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# Efficiency evaluation of chemical and physical methods for the removal of spray paints from marble substrates

M Bargi<sup>1</sup>, M P Morigi<sup>2</sup>, R Fontana<sup>3</sup>, E Pampaloni<sup>4</sup>, J Striova<sup>5</sup> and B Salvadori<sup>6</sup>

<sup>1</sup>Istituto per l'Arte e il Restauro-Palazzo Spinelli, Via Maggio, 13, 50125, Florence, Italy

<sup>2</sup>X-Ray Imaging Group, Dipartimento di Fisica e Astronomia, Viale B. Pichat 6/2, 40127, Bologna, Italy

<sup>3,4,5</sup>CNR – Istituto Nazionale di Ottica Applicata, Largo E. Fermi 6, 50125, Florence, Italy

<sup>6</sup>CNR – Istituto di Scienze del Patrimonio Culturale, Via Madonna del Piano, 10, 50019, Sesto Fiorentino, Florence, Italy

<sup>1</sup>matilde.bargi@gmail.com, <sup>2</sup>mariapia.morigi@unibo.it, <sup>3</sup>raffaella.fontana@ino.it, <sup>4</sup>enrico.pampaloni@ino.it, <sup>5</sup>jana.striova@ino.cnr.it, <sup>6</sup>barbara.salvadori@cnr.it

**Abstract.** The graphic vandalism is considered one of the most important topics in the field of conservation of cultural heritage. The most widespread means used for the acts of vandalism are the felt-tip pens and the aerosol paints. These tools irreversibly damage the stone substrates, changing their appearance and conservation state. The aim of this article is to compare and characterize four different cleaning approaches in terms of their efficacy and invasiveness in the removal of the specific brand spray used as dirtying material.

## 1. Introduction

The graphic vandalism is considered one of the most important topics in the field of conservation of cultural heritage. Typical manifestations of this widespread phenomenon are inscriptions tags, pencils and spray drawings on public and private buildings without sparing historical monuments. Felt-tip pens and aerosol paints are the most common means used for the acts of vandalism. These tools irreversibly damage the stone substrates, changing their appearance and conservation state [1]. The aim of this research was to compare and characterize four different cleaning approaches in terms of their efficacy and invasiveness in the removal of the specific brand spray used as dirtying material.

To reach it, five different spray paints (Red, Green, Blue, Yellow and Black) produced by Nova S.p.a [2] were chosen and sprayed on four marble samples. After that, a systematic removal of aerosol paint signs from the marble substrate was tested with four different approaches: chemical, physical (laser ablation) and a two-step combination of them (chemical cleaning followed by laser ablation and vice versa). For the chemical cleaning, the Art-Shield4 remover was chosen, based on its widespread use among restorers. The physical approach exploited a Q-switched Nd:YAG laser ( $\lambda=532$  nm, Thunder Art, El.En. spa). The systematic evaluation and comparison of cleaning efficiency was carried out for each method and colour paint sprayed on marble, monitoring the removal of paint through a multi-



analytical approach. FT-IR reflectance spectroscopy and XRF spectroscopy allowed us to characterize each paint and monitor the depletion of binder and filler after cleaning, respectively. The morphological effects of cleaning approaches on the substrate were evaluated by Laser Scanner microprofilometry. Colorimetric analyses and photographic documentation were used to compare the surface chromatic evolution and ascertain the presence of remnants. The penetration depth of the paints and the presence of residues underneath the surface were checked in cross section with optical microscopy, before and after cleaning.

## 2. Material and methods

### 2.1. Marble specimens and spray paints

Four Carrara Marble specimens (13 cm × 10 cm × 1.4 cm) were polished with sand paper (180 grit). Each surface was divided in five areas (2×8 cm) and painted with five different spray paint colours produced by Nova spa (Table 1) [2].

Table 1 Nova spa spray paints.

Colour Paint	Chosen Shades
Red paint	RAL 3000 FIRE RED
Green paint	RAL 6001 EMERALD GREEN
Blue paint	RAL 5015 ELECTRIC BLUE
Yellow paint	FIAT 279 TAXY YELLOW
Black paint	RAL 9005 GLOSSY BLACK

### 2.2. Cleaning methods

Chemical and laser cleaning were carried out on two samples (C and L, respectively). Moreover, on the other two (LC and CL) we applied a combination of chemical and laser cleaning. On the CL sample, we carried out first the chemical removal and then the laser one; instead, on the LC sample laser cleaning was applied first, followed by the chemical one. As mentioned above, the chemical cleaning was carried out using the graffiti remover Art-shield 4 (CTS, Vicenza) [3], a mixture of glycol ethers. The Art-shield 4 was left to act on the whole marble surface for a period of 15 minutes and then rinsed with deionized water. This procedure was repeated until homogeneous (and best possible) cleaning results were obtained for each colour.

The samples that have undergone laser cleaning are L, CL and LC. Each coloured area is divided in four subareas that correspond to P0 where there is the reference colour area, P1 where the laser cleaning was carried out for one time, P2 where the laser cleaning was carried out for two times and P3 where laser cleaning has been used as many times as to ensure the best possible results.

For the laser cleaning, a Nd:YAG (Thunder Art, El.En. spa) Q-switched laser with a pulse duration of around 8 ns was employed. A fundamental wavelength at 1064 nm and its first harmonic at 532 nm were tested for the removal of sprays. The laser spot on the surface has an elliptical shape with an area of  $A = 0.33 \text{ cm}^2$ .

Through a series of preliminary tests, we chose the harmonic at 532 nm with an energy of 70 mJ to perform systematic and comparative cleaning tests. To evaluate the effectiveness of each cleaning procedure, the marble was characterized before the painting at time  $t_0$ , after the painting at time  $t_1$  and after the cleaning at time  $t_2$ .

## 3. Investigation techniques

### 3.1. Characterization of the spray paints

Each paint was sprayed on glass slides and scratched to collect it as a powder. The analysis of elements in inorganic pigments, fillers and extenders ( $Z > 10$ ) was carried out with a Bruker Tracer III-SD X-Ray

Fluorescence Spectrometer, equipped with Rh anode and Pd slit and an Al-Ti filter. Working conditions were: anodic current 12  $\mu\text{A}$ , voltage 40 kV, acquisition time 60s. The spectra were processed with Artax 7.4.0.0 software.

The chemical characterization of the powdered spray paints was carried out with an Alpha Bruker portable FT-IR spectrometer, equipped with an ATR diamond in the range 4000-400  $\text{cm}^{-1}$ , 128 scans, resolution 4  $\text{cm}^{-1}$ . The spectra were processed with an OPUS 7.2 Software. The same spectrometer equipped with a front-reflection module and a video camera (spectral range: 7500-375  $\text{cm}^{-1}$ , spot diameter: 6 mm; 128 scans, resolution 4  $\text{cm}^{-1}$ ) was used to monitor the cleaning outcome.

### 3.2. Evaluation of cleaning

Paint thickness as well as the efficiency and invasiveness of the cleaning methods were evaluated through Laser Scanner Micro-profilometry, realized by INO (Istituto Nazionale di Ottica), composed of conoscopic probe mounted on two motorized high-precision linear stages that can scan a maximum area of 28×28  $\text{cm}^2$ . The conoscopic probe has a height resolution of about 1  $\mu\text{m}$ , an accuracy better than 6  $\mu\text{m}$ , and a transverse resolution of 20  $\mu\text{m}$ . The instrument works at a standoff distance of 4 cm with measurement range of  $\pm 4\text{mm}$ . The areas (3×10  $\text{cm}^2$ ) were measured with a resolution of 50  $\mu\text{m}$ . Appropriate masks were prepared for each specimen to enable the monitoring of definite areas throughout the cleaning process. Macrophotography and microscopic observation, both on surface and in cross section, documented each cleaning step. Colour changes of the surface were monitored with a Spectrophotometer CM-2600d Konica Minolta. The instrument was set to operate with an 8 mm measurement area, the D65 as illuminant and the CIE 10° standard observer.

The organic paint residues on the surface were investigated using a Bruker Alpha reflection FT-IR spectrometer, whereas the residues of fillers and extenders were checked with the Bruker Tracer III-SD X-Ray Fluorescence Spectrometer, both mentioned in section 3.1.

## 4. Results

### 4.1. Paint chemical characterization

Each paint was characterized both from a chemical and morphological point of view. The FT-IR and the XRF analyses were performed both on the painted marble samples (RC, GC, BC, YC and KC) and on the reference ones (R, G, B, Y and K) where each colour had been sprayed onto glass slides.

The FT-IR spectral profiles, reported in Figure 1, are typical of an acrylic polymer, showing absorption bands at 2957  $\text{cm}^{-1}$  and 2871  $\text{cm}^{-1}$  corresponding to methyl C-H asymmetric and symmetric stretching vibrations. The strong band at 1729  $\text{cm}^{-1}$  (C=O stretching) and the vibrations at 1452  $\text{cm}^{-1}$  (C-H bending), 1239  $\text{cm}^{-1}$  (C-O stretching), 1150  $\text{cm}^{-1}$  (C-O-C bending) confirm the presence of an acrylic compound. These results are in agreement with the composition declared by the technical sheets of the spray paints [4]

The absorption bands detected in samples RC, BC and GC at 464, 448 and 433  $\text{cm}^{-1}$  suggest the presence of an oxide.

It is important to underline that the results obtained from FT-IR spectroscopy refer mainly to the binder composition, even though some bands could be assigned both to the binder and to the colorant. Indeed, in GC, BC and YC the absorption bands at 1452  $\text{cm}^{-1}$ , 1064  $\text{cm}^{-1}$ , 750  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$  assigned to aromatic groups may be related to the binder as well as to the presence of copper phthalocyanine or arylide yellow (Figure 1).

Table 2 reports the major elements detected in each paint by XRF spectroscopy. The presence of Titanium (Ti) in the Red, Green, Blue and Yellow paint suggests the use of titanium dioxide as a filler.

In the green paint, Copper (Cu) can be attributed to the presence of Cu-phthalocyanine, as also suggested by the FT-IR analysis. Instead, Vanadium (V) and Bismuth (Bi) lines suggest the presence of Bismuth Vanadate, which is a yellow compound. Bi and V have been also found in the yellow paint. This suggests the possible blend of yellow and blue colours to obtain the green paint.

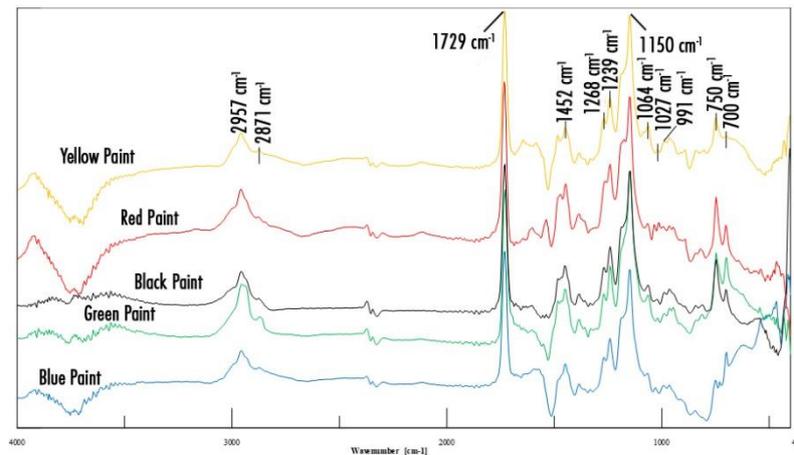


Figure 1 Red, Green, Blue, Yellow and Black paints FT-IR spectra.

Table 2 Elements detected by XRF on paints applied on marble and glass. Major elements are in bold.

Paint	Paint on Marble (Ca, Fe, Zn)	Paint on glass slides	Pigments
Red	Ca, <b>Ti</b> , <b>Mn</b> , Fe, Cu, Zn, Sr, Zr, Ru, Rh, Pd	Ca, <b>Ti</b> , <b>Mn</b> , Fe, Cu, Zn, Rb, Sr, Zr, Ru, Rh, Pd	Red Ochre Titanium dioxide
Green	Ca, <b>Ti</b> , V, Fe, <b>Cu</b> , <b>Bi</b> , Sr, Zr, Ru, Rh, Pd	Ca, <b>Ti</b> , V, Fe, <b>Cu</b> , Zn, <b>Bi</b> , Sr, Zr, Ru, Rh, Pd	Bismuth Vanadate Copper phthalocyanine Titanium dioxide
Blue	Ca, <b>Ti</b> , Fe, <b>Cu</b> , Sr, Zr, Ru, Rh, Pd	Ca, <b>Ti</b> , Fe, <b>Cu</b> , Zn, Rb, Sr, Zr, Ru, Rh, Pd	Copper phthalocyanine Titanium dioxide
Yellow	Ca, <b>Ti</b> , V, Fe, Cu, <b>Bi</b> , Sr, Zr, Ru, Rh, Pd	Ca, <b>Ti</b> , V, Fe, Cu, Zn, <b>Bi</b> , Sr, Zr, Ru, Rh, Pd	Bismuth Vanadate Titanium dioxide
Black	Ca, Fe, Cu, Zn, Sr, Zr, Ru, Rh, Pd	Ca, Fe, Cu, As, Rb, Sr, Zr, Ru, Rh, Pd	Organic black (no characteristic elements)

#### 4.2. Morphological characterization

The paint morphology was characterized through the cross-section observation and with the laser scanner micro-profilometry.

The cross-section observation by optical microscopy showed that all the paint layers were around 20  $\mu\text{m}$  thick and the penetration depth was around 300  $\mu\text{m}$ , except for the yellow paint where the penetration depth was around 400  $\mu\text{m}$  probably due to the high fluidity of this paint. These values were estimated thanks to the presence of colour densification at the grain boundaries.

The lasers scanner micro-profilometry (performed on L, LC and CL samples) provided the paint thickness calculated by subtraction of the painted marble z (height) values from those of the bare marble ( $t_1-t_0$ ). The paint thicknesses are reported in the Table 3.

Table 3 Paints average thickness

Colour paint sample	Average spray thickness	Maximum and minimum value
Red paint (RL t1-t0)	40 $\mu\text{m}$	20-60 $\mu\text{m}$
Red paint (RCL t1-t0)	50 $\mu\text{m}$	20-80 $\mu\text{m}$
Red paint (RLC t1-t0)	15 $\mu\text{m}$	10-40 $\mu\text{m}$
Green paint (GCL t1-t0)	50 $\mu\text{m}$	40-80 $\mu\text{m}$
Blue paint (BL t1-t0)	40 $\mu\text{m}$	20-60 $\mu\text{m}$
Blue paint (BCL t1-t0)	50 $\mu\text{m}$	20-80 $\mu\text{m}$
Blue paint (BLC t1-t0)	15 $\mu\text{m}$	10-40 $\mu\text{m}$
Black paint (KL t1-t0)	40 $\mu\text{m}$	20-60 $\mu\text{m}$
Black paint (KCL t1-t0)	50 $\mu\text{m}$	20-80 $\mu\text{m}$
Black paint (KLC t1-t0)	15 $\mu\text{m}$	10-40 $\mu\text{m}$
Yellow paint (YCL t1-t0)	20 $\mu\text{m}$	10-80 $\mu\text{m}$

### 4.3. Cleaning efficacy

Figures 2a and 2b report respectively FT-IR and XRF analyses as a function of the cleaning approaches applied to the red paint, as a representative case of all the paints. The macrophotographs and stereomicroscopic observations of the red paint sample are reported in Figures 3 and 4 respectively. The FT-IR spectra in Figure 2a of laser-cleaned surfaces reveal a small absorption band at  $1729\text{ cm}^{-1}$  that is the evidence of the colour residues also visible macroscopically and under stereomicroscope. A weak absorption band is also visible after chemical followed by laser cleaning. Instead, this peak is not visible after the standalone chemical method and the laser ablation followed by chemical cleaning.

This result is not consistent with the visual observation of the surface and the observation in cross section after chemical cleaning. This can be due to the very small penetration depth of the incident radiation in the FT-IR reflectance technique, which is actually a surface method, and to its sensitivity limits. Neither colour residues underneath the surface nor minimal residues eventually present on the surface that are visible in the cross-section (Figure 5) are detectable with this technique. The complete depletion of paint elements detected by XRF suggests the comparable cleaning efficiency of all the methods (Figure 2b). However, the FT-IR results show that the chemical and the combined techniques are more efficient than the laser as a standalone method in removing spray paints from the marble substrate.

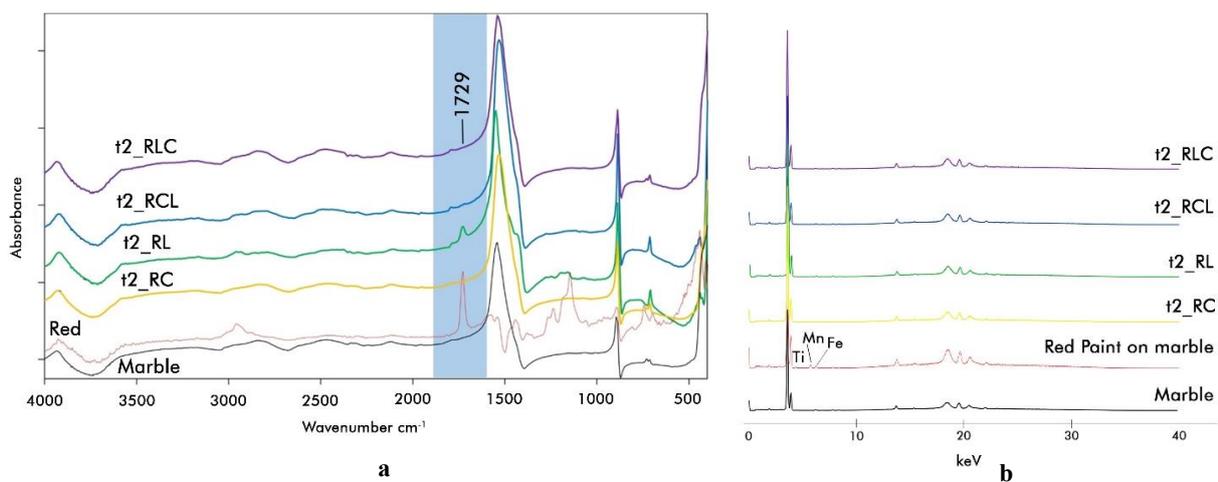


Figure 2 Spectra a) FTIR and b) XRF as a function of the cleaning method applied to removed red paint. The reference spectra are reported at the bottom.

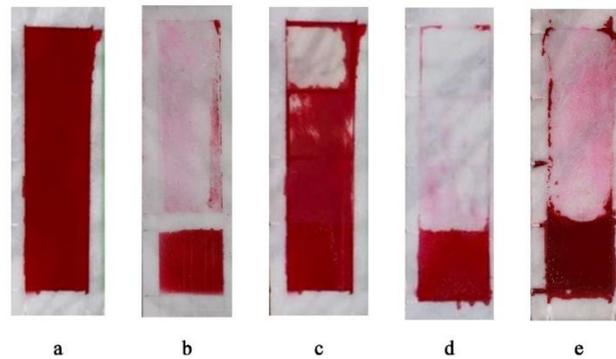


Figure 3 Red sample macrophotographs obtained after (a) (a) painting (red paint t<sub>1</sub>); (b) chemical cleaning (RC t<sub>1</sub>); (c) laser cleaning (RL t<sub>1</sub>); (d) chemical followed by laser cleaning (RCL t<sub>1</sub>); (e) laser followed by chemical cleaning (RLC t<sub>1</sub>).

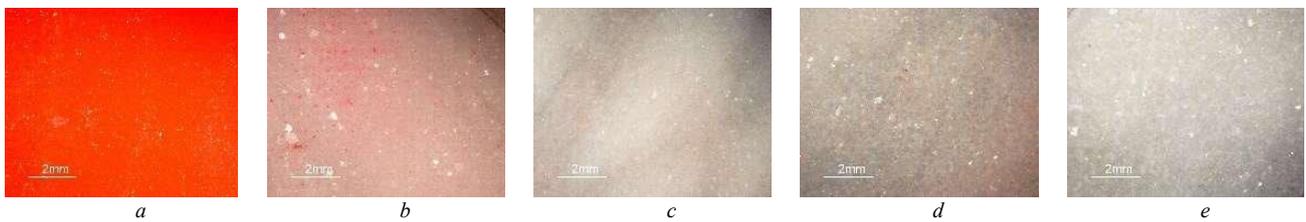


Figure 4 Stereomicroscope observation of surface area after (a) painting (red paint t<sub>1</sub>); (b) chemical cleaning (RC t<sub>1</sub>); (c) laser cleaning (RL t<sub>1</sub>); (d) chemical followed by laser cleaning (RCL t<sub>1</sub>); (e) laser followed by chemical cleaning (RLC t<sub>1</sub>).

The comparison of colorimetric results [5] (Figure 6) as well as the observation of cross sections (see example for red sample in Figure 5) shows that the most efficient action was exerted by the laser followed by chemical approach for all but the blue sample.

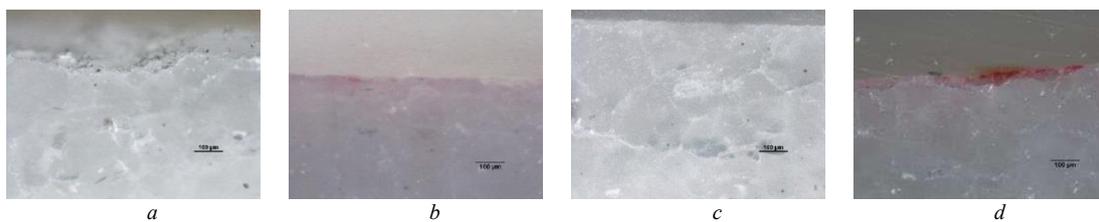


Figure 5 Microscopic observation of cross section relative to red painted marble for (a) laser cleaning, (b) chemical followed by laser cleaning, (c) laser followed by chemical cleaning, (d) chemical cleaning - Magnification 10X

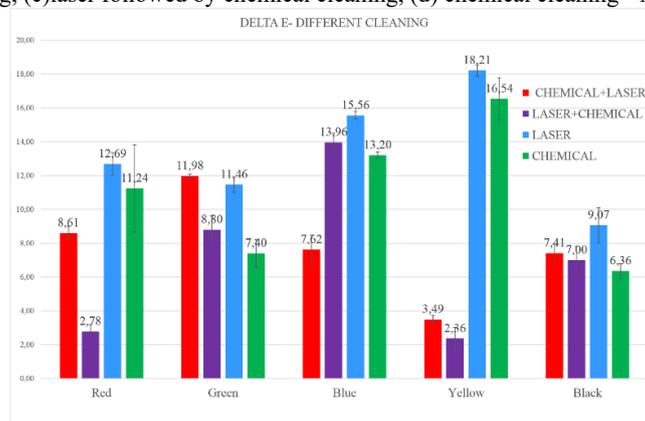


Figure 6 Colour changes expressed as  $\Delta E$  for the different colours and cleaning methods

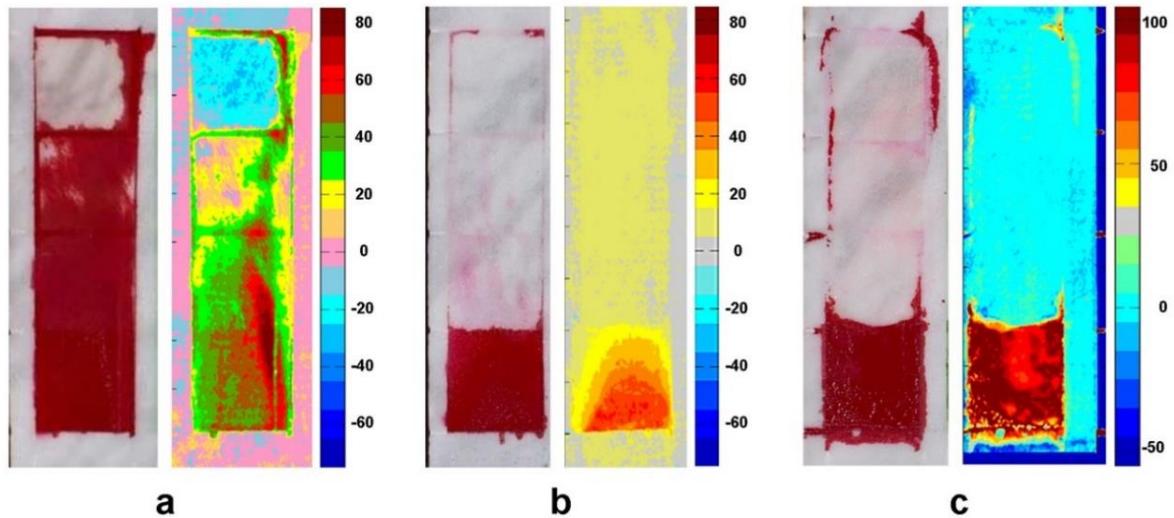


Figure 7 Height difference image for marble with red paint, (a) RL t2-t0, (b) RLC t2-t0 (c) RCL t2-t0. Scale bar reported in microns

The morphological effects of cleaning approaches on the substrate were evaluated by microprofilometry (Figure 7). The results prove that the laser cleaning when used as a standalone method was damaging the substrate on the micrometric scale under the conditions used. This is clearly caused by the attempt to remove completely the paint. The visual evaluation, by which the operator checks the output of each cleaning step, may be deceptive as the surface may seem to present colour residues but this is simply owed to the colour penetrated the substrate. Laser alone is not capable of the substance removal from underneath the surface. Contrarily, no damage is detected with a combined approach in which the laser is not applied as a standalone method, but rather in combination with chemical cleaning. Such approach proved very beneficial in safeguarding the substrate integrity both when laser is applied first followed by chemical cleaning and vice versa. This is confirmed by the observation of the cross sections showing the local damage for laser cleaning at micrometric scale and substrate preservation for other cleaning approaches. From the morphological point of view, the best suitable approach would be the combined technique (laser followed by chemical cleaning or the other way around). The results of colorimetry and observation in cross section confirmed that it is more beneficial to apply the chemical cleaning after the laser ablation to remove the possible disintegrated paint debris left on the surface, to allow also extracting some paint from the porous substrate structure minimizing the risk of the paint migration.

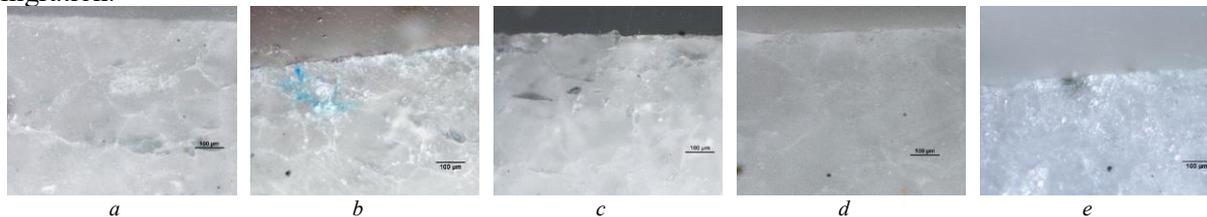


Figure 8 Microscopic observation of cross section relative to laser followed by chemical cleaning on (a) red paint, (b) blue paint, (c) black paint, (d) yellow paint, (e) green paint– Magnification 10X

To summarize, evaluating the entire set of results, the laser followed by chemical cleaning method was individuated as the most efficient method to completely remove the paint layer from the marble substrate without damaging it (see cross sections in Figure 8). In addition, the Art-Shield 4 removed almost all the colour remnants present on and underneath the marble surface. The microscopic paint residues (not visible at macroscopic scale) are less than 10 µm under the marble surface, except for the blue paint that has a consistent colour remain. The other combined technique (chemical followed by

laser) shows better results than the standalone techniques, but observing the cross sections it is possible to note some paint remains underneath the marble surface (50  $\mu\text{m}$  in depth).

## 5. Conclusion

This work evaluated the efficiency and invasiveness of different cleaning approaches for spray paints on marble. Chemical cleaning, laser cleaning and chemical and laser coupled methods were compared through a multi-analytical approach.

After a preliminary characterization of the paint composition, each cleaning procedure was evaluated through FT-IR reflectance spectroscopy, XRF spectroscopy, laser scanner micro-profilometry, colorimetric analysis and photographic documentation both on surface and in cross section. The measurements were carried out on unpainted marble and on painted marble before and after cleaning. Visual observation under stereomicroscope and photographic documentation allowed monitoring of the paint removal; colorimetric analyses confirmed the results of visual evaluation. FTIR and XRF spectroscopy proved to be useful to check the depletion of binder and filler components on the surface.

The laser scanner micro-profilometry allowed to measure the spray paint thickness and to evaluate the invasiveness of the cleaning treatments for the marble substrate. This technique showed that, from the morphological point of view, the best suitable approach would be the combined technique (laser followed by chemical cleaning or the other way around). In more detail, the results of colorimetry and microscope observation on surface and in cross section suggested that it is more beneficial to apply the chemical cleaning after the laser ablation to remove the possible disintegrated paint debris left on the surface, to allow also extracting some paint from the porous substrate structure minimizing the risk of the paint migration.

Finally, it should be noticed that the cleaning results could be influenced by the colour thickness or by the spray paint composition.

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