

PULL_SI		Melanin NPs dispersion in H_2O (18 mg/mL)		Stirring + 10 minutes of sonication		24-25 kV		

*Please note: pullulan is soluble in water; therefore, it must be handled wearing gloves.
**Please note: the use of electrospun fabrics for the removal of overpainting from street artworks has been optimised selecting γ-valerolactone as solvent. If different solvents are to be used, the stability of the fabrics in the solvents must be evaluated. As far as the PULL_SI fabric is concerned, it must be used with high-boiling solvents, otherwise, the solvent will evaporate during irradiation.

3.1.2 Application of non-photothermal mats

Cleaning systems based on **non-photothermal mats** are useful for the removing of unwanted acrylic spray paint. Figure 3.1 shows a schematic representation of the application of the non-photothermal mat use. The mat is first saturated with the selected solvent, then it is applied on the graffitied surface for some minutes.

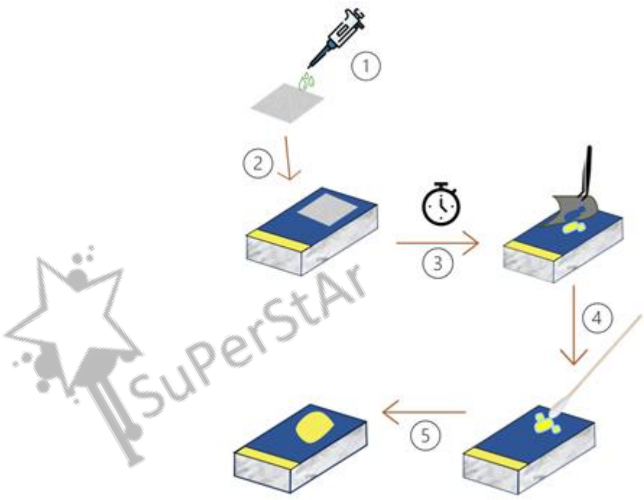

Figure 3.1. Schematic representation of the use of a non-photothermal mat of pullulan (PULL).

A correct application entails the following 5 steps:

1. the electrospun mat, with the required size, has to be saturated with GVL at a ratio of 4.5 μL/mg;
2. place the electrospun mat on the graffitied area;
3. wait for 5 minutes;
4. remove the electrospun mat from the surface;
5. finally remove some varnish residues with dry cotton swabs.

3.1.3 The restorers' feedback

Workshop at the Central Institute for Restoration of Rome (ICR) in November 2023
During the workshop organized at the Central Institute for Restoration in Rome, the involved students tested three different cleaning systems (cotton swabs, PHB gel, and ES pullulan) combined with GVL to remove an acrylic blue paint from an alkyd yellow paint. At the end of the experiments, they answered a questionnaire about their impressions on preparation, user-friendliness, efficacy and spatial control of cleaning systems. The participants were more satisfied with the cleaning performance of the ES pullulan than the traditional cotton swab, and with the preparation and application of the ES pullulan compared to the gels.

Workshop at the Venaria Reale (Turin) in February 2025
During the workshop at the Center of Conservation and Restoration "Venaria Reale" in Turin a practical activity for conservators and restorers was planned for testing and comparing directly the new chemical system to more common ones (such as ES pullulan, cotton swabs and PHB gel added to GVL) for cleaning an acrylic blue paint from an alkyd yellow paint. Finally, participants filled out a questionnaire about the cleaning systems used in terms of ease of preparation, solvent retention, and efficacy, uniformity and control in cleaning. The electrospun mats have been found to be more useful considering cleaning control and uniformity, while cotton swabs were preferred in terms of material preparation, of ease of application and of efficacy in removing the unwanted layer.

3.1.4 Application of photothermal mats

Photothermal mats are preferable when the unwanted paint is highly insoluble, such as a cross-linked alkyd spray paint.

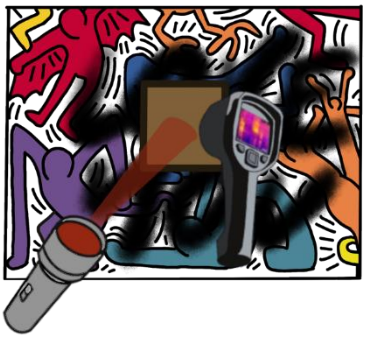

Figure 3.2. Schematic representation of the use of the photothermal mats PULL_SI.

Figure 3.2 reports a schematic representation of the use of the photothermal mats. The mat is irradiated with a red LED, and a thermal camera monitors the surface temperature.
For a correct application, follow these steps:

1. the fabric must be cut to the required size;

2. then, add solvent at a ratio of 2 μL/mg;
3. place the tissue on the area to be treated and irradiated with a red LED (660 nm) for 2 minutes and 30 seconds. The optimized temperature of 30 °C monitored with a thermal imaging camera on the irradiated surface of the tissue is sufficient. Therefore, adjust your lamp irradiance accordingly;
4. remove the unwanted varnish residues with dry cotton swabs.

Please note: the materials are prototypes and have been tested only on a lab scale (cleaned areas of 0.5 cm^2); therefore, conditions and parameters may need to be adjusted for applications on a larger scale.

3.1.5 Reusability

The materials can be reused up to 3 times. It was observed that although the microstructure and the photothermal properties are retained for up to 10 uses, a partial loss of cohesion of the fibers was observed after the third use. Additionally, if a high boiling point solvent is selected, the mat should be completely dry before reusing. Complete drying can be obtained by placing the mat in a vacuumed desiccator for 3 hours or in air overnight. Heating is advised against as it could damage the mat.

3.1.6 The restorers' feedback

During the workshop organized by the project at the Venaria in Turin, a demonstration was given of the use of the photothermal mats. During the demonstration, both the setup and the cleaning process were demonstrated. The latter was carried out on a model sample consisting of a layer of blue cross-linked alkyd varnish to be removed from a layer of yellow acrylic varnish. A questionnaire was submitted at the end of the demonstration; 88% of the participants stated that it will be useful to produce these mats at a larger scale to be used in practice.

3.2 Laser cleaning method: set-up and optimization of cleaning procedures

The sequence of operations for an effective and surface-respectful laser cleaning varies depending on the specific case. Each intervention must be tailored to the conditions of the object and to the materials to be removed or preserved.

The following recommendations specifically apply to Q-Switch (QS) and Long Q-Switch (LQS) laser cleaning of murals made with synthetic paints.

The laser-material interaction depends on the chemical and chromatic properties of the materials. In the case of painted surfaces, the effectiveness and impact of the laser vary according to the binder type, as well as the nature and color of the pigments.

For this reason, a preliminary study of the surfaces to be treated is essential. This can be carried out through visual examination or microscopy to detect any heterogeneities (Figure 3.3) and understand the stratigraphy of the painting. If necessary, visual observations can be complemented by chemical analyses to identify the materials to be removed and those to be preserved.

Given the variability of materials, optimizing laser parameters is crucial to ensure a safe and effective intervention. The preparation and use of mock-ups is a valuable approach to determine the optimal laser settings or, at the very least, to exclude the most hazardous operating conditions before proceeding with the actual artwork treatment.

When planning laser cleaning, the following aspects, emerged as a result of the experiments carried out during the project, should be considered:

- the overall results of cleaning strongly depend on the type of binder;
- the aging of the paint film does not significantly influence the effectiveness of laser cleaning;
- the laser can remove the unwanted paint but also erode the most superficial part of the original layer, revealing a surface diminished in binder content but enriched in pigments and fillers; this potential erosion and loss of cohesion could necessitate additional maintenance measures;
- a protective coating forming a layer between the painted surface and the unwanted material to be removed facilitates laser cleaning and improves its effectiveness.

Keep two out of three parameters fixed: wavelength = 1064 nm, frequency = 5 Hz [15]. Increase the

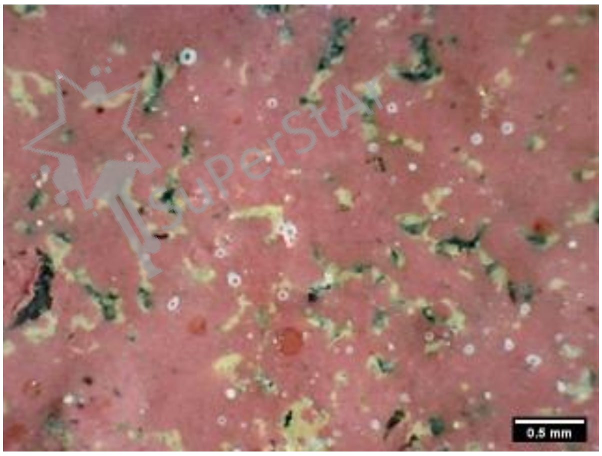

Figure 3.3. Detail of a mural made by layers of overlapping spray paints.

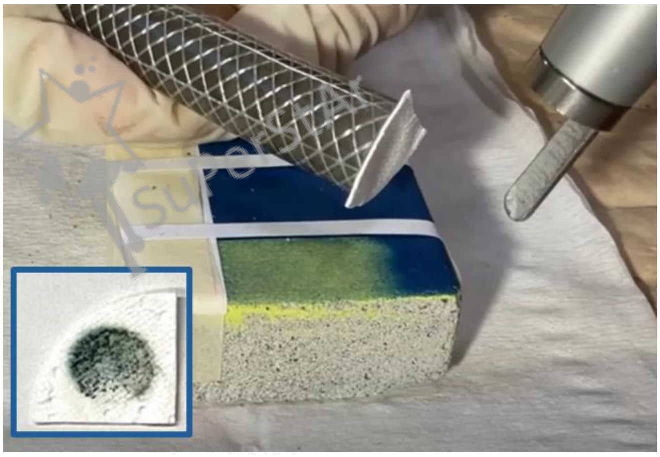

Figure 3.4 Sampling of the ablated material using a micro-aspirator and a quartz fiber membrane.

laser fluence[16] gradually, while observing the cleaning effect.

Under the same laser fluence, dark colored surfaces absorb more laser energy and are consistently better cleaned than light colored surfaces. To better preserve the underlying paint layers and completely remove overlapping materials, especially if dark, it is preferable to repeat two or more cleaning cycles rather than increasing the laser fluence.

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[15] Bertasa, M.; Ricci, C.; Scarcella, A.; Zenucchini, F.; Pellis, G.; Croveri, P.; Scalarone, D. Overcoming Challenges in Street Art Murals Conservation: A Comparative Study on Cleaning Approach and Methodology. *Coatings* 2020, 10, 1019. https://doi.org/10.3390/coatings10111019.

[16] Laser fluence or laser density is the energy delivered per unit area which can be obtained by dividing the energy per pulse by the spot size.

3.2.2 Empirical evaluation of laser-cleaned surfaces

The method is based on five critical parameters and is used to assess the efficacy and selectivity of the laser cleaning process (Figure 3.5). Each parameter is assessed by the same researcher. The researcher assigns a score ranging from 1 to 9 for each parameter; a higher score indicates a better performance.

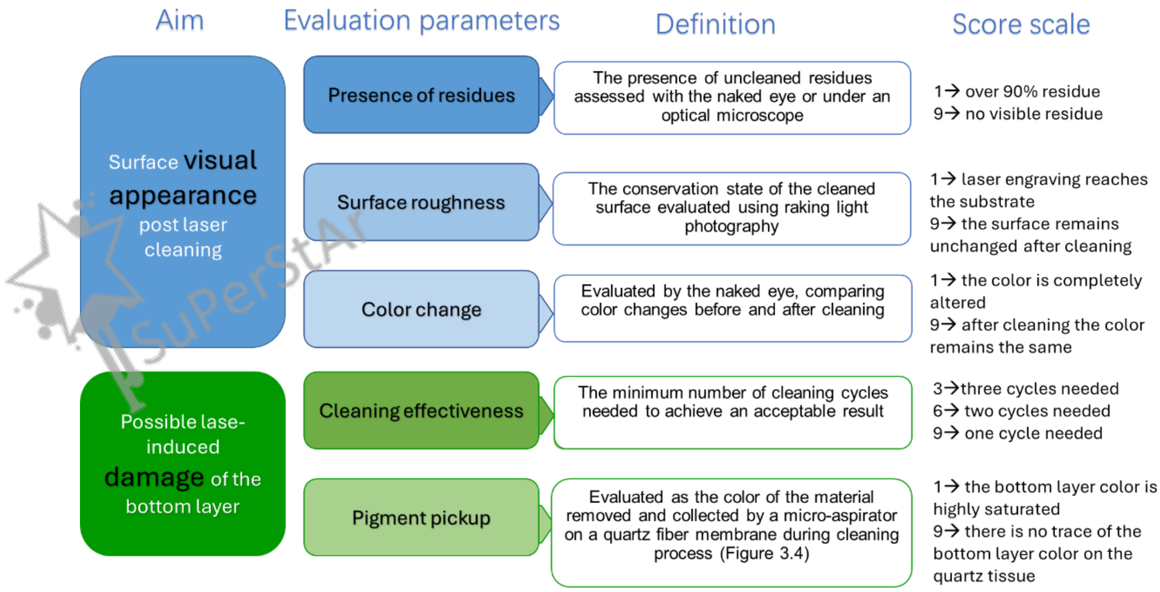

Figure 3.5. Summary diagram of the empirical evaluation methodology of laser-cleaned surfaces.

3.2.3 Analytical evaluation of laser-cleaned surfaces[17]

An objective and more detailed numerical evaluation of the effectiveness of cleaning is obtained as described in Figure 3.6.

[17] Zhang, Y.; Zenucchini, F.; Ricci, C.; Croveri, P.; Scalarone, D. Analytical Evaluation of Laser Cleaning Effectiveness in the Context of Contemporary Muralism. *Applied Science* 2024, 14, 4799. https://doi.org/10.3390/app14114799.

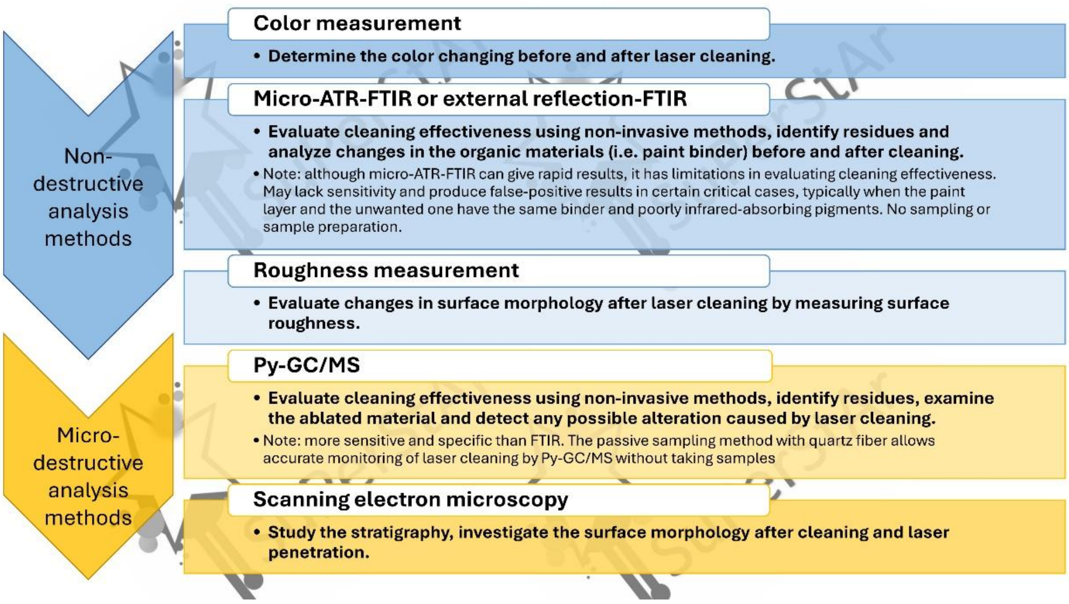

Figure 3.6. Summary diagram of the analytical evaluation methodology of laser-cleaned surfaces.

4. Guidelines for the *in lab and in situ* testing of protective treatments

4.1 Selection of the commercial protectives – criteria

In the context of restoration, four main classes of products—established and approved for use—are currently available on the market [18]:

- acrylic based coatings;
- silane and silicon based coatings;
- fluorinated and partially fluorinated coatings;
- wax based coatings.

These coatings are, in general, transferred to the conservation of contemporary muralism from other fields of application (stone materials, ceramics, anti-graffiti, etc.).

The experimental work carried out during the project allowed us to assess that the effectiveness and durability of the coatings depend on:

- the type and chemical nature of painting materials;
- the state of conservation of the painted surface;
- the application methodology (brush or spray, concentration, choice of solvents).

The adhesion between the protective coating and the paint layers is crucial. The exposure of the site to direct solar irradiation and rain runoff are the main deteriorating factors. The

[18] Pagnin, L., Guarnieri, N., Izzo, F. C., Goidanich, S., & Toniolo, L. (2023). Protecting Street Art from Outdoor Environmental Threats: What Are the Challenges?. Coatings, 13(12), 2044.

selection of the suitable coating can be done on the basis of preliminary testing onsite, according to the protocol presented in §4.3.

4.2 Application methodologies

In the framework of the Superstar research activities, a selection of commercial protective treatments has been applied according to the recommendation of the technical data sheet of the suppliers, whereas the amount and the dilution of the coating should be adapted to the situation of the surfaces. The experiment demonstrate that, low porosity, newly painted surfaces behave quite different from porous and aged substrates, and thick coating layers do not improve the effectiveness of the treatment, and that application by brush is highly recommended.

In Table 4.1 the recommended amount of product for each coating is indicated, as observed during experiments on laboratory mock-ups. Acrylic-based products are labelled as “A” and silane/fluoro-silane-based formulations are labelled as “S” and “SF”, respectively. The coatings were applied pure, except for A2 and S1, which require dilution. S1 coating was diluted at 10% in distilled water. Initially, half of the water was added to the product and stirred for 5–7 minutes. The remaining water was then added and mixed for an additional 2 minutes.A2, for example, required dilution in toluene or acetone, however these solvents cause also the dissolution of acrylic paint. For this reason, the solubility triangle approach was considered to prepare the correct dilution. After several tests on acrylic paint specimens, the A2 coating was diluted initially at 30% in ethyl acetate to ensure the complete dissolution of the coating and furtherly diluted to a final 15% in isopropanol, to lower the polarity factor and avoid the solubilization of the acrylic paint during treatment. On the treated surface, the calculated amount of coating (Table 4.1) was applied using a pipette and then spread with a soft bristle brush (20 mm).

Table 4.1. Application modality and amount of products used for the protective treatments on laboratory mock-ups.

Coating	**Application modalities**	**Recommended amount of product per surface unit (L/m^2)**	**Amount of product on mock-ups, after curing (g)**
A1	Pure	0.10–0.15	0.34 ± 0.03
A2	30% in ethyl acetate or 15% in isopropanol	0.1–0.3	0.14 ± 0.02
S1	10% in distilled water	0.1–0.2	0.15 ± 0.05
S2	Pure	0.4	0.30 ± 0.05
SF3	Pure	0.1–0.2	0.15 ± 0.05

4.3 Protective treatments: in lab and in situ testing protocol[19]

4.3.1 Laboratory testing protocol

The testing protocol applied in the framework of the project is directly derived by the standard EN protocol for the control of protective treatments on stone materials. The protocol and each testing method have been adapted to the measurement of painted surfaces (Table 4.2).

In this regard, the study of the morphology of the surface, both painting and protective film, is crucial, because it can reveal the roughness, the adhesion and defects of the two layers, and the physical-mechanical damage after ageing. Both optical and scanning electron microscopy, working at different scales, can provide information on the coating ability and stability after ageing. For what concerns roughness, the optical measurements are possible only on opaque painting films.

The aesthetic compatibility is assessed through VIS reflectance spectroscopy measuring the color coordinates of the surfaces, before and after treatment. These measurements are carried out according to the EN protocols, indicated in Table 4.2.

The compatibility evaluation includes to determine the change in the color coordinates of the surface, in order to detect changes in the perception of the painting surface, that can be due to the application of protective coatings and to the ageing process; therefore, it is important to state if such changes are due to the treatment application, or to undesired process that affect the painting layers. The coating can also change the gloss of the paint surfaces. Measurements before and after treatments, and after ageing are thus necessary to evaluate any possible changes affecting aesthetic appearance.

Table 4.2. List of laboratory testing methods selected for the characterization and monitoring protocol before and after the application of the protective treatments.

Testing methods	Reference standard protocol	Aim of the tests
Optical Microscopy (OM)	n.a.	Surface morphological studies
Scanning Electron Microscopy (SEM)	n.a.	Surface morphological studies
Laser optic profilometry	n.a.	Surface morphological studies
Vis-Reflectance spectroscopy	EN 15886:2000	Color stability evaluation
Glossmetry	EN 2813:2016	Gloss surface characterization
Contact angle measurements	EN 15802:2009	Surface contact angle evaluation
Water absorption by capillarity	UNI 10859:2000	Evaluation of absorption dynamic of liquid water by capillarity

[19] L. Pagnin, S. Goidanich, F.C. Izzo, Y. Zhang, D. Scalarone, L. Toniolo, Compatibility and Efficacy Evaluations of Organic Protective Coatings for Contemporary Muralism. *Coatings,* 15 (2025) 166. https://doi.org/10.3390/coatings15020166.

ATR-FTIR spectroscopy	n.a.	Surface molecular characterization and stability

Since the ability of coatings to protect the paintings is essentially due to the ability to avoid or reduce the contact of the painting film with liquid water (rain and surface humidity condensation), the study of the behavior of treatments towards liquid water is the most important part of the testing protocol. In this respect, in laboratory conditions, the measurements of the static contact angle before and after treatments allow to assess the changes of surface wettability (Figure 4.1). They are carried out according to the EN protocols indicated in Table 4.2.

The evaluation of water absorption by capillarity test allows us to study the behavior of the surface towards the prolonged contact with liquid water. Effect of water contact and capillary rise phenomena are already changed and reduced by the application of a paint layer on the surface; nevertheless, the conservation and long-term stability of the paint layers depend on the possibility to further limit contact with water, and in particular its absorption into the porous microstructure of the substrate.

Finally, the evaluation of the chemical stability of the materials (the protective coatings) is assessed by diamond ATR-FTIR spectroscopy directly on the paint models, before and after the different artificial ageing procedures.

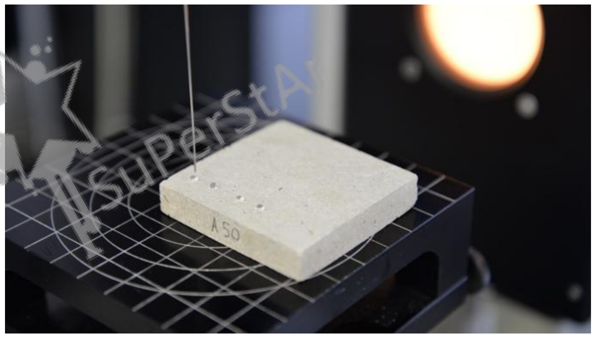

Figure 4.1. Contact angle measurements on mock-ups with benchtop equipment.

4.3.2 In situ testing protocol

The testing protocol set-up and optimized for the evaluation and effectiveness of protective treatments on outdoor surfaces, in situ, is reported in Table 4.3. Sample areas of about 10x10 cm size are selected for the application of protective treatments, paying attention to the homogeneity of the surface; one reference area is kept untreated for comparison. The application of protectives should be carried out in the same condition adopted for the in lab experimental work (solvents and concentration as recommended by the technical datasheet). Also in this respect, the testing methods were derived by the standard EN protocol for the control of protective treatments on stone materials and were adapted to the assessment of painted surfaces. The testing protocol is summarized in Table 4.3.

The morphological study of the surface is carried out using a digital microscope, and therefore, only a limited magnification is available (depending on the type and quality of the digital microscope); it is not possible, in a completely non-invasive way, to investigate the morphology of the paint layer before and after the treatment application. A complete assessment highlights specific defects, cracks, and distribution of the product.
The assessment of the aesthetic compatibility by VIS reflectance spectroscopy and glossmetry is carried out in the same conditions and with the same approach used in laboratory, according to the standard EN protocols.

Table 4.3. List of testing methods selected for the characterization and monitoring protocol before and after the application of the protective treatments on real case studies (*In situ* testing protocol).

Testing methods	Reference standard protocol	Aim of the tests
Digital portable microscopy	n.a.	Surface morphological studies at low magnification
Vis-Reflectance spectroscopy	EN 15886:2000	Color stability evaluation
Glossmetry	EN 2813:2016	Gloss surface characterization
Contact angle measurements	EN 15802:2009	Surface contact angle evaluation by portable instrument
Water absorption by contact sponge method	UNI 11432:2011 EN 17655:2022	Evaluation of amount of liquid water absorbed by capillarity on vertical surface

The data on the surface wettability are obtained with a portable instrument on a vertical surface, operating in different conditions from those usually applied for performing the measurements with the laboratory equipment. The laboratory protocol is therefore adapted to the instrument and equipment to be used *in situ*. The number of measuring points for each testing area is limited, essentially due to the surface inhomogeneity and defects. From recent experimental work, it was demonstrated that the obtained average values are reliable and can be compared with those obtained in lab conditions.
Water capillary absorption is measured using the contact sponge method, without causing any damage to the surface. This method, developed and set-up for stone materials, has been transferred to painted surfaces. In this case, the amount of absorbed water is rather low and, sometimes, below the detection limit of the portable balance that can be used *in situ*. Indeed, the difference in absorbed water between the treated and untreated surface is quite low, as we were only able to evaluate it on laboratory mock-ups with 4 digit laboratory balance.

4.3.3 Durability of protective treatments: in lab artificial ageing procedures

Artificial ageing procedures were set-up in the framework of the Superstar project for laboratory conditions. Two different ageing conditions were selected: rain and solar irradiation.

Rain ageing was performed using a prototype rain chamber (Figure 4.2), developed and set-up in the Laboratory MaMeCH at Politecnico di Milano[20].


Figure 4.2. Prototype of the rain chamber.

The rain ageing conditions should be adapted to simulate the appropriate rain regime. It is possible to simulate approximately 10 years of rain, alternating wet and dry periods, in about 15-30 days of accelerated artificial ageing. The quality of rain depends on the water conductivity and pH. For example, in the framework of the project, the test was conducted for a total of 15 days, with 7 hours of raining time per day: 1 hour of soft rain (~30 mm/h) followed by 6 hours of heavy rain (~80 mm/h); then, 17 hours of drying at room temperature. At the end of each ageing day, the samples were rotated by 90° and their positions along the Y-axis of the sample platform were shifted. Rain consisted of demineralized water (average pH 6.2 value, and conductivity of 1.45 μS/cm). The experiment run for a total time of 105 h, with a total rainfall of 7320 mm, corresponding to about 10 years of outdoor exposure in Central-Southern Europe. Solar irradiation was carried out in a solar box equipment Q-Sun Xe-3 test chamber (Q-Lab) equipped with 3 Xenon lamps for a total exposure time of 1440 h (60 days), moving mock-ups each week in the four quarters of the samples tray to avoid possible irradiation differences. Ageing followed a day cycle divided into two phases: 20 h of irradiation (68 W/m^2), 50 °C air temperature, and 40% relative humidity, followed by 4 h of dark, at 35 °C and 80% relative humidity. The ageing progress was monitored by lab testing protocol after 720 h and 1440 h.

[20] Roveri M, Goidanich S, Toniolo L. Artificial ageing of photocatalytic nanocomposites for the protection of natural stones. Coatings 2020;10. https://doi.org/10.4067/S0718-07052019000200047

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