High efficiencies for laser cleaning of glassware irradiated from the back: application to glassware historical objects

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Abstract
We present a systematic study of laser cleaning of black paint deposited on both standard and frosted glasses. We performed laser cleaning of black paint layers of different thicknesses in both front- and backside laser irradiation geometries. Using laser ablation induced photoacoustics (LAIP), we determined the ablation threshold of the paint that turns out to be independent of the paint thickness and substrate’s properties. To characterize the efficiency of the cleaning process as a function of the number of laser shots, we measured the transmission of the glass in the ablated region and simultaneously the amplitude of the acoustic signal generated by the ablation process. We show that laser cleaning is much more effective when the glass sample is irradiated from the back. To explain this effect, we propose a phenomenological model. This model also predicts the existence of a critical thickness, above which backside cleaning is no longer efficient. The method of back incidence laser cleaning was successfully applied to two real objects, namely a piece of advertising glass covered with black paint and an antique glass bottle with black dirt inside, both archeological objects founded in excavations made in the city of Buenos Aires.

1 Introduction

Laser cleaning is a technique that allows removing surface layers or small contaminant particles deposited over different kinds of substrates. It uses a pulsed laser with a fluence being high enough to achieve the removal of the unwanted material, but low enough to avoid damage on the substrate [1, 2].

The most common laser cleaning procedures are (1) vaporization induced by laser ablation, in which the laser pulse produces phase explosion [3], (2) dry laser cleaning, which consists in an escape of material from an adhesion potential under the forces induced by thermal expansion [4] and (3) wet laser cleaning, in which the laser pulse produces ablation of a material being covered by a thin liquid film [5].

Following the initial work from Petrov’s, Zapka’s and Allen’s groups at the end of the 1980s and early 1990s [6–8], many papers and patents were published showing how lasers can be used to clean surfaces as well as applications to industrial problems and cultural heritage conservation [9–13]. Some of these works are dedicated to laser cleaning of glassware and transparent objects [14–23]. In these cases, the incidence geometry is an important factor that can improve the cleaning efficiency. Previous studies on the removal of fingerprints [14], ink and candle soot [15] provide some evidence that laser incidence from the back leads to a better cleaning quality than front irradiation. The possibility of using backside irradiation to clean glasses of difficult access (like cleaning of windows in high buildings from inside) was also proposed [16]. On the same line, Beyer et al. [21] have shown that rear-side ablation of painted float glass is more efficient than frontside ablation. Also it was demonstrated that laser cleaning with incidence on the rear surface can be applied to opaque thin films and
paper sheets [24]. In spite of the different works mentioned before, some basic physical phenomena underlying this method still remain unknown. To elucidate the mechanisms of laser cleaning of glassware and to be able to control the cleaning process, systematic investigations taking into account laser fluence, dirt thickness, incidence geometry of the laser pulse and surface morphology of the glassware are needed. In this paper, we investigate, using laser ablation, the dependence of the cleaning efficiency of glassware on the surface roughness, the thickness of the material to be removed, the laser fluence and the incidence geometry of the laser pulses. To carry out these investigations, we first produced technical reference samples to simulate dirt over real glassware objects. These samples were pieces of flat glass covered with layers of different thicknesses of black paint (to simulate dark dirt). We worked on smooth, transparent and frosted glasses. We then determined the ablation threshold of the material to be removed, as well as that of the glasses, defined as the minimal laser fluence needed to initiate the removal of the paint layers. In a further step, we determined the efficiency of the cleaning process in all samples for both front and back incidence geometries, using the number of shots necessary to remove the dirt layer as a reference. We implemented and employed a photoacoustic monitoring method (LAIP) to determine the ablation onset and the subsequent rise of the ablation rate with increasing laser fluence [25, 26]. Additionally, we measured the transmission of the glass plate on the area where ablation occurs using a CW laser and a photodiode. Notice that the transmission after laser treatment is an indicator of the efficiency of the cleaning process. We also propose a simple model, based on general considerations of laser–matter interaction to explain our results. Once the empirical conditions for efficient laser cleaning were determined, the method was successfully applied to two real objects: a piece of advertising glass covered with black paint and an antique glass bottle with black dirt inside, both archeological objects found in excavations made in the city of Buenos Aires.

2 Experimental

The experimental setup used to perform the measurements is shown in Fig. 1.

In this setup, a Q-switched Nd:YAG laser with a pulse duration of 7 ns (FWHM), operating at 1064 nm impinges normally to the sample surface. The laser profile was flattened out by a pinhole. A neutral density wedge filter was used to change the energy of the laser pulse from 0.8 to 200 mJ. The laser was then focused on the sample using a plano-convex lens to produce a spot of 1 mm in diameter. The pulse energy was measured using an energy meter with a pyroelectric detector (models RjP-735 and l Rm-6600, from Laser Probe Inc.), splitting the laser pulse by means of a calibrated beam splitter. Taking into account the spatial energy distribution of the laser pulse and the effective area of the laser spot, the fluences \( F \) calculated in this work exhibit an uncertainty of c.a. 10%. To monitor the transparency of the glass plate on the ablation spot, the intensity of a commercial He–Ne laser (632.8 nm) was measured by means of a standard photodiode and a digital oscilloscope. An electret condenser microphone (Panasonic WM-61A) was used to measure the sound produced during ablation. The acoustic signals were amplified and registered on a

![Fig. 1 Experimental setup used for laser ablation and cleaning of painted glassware](image-url)
digital oscilloscope (sample rate 300 MHz). The amplitude of the first peak-to-peak acoustic signal (S) was measured as a function of the laser fluence.

Samples were made on commercial transparent smooth and frosted glass substrates of 3 mm thickness by multiple applications of commercial black paint satin matte in spray to produce the different paint thicknesses in a range between 50 and 120 μm (composition: xylene 10–30%; propellent 50–70%; resin 25–35%; black pigments c.s.p 100. Density of the concentrate at ambient temperature: 0.85–1.15 g/cm³). The thickness of each paint layer was determined using a universal measure machine MU-214 B (Société Genevoise D’instruments de Physique, Genève, Switzerland).

3 Results and discussion

3.1 Ablation thresholds

To determine the laser ablation thresholds of the paint, an acoustic method was used. It is based on the measurement of the intensity of the acoustic signal produced during ablation, as a function of the laser fluence [25, 26]. An example of an ablation curve is shown in Fig. 2 for the case of black paint on smooth glass and three different thicknesses.

Each point on the plot corresponds to a measurement in an untreated area of the sample. As it can be seen, two main regions can be identified: the first one is located below the ablation threshold, in which no ablation takes place and no acoustic signal can be detected, whereas in the second region, the acoustic signal increases with the laser fluence.

A linear minimum square fit was applied to the first linear part of the curve (see inset in Fig. 2). The interception of the fitted straight line with the horizontal axis is taken as the ablation threshold. It indicates the value of fluence at which significant material removal starts.

As it can be seen, all three curves for the different thicknesses clearly coincide in this region, which demonstrates that the threshold value of black paint \( F_0 = 0.48 \pm 0.05 \text{ J/cm}^2 \) is the same in all cases. The same curves where obtained for smooth and frosted glasses and for thickness between 40 and 120 μm. From these results, we conclude that laser ablation threshold for painted glass is a property of the paint, and is independent of the thickness of the paint layer and of the characteristics of the substrate.

Figure 3 shows the ablation curve for smooth and frosted glass substrates used in this work. As it can be seen, the ablation threshold fluence in both cases is much higher than that of the paint. Ablation threshold fluences of \( F_s = 8.20 \pm 0.08 \text{ J/cm}^2 \) and \( F_F = 4.10 \pm 0.08 \text{ J/cm}^2 \) for smooth and frosted glasses, respectively, were determined, in agreement with previous measurements [27]. It is interesting to mention that \( F_s \) is more than twice the value of \( F_F \), reflecting the influence of the structure of the surface in the magnitude of this parameter. In agreement with these results, optical inspection of the glass surface under the microscope, after single laser shot shows damage at values close to the ablation threshold and above it, while no evidence of cracks or damage can be seen for fluence values below the threshold, as it is shown in Fig. 4.

A problem relevant to laser cleaning is that of laser-induced damage (LID). LID depends on several physical factors, among them the most important ones are: the nature of the material itself, laser pulse duration, the overall fluence, and number of previous shots already impacted on
the surface (laser-induced fatigue). Values for the threshold fluence of different glasses vary greatly from a few J/cm\(^2\) to more than 100 J/cm\(^2\) depending on the composition of the glass but also differ by orders of magnitude in the duration of the pulse, being much lower for shorter (fs–ps) than for longer (ns) pulses [28].

Figure 4 shows microscopic images of frosted (upper part) and smooth glasses (lower part) irradiated with a single pulse of the laser used in this work, below, above and at the ablation threshold fluence (ATF). Figure 4a, corresponds at laser irradiation with half of ATF. In Fig. 4b, a typical image of the effect of the laser irradiation at fluences of the order of the ATF is depicted, showing a modification of the surface of the sample. Figure 4c shows the damage produced in the glass at fluences above the ATF. From these results, we can conclude that when cleaning at fluences below the ATF of the substrate, no damage is produced on the samples.

3.2 Laser cleaning

To perform the laser cleaning process, two laser incidence geometries were investigated:

1. A frontside (FS) incidence in which the laser pulse impinges directly on the paint layer and

2. A backside (BS) or rear incidence in which the laser pulse impinges from the opposite side and through the glass plate. These two geometries are shown in Fig. 5

To characterize the efficiency of the cleaning process with both incidence geometries, we made two types of independent measurements. On the one side, we measured the transmission of the ablated region as a function of the number of laser shots N. Simultaneously, we measured the intensity of the acoustic signal produced during the ablation vs. the number of laser shots. Figure 6 shows an example of these measurements performed at a fluence of 4.55 J/cm\(^2\), for the case of a black paint layer of 50 μm thickness deposited on smooth glass.

Both measurements provided important and complementary information. Transmission result in Fig. 6 indicates that cleaning starts from the first laser shot and advances rather quickly to reach a more or less stable plateau. The number of

![Fig. 4](image_url)

**Fig. 4** Microscopic images of frosted (upper part) and smooth glasses (lower part) irradiated with a single pulse of the laser used in this work, below, above and at the ablation threshold fluence (ATF). **a** Laser fluence is half of ATF. **b** Laser fluence is of the order of the ATF. **c** Laser fluence is two times larger than ATF

![Fig. 5](image_url)

**Fig. 5** The two laser incidence geometries used in this work for laser cleaning: frontside and backside incidence
pulses required to reach the plateau depends on the incidence geometry. The asymptotic value of this plateau indicates the maximum achievable transmission \((T_m)\), which represents the highest degree of cleanliness attainable. The acoustic measurements show more clearly the cleaning process. The number of pulses required to obtain a null signal (signal under the noise) is easy to determine. A null acoustic signal means that the \(T_m\) was achieved.

It is important to mention that in both laser cleaning geometries there is a maximum achievable transmission with values below 100%. This is due to the presence of an organic patina remaining after removing the black part of the paint. This patina is a semitransparent thin film that can be easily removed by wiping the surface with a tissue soaked in alcohol. The nature of this patina depends on the composition of the paint and it is strongly dependent on the amount of resin contained in the paint (we have observed that this patina was different for different types of black paint and different colors of paint). Notice, that this remaining film was also observed by Beyer et al. [21] using a different type of paint, sample preparation and substrate. However, in contrast to our results, in that work this patina was only observed for BS incidence.

Figure 7 shows the typical behavior of the maximum achievable transmission as a function of the fluence. It can be clearly seen that the cleaning process improves with increasing the fluence up to a value at which it reaches a plateau. Simultaneously, the acoustic signal reaches a null value more quickly (less numbers of pulses) as the fluence is increased. This behavior was the same, independently of the thickness (between 40 and 120 μm) and for both geometries. Figure 7 corresponds to the case of a black paint layer deposited on frosted glass and BS incidence. The different symbols correspond to different thicknesses of the paint.

In the case of frosted glass, \(T_m\) was always near 20% higher than for smooth glass, for BS geometry. Also, \(T_m\) was always approximately 10% higher than in the case of FS geometry for thicknesses up to 100 μm.

Table 1 summarizes the results obtained for laser cleaning of black paint layers of different thickness in both glass substrates. In the table, the maximum transmission achieved, the number of pulses required in each incidence geometry and the relative efficiency are shown. We define the relative efficiency \((N_f/N_b)\) as the number of pulses required to reach the maximum transmission with FS incidence \((N_f)\) divided by the number of pulses required

![Fig. 6](image_url) Typical measurements performed to characterize the laser cleaning processes with FS and BS incidences. a Transmission vs. number of laser shots N. b Normalized acoustic signal vs. number of laser shots N. Sample: black paint layer of 50 μm thickness on smooth glass. Fluence: 4.55 J/cm²

![Fig. 7](image_url) Maximal transmission achievable for frosted glass covered by black paint layers as a function of the laser fluence. Ablation was performed using BS incidence. The different symbols correspond to different thicknesses of the paint (see inset)
to achieve the maximum transmission with BS incidence ($N_b$).

Results of Table 1 show that the laser cleaning process with BS incidence through the glass is, for all samples, much more efficient than frontside incidence. BS incidence requires about one order of magnitude less laser shots with respect to FS incidence to achieve maximal transmission. Moreover, BS incidence reaches even a higher final transparency. Note also (see Fig. 6) that one or two pulses impinging from the back side are able to overcome the maximum value of $T_m$ reached using FS geometry. In addition, we notice that in BS geometry, for both smooth and frosted glasses, the same number of pulses is needed to reach $T_m$, independently of the thickness. Therefore, it can be concluded that the extraction factor (i.e., extracted volume per pulse) increases for increasing layer thickness. On the contrary, the number of pulses required to reach $T_m$ in FS geometry increases with the thickness. This result is in agreement with the observations made by Beyer et al. [21]. It is important to point out that under our experimental conditions, for very thin films (less than 20 μm) of paint, we found complete cleaning using a single pulse in both FS and BS geometry.

Results on frosted glass with BS geometry show that it is necessary to apply more laser shots (at least one more) than in smooth glass, to obtain the $T_m$. This result can be explained taking into account the fact that in frosted glass the impinging light is scattered at the interface glass/paint, before reaching the paint. Then, part of the laser energy is lost by this effect.

In frosted glass, independently of the incidence geometry, $T_m$ values are always higher than for smooth glass (with BS geometry, $T_m$ reaches almost 90%). This means that the patina effect (i.e., the adherence of the patina) is less important in frosted glass. The patina effect is also more pronounced in both types of substrates for thicknesses larger than 100 μm. In these cases, the values of $T_m$ obtained are similar for both geometries but lower than for smaller thicknesses.

### 3.3 Phenomenological model

A complete microscopic explanation of the results presented above is not possible at the moment. First, an atomistic description of the sample taken into account the dimensions of the laser spot (approximately 1 mm diameter) and the thickness of the paint would involve such an enormous amount of atoms that cannot be treated by state-of-the art methods. Note, that a small simulation cell of submicrometer dimensions already contains hundreds of millions of atoms. Moreover, even for submicrometer cells, atomistic simulations cannot achieve time lengths of the order of 0.1 μs within realistic computer times, which prevent the description of the action of nanosecond laser pulses. Second, simulations in submicrometer cells are only possible within the molecular dynamics two-temperature model (TTM-MD) scheme [29–33]. This method is based on the knowledge of the interatomic potential and treats the excited carriers as free electrons. However, for black paint, the interatomic potential is unknown and excited electrons in polymers cannot be treated as free with a parabolic dispersion relation. Therefore, atomistic simulations are inapplicable to study the problem posed by our experimental results. For this reason, we present below a phenomenological model which aims at explaining the most striking effect observed in this type of measurements, namely the remarkable increase of the laser cleaning efficiency for BS irradiation. The quantities playing a key role are the thickness $D$ of the paint film and the penetration depth $\delta$ of the light into the paint. In our discussion, we will always assume normal incidence. We set the $z$-axis parallel to the laser propagation direction and perpendicular to the sample surface. For the seek of clarity, we also define the ablation depth $L$ as the interval along $z$-axis inside the sample for which the condition $I(z) > I_{abl}$ is satisfied, being $I_{abl}$ the ablation threshold. The laser intensity profile at the surface of the irradiated region (laser spot) is assumed to be given by a Gaussian $I(x, y) = I_0 \exp\left(-\beta \left(x^2 + y^2\right)\right)$, where $z_0$ defines the coordinate.
High efficiencies for laser cleaning of glassware irradiated from the back: application to...

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Fig. 8 Schematic description of the interaction of an intense nano-second laser pulse with a paint film on a glass substrate for the case \(D > L\) (see text) and frontside incidence. a The region of the sample irradiated with intensity over the ablation threshold \(I_{abl}\) is in dark gray. The arrows indicate the forces acting on the part of the material for which \(I(x, y, z) < I_{abl}\). The excited volume expands upwards. b Subsequent vaporization leads to ablation and material removal.

Fig. 9 Schematic description of the interaction of the intense laser excitation of a paint film on a glass substrate for the case \(D < L\) (see text) and backside incidence (through the glass substrate). a The region of the sample irradiated with intensity over the ablation threshold \(I_{abl}\) is dark gray. The arrows indicate the forces acting on the part of the material for which \(I(x, y, z) < I_{abl}\). b Since lateral expansion is not possible, the excited region expands upwards, detaches from the substrate and produces stress on the unexcited part above it, which then fragments. Then, the removal of the excited volume and the unexcited part above it follows.

of the surface of the irradiated region on the \(z\)-axis. Thus, the volume \(V(x, y, z)\) exposed to laser intensity larger than the ablation threshold, marked in dark gray in Figs. 8 and 9, is composed by all points \((x, y, z)\) for which the following inequality is satisfied:

\[
I_{\text{max}} e^{-\beta(x^2 + y^2)} e^{-\alpha z} < I_{abl}.
\]

In Eq. (1), \(\alpha = 1/\delta\), being \(\delta\) the penetration depth of the black paint, whereas \(\beta\) depends on the characteristics of the laser spot. From the above expression it is clear that the ablation depth produced with a Gaussian pulse is actually dependent on \(x\) and \(y\). This situation is taken into account in the schematic description shown in Figs. 8 and 9.

Using general physical arguments, one can distinguish three different situations:

1. \(L > D\). In this case, the ablation depth is larger than the thickness of paint. Then, the paint film is excited with intensity higher than \(I_{abl}\) over its whole thickness. Notice that this happens independently whether the laser pulse is incident from the front or from the back. Therefore, the complete removal of the paint occurs on the irradiated region. Thus, the efficiency of the cleaning processes is the same for direct and backside incidence. As mentioned in Sect. 3.2, in our experiments, this happens for thicknesses smaller than 20 \(\mu\)m and at laser fluences below the ATF of the glass.

2. \(D > L\). Under this condition, the effectiveness of the laser cleaning process is no longer independent of the incidence direction. We consider the two cases of FS and BS incidence separately:

2.i Frontside incidence: if the laser pulse excites the paint film directly from the front side, the excited volume \(V_F(x, y, z)\) (Eq. 1) will include the surface of the paint and a region of thickness \(L\) below it (Fig. 8a). In \(V_F(x, y, z)\), electrons acquire an extremely high temperature, which leads to a rapid increase of the electronic pressure. Through electron–phonon coupling, a large part of the absorbed energy is transferred to the atoms, which increases its temperature and pressure to high values.

This nonequilibrium situation, represented by a large pressure difference between \(V_F(x, y, z)\) and its surroundings, leads to a build-up of large forces, which are indicated by the arrows in Fig. 8a.

Consequently, a relaxation process starts which consists in the propagation of pressure waves, and the excited volume will tend to exert pressure downwards and laterally onto the remaining part of the painted film. Notice that lateral and downward expansions are not possible due to inertial confinement. Therefore, the excited volume can only expand upwards. The rapid expansion, which most likely occurs along the binodal, is followed by ablation in form of vaporization [3]. Through laser ablation, the irradiated volume \(V_F(x, y, z)\) is removed. Since \(D > L\) only partial cleaning is obtained. This situation is schematically shown in Fig. 8b.

2.ii Backside incidence: for laser irradiation from the backside, the volume \(V_B(x, y, z)\) (Eq. 1) excited by the laser pulse includes the interface between paint and glass, but not the surface of the painted film, because of the condition \(D > L\) (see Fig. 8a). Therefore, \(V_B(x, y, z)\) cannot expand at all at the beginning due to inertial confinement. Since in our experiments we use nanosecond laser pulses, a certain expansion will occur during the excitation, which will be, however, much smaller than in the case of front side irradiation. The small expansion will be upwards, but not lateral, due to stronger confinement. Consequently, the laser pulse induces, to a certain extent, an isochore heating. The temperature and pressure inside the excited volume will rapidly increase, and be certainly higher than in the case of frontside incidence.

This situation is represented in Fig. 9a, where the region colored in dark gray indicates the excited volume \(V_B(x, y, z)\).

Now, this highly excited region will exert a huge pressure on
the less excited or unexcited part of the paint film surrounding it (the corresponding forces are represented by the black arrows in Fig. 9a), and also on the glass substrate.

Since the superheated material in $V_R(x, y, z)$ cannot expand laterally, it will relax upwards in the vertical direction, detaching from the glass substrate and pushing the unexcited part of the paint film lying above it (see Fig. 9b). This situation is similar to what happens for FS femtosecond laser excitation of metallic films (see Figure 4 in Ref. [32]). In other words, BS nanosecond laser irradiation induces superheating due to confinement conditions. The huge stress built up in the unexcited region breaking off the paint film and the consequent removal of material. Consequently, ablation of the film over the whole thickness at the laser spot happens, which means a 100% cleaning efficiency (Fig. 7b).

We expect here vaporization to play a minor role.

(3) $D > > L$. In this case, BS incidence cannot lead to ablation in the same way as (2.ii) because the unexcited part of the paint lying above $V_R(x; y; z)$ is too large to be pushed upwards by the pressures developed in this excited volume. In this case, isochore heating of $V_R(x; y; z)$ occurs, which might lead to a microexplosion. Depending on the thickness, the resulting pressure wave can produce spallation [34, 35] or can be damped out leaving the paint surface unaffected. Interestingly, in these later cases, the cleaning efficiency of front side incidence would be higher than for backside incidence. This means that for increasing thickness the relative cleaning efficiency would be inverted. From the discussion of situations (2) and (3) it is clear that for a given fluence (and consequently a given $L$) there will be a critical paint thickness $D_C$ for which the cleaning efficiencies of FS and BS irradiation are equal.

Based on this analysis, we can write the difference between the cleaning efficiency for backside incidence, $E_B$ and frontside incidence, $E_F$, as $\Delta E = E_B - E_F = f(D_C - D)$, where $f(x)$ is an arbitrary, not necessarily monotonous function of $x = D_C - D$, but satisfying $f(0) = 0$ and $\left.\frac{df}{dx}\right|_{x=0} > 0$.

Taking into account these properties, we can expand $f(x)$ around $x = 0$ and obtain

$$\Delta E = \frac{df}{dx} \bigg|_{x=0} (D_C - D) + \cdots .$$

This means that for thicknesses slightly smaller than $D_C$, the cleaning efficiency of rear-side irradiation will be only slightly better than for frontside incidence. This case has not been achieved in our experiments since the critical thickness $D_C$ seems to be considerably larger than 120 µm which is the maximum thickness studied in this work.

Notice that the BS laser cleaning technique modeled here is essentially different from the so-called “verso” laser cleaning, which is based on acoustic wave propagation through the substrate leading to detachment of particles [22].

### 3.4 BS laser cleaning of patrimonial objects

We applied the BS laser cleaning method to two real life samples. The first one was an advertisement made in smooth and frosted glasses partially covered with black paint (Fig. 10a). This piece belongs from an antique shop, already demolished, that was located in the historical center of the city of Buenos Aires.

As it can be seen, the paint covers partially the rough surface of the glass. The pulsed laser was directed using BS incidence from the opposite side of the paint. The cleaning process was monitored by the LAIP method already described. The ablation of the paint in the laser spot was let to continue until the acoustic signal disappeared. Then, the laser spot was moved to next adjacent place. The cleaning process was performed at fluences of 1.2 J/cm². At a repetition rate of 10 Hz, this procedure was relatively fast and the cleaning of the whole surface was accomplished in a few minutes. After cleaning the surface with the laser, the remaining organic patina formed was removed by wiping the surface with a tissue soaked in alcohol. Figure 10c shows the final state after laser cleaning.

As a second application, BS laser cleaning was performed on a patrimonial bottle found in archeological excavations in one of the earliest houses of the city of Buenos Aires. In this case, the BS incidence method turns out to be an efficient procedure for cleaning due the fact that black dirt was strongly stuck to the inner walls of the bottle (Fig. 11a). Frontal laser incidence on the dirty surface was impossible in this case. For practical reasons, a piece of tissue was inserted prior to laser cleaning to collect the expelled material and avoid redeposition on the opposite face inside the bottle. The method was very efficient and thorough in removing basically all black dirt at fluences of 1 J/cm². The remaining patina was removed by washing the bottle in an ultrasonic bath with soap and water. The final result of the laser cleaning and wash processes is shown in Fig. 11c, together with a partial cleaning (Fig. 11b) stage. The upper circle in Fig. 11 is a microscopic image of a cleaned section. As it can be seen, no damage of the glass can be observed.

### 4 Conclusions

In this work, we analyzed laser cleaning, based on laser ablation, of glassware and transparent objects. By measuring the ablation thresholds of paint films using a photoacoustic method (LAIP), we found that they are a joint property of the system dirt-glass and do not depend on the thickness of the paint layer. Our results also show that the ablation threshold is independent of the microstructure of the substrate (frosted or transparent glass). Based on these results, we propose that for systems composed by a substrate covered with a film of
other material, the threshold fluence for ablation depends only on the intrinsic properties of the film.

By means of transmission measurements and LAIP, we determined the cleaning efficiency for both front- and backside incidence geometries, showing that laser irradiation from the back side through the glass was at least one order of magnitude more effective than frontside irradiation. Real time monitoring of the cleaning process with LAIP was possible because there is a direct relationship between the amplitude of the acoustic wave produced in the ablation process and the amount of ablated material.
A null acoustic signal indicates that no more material is
removed, so the laser cleaning process can be finished.

We developed a simple phenomenological model that
accounts for the remarkably higher cleaning efficiency
for rear-side irradiation obtained in our experiments.
The model is based on the analysis of the processes tak-
ing place in the case of rear-side irradiation, which are
essentially different from those occurring for frontside
incidence. The most important effect induced by backside
irradiation is the creation, by an almost isochoric heating,
of a superheated layer which bends upwards due to the
impossibility of lateral expansion. This leads to a detach-
ment of the paint from the substrate and to an ejection
of material due to the high pressures accumulated in the
heated region. We propose a mathematical relationship
between cleaning efficiency, thickness and laser fluence,
which should be tested in further experiments.

The method reported here was successfully applied to
two real life samples: a painted advertisement glass and an
antique bottle of patrimonial value founded in archeologi-
cal excavations made in the city of Buenos Aires. Laser
cleaning using backside incidence was very successful in
both cases.

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