

Article

Analytical Evaluation of Laser Cleaning Effectiveness in the Context of Contemporary Muralism

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Abstract: Contemporary murals and street art play a critical role in urban culture, serving as platforms for social activism and reflecting the vibrancy of city life. This study within the SuperStaAr project framework examines the challenge of graffiti removal while safeguarding the original synthetic paint layers. Through a detailed investigation using Q-Switch and Long Q-Switch lasers (Nd:YAG), we evaluate the effectiveness and safety of laser cleaning techniques on both unaged and artificially aged mural mock-ups. The initial findings highlight the Q-Switch and Long Q-Switch lasers as promising for removing graffiti without compromising the paint integrity. Our assessment criteria—encompassing residue presence, surface roughness, color changes, cleaning effectiveness, and pigment pickup—were validated through empirical evaluation and supported by colorimetric, micro-ATR-FTIR, and Py-GC/MS analyses. Notably, the incorporation of a passive sampling system for Py-GC/MS analysis facilitates a deeper understanding of the ablated materials without direct sampling from the artwork. This research contributes a foundational framework for the evaluation of laser cleaning in mural conservation, emphasizing the importance of tailored strategies to enhance the sustainability of urban art conservation efforts.

Keywords: laser cleaning; street art; sustainable conservation; cultural heritage; acrylic paint; alkyd paint



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1. Introduction

The preservation of cultural heritage has undergone a significant transformation in recent decades, driven by innovative technologies that have overcome the limitations of traditional restoration methods. Among these advancements, the widespread adoption of laser cleaning technology has emerged as a transformative force, successfully applied to a remarkable array of historical treasures. Over the past two decades, laser cleaning has been widely employed to preserve diverse materials including stones, paintings, and archaeological finds such as metals, textiles, wood, glass, bones, and more [1–7]. Unlike conventional cleaning methods that often involve the use of solvents, which might be harmful to the environment and operators, laser ablation technology offers a sustainable alternative that overcomes the limitations of chemical processes. Given the immense challenges posed by global climate change, the development and promotion of this technology become crucial options for practical conservation work.

Laser ablation is a process that involves the precise removal of material from a surface by exposing it to an intense laser beam. The selectivity of laser ablation arises from the specific interaction between the laser irradiation and the material properties. Different materials absorb and respond to laser beams in unique ways, a phenomenon known as the ablation threshold [8]. Wavelength and pulse duration are the main distinguishing features of laser systems; in the practical working process, average power and frequency can be

adjusted, allowing for the fine-tuning of the interaction. Recent studies have demonstrated that the shape of the laser beam and the overlapping rate are crucial for achieving homogeneous ablation and avoiding the edge effect of laser pulses when scanning a surface [9]. The optimization of these parameters in addition to the choice of the instrument are the key points of laser application and have been extensively studied based on specific materials. For instance, the UV region laser irradiation is highly absorbed by most aged varnishes [10] and often used to remove or to thin down aged coatings, while IR region laser irradiation is commonly used to eliminate black crust caused by urban pollution, cleaning spray painting vandalism on stone surfaces [11–13], and in more recent times, organic materials [14,15].

In the field of cultural heritage conservation, one of the most diffused issues is the removal of unwanted graffiti from historical monuments and architectural structures. Graffiti vandalism on cultural monuments is causing significant problems both on surfaces' esthetical appearance and on historical material preservation. Recent studies have demonstrated the efficiency, safety, and feasibility of laser cleaning instruments, either used independently or in combination with chemical methods, even for on-site work [12,16–18].

Unwanted graffiti also threatens another integral part of our cultural heritage—contemporary muralism. Despite the initial controversy, street art and murals are often considered decorative and didactic elements that reflect and express topics of social concern, deeply integrated into the social life of citizens and local communities. In addition to spontaneous creations, many large-scale urban murals are being executed under the commission of local institutional projects. They are usually created within frameworks of festivals and the regeneration of degraded urban areas, satisfying the needs of communities and attracting tourism interests [19]. Today, there are numerous urban murals that are beginning to receive attention from the heritage safeguarding bodies and local authorities who are in charge of the management of urban decorum, creativity, and culture [20,21]. However, the degradation phenomenon of outdoor paints is particularly severe since they are constantly exposed directly to various degradation factors, including human vandalism, sunlight, rain, and urban pollution.

The conservation of contemporary murals remains a relatively new and evolving topic. While some progress has been made in recent years, there is still not a standard protocol or shared guidelines for the general approach to the conservation and maintenance of these artworks. A significant challenge lies in cleaning unwanted graffiti without compromising the integrity of the original paint layer. Equally significant is the need to define widely useful criteria for proper methodologies and scientific evaluation. As mentioned previously, the efficacy of laser irradiation relies on the different ablation thresholds of the materials. However, graffiti itself is often created by materials similar to those used to make the mural, reducing the laser ablation threshold and creating a complex interplay of materials. Murals and graffiti are typically made with commercially available spray cans, rollers, or brushes, and they often employ synthetic paints primarily composed of alkyd, acrylic, styrene resins, or various combinations thereof [21–25]. This complexity adds layers of difficulty to optimizing laser operating parameters and establishing the criteria for evaluating effectiveness.

In this study, we explore and present a pilot protocol specially designed to evaluate the effectiveness and safety of laser cleaning on contemporary murals. The protocol provides for the empirical evaluation of some specific criteria and their validation through a set of instrumental chemical analyses, intrinsically non-invasive or involving passive sampling. We employed two types of lasers, Q-Switch (QS) and Long Q-Switch (LQS), to target both fresh and artificially aged mock-ups, reflecting the diverse conditions that urban art encounters over time. Three types of paints were carefully selected from commercially available products: acrylic spray, alkyd spray, and acrylic-styrene water-based paint applied by brush. Additionally, to facilitate the clear observation of cleaning results, we selected three contrasting paint colors, namely yellow, blue, and fluorescent blue.

In particular, we created 13 different combinations of paints to simulate hypothetical vandalism. We established five criteria that can be applied in real time to evaluate the

effectiveness and safety of this cleaning methodology by constructing radar diagrams, representing empirical evaluations of significant parameters for cleaning monitoring. In a subsequent phase, these parameters were analytically assessed using specific techniques, including Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), optical microscopy, colorimetric measurements, and Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS). These instrumental responses enabled us to validate or reject the initial empirical evaluations.

In particular, for the latter analysis, we adopted an inert and thermally stable material, a quartz tissue, to sample the laser-ablated material during the cleaning process. This sampling method provides the possibility for the rigorous analysis of the laser-ablated material by Py-GC/MS, which is crucial for evaluating possible thermal damage to the original paint layer without having to take another sample from the clean surface. We believe this method can be adopted in a broader range of scientific activities involving laser ablation technology.

This study contributes to advancing the conservation of contemporary murals and street art by offering a simple, scientifically backed protocol for laser cleaning evaluation. By bridging the gap between empirical assessment and analytical techniques, we aim to provide conservators and cultural heritage experts with a reliable tool to ensure the preservation of these vibrant expressions of our modern culture. Furthermore, as laser technology continues to evolve, its applications in cultural heritage conservation are expected to expand, offering new avenues for safeguarding the art that enriches our urban landscapes.

2. Materials and Methods

2.1. Materials

2.1.1. Sample Preparation

The mock-ups were prepared by applying a layer of spray or brush paint on cement mortar, as often found in murals and street artworks. Subsequently, a second layer of paint was applied by spray to simulate an act of vandalism (Figure 1a).

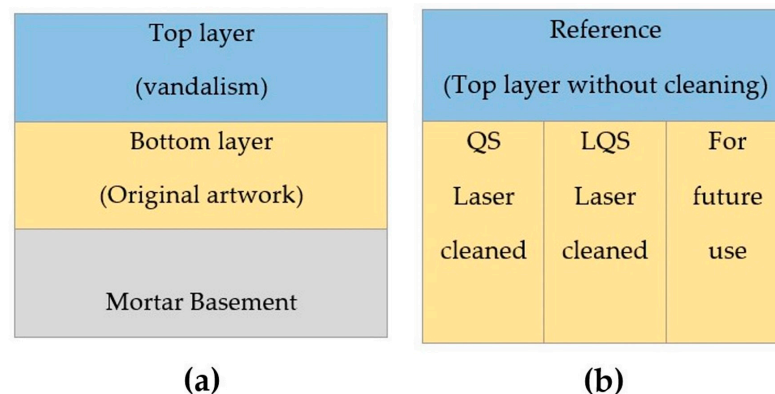


Figure 1. (a) Stratigraphy of mock-ups; (b) three cleaning sections of each sample.

The mortar specimens were prepared following this recipe: 2.5 parts (in volume) of mixed sand, composed of 2 parts of natural fine sand (Sabbia AXTON fine naturale di fiume) and 1 part of coarse sand (Sabbia AXTON vagliata); 1 part of cement (i.work TECNOCEM A-LL 32,5 R); and 0.65 to 1 parts of water.

The cement used was Portland limestone cement type II, known for its high early strength. It meets the requirements specified in EN standard 197-1 and contains 80–94% clinker excluding calcium sulfate and additives, with the remaining fraction consisting of limestone ($\text{TOC} \leq 0.20\%$, mass (LL)) and possibly other minor constituents.

Variations in water volume occurred due to the varying humidity of the sand and environmental conditions. During the preparation process, we adjusted the water content to achieve a consistent mortar consistency. Silicone molds were used to ensure uniform

size and shape ($5 \times 5 \times 2$ cm). After preparation, the cement samples were air-dried for approximately one month and then polished with 180-grit sandpaper to remove the shiny effect from the front surface and even out the backside.

For the painting materials used in this study, three types of spray products were selected, each characterized by a specific binder: an alkyd resin for Montana 94, an acrylic resin for Flame Orange and for the fluorescent colors, Urban Fine-Art Neon, and a styrene-acrylic resin for Alpha Acrilmat. Products containing secondary binders were excluded in order to better correlate the action of the laser to the type of binder. Additionally, a styrene-acrylic water-based paint by Sikkens was chosen as representative of the paints applied by brush or roller. Table 1 provides a complete list of the products used for preparing the reference models.

Table 1. List of the materials used for mock-up preparation.

Materials	Manufacturer	Product	Color	Ref. Code
Cement mortar	Italcementi	i.work TECNOCEM A-LL 32,5 R—type II limestone Portland cement	-	-
		Fine natural river sand (Granulometry: 0–1 mm)	-	-
	Axton	Coarse sand	-	-
Spray paint	Molotow	Flame Orange	FO-102 Zinc Yellow	558.002
	Montana Colors	Montana 94	FO-514 True Blue	558.059
			RV 1021 Light Yellow	EX0141021M
			RV 154 Tornado Blue	EX019W0154M
Paint (brush, roll)	Molotow	Urban Fine-Art Neon	404 Neon Blue Fluorescent	337.304
	Sikkens	Alpha Acrilmat	G3.46.83 Yellow	-

In total, 26 mock-ups were prepared, consisting of two sets of 13 samples. One set of specimens was used as it was, after at least one month of preparation. The second set was artificially aged for 1500 h under artificial solar light.

According to the spray producer, the paint required a total drying time of 2–72 h. For the 13 unaged samples, to ensure consistent results, the second paint layer was applied at least 72 h after the application of the first layer. The cleaning procedure was conducted 72 h after the application of the second layer. For the aged sample set, after applying the bottom layer, the samples were aged for 1500 h in a Q-Sun Xe-1 Xenon Test Chamber (Q-Lab Corporation, Westlake, OH, USA) at a constant temperature of 50 °C. The irradiance was set at 0.68 W/m² at 340 nm, using the Daylight Q filter with a cut-on at 295 nm, simulating exposure to direct sunlight. Following the aging process, a second paint layer was applied, and cleaning was performed after 72 h.

The nomenclature of the mock-ups is based on their binder type, color, and stratigraphy, as listed in Table 2. Based on the authors' observation of the materials most used in murals and graffiti vandalism in Italy, the brush-applied yellow paint (StyY) was only used for the bottom layer, while the fluorescent blue paint (AcrFB) was only applied for the top layer.

Table 2. Nomination list of samples.

Mock-Up Name	Bottom Layer			Top Layer		
	Product	Color	Main Binder	Product	Color	Binder
AlkY–AlkB	Montana 94	Yellow	Alkyd	Montana 94	Blue	Alkyd
AlkY–AcrB	Montana 94	Yellow	Alkyd	Flame Orange	Blue	Acrylic
AlkY–AcrFB	Montana 94	Yellow	Alkyd	Urban Fine-Art Neon	Blue Fluorescent	Acrylic
AlkB–AlkY	Montana 94	Blue	Alkyd	Montana 94	Yellow	Alkyd
AlkB–AcrY	Montana 94	Blue	Alkyd	Flame Orange	Yellow	Acrylic

Table 2. Cont.

Mock-Up Name	Bottom Layer			Top Layer		
	Product	Color	Main Binder	Product	Color	Binder
AcrY-AlkB	Flame Orange	Yellow	Acrylic	Montana 94	Blue	Alkyd
AcrY-AcrB	Flame Orange	Yellow	Acrylic	Flame Orange	Blue	Acrylic
AcrY-AcrFB	Flame Orange	Yellow	Acrylic	Urban Fine-Art Neon	Blue Fluorescent	Acrylic
AcrB-AlkY	Flame Orange	Blue	Acrylic	Montana 94	Yellow	Alkyd
AcrB-AcrY	Flame Orange	Blue	Acrylic	Flame Orange	Yellow	Acrylic
StyY-AlkB	Alpha Acrilmat	Yellow	Styrene Acrylic	Montana 94	Blue	Alkyd
StyY-AcrB	Alpha Acrilmat	Yellow	Styrene Acrylic	Flame Orange	Blue	Acrylic
StyY-AcrFB	Alpha Acrilmat	Yellow	Styrene Acrylic	Urban Fine-Art Neon	Blue Fluorescent	Acrylic

2.1.2. Cleaning Instrument

We adopted two types of laser instruments, both produced by the El.En. Group (Firenze, Italy). The instrument features are presented in Table 3.

Table 3. Laser instrument features.

Laser Type	Q-Switch	Long Q-Switch
Model	Thunder Art	EOS 1000
System	Nd:YAG	Nd:YAG
Wavelength	1064 nm 532 nm 355 nm	1064 nm
Pulse duration	8 ns	100 ns–200 µs
Frequency	1–20 Hz	1–10 Hz 15 Hz 20 Hz
Energy	0–900 mJ	130 mJ (1 pulse) 250 mJ (2 pulses) 380 mJ (3 pulses)
Spot size	4–10 mm	1–6 mm
Beam delivering	7-mirror articulated arm	Optic fiber

All the cleaning tests were conducted using some fixed parameters for a better comparison; these are wavelengths of 1064 nm and a frequency of 5 Hz. Prior research [26] has demonstrated that an Nd:YAG laser system operating at 1064 nm can effectively thin overpainting layers composed of pigments and binders. The choice of a frequency of 5 Hz was based on prior experience [21].

Before starting the systematic cleaning process, the operational parameters were identified through a series of tests on two samples, AcrY-AlkB and AlkB-AcrY. The goal was to determine the ideal combination of energy and spot size for effectively removing this specific top layer. These two factors determine the energy delivered per unit area, known as laser fluence or laser density, which can be obtained by dividing the energy by the beam area. The laser fluence was gradually increased during the test while observing the cleaning effect visually. For the Q-Switch laser system, the laser articulated arm was coupled with a homogenizer hand peace, and the ideal fluence was obtained operating at 266 mJ and a spot size of 10 mm. Instead, the Long Q-Switch laser yielded good results operating at 130 mJ with a spot size of 4 mm. Subsequent tests were based on these parameters.

Additionally, as expected, we noticed that blue-colored surfaces generally absorb more laser energy than yellow ones. Consequently, under the same laser fluence, the blue surface is consistently better cleaned than the yellow one. To better preserve the bottom layer, cleaning of the yellow surfaces was conducted by repeating two or more cleaning cycles rather than increasing the laser fluence.

2.1.3. Cleaning Method

Each sample was divided into three sections (Figure 1b). The first section was cleaned using the Q-Switch laser, the second section was cleaned using the Long Q-Switch, and the last section was preserved for future use. Operational parameters are listed in Table 4.

The cleaning process was performed using the parameters presented in the table.

Laser pulse overlap (O) is calculated with the formula in [27]:

$$O = \left(1 - \frac{v_s}{d_f \times f_{REP}} \right) \times 100\%,$$

where v_s is the scanning velocity, d_f is the circular focus diameter, and f_{REP} is the repetition rate (frequency). For the QS laser instrument, the scanning velocity was estimated to be approximately 25 mm/s, and the pulse overlap on the surface was about 50%. Similarly, the scanning speed of the LQS laser was estimated to be around 10 mm/s, resulting in an overlap area of about 55%. It should be noted that the scanning speed is based on the experience of the laser operator and is not fixed, allowing for real-time adjustments to optimize cleaning results.

Initially, one cleaning cycle was conducted for each sample and, if necessary, the process was repeated up to a maximum of three cycles to achieve an acceptable result while avoiding severe damage to the bottom layers. After every cleaning cycle, the result was assessed using an optical microscope.

Table 4. Laser operational parameters.

Laser System	Q-Switch	Long Q-Switch
Frequency	5 Hz	5 Hz
Pulse duration	8 ns	100 ns
Energy setting	266 mJ	130 mJ
Spot size	10 mm	4.5 mm
Fluence	0.34 J/cm ²	1.17 J/cm ²

2.2. Instrumentation

2.2.1. Optical Microscope

All the samples were photographed under a stereoscopic optical microscope (Olympus, Tokyo, Japan) OLYMPUS SZ X10 interfaced with a digital camera OLYMPUS ColorView I. This focused on capturing the differences in appearance before and after cleaning. Additionally, a portable digital microscope Micriuvw (Italeco, Italy) with UV and white LED was used to assist in the cleaning process.

2.2.2. Micro-Attenuated Total Reflection-Fourier Transform Infrared (Micro-ATR-FTIR)

Micro-ATR-FTIR was used to analyze the paint material and cleaning efficiency in a non-invasive manner. For each cleaning test section, the spectra were collected before and after cleaning using a Perkin Elmer Spectrum Spotlight 300 FT-IR spectrometer (Waltham, MA, USA) equipped with a Germanium ATR crystal. All spectra were collected in the wavenumber range of 750–4000 cm^{−1}, with a resolution of 4 cm^{−1} and 16 scans per spectrum.

2.2.3. Raking Light Photography (RLP)

Raking Light Photography is a crucial yet straightforward technique for evaluating the topographic features of a surface and revealing surface irregularities and textures not visible under normal lighting conditions. In this technique, the sample surface is illuminated from one side in the visible spectrum at an oblique angle, enhancing the surface texture by contrasting illuminated and shadowed areas [28].

In this study, RLP observations were conducted during the laser cleaning process using a minimal instrument setup to streamline the evaluation process. The sample surface

was illuminated from the left side with two parallel LED halogen lights. The height of the LEDs was adjusted to be level with the sample, while the camera was positioned directly above the sample, perpendicular to the surface.

2.2.4. Colorimetric Measurement

To monitor the color changes after cleaning, colorimetric measurements were performed using a CM-700d Portable Spectrophotometer (Konica Minolta, Japan). In SCI (specular component included) mode, three points for each cleaning test section were measured and three measurements were automatically repeated for each point. The average value of color coordinates L^* , a^* , b^* was calculated, and the change in color (ΔE) was determined for each section by comparing the values of L^* , a^* , b^* obtained before and after cleaning.

Color in this context is typically described using the CIELAB color space, which is defined by the International Commission on Illumination (CIE). Component L^* represents the brightness or darkness of a color and ranges from 0 (black) to 100 (white). Component a^* measures the position of the color on the red–green axis; positive values represent redness, while negative values represent greenness. Component b^* measures the position of the color on the yellow–blue axis; positive values represent yellowness, while negative values represent blueness. The change in color ΔE quantifies the perceptual difference between two colors and was calculated using the following formula, known as the CIE76 formula:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}.$$

2.2.5. Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

During the cleaning, the ablated paint material was collected using a system that combined a micro-aspirator and quartz tissue CELSUS[®]. Under pyrolysis conditions, the quartz fabric is inert and does not release any organic contaminants. Therefore, Py-GC/MS analyses were performed directly on the fluffy tissue with ablated material trapped on it, and paint pyrolysis markers were detected and identified.

A micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab, Koriyama, Japan) coupled to a GC/MS system was used. Samples were placed into a stainless-steel cup inserted into the micro-furnace. The pyrolysis temperature was set at 500 °C for 12 s, the interface temperature was 320 °C, and the temperature of the GC injector was maintained at 250 °C. The GC was an 8860 GC System (Agilent Technologies, Sta. Clara, CA, USA) gas chromatograph with a methylphenyl-polysiloxane cross-linked 5% phenyl methyl silicone (30 m, 0.25 mm i.d., 0.25 µm film thickness) capillary column. Helium was used as the carrier gas (1.0 mL/min), and the split ratio was 1/20 of the total flow. The mass spectrometer coupled to the GC apparatus was a 5977B Mass Selective Detector (Agilent Technologies, Sta. Clara, CA, USA). The mass spectra were recorded under electron impact at 70 eV, and a scan range of 45–800 m/z. The following temperature program was used for the gas chromatographic separation: isotherm of 2 min at 50 °C and ramp of 10 °C/min up to 300 °C. All instruments were controlled by Agilent MassHunter Workstation (ver. 10.1.49) software. The mass spectra assignment was performed by mass library searches and by comparison with the literature data.

3. Results

3.1. Characterization of Painting Material

An initial material characterization was conducted using micro-ATR-FTIR analysis to confirm the chemical composition of the paints. The spectra are presented in Figure 2.

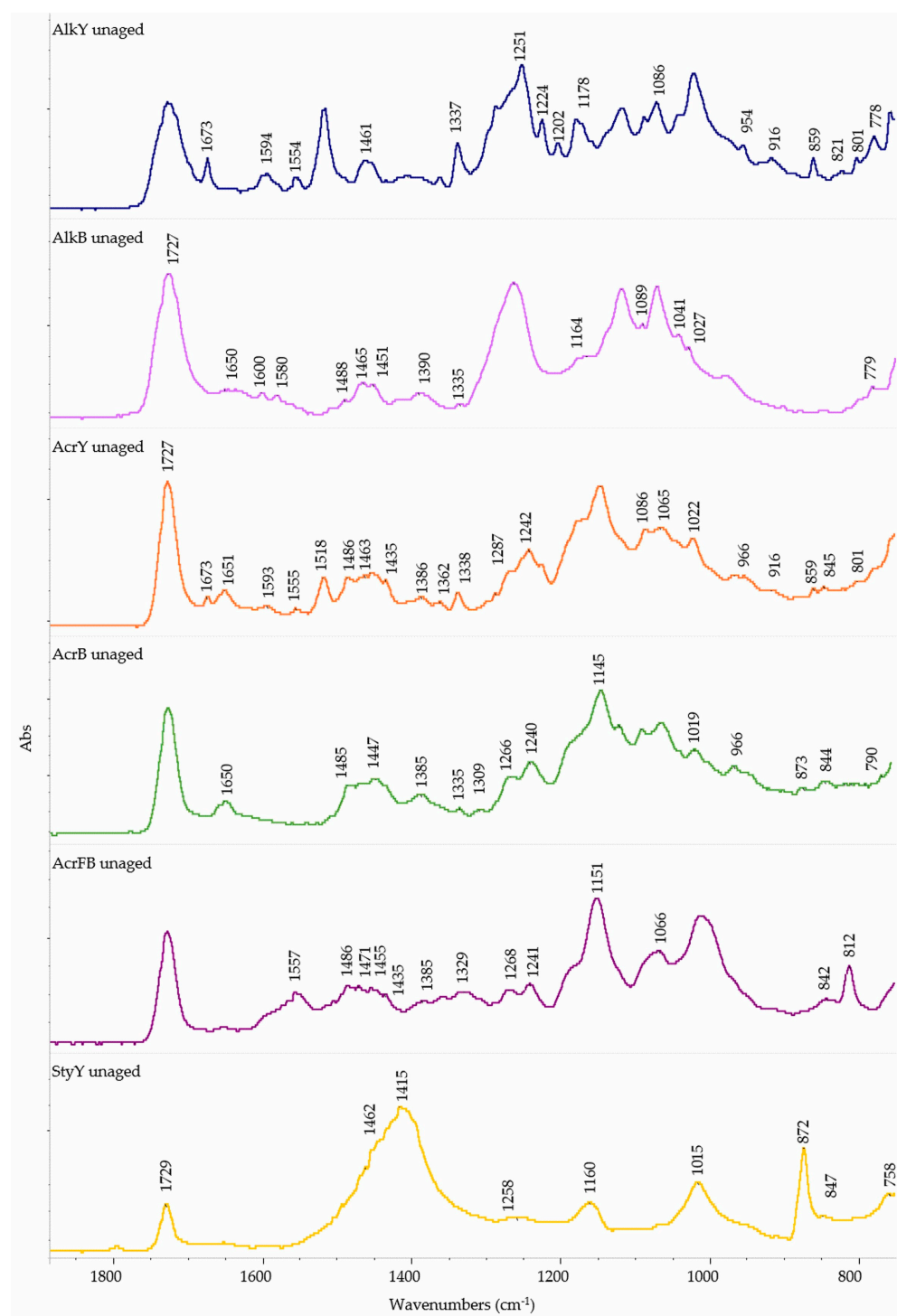


Figure 2. Micro-ATR-FTIR spectra of the paints used to prepare the mock-ups listed in Table 2.

Spectra of Montana 94 spray paints (AlkY and AlkB) showed typical absorption peaks of alkyd resins at approximately 1730 ($\nu(\text{C}=\text{O})$), 1600, 1580 and 1488 ($\nu(\text{C}=\text{C})$), 1250 ($\nu(\text{C}-\text{O})$ of COO ester groups), 1120, 1086 and 1040 cm^{-1} ($\nu(\text{C}-\text{O})$). Many absorption peaks of pigment PY74 were identified in AlkY (1673, 1594, 1554, 1516, 1461, 1337, 1224, 1202, 1178, 1086, 954, 916, 859, 801, 778 cm^{-1}) and a few peaks of pigment PB15 were identified in AlkB (1335, 1164, 1089 cm^{-1}) [29,30].

As expected, the Flame Orange paints (AcrY and AcrB) showed an acrylic binder, evident from peaks at 1727 ($\nu(\text{C}=\text{O})$), 1486 ($\delta(\text{CH}_2)$ of CH_2 groups), 1450 ($\delta_{\text{as}}(\text{CH}_2)$ of

CH₃ groups), 1239, 1143 and 1063 ($\nu(\text{C}-\text{O})$), 966 (ρCH_3), and 845 cm^{-1} (acrylate side chain vibration) [29]. The yellow spray showed peaks at 1674, 1518, 1463, 1335, 1225, 1086, 916, 859, and 801 cm^{-1} , indicating the presence of organic pigment PY74. In the blue spray AcrB, peaks at 1507, 1335, 1120, 1090, and 900 cm^{-1} were assigned to pigment PB15.

For the fluorescent blue spray (AcrFB), in addition to the typical peaks of the acrylic binder (1728, 1486, 1455, 1241, 1148, 1066, 842 cm^{-1}), the spectrum revealed the presence of another polymer, a poly(aryl sulfonamide), having characteristic peaks at 3367 and 3280 cm^{-1} for the N-H stretching, 1323 cm^{-1} for the antisymmetric vibrations of the sulphonyl group, and 1557 and 812 cm^{-1} for the vibrations of the aromatic rings [30]. This polymer serves as a carrier for the fluorescence pigment.

In Alpha Acrilmat paints (StyY), the styrene-acrylic binder was identified, with contributions from the acrylic component (1729, 1160, 760 cm^{-1}) and styrene (3061, 3028, 1601, 1584 cm^{-1}). No typical yellow pigments were identified, but peaks at 1015 cm^{-1} (talc absorption) and at 1048 and 872 cm^{-1} (related to calcium carbonate) indicated the presence of fillers in the paint.

3.2. Empirical Evaluation

During the cleaning process, five parameters were identified to evaluate the effectiveness and safety of laser cleaning on different samples, allowing the construction of radar charts for direct assessment [31]. Each criterion is assessed by the same author who prepared all the samples and assisted in the cleaning process. The author assigns a score ranging from 1 to 9 for each criterion; a higher score indicates better performance. The five parameters are as follows:

- Presence of residues, i.e., the presence of uncleaned residues assessed with the naked eye during the cleaning procedure and under an optical microscope;
- Roughness of the surface (topography integrity), i.e., the conservation state of the cleaned surface evaluated using grazing light photography;
- Color change, evaluated by the naked eye, comparing color changes before and after cleaning, and then further verified by colorimetric measurements;
- Cleaning effectiveness, i.e., the minimum cleaning cycles needed to achieve an acceptable result;
- Pigment pickup, assessed as the color of the bottom layer of paint absorbed onto the quartz fiber membrane during the cleaning process. This material is then analyzed by Py-GC/MS in a second stage.

The first three criteria aim to evaluate the aesthetic appearance of the mock-up after each cleaning process, while the last two are intended to identify whether the cleaning process causes severe damage to the bottom layer. The empirical evaluation scale is established as follows: For the presence of residue, scores range from nine, indicating no visible residue, to one, indicating over 90% residue. Surface roughness is scored from nine if the surface remains unchanged after cleaning to one if the engraving reaches the substrate (mortar basement). Color change is evaluated with a score of nine if the color remains the same after cleaning, and one if the color is completely altered. Cleaning effectiveness is based on the number of cycles required, with a score of nine for one cycle, six for two cycles, and three for three cycles. Pigment pickup is scored nine if there is no trace of the bottom layer color on the quartz tissue, and one if the bottom layer color is highly saturated. All the empirical scores are listed in Table 5.

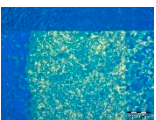
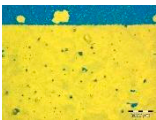
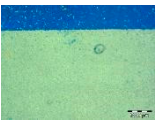
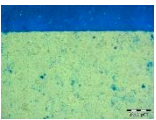
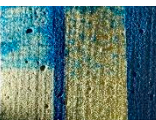
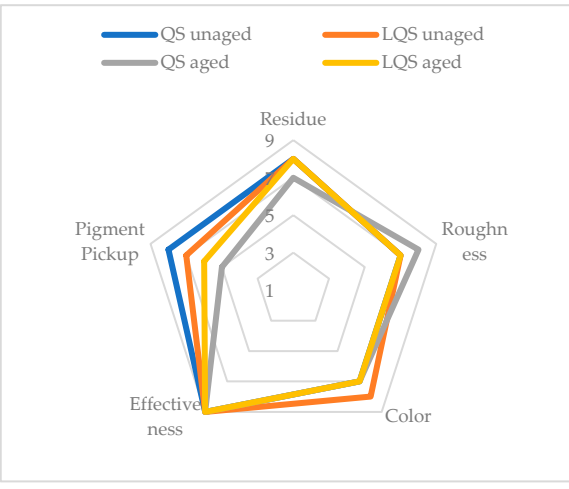
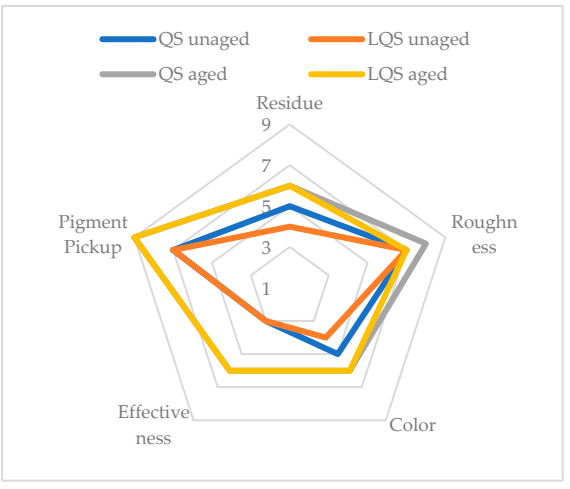
Table 5. Empirical evaluation of laser cleaning effectiveness.

Sample	Condition	Laser	Residue	Roughness	Color	Effectiveness	Pigment Pickup	Total
AlkY–AlkB	Unaged	QS	8	7	6	9	8	38
		LQS	6	6	6	9	7	34
	Aged	QS	8	8	5	6	6	33
		LQS	7	7	6	9	7	36
AlkY–AcrB	Unaged	QS	6	7	6	6	8	33
		LQS	6	6	6	6	7	31
	Aged	QS	7	8	5	6	7	33
		LQS	7	7	6	6	8	34
AlkY–AcrFB	Unaged	QS	6	7	7	9	6	35
		LQS	6	7	8	9	7	37
	Aged	QS	9	7	6	9	6	37
		LQS	8	6	7	9	7	37
AlkB–AlkY	Unaged	QS	6	6	7	6	5	30
		LQS	6	6	7	6	8	33
	Aged	QS	6	7	8	6	6	33
		LQS	5	5	6	6	7	29
AlkB–AcrY	Unaged	QS	7	7	7	6	6	33
		LQS	6	6	7	6	8	33
	Aged	QS	8	7	9	6	7	37
		LQS	6	6	7	6	8	33
AcrY–AcrB	Unaged	QS	7	6	6	9	9	37
		LQS	5	5	6	6	7	29
	Aged	QS	4	6	4	6	8	28
		LQS	5	5	5	6	7	28
AcrY–AlkB	Unaged	QS	8	7	6	9	7	37
		LQS	6	6	6	6	6	30
	Aged	QS	6	5	5	6	6	28
		LQS	6	6	6	9	7	34
AcrY–AcrFB	Unaged	QS	8	7	7	9	8	39
		LQS	8	7	8	9	7	39
	Aged	QS	7	8	7	9	5	36
		LQS	8	7	7	9	6	37
AcrB–AcrY	Unaged	QS	9	8	7	6	8	38
		LQS	7	7	7	6	6	33
	Aged	QS	8	8	7	6	6	35
		LQS	7	7	7	6	7	34
AcrB–AlkY	Unaged	QS	7	7	8	6	6	34
		LQS	7	7	7	9	7	37
	Aged	QS	6	8	8	6	6	34
		LQS	6	9	7	9	9	40
StyY–AcrB	Unaged	QS	5	7	5	3	7	27
		LQS	4	7	4	3	7	25
	Aged	QS	6	8	6	6	9	35
		LQS	6	7	6	6	9	34
StyY–AlkB	Unaged	QS	6	7	5	6	8	32
		LQS	4	7	3	3	8	25
	Aged	QS	7	8	6	6	9	36
		LQS	7	7	6	6	8	34
StyY–AcrFB	Unaged	QS	6	7	6	9	8	36
		LQS	5	6	5	6	9	31
	Aged	QS	7	8	6	9	8	38
		LQS	7	7	6	6	9	35

The total score was found to depend significantly on the binder type of the painting material. Samples containing a styrene-acrylic binder (StyY) generally received a lower overall valuation, while samples with a fluorescent blue layer (AcrFB) achieved higher total scores. The comparison between samples AcrY–AcrFB and StyY–AcrB, representing the highest and lowest global evaluations, respectively, is detailed in Table 6.

Table 6 shows that within the same sample, the radar charts for QS and LQS laser instruments showed similar cleaning effects under both fresh and aged conditions. For example, the chart for sample AcrY–AcrFB exhibited a balanced result, with high scores for all five criteria. In contrast, the shape of the chart for sample StyY–AcrB was flatter, indicating significantly lower scores for parameters such as “color”, “residue”, and “effectiveness”. Combining the results of all samples, as shown in the complete set of charts reported in the Supplementary Materials, it was observed that these are the three parameters that contributed the most to the evaluation of satisfaction with the cleaning process.

Table 6. Cleaning results of samples AcrY–AcrFB and StyY–AcrB.

Sample	AcrY–AcrFB			StyY–AcrB		
Instrument	QS	LQS	Raking Light	QS	LQS	Raking Light
Unaged						
Aged						
Radar chart						

3.3. Analytical Results

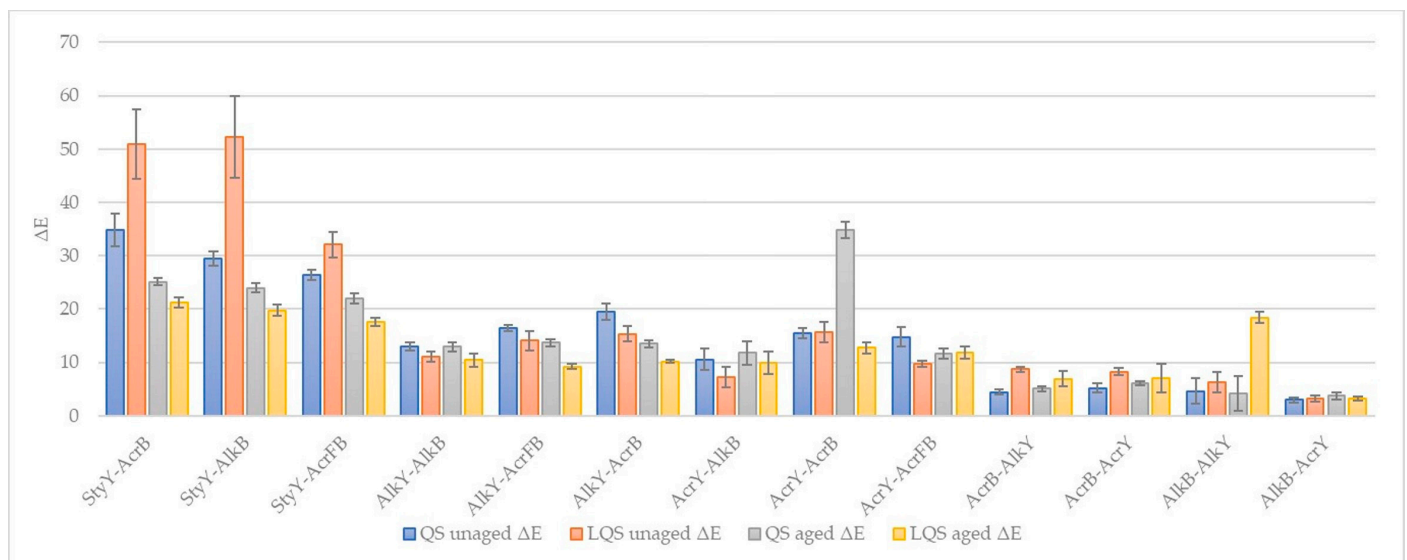
3.3.1. Color Change: Colorimetric Measurements

The colorimetric measurements substantiated our empirical evaluation, with the data reported in Table 7.

Figure 3 illustrates that samples containing a styrene-acrylic binder layer (StyY) exhibit higher ΔE values, indicating a substantial color difference between the bottom layer after cleaning and its original color. This observation corresponds to a poor cleaning result, leading to a higher number of cleaning cycles and lower scores for the “effectiveness” criterion. Conversely, samples using the blue spray as the bottom layer, such as AcrB–AlkY, AcrB–AcrY, AlkB–AlkY, and AlkB–AcrY, show satisfactory ΔE values.

Table 7. Average color change (ΔE) and standard deviation ($\sigma\Delta E$) of all samples after laser cleaning.

Condition	Unaged				Aged			
Laser	QS ΔE	QS $\sigma\Delta E$	LQS ΔE	LQS $\sigma\Delta E$	QS ΔE	QS $\sigma\Delta E$	LQS ΔE	LQS $\sigma\Delta E$
StyY–AcrB	34.85	3.09	50.90	6.56	25.17	0.74	21.19	0.97
StyY–AcrFB	26.39	1.33	32.10	7.67	22.02	0.82	19.80	1.07
StyY–AlkB	29.40	0.93	52.27	2.38	24.00	1.01	17.68	0.78
AlkY–AlkB	13.03	0.82	11.13	0.99	12.93	0.86	10.49	1.25
AlkY–AcrFB	16.48	0.62	14.09	1.84	13.73	0.66	9.24	0.48
AlkY–AcrB	19.52	1.50	15.40	1.52	13.51	0.72	10.20	0.28
AcrY–AlkB	10.60	2.06	7.29	1.92	11.83	2.19	9.95	2.17
AcrY–AcrB	15.52	0.94	15.77	1.90	24.64	1.53	12.77	1.05
AcrY–AcrFB	14.82	1.77	9.71	0.53	11.67	0.88	11.88	1.13
AcrB–AlkY	4.48	0.46	8.76	0.50	5.07	0.57	6.93	1.45
AcrB–AcrY	5.19	0.89	8.25	0.68	6.17	0.37	7.12	2.70
AlkB–AlkY	4.62	2.38	6.34	1.86	4.13	3.25	18.47	1.06
AlkB–AcrY	2.97	0.53	3.27	0.63	3.73	0.72	3.22	0.44

**Figure 3.** Color change (ΔE) of all samples after laser cleaning.

It is also worth noting that the error bars in Figure 3 are correlated with the “residue” criterion, where larger $\sigma\Delta E$ values suggest a greater color difference between different points measured within the same cleaning section. This aligns with our empirical evaluation: in samples containing StyY, not only is it difficult to reveal their original color, but they also exhibit an uneven surface with significant residue after multiple cleaning cycles.

3.3.2. Roughness: Raking Light Photography

Surface roughness evaluations were based on naked-eye observations and raking light photography, comparing surface roughness before and after laser cleaning. Caps of the spray cans often gave remarkably uneven paint films, characterized by small bubbles or local agglomerations. The roughness of the original surface is primarily influenced by the evenness of the paint film. Therefore, we assessed this parameter within the same sample instead of making comparisons among different samples.

Table 8 displays grazing light photos of sample AcrY–AcrB and their evaluation scores. It is evident that under both unaged and aged conditions, the surface treated with the LQS laser instrument appeared more engraved compared to the surface treated with the QS laser. Consequently, higher roughness indicates potential damage to the bottom layer (in

the case of unaged LQS) or poor cleaning with a large amount of top layer residue (in the case of aged LQS).

Table 8. Raking light photography of sample AcrY–AcrB with roughness evaluation score.

Condition	Unaged		Aged	
AcrY–AcrB				
Laser type	QS	LQS	QS	LQS
Score	6	5	6	5

3.3.3. Residues and Effectiveness: ATR–FTIR and Py–GC/MS

We employed micro–ATR–FTIR and Py–GC/MS analyses to evaluate residues and cleaning effectiveness, utilizing non-invasive methods. Micro–ATR–FTIR analyses were carried out directly on the uncleaned and cleaned areas without sampling or sample preparation, while Py–GC/MS analysis involved sampling with the quartz tissue (Figure 4).

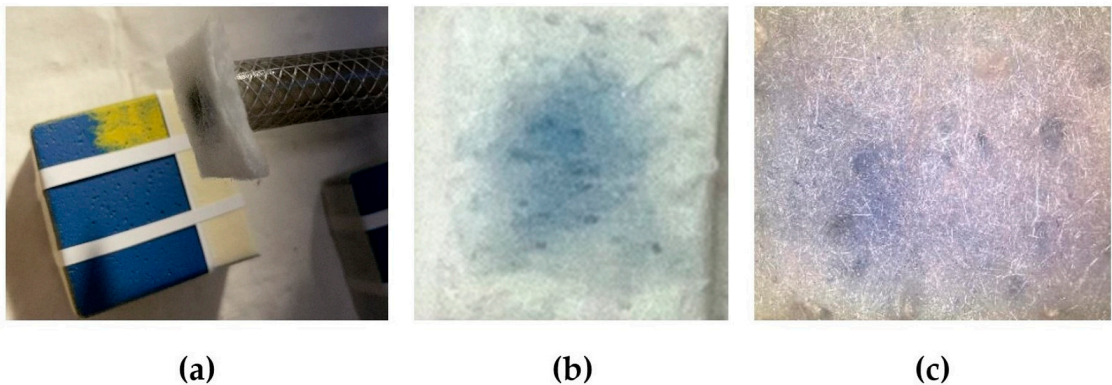


Figure 4. (a) Quartz tissue combined with a micro aspirator during the cleaning process; (b) photo of quartz tissue after the cleaning process; (c) quartz tissue under microscope.

Micro–ATR–FTIR yielded rapid and indicative results, generally aligning with our empirical evaluation. Figure 5a shows the spectrum of sample AcrB–AcrY cleaned with the QS laser under unaged conditions, along with two reference spectra of AcrB and AcrY. The spectrum after the cleaning process closely resembled that of AcrB, indicating the presence of the blue pigment at 1508, 1120, 1090, and 900 cm^{−1}, with no significant peaks suggesting the presence of yellow pigment.

Py–GC/MS analysis also indicated a satisfactory cleaning effect. Figure 5b shows the chromatogram of the same sample, revealing three principal components: peaks 1 and 2 correspond to MMA (methyl methacrylate) and nBMA (butyl methacrylate), respectively, associated with the acrylic binder, while peak 3 is 1,2-benzenedicarbonitrile, a marker of phthalocyanines used as blue pigments [32,33]. This result indicates that no residue remains on the cleaned surface, in line with our empirical evaluation, where this cleaning case received the highest score (nine) for the “residue” parameter among all samples.

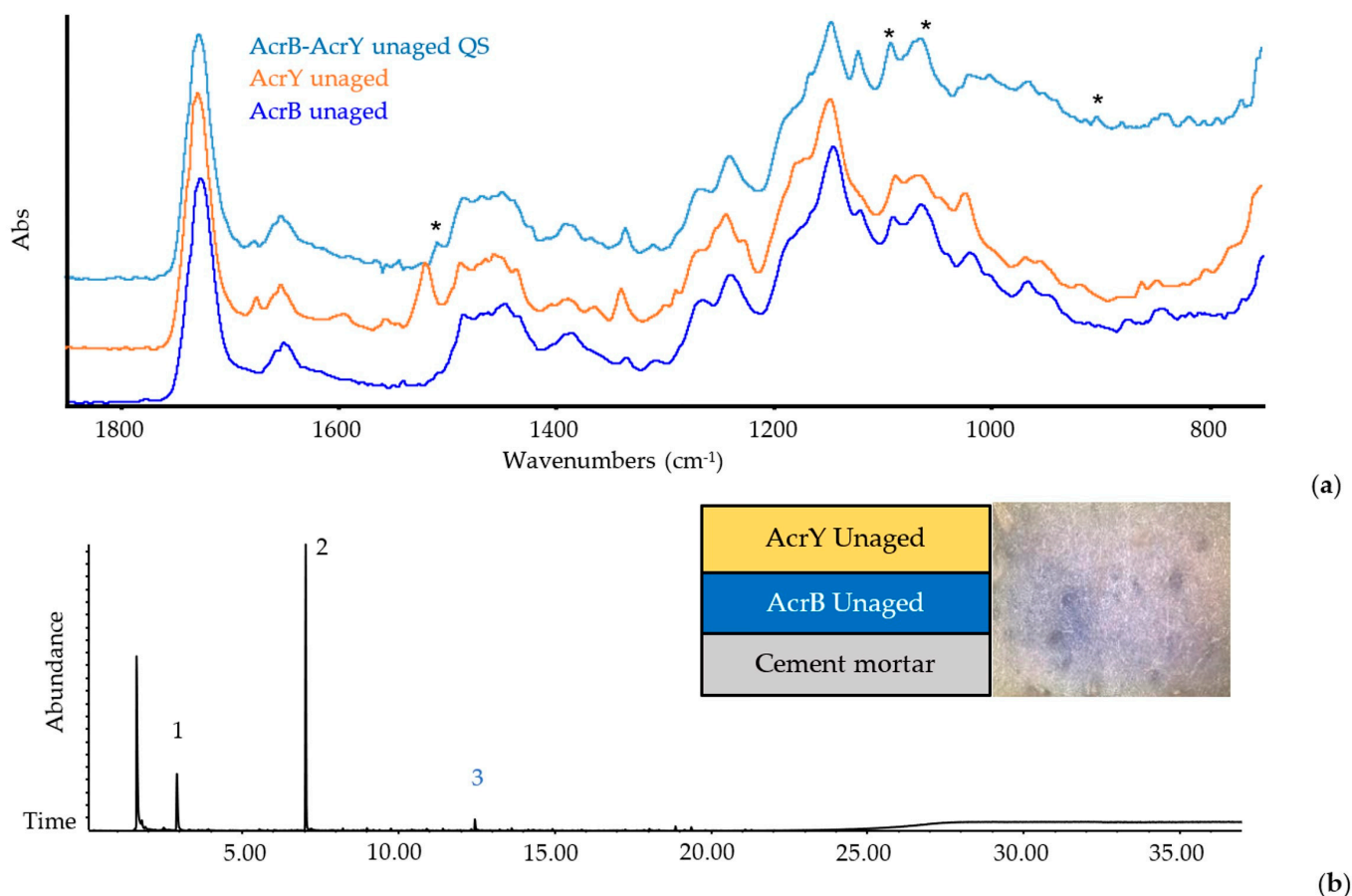


Figure 5. (a) Micro-ATR-FTIR spectrum of unaged AcrB, AcrY, and AcrB-AcrY cleaned with QS laser (asterisks indicate PB15 signals); (b) pyrogram of unaged AcrB-AcrY cleaned with QS laser.

However, in some critical cases, micro-ATR-FTIR may lack sensitivity and produce false-positive results, especially when the first paint layer and the unwanted one share the same binder and poorly infrared-absorbing pigments. Figure 6a shows the effect of the two-cycle cleaning of the QS laser on the aged sample AlkY-AlkB by micro-ATR-FTIR analysis, where the spectrum matches well with the aged AlkY reference. Peaks at 1674, 1516, 1463, 1337, 1224, 1202, and 1178 cm^{-1} are related to the presence of pigment PY74, with no significant peaks contributing to the blue pigment. However, with significantly higher sensitivity, the pyrogram in Figure 6b of the same sample reveals peaks related to the blue pigment in the aged AlkY-AlkB. Peak 1 (benzoic acid), peak 4 (phthalic anhydride), peak 8 (hexadecenoic acid), and peak 9 (octadecanoic acid) are related to the alkyd binder; peak 2 (2-methoxy-benzenamine), peak 3 (1-isocyanato-2-methoxy-benzene), and peak 7 (2-methoxy-4-nitro-benzenamine) are markers of PY74 [34]. Furthermore, we observed the presence of peak 5 and peak 6, tentatively assigned to 3-benzoylpropionic acid methyl ester ($m/z = 105, 77, 68$) and 2-ethylpropyl benzoate ($m/z = 105, 77, 123$), both of which were also identified in the pyrogram of spray AlkB (Figure 6c) used as a reference. Although their chemical compositions remain uncertain, their presence could be linked to the production process of synthetic blue pigments. This result highlights the capability of Py-GC/MS to provide a more detailed and accurate analysis of residues.

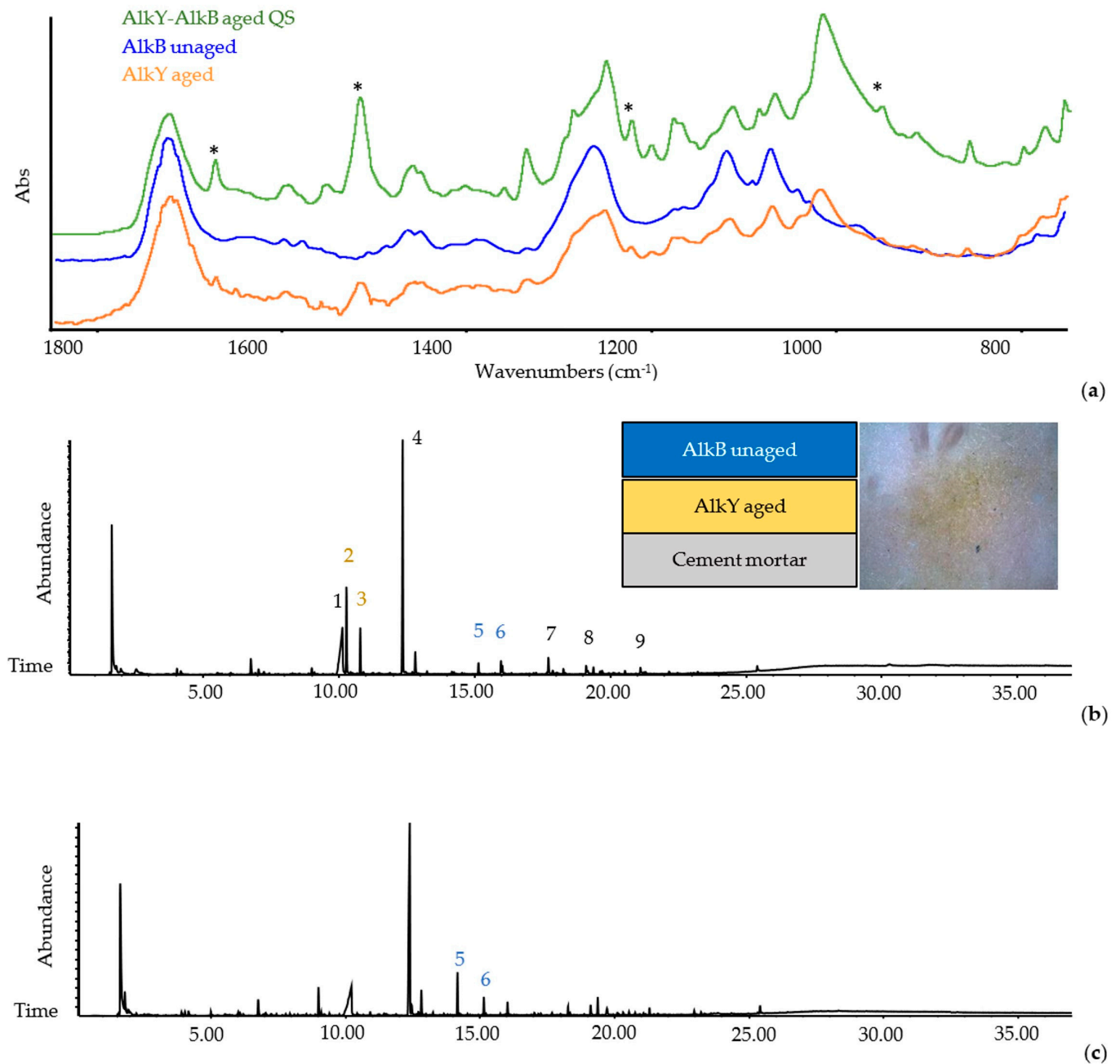


Figure 6. (a) Micro-ATR-FTIR spectrum of AlkB (unaged), AlkY (aged), and aged AlkY-AlkB cleaned with QS laser (asterisks indicate PY74 signals); (b) pyrogram of aged AlkY-AlkB cleaned with QS laser; (c) pyrogram of aged AlkB spray.

An in-depth study of the selectivity of the laser cleaning method revealed intriguing details. As illustrated in Figure 7, the spectra of the aged sample AlkY-AlkB, after undergoing the cleaning treatment with the removal of the blue layer, match better to the unaged reference of AlkY rather than the aged reference. In fact, following the artificial aging process, the peak of the alkyd binder at 1727 cm⁻¹ (C=O stretching vibration) becomes broader compared to the unaged one, with the baseline ranging from 1767–1684 cm⁻¹ up to 1820–1684 cm⁻¹ (gray area in Figure 7). This broadening effect hints at the potential erosion of the bottom layer after laser treatment, i.e., as a result of the paint-laser interaction, the aged surface layer of the bottom paint has been removed together with the vandalism layer, revealing a deeper and unaged paint.

Moreover, in Figure 7, it is noticeable that, post-cleaning, the relative absorption of the peaks associated with pigment PY74 (yellow area) and filler (green area) is more intense than the peaks of the binder. This suggests that, after the cleaning process, the paint film is richer in pigment and filler but poorer in binder. This alteration may lead to a loss of cohesion in the original paint, necessitating further maintenance.

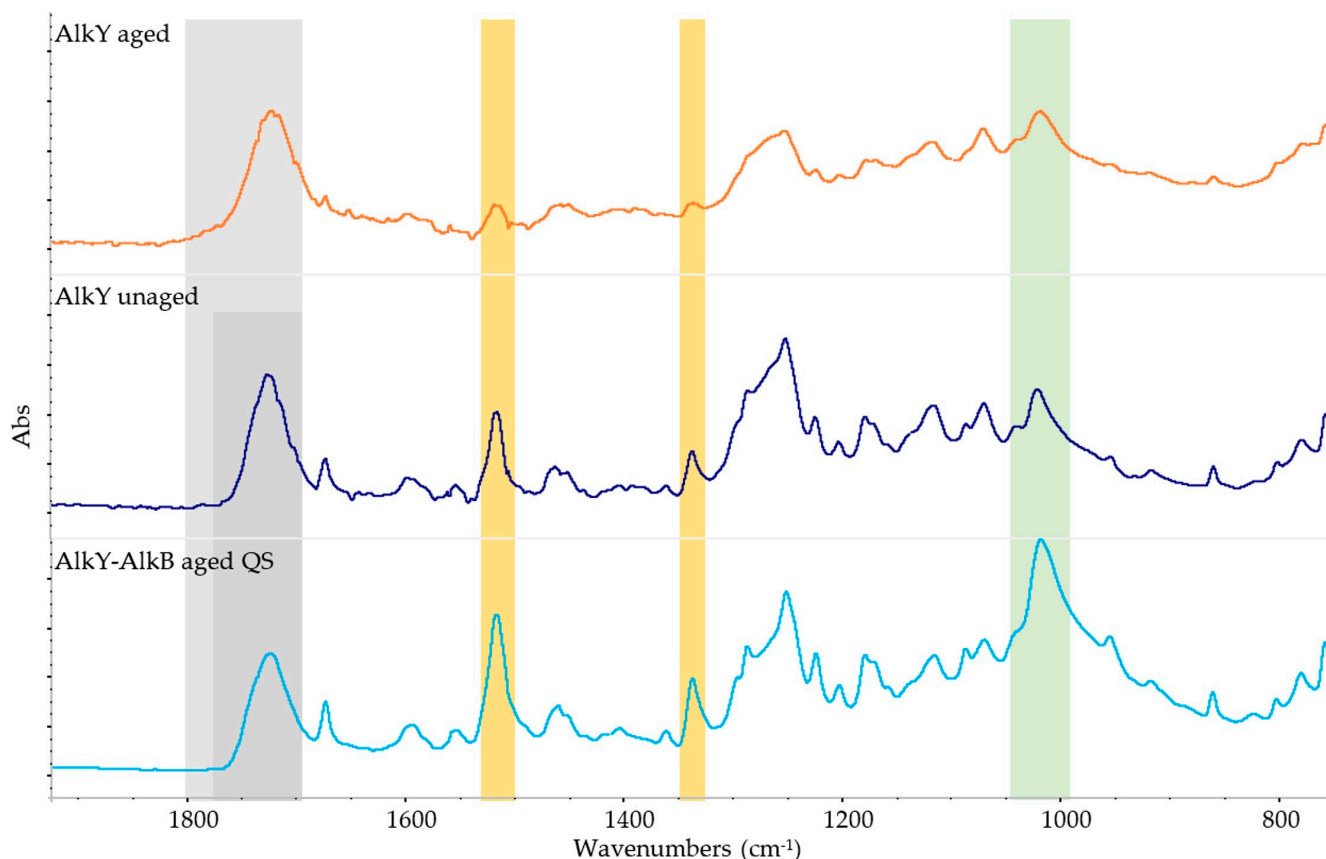


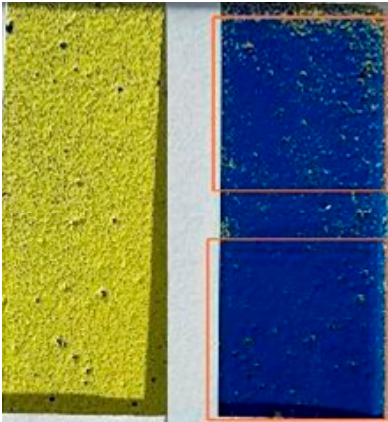
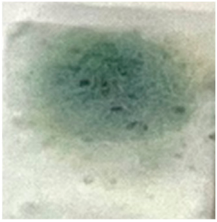
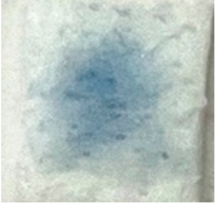
Figure 7. Micro-ATR-FTIR spectrum of AlkY (unaged), AlkY (aged), and aged AlkY-AlkB cleaned with QS laser.

3.3.4. Pigment Pickup and Cleaning Cycle

The decision on the number of necessary cleaning cycles is guided by meticulous observations of the sample and quartz tissue after each treatment. Table 9 presents images highlighting the need for a second cleaning cycle, due to the presence of numerous yellow paint residues after the first cycle (zone a), and the efficacy of this additional cycle has been validated through Py-GC/MS analysis, as depicted in Figure 8.

The analysis of the quartz tissue after the initial cleaning cycle illustrates fragments of the acrylic binder (peaks 1 and 2 denoting MMA and nBMA, respectively) and the yellow pigment PY74 (peak 3, 2-methoxy-benzenamine; peak 4, 1-isocyanato-2-methoxy-benzene; peak 5, 2-methoxy-4-nitro-benzenamine). After the second cleaning cycle, the pyrogram exclusively reveals the blue pigment, with the marker peak 3 (1,2-benzenedicarbonitrile), without traces of the yellow pigment. This thorough process resulted in a 38/45 overall empirical evaluation for this cleaning case, attesting to its satisfactory outcome, although the presence of evident traces of the blue pigment in the ablated material indicates a certain invasiveness of the laser on the paint layer to be preserved.

Table 9. Photo of unaged sample AcrB-AcrY and quartz tissue after cleaning with QS laser.

AcrB–AcrY Unaged	Cleaning Cycle	Pigment Pickup
	QS laser (zone a) one cleaning cycle	
	QS laser (zone b) two cleaning cycles	

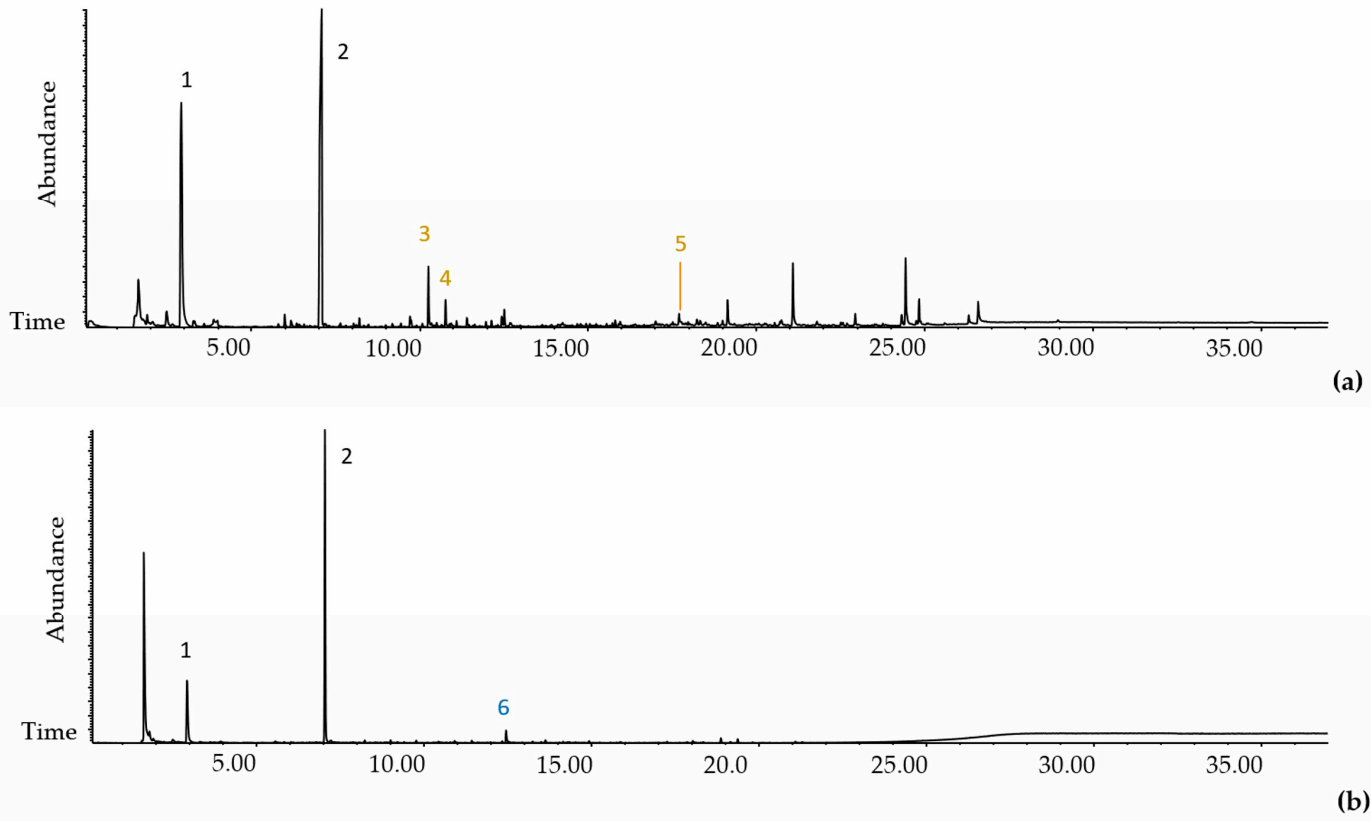


Figure 8. Pyrograms of unaged AcrB–AcrY after one (a) and two cleaning cycles (b) with QS laser.

4. Conclusions

In this study, we conducted an extensive investigation into the laser cleaning of synthetic sprays on both unaged and artificially aged mock-ups, presenting a specific protocol for assessing the effectiveness and safety of laser cleaning on contemporary murals. Through micro-ATR-FTIR analysis, we confirmed the chemical composition of the painting materials. Different binders such as acrylic, alkyd, and styrene-acrylic, along with specific pigments, were identified, providing a foundational understanding for subsequent cleaning assessments.

Five empirical evaluation criteria were identified and validated analytically, providing a practical insight into the effectiveness of laser cleaning. This approach, expressed through radar charts, demonstrated the influence of the binder type on the overall cleaning performance.

The results are further validated by non-invasive analytical measurements. Colorimetric measurements revealed significant ΔE values for samples with styrene-acrylic binders, indicating substantial color changes after cleaning. Micro-ATR-FTIR and Py-GC/MS analyses were employed for a deeper understanding of the cleaning process. In particular, micro-ATR-FTIR provided rapid results aligned with empirical observations, but it exhibits limitations in assessing cleaning effectiveness, particularly in cases where the first paint layer and the unwanted top layer share the same binder and contain poorly infrared-absorbing pigments, which leads to potential false negatives. In contrast, Py-GC/MS analysis demonstrated superior sensitivity and specificity compared to FTIR, making it the preferred choice for validating empirical evaluations. The adoption of a passive sampling method with a quartz fiber filter facilitated precise monitoring of laser cleaning action through Py-GC/MS without the need to extract samples directly from the surface of the mock-ups or artwork.

Both Q-Switch and Long Q-Switch laser instruments demonstrated comparable cleaning effects, proving especially effective for restoring vandalized murals, with the sole exception of cases where the base paint is styrene-acrylic. The aging of the paint film does not significantly influence the effectiveness of laser cleaning. However, some extra attention must be paid: while the laser effectively removes unwanted paint, it may also erode the most superficial layer of the underlying paint, 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.

Our study contributes with empirical insights and establishes a first framework for evaluating laser cleaning procedures that will be further developed and refined in the future. The interplay between binder types, pigments, and laser parameters is crucial, emphasizing the need for a simple and feasible approach to preserve the aesthetic and structural integrity of murals during restoration efforts. As laser cleaning technology evolves in cultural heritage conservation, the passive sampling system for Py-GC/MS analysis promises to provide detailed information on the ablated material components while preserving the integrity of artworks. Furthermore, it is easily adaptable to different application contexts.

Our findings provide valuable considerations for conservators, restorers, and researchers engaged in the preservation of street art and murals. Future research aims to explore different types of lasers (Ytterbium-doped active fiber laser) and investigate the behavior of anti-graffiti coatings under laser cleaning processes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14114799/s1>, Table S1: Cleaning results of 26 samples.

Author Contributions: Conceptualization, Y.Z. and D.S.; methodology, Y.Z., D.S., and F.Z.; validation, F.Z. and C.R.; formal analysis, Y.Z.; investigation, Y.Z. and F.Z.; data curation, C.R.; writing—original draft preparation, Y.Z.; writing—review and editing, D.S.; supervision, D.S., P.C., and F.Z.; funding acquisition, D.S. and P.C. All authors have read and agreed to the published version of the manuscript.

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References

1. Zanini, A.; Trafeli, V.; Bartoli, L. The Laser as a Tool for the Cleaning of Cultural Heritage. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *364*, 012078. [\[CrossRef\]](#)
2. Prokuratov, D.; Samokhvalov, A.; Pankin, D.; Vereshchagin, O.; Kurganov, N.; Povolotckaia, A.; Shimko, A.; Mikhailova, A.; Balmashnov, R.; Reveguk, A.; et al. Investigation towards Laser Cleaning of Corrosion Products from Lead Objects. *Heritage* **2023**, *6*, 1293–1307. [\[CrossRef\]](#)
3. Martínez-Weinbaum, M.; Lozano-Carbó, M.; Maestro-Guijarro, L.; Carmona-Quiroga, P.M.; Oujja, M.; Castillejo, M. Comparison of the Use of Traditional Solvents and Nanosecond 213 Nm Nd:YAG Laser in Thinning Naturally Aged Varnish on a Contemporary Oil Easel Painting. *Heritage* **2023**, *6*, 957–967. [\[CrossRef\]](#)
4. Rahman, M.A.; de la Fuente, G.F.; Miguel Carretero, J.; Abad, M.P.A.; Alcalde, R.A.; Chapoulie, R.; Schiavon, N.; Angurel, L.A. Ultra-Short Pulse Laser Cleaning of Contaminated Pleistocene Bone: A Comprehensive Study on the Influence of Pulse Duration and Wavelength. *Heritage* **2023**, *6*, 2503–2519. [\[CrossRef\]](#)
5. Maingi, E.M.; Alonso, M.P.; Angurel, L.A.; de la Fuente, G.F.; Dubernet, S.; Chapoulie, R.; Mellouët, O.; Vally, E. Chemical and Laser Cleaning of Corrosion Encrustations on Historical Stained Glass: A Comparative Study. *Heritage* **2023**, *6*, 1942–1957. [\[CrossRef\]](#)
6. Scaglia, V.; Zenucchini, F.; Piccirillo, A.; Ricci, C. Laser Cleaning of an Eighteenth-Century Waistcoat from the Civic Museums of Modena: Preserving Silk and Metallic Threads. In *Lasers in the Conservation of Artworks XIII, Proceedings of the Lasers in the Conservation of Artworks XIII, Florence, Italy, 12–16 September 2022*; CRC Press/Balkema: Boca Raton, FL, USA, 2024; pp. 173–182.
7. Zenucchini, F.; Ricci, C.; Piccirillo, A.; Cavaleri, T.; Cacciari, I.; Borla, M.; Aicardi, S.; Buscaglia, P. Laser Cleaning in the Conservation of Archaeological Artifacts: Polychrome Wooden Objects from Ancient Egypt. In *Lasers in the Conservation of Artworks XIII, Proceedings of the Lasers in the Conservation of Artworks XIII, Florence, Italy, 12–16 September 2022*; CRC Press/Balkema: Boca Raton, FL, USA, 2024; pp. 79–95.
8. Cooper, M. Lasers in the Preservation of Cultural Heritage: Principles and Applications. *Phys. Today* **2007**, *60*, 58–59. [\[CrossRef\]](#)
9. Lopez, M.; Bai, X.; Wilkie-Chancellor, N.; Detalle, V. Contribution to Controlled Method of Varnish Removal from Easel Paintings by ns Pulsed Nd:YAG Laser. *Heritage* **2023**, *6*, 3307–3323. [\[CrossRef\]](#)
10. Kokkinaki, O.; Dimitroulaki, E.; Melessanaki, K.; Anglos, D.; Pouli, P. Laser-Induced Fluorescence as a Non-Invasive Tool to Monitor Laser-Assisted Thinning of Aged Varnish Layers on Paintings: Fundamental Issues and Critical Thresholds. *Eur. Phys. J. Plus* **2021**, *136*, 938. [\[CrossRef\]](#)
11. Gomes, V.; Dionísio, A.; Pozo-Antonio, J.S. Conservation Strategies against Graffiti Vandalism on Cultural Heritage Stones: Protective Coatings and Cleaning Methods. *Prog. Org. Coat.* **2017**, *113*, 90–109. [\[CrossRef\]](#)
12. Siano, S.; Giamello, M.; Bartoli, L.; Mencaglia, A.; Parfenov, V.; Salimbeni, R. Laser Cleaning of Stone by Different Laser Pulse Duration and Wavelength. *Laser Phys.* **2008**, *18*, 27–36. [\[CrossRef\]](#)
13. Siano, S.; Agresti, J.; Cacciari, I.; Ciofini, D.; Mascalchi, M.; Osticioli, I.; Mencaglia, A.A. Laser Cleaning in Conservation of Stone, Metal, and Painted Artifacts: State of the Art and New Insights on the Use of the Nd:YAG Lasers. *Appl. Phys. A Mater. Sci. Process* **2012**, *106*, 419–446. [\[CrossRef\]](#)
14. Pereira-Pardo, L.; Korenberg, C. The Use of Erbium Lasers for the Conservation of Cultural Heritage: A Review. *J. Cult. Herit.* **2018**, *31*, 236–247. [\[CrossRef\]](#)
15. Pereira-Pardo, L.; Melita, L.N.; Korenberg, C. Tackling Conservation Challenges Using Erbium Lasers: Case Studies at the British Museum. *J. Inst. Conserv.* **2020**, *43*, 25–43. [\[CrossRef\]](#)
16. Samolik, S.; Walczak, M.; Plotek, M.; Sarzynski, A.; Pluska, I.; Marczak, J. Investigation into the Removal of Graffiti on Mineral Supports: Comparison of Nanosecond Nd:YAG Laser Cleaning with Traditional Mechanical and Chemical Methods. *Stud. Conserv.* **2015**, *60* (Suppl. S1), S58–S64. [\[CrossRef\]](#)
17. Ramil, A.; Pozo-Antonio, J.S.; Fiorucci, M.P.; López, A.J.; Rivas, T. Detection of the Optimal Laser Fluence Ranges to Clean Graffiti on Silicates. *Constr. Build. Mater.* **2017**, *148*, 122–130. [\[CrossRef\]](#)
18. Ricci, C.; Gambino, F.; Nervo, M.; Piccirillo, A.; Scarcella, A.; Zenucchini, F.; Pozo-Antonio, J.S. Developing New Cleaning Strategies of Cultural Heritage Stones: Are Synergistic Combinations of a Low-Toxic Solvent Ternary Mixtures Followed by Laser the Solution? *Coatings* **2020**, *10*, 466. [\[CrossRef\]](#)
19. Ocakçı, M. A Survey about the Effects of the Commissioned Street Art on Physical and Social Spaces. *Idealkent* **2020**, *11*, 938–962. [\[CrossRef\]](#)
20. Chatzidakis, M. Street Art Conservation in Athens: Critical Conservation in a Time of Crisis. *Stud. Conserv.* **2016**, *61*, 17–23. [\[CrossRef\]](#)
21. 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. [\[CrossRef\]](#)

22. Germinario, G.; van der Werf, I.D.; Sabbatini, L. Chemical Characterisation of Spray Paints by a Multi-Analytical (Py/GC–MS, FTIR, μ -Raman) Approach. *Microchem. J.* **2016**, *124*, 929–939. [[CrossRef](#)]
23. Bosi, A.; Ciccola, A.; Serafini, I.; Guiso, M.; Ripanti, F.; Postorino, P.; Curini, R.; Bianco, A. Street Art Graffiti: Discovering Their Composition and Alteration by FTIR and Micro-Raman Spectroscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2020**, *225*, 117474. [[CrossRef](#)]
24. Marazioti, V.; Douvas, A.M.; Katsaros, F.; Koralli, P.; Chochos, C.; Gregoriou, V.G.; Boyatzis, S.; Facorellis, Y. Chemical Characterisation of Artists' Spray-Paints: A Diagnostic Tool for Urban Art Conservation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2023**, *291*, 122375. [[CrossRef](#)] [[PubMed](#)]
25. La Nasa, J.; Orsini, S.; Degano, I.; Rava, A.; Modugno, F.; Colombini, M.P. A Chemical Study of Organic Materials in Three Murals by Keith Haring: A Comparison of Painting Techniques. *Microchem. J.* **2016**, *124*, 940–948. [[CrossRef](#)]
26. Siano, S.; Osticioli, I.; Pavia, A.; Ciofini, D. Overpaint Removal from Easel Paintings Using an LQS Nd:YAG Laser: The First Validation Study. *Stud. Conserv.* **2015**, *60*, S49–S57. [[CrossRef](#)]
27. Schnell, G.; Duenow, U.; Seitz, H. Effect of Laser Pulse Overlap and Scanning Line Overlap on Femtosecond Laser-Structured Ti6Al4V Surfaces. *Materials* **2020**, *13*, 969. [[CrossRef](#)]
28. Lanteri, L.; Calandra, S.; Briani, F.; Germinario, C.; Izzo, F.; Pagano, S.; Pelosi, C.; Santo, A.P. 3D Photogrammetric Survey, Raking Light Photography and Mapping of Degradation Phenomena of the Early Renaissance Wall Paintings by Saturnino Gatti—Case Study of the St. Panfilo Church in Tornimparte (L'Aquila, Italy). *Appl. Sci.* **2023**, *13*, 5689. [[CrossRef](#)]
29. Pintus, V.; Wei, S.; Schreiner, M. Accelerated UV Ageing Studies of Acrylic, Alkyd, and Polyvinyl Acetate Paints: Influence of Inorganic Pigments. *Microchem. J.* **2016**, *124*, 949–961. [[CrossRef](#)]
30. Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed.; Wiley: Hoboken, NJ, USA, 2004.
31. Joosten, I.; Voor, R.; Erfgoed, C. Dry Cleaning Approaches for Unvarnished Paint Surfaces. In Proceedings of the Cleaning 2010 Conference, Valencia, Spain, 26–28 May 2010; Smithsonian Institution: Washington, DC, USA, 2013.
32. Pellis, G.; Bertasa, M.; Ricci, C.; Scarcella, A.; Croveri, P.; Poli, T.; Scalarone, D. A Multi-Analytical Approach for Precise Identification of Alkyd Spray Paints and for a Better Understanding of Their Ageing Behaviour in Graffiti and Urban Artworks. *J. Anal. Appl.* **2022**, *165*, 105576. [[CrossRef](#)]
33. Ghelardi, E.; Degano, I.; Colombini, M.P.; Mazurek, J.; Schilling, M.; Learner, T. Py-GC/MS Applied to the Analysis of Synthetic Organic Pigments: Characterization and Identification in Paint Samples. *Anal. Bioanal. Chem.* **2015**, *407*, 1415–1431. [[CrossRef](#)]
34. Sonoda, N. Characterization of Organic Azo-Pigments by Pyrolysis–Gas Chromatography. *Stud. Conserv.* **1999**, *44*, 195–208. [[CrossRef](#)]

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