The art of CO_2 for art conservation: a green approach to antique textile cleaning†

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The use of CO_2 as a dry-cleaning solvent for old silk textiles was investigated. The cleaning procedures under study were tested on the 18th century religious garments from Virgin and Child from Palácio das Necessidades, Lisbon. The effect of using different cleaning solvent streams, supercritical and liquid CO_2, CO_2 + isopropanol and CO_2 + isopropanol + water, was evaluated concerning the dirt particles extracted, weight loss and colour variation of the scapulary samples tested. Particularly, the use of liquid CO_2 and the addition of water as a co-solvent had a strong positive effect on removal of dirt particles. CO_2-assisted cleaning proved to be a very safe method for the cleaning of very deteriorated silk textiles. The fibres and the textile structure were not physically damaged and the method did not promote the loss of material, which is an enormous advantage for the cleaning of textiles of historic or artistic value.

Introduction

Conservators are committed to the development of safe techniques to clean textiles of historic or artistic value. Cleaning procedures must be designed to physically preserve the fibres and their structure and to avoid the shrinkage of materials, as happens during traditional wet cleaning. This is particularly important in severely damaged textiles, as in the case for the garments of the Virgin and Child (Fig. 1), an 18th century sculpture from Palácio das Necessidades in Lisbon, Portugal. The Virgin's garments are composed of several pieces that were heavily damaged; the fibres could easily suffer disintegration by simple handling. Our goal has been to develop new methods and procedures for cleaning the antique and fragile clothes of the Virgin and Child, since the previously performed wet cleaning tests damaged them unacceptably. The results of our preliminary studies were described by Sousa *et al.*[1] Our first "green" approach to antique textile cleaning investigated the harmfulness of the dry supercritical CO_2 ($scCO_2$) method in relation to colour variation due to solubilization of mordant ions, as well as loss of textile material, be it in weight or dimension, and efficacy by evaluating the amount of removal of external dirt particles. The comparison with the wet cleaning demonstrated that $scCO_2$ is a very safe solvent for cleaning very deteriorated silk textiles. As well as its safety as cleaning agent, CO_2 is considered a "green" solvent. Stricter regulation is pushing researchers to find modern environmental technologies and alternatives to perchloroethylene and other toxic organic solvents generally used in dry cleaning, which is the only method that could also be applied to this case study. Studies have linked prolonged perchloroethylene exposure to liver or kidney damage, short-term contact can cause headaches, nausea, and irritation of the skin, eyes, nose and throat.[2]

Fig. 1 Virgin and Child, an 18th century sculpture from Palácio das Necessidades, Lisbon. Photo copyright: Portuguese Institute of Conservation and Restoration (IPCR), Department of Textiles Conservation.

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Special concern must be taken to avoid the use of these hazardous substances by conservators and to minimize the emission of these compounds. $ScCO_2$ is considered a "green" alternative—CO_2 is non-flammable, relatively non-toxic and relatively inert—because after the extraction process it can be easily released as a gas simply by returning to atmospheric pressure and temperature conditions.[3] Therefore, no toxic residues will be present in the extracted materials or in the extracted compounds. Furthermore, processes involving CO_2 as a solvent do not increase CO_2 emissions but reuse the waste CO_2 produced by other industries.

Supercritical CO_2 has already been tested and applied in conservation and restoration operations, such as cleaning, protection and consolidation. CO_2 has demonstrated a great potential in replacing current conventional processes used in the conservation and restoration of paper, wood, waterlogged, ethnographic materials, stone and textiles.[4–8]

In this paper, we present the results obtained for the cleaning of scapulary samples from the 18th century religious garments from the Virgin and Child sculpture, with CO_2 at liquid and supercritical conditions with and without the use of co-solvents. Different sequences of cleaning extractions in continuous conditions were tested. The best cleaning procedure was established by analysis of loss of textile material, colour variation and dirt removal.

Experimental

Materials

The co-solvent isopropanol (IPA) was an analytical reagent puriss. P.A., purchased from Fluka Riedel-de-Haën. All reagents were used as received without further purification.

CO_2 was obtained from Air Liquide with 99.998% purity.

Characterization of textile samples

The silk textile samples from the sculpture Virgin and Child were collected from the scapulary of the Virgin (Fig. 2(a)). All the square samples used in the tests with co-solvents were cut in 1 cm^2 pieces from a bigger sample of the scapulary (7 cm × 5 cm, Fig. 2(b)). This bigger sample was separated from the scapulary just by simple handling, since the fibres are very weak and are at risk of disintegration.

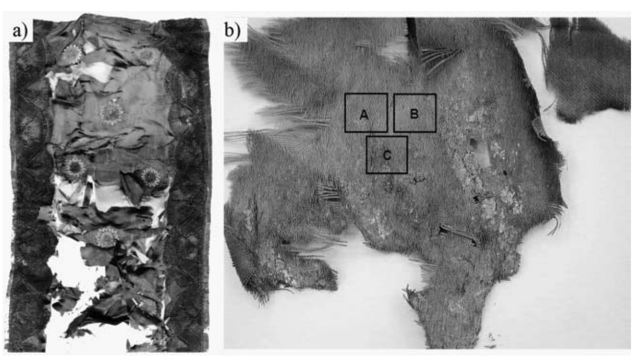

Fig. 2 (a) Detail of the Virgin and Child scapulary; (b) sample with 7 cm × 5 cm dimensions showing samples A, B and C of 1 cm^2.

The textile fibres were characterized through optical microscopy in longitudinal and cross sections and infrared spectroscopy as described in earlier work.[1] The scapulary samples were identified as silk *Bombyx mori*, and display a brownish colour with the following average colour coordinates: $L = 44.9$ (± 1.43), $a^* = 4.9$ (± 0.71) and $b^* = 13.8$ (± 1.68).

In order to control physical losses, textile samples were weighed, before and after the dry-CO_2 cleaning procedures, in a Startorius Research balance with 0.00001 g accuracy.

Characterization of the dirt particles

The garments from the sculpture the Virgin and Child are an example of a silk textile heavily deteriorated and soiled. The silk fibres have lost their mechanical properties and are collapsing, with consequent loss of material. The presence of soil particles will catalyze the textile degradation, and therefore a cleaning operation will be the first step for a complete restoration of the garments. The dirt particles that were present in the fibres from the Virgin and Child were characterized by infrared spectroscopy whenever possible. The sampling of the soil particles was performed in 4 samples with *circa* 1 cm^2, and in a bigger sample of *circa* 7 × 10 cm; the particles were separated by colour and form. The results obtained were consistent and it was possible to conclude that the main exogenous compounds were calcium carbonate and calcium sulfate particles (see Fig. 3(a)), with dimensions between 10–20 μm. Other black particles, probably carbonaceous particles, of similar dimensions were present in lower amounts, but could not be analyzed as sampling was very difficult due to their loss of cohesion. Besides the above described particles, which are expected and common in air, large amounts of cellulose fibres, as small crusts, were also characterized since they could be removed physically. These crusts were most probably a result of contamination by the paper used for the storage protection of the sculpture, this was confirmed by comparing the infrared spectra of the crust and paper, which is shown in Fig. 3(b). Contrary to the airborne particles of gypsum and calcium carbonate, this soil was an unexpected contamination, which complicated the extraction of dirt particles with $scCO_2$.

CO_2-assisted cleaning experiments

The scapulary samples were cleaned in a laboratory scale apparatus shown schematically in Fig. 4, which is an improved version of the previous one described by Sousa *et al.*[1] The measurements were carried out in a visual 4.5 mL stainless steel cell equipped with two sapphire windows, which allows full visualization of the sample during the cleaning process. First the sample is carefully placed within a metallic support and introduced into the cell. The cell is then immersed in a thermostated water bath, and the system is pressurized with fresh CO_2 until the desired pressure is brought into the cell (approximately 20 MPa) using a Gilson liquid pump at a CO_2 flow rate of 0.98 g min^{-1}. Then a CO_2 (or a CO_2 + co-solvent stream) passes through the vessel with a flow rate of 1.5 mL min^{-1} for two hours. The co-solvent is introduced using a slave pump connected and controlled by the master pump. The solvent mass compositions used were:

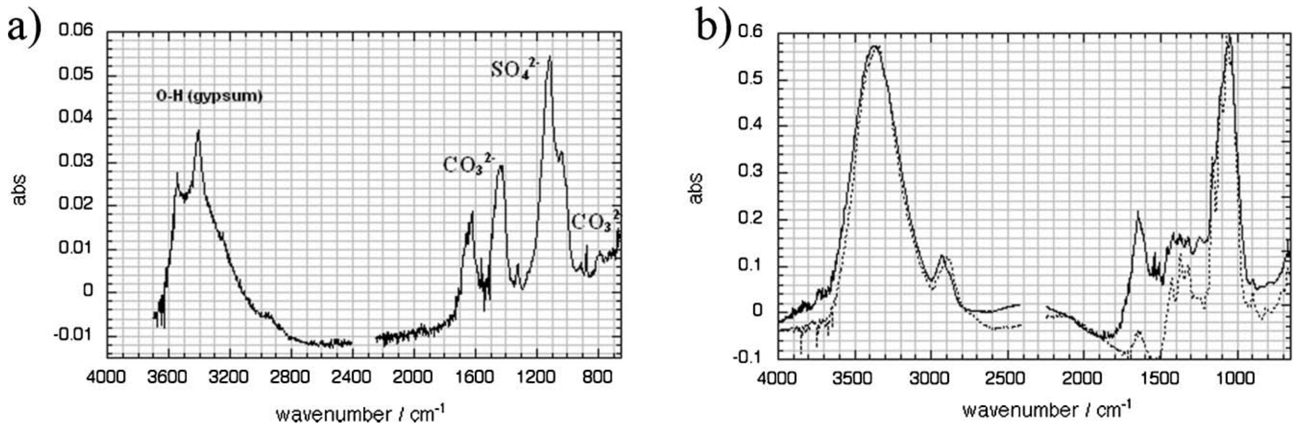

Fig. 3 (a) Infrared spectrum of soil particles where gypsum ($CaSO_4 \cdot 2H_2O$) and calcium carbonate are present; (b) representative infrared spectra for the whitish crust (full line) compares well with the spectra obtained for the paper used for storage protection (dotted line).

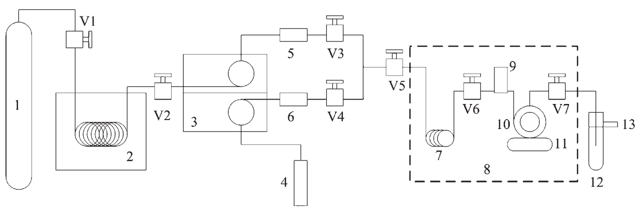

Fig. 4 Experimental cleaning apparatus: (1) CO_2 cylinder; (2) refrigeration unit; (3) high-pressure liquid pump, master and slave Gilson pumps; (4) co-solvent; (5) and (6) check-valves; (7) pre-heater; (8) thermostated bath; (9) pressure transducer; (10) high-pressure visual cell; (11) cell support; (12) trap; (13) vent; (V1) to (V7) high-pressure valves.

98.35% CO_2 + 1.65% isopropanol , 98.13% CO_2 + 1.64% isopropanol + 0.23% H_2O, and 97.83% CO_2 +1.66% isopropanol + 0.51% H_2O. Experiments at supercritical conditions were conducted at 40 °C and 20 MPa, and 25 °C and 20 MPa when using liquid CO_2. At the end of the experiment the samples were further cleaned with only CO_2 to remove traces of any co-solvent.

At the exit, the extract (co-solvents and residues) was collected by precipitation, due to the decompression, in a glass tube immersed in an ice bath.

Safety warning. These experiments involve high pressures and must only be carried out in an apparatus with the appropriate pressure rating at the dry-cleaning temperature. The technology involved needs to be operated by qualified high pressure engineers.

Optical microscopy

To ascertain the removal of the dirt particles, the samples were analyzed by Zeiss Axioplan Z Imaging optical microscopy with a Canon Power Shot G3 digital camera (Model PC1032), before and after the cleaning. The quantification of dirt particles extracted with the CO_2 cleaning was performed through digital image treatment using the program Paint Shop Pro. This program allows the measurement of the dirt particulate area before and after the cleaning in the photographs obtained with the optical microscope.

Micro Fourier transform infrared spectroscopy

Infrared spectra were acquired with a Nicolet Nexus spectrophotometer interfaced with a Continuμm microscope, with a MCT-A detector cooled by liquid nitrogen. The spatial resolution is 30 μm. All the spectra presented were obtained in transmission mode, using a Thermo diamond anvil compression cell. The spectra were obtained in the range of 4000–650 cm^{-1}, with a resolution of 4 cm^{-1} and 128 scans. They are shown here as acquired, except for the removal of the CO_2 absorption at approx. 2300–2400 cm^{-1}.

Colourimeter

Colour determinations were made using a Datacolor International colourimeter. The optical system of the measuring head uses diffuse illumination from a pulsed Xenon lamp over a 8 mm diameter measuring area, with a 10° viewing angle geometry. The reference source was D65 and the calibration was performed with a bright white tile standard plate and with a black trap standard. With the aid of a positioning Melinex mask, the measuring head was positioned on the same area of each textile sample; for each determination of the L, a^*, b^* values, the mean value of six measurements was calculated.

Results and discussion

Table 1 summarizes the cleaning experiments undertaken with different solvent streams and includes the percentage of dirt extraction and corresponding weight loss of the three extensively soiled scapulary samples, shown in Fig. 2(b), named A, B and C.

The investigation of the best cleaning procedure with real sample tissue is always difficult, as a real sample can not be exactly duplicated. This is confirmed by the different extent of cleaning obtained with $scCO_2$ (entries 1 and 5, Table 1) for samples A and B.

In our previous work, $scCO_2$ was able to remove about 50–70% of usual dirt particles found in textiles. However, the tissue samples under study, A, B and C, were extensively dirty and the help of co-solvents was needed.

Table 1 Percentage of dirt particles extracted and loss in mass of the samples from the scapulary of Virgin and Child sculpture after cleaning with different streams

Entry	Sample	Cleaning stream composition[a]	Extracted dirt particles (%)	Δ weight (%)
1	A	$scCO_2$	25	2
2	A	98.34% $scCO_2$ + 1.66% IPA	−42	5
3	A	98.34% liquid CO_2 + 1.66% IPA	10	2
4	A	98.13% liquid CO_2 + 1.64% IPA + 0.23% H_2O	53	2
5	B	$scCO_2$	35	2
6	B	Liquid CO_2	53	3
7	C	97.83% liquid CO_2 + 1.66% IPA + 0.51% H_2O	51	10

[a] IPA = isopropanol

Sample A was first cleaned with $scCO_2$. This operation removed about 25% of the soiling without significant weight loss (entry 1, Table 1). The addition of isopropanol as a co-solvent to $scCO_2$ did not improve the efficiency of the cleaning of sample A, as can be seen from entry 2 of Table 1. In fact, it seems that the percentage of dirt increased. A possible explanation for this fact is the migration of dirt particles existing inside the fibres to the surface of the textile due to the high diffusivity of the $scCO_2$ + isopropanol stream. Sample B was also cleaned using $scCO_2$, which was able to remove 35% of dirt particles (entry 5, Table 1). This sample was then cleaned with liquid CO_2, this procedure had a significant impact on the cleaning, since more than 50% of dirt particles were extracted (entry 6, Table 1), as can be seen in Fig. 5(a) and (b). This can be explained by the higher density of the liquid CO_2 which allows a better removal of dirt particles at the textile surface.

Sample A was further treated with liquid CO_2 and isopropanol as a co-solvent (entry 3, Table 1). This cleaning stream was able to remove only 10% of the remaining dirt of the previous experiment. The addition of a small percentage of water as a co-solvent to the stream liquid CO_2 + isopropanol had a very positive influence on the removal of dirt particles of sample A (entry 4, Table 1). It was possible to remove more than 50% of remaining dirt particles that were strongly linked to the textile and were not extracted with the previous experiments (entries 1–3, Table 1), as can be seen in Fig. 6(a) and (b).

The variation in the water content, from 0.23% to 0.51%, in the solvent stream did not have an impact on the percentage of cleaning (entries 4 and 7, Table 1). However, the stream with the highest water content promoted the humidification of the textile to a considerable amount (entry 7, Table 1), and the physical losses increased to 10% instead of the usual 3%.

Only in the tests performed with liquid CO_2 + water + isopropanol as co-solvents did the luminosity of the textile samples decrease as a result of the extraction of white dirt particles. The other samples with cellulose crusts only showed colour variation within the experimental error. In all the tests performed, the hue did not significantly change, which means that the mordant were not extracted with the CO_2 cleaning and did not change the final colour of the textile.

Conclusions

The use of water as a co-solvent had a positive effect on the cleaning of the dirtier areas of the Virgin and Child's textiles. The CO_2-assisted cleaning process did not physically damage the fibres nor their structure and did not promote the loss of material, which is an enormous advantage when cleaning textiles of historic or artistic value.

In this work, a two-step process was proposed to clean the textiles from the garments of the Virgin and Child. In the first step, the textile was cleaned with supercritical CO_2 which was able to remove about 50–70% of usual dirt particles found in textiles and 25–35% of dirt in the more extensively soiled areas. In the second extraction, the textile was cleaned with liquid CO_2, further removing approximately 50% of dirt particles from the more extensively soiled areas. The addition of

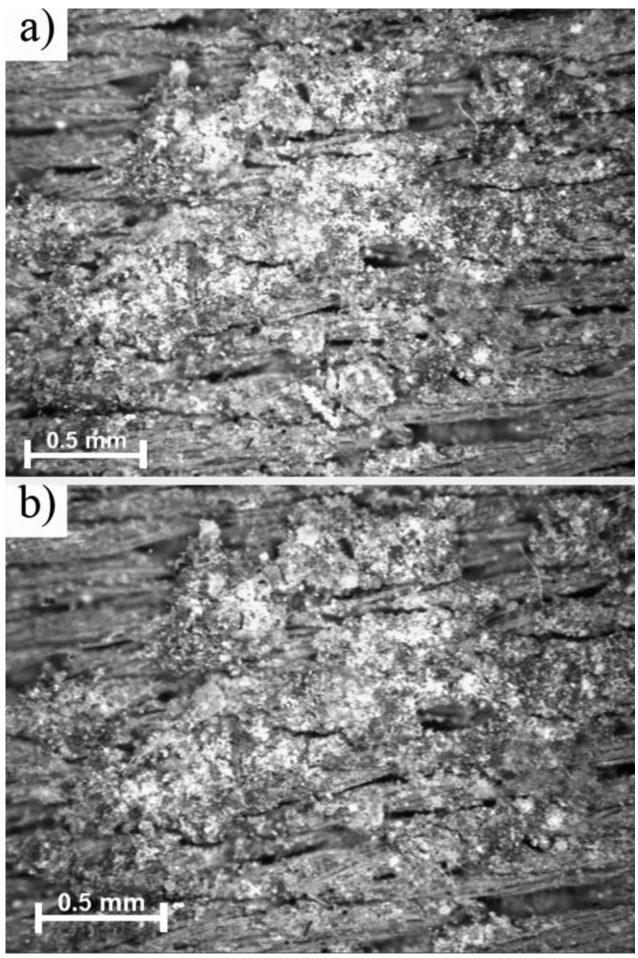

Fig. 5 Image of textile sample B corresponding to entry 6 of Table 1: (a) before; (b) after cleaning.

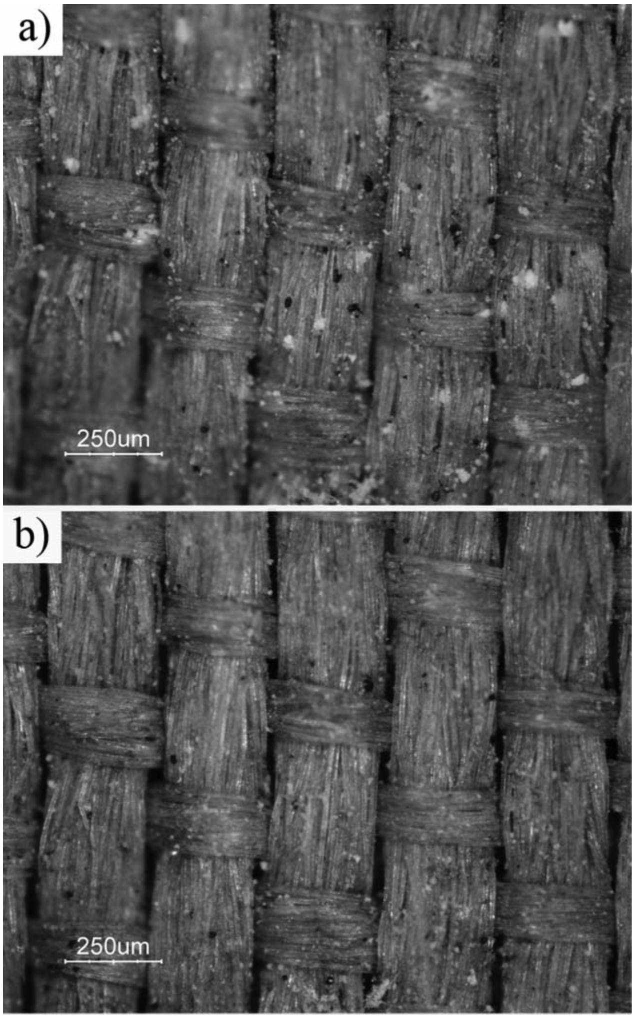

Fig. 6 Image of textile sample A corresponding to entry 4 of Table 1: (a) before; (b) after cleaning.

co-solvents (isopropanol and isopropanol + water) promoted the extraction of polar particles strongly attached to the textile, such as carbonates and sulfates, removing another 20% of dirt. The addition of water was required for sufficient removal of dirt particles in areas of the textile where the amount of carbonaceous particles was probably higher.

It should be pointed out that other wet cleaning methods used in conservation and restoration of textiles cannot be applied to this case study because they can cause severe damage contrary to the CO_2 cleaning. The liquid and/or supercritical CO_2, either with or without the use of co-solvents, represents an enormous advantage for the cleaning of textiles of historic or artistic value, and allows the preservation of textile cultural heritage within the limits of disintegration. The technology involved needs experts and the cooperation between high pressure engineers and conservation scientists to make accessible further applications of supercritical technology on an appropriate scale.

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