Pozhidaev *et al. Herit Sci* (2019) 7:90
https://doi.org/10.1186/s40494-019-0329-z

Heritage Science

RESEARCH ARTICLE Open Access

# Research of a complex fire-induced pollution on the marble relief from the Pushkin state museum of fine arts collection

V. M. Pozhidaev[1], V. M. Retivov[2], A. V. Kamaev[1], S. K. Belus[2], A. S. Nartov[2], V. A. Rastorguev[3], I. V. Borodin[3], E. Y. Tereschenko[1,4*], R. A. Sandu[1,2], E. B. Yatsishina[1] and M. V. Kovalchuk[1,4]

## Abstract

**Background:** Fundamental restoration of sculptures must include the research of pollution composition and exhibit surface condition as well as accurate identification of the materials of sculptures, bas-reliefs and coatings. In the recent years, studies of marble objects aimed at identification of contamination nature and composition have been developed. It should be noted that some exhibits have individual features as objects of restoration due to complex exposure to the environment, e.g. to fire.

**Results:** The article describes the results of surface contamination study on two exhibits from the Pushkin State Museum of Fine Arts collection. Marble relief sculpture "The Flagellation of Christ" was the main object of the study. Glazed terracotta (majolica) "Madonna Friedrichshain" was studied as a control sample with the same type of contaminations but with less sensitive surface. According to the results of different gas chromatography and X-ray fluorescence analyses, pollution compounds were identified as fatty alcohols, fatty acids and esters, part of which being residues of pyrolysis gasification, including those containing iron and lead. In order to gently clean the exhibits, several variants of chemical compounds were proposed based on various chelating agent mixtures, and, after studying their comparative effectiveness, the optimal scheme was chosen for removing existing contamination. For verification of marble exhibits safety, selected cleaning mixtures were tested on polished Carrara marble sample.

**Conclusion:** The most suitable scheme of organic contaminations removal including those containing iron and lead was suggested as part of restoration process. There is a number of working schemes of cleaning the surface of exhibits, however our proposed scheme interacts with the marble surface more gently because the target cleaning mixture composition was formulated taking into account the nature of pollutants and the least possible impact on the sample surface.

**Keywords:** Surface pollution cleaning, Gas chromatography-mass spectrometry, Targeting design of cleaning mixture, XRF, Marble, Majolica

## Introduction

Fundamental restoration of sculptures is impossible without conducting integrated studies of contamination composition and exhibit surface condition and accurate identification of the materials of sculptures, bas-reliefs and coatings. Studying the contamination before cleaning marble objects has been common practice in recent years [1–12]. Most often, these are pollutions associated with the environment [1–9] or appeared due to contact with other materials [10–12]. A wide range of methods is used to study pollutants: IR-spectroscopy [1–8], optical microscopy [1, 2, 5, 7], scanning electron microscopy [1–3, 5], gas chromatography [7–9], energy-dispersive X-ray microanalysis [1, 5], X-ray fluorescence [7] and others. However, individual character of pollutions occurring in most exhibits requires the personalized approach to their

*Correspondence: helena.tereschenko@gmail.com
[4] Shubnikov Institute of Crystallography, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Moscow, Russia
Full list of author information is available at the end of the article

removal. Sanne Spile et al. [11] described some working techniques used during the cleaning of the Carrara Bianco marble surface.

In this paper, we are describing the development of purification scheme based on the targeting treatment of marble surface with the complexing agents selected in accordance with this particular type of contamination. The publication is a result of the research work conducted by the staff of the NRC «Kurchatov Institute» with sculptures from the Pushkin State Museum of Fine Arts holdings and originating from the collection of the Kaiser-Friedrich-Museum, which currently does not exist. In 2015, the Pushkin Museum and the Berlin Bode Museum (the legal successor of the Kaiser-Friedrich-Museum) launched a joint project with the purpose of returning to scientific use and restoring these works that had been considered irretrievably lost during the World War II for a long period of time.

The marble relief "The Flagellation of Christ" was acquired in 1892 in Florence for the Berlin Museum from the famous Florentine family Peruzzi [13]. It was bought by Wilhelm von Bode (1845–1929) for Berlin collections. He was the head of the state museum collections and the author of numerous scientific papers on the history of German, Dutch and Italian fine art and sculpture [14]. Wilhelm von Bode supposed that the marble relief was the original work of the famous master of Italian sculpture of the XV century, Donato di Niccolo di Betto Bardi, better known as Donatello (c. 1386–1466). He suggested that the relief version was created in the 1420 s, in the early period of the sculptor's creativity. This attribution was adopted by many researchers and remained common for a long time [15–18]. Later, the relief was excluded from the list of Donatello's works by the most authoritative researchers of his creative works in the post-war period when it was no longer physically available to historians and critics of art. H.W. Janson, the author of the fundamental monograph about Donatello, attributed the authorship of the marble relief to an unknown follower of the artist's style who worked in the late fifteenth century. The relief's marble is white with characteristic fine crystallization, so it was supposed that it could be Carrara marble, but there is no clear evidence.

Also, in this research, we examined the relief sculpture depicting Madonna and Child called "Madonna Friedrichshain". It was named after Graf von Dönhoff - Friedrichstein who donated the sculpture to the museum in Berlin. It was bought in Florence in 1888 [19, 20], and its authorship is associated with the name of the Florentine sculptor Luca Della Robbia (1400–1482), who worked a lot in the technique of glazed terracotta [21]. Later, "Madonna Friedrichshain" became a household name in the literature for all similar images of Madonna: another version, very close in manner to this one, is stored in the Museum of Albright-Knox, Buffalo, United States [20, 22, 23]. John Pope Hennessy, authoritative English historian of Renaissance sculpture, dated this relief sculpture about 1438 in his work about Luca Della Robbia [24]. He named not only stylistic considerations as arguments for such attribution, but also some of the technical imperfections of workmanship. In particular, John Pope Hennessy mentioned glazing errors that led to cracks in the glaze surface of relief sculpture that almost never occurred in the works of masters of the later period. That caused him to conclude that Berlin "Madonna Friedrichshain" is a product of some technical experiment, during which the master were perfecting his methods of work.

This paper is just a small part of the complex research program and is devoted to determination of composition and origin of contaminations on the two objects of art from the Pushkin Museum collection that were prepared for the restoration, development of cleaning reagents mixture and testing its effectiveness for the exhibit treatment.

## Experimental part

### Sample collection

Exhibit I: The main object of the study was marble basrelief "Flagellation of Christ" (S5, 46.5 × 57.5 cm).

Exhibit II: Majolica "Madonna with Child in her arms" (S17, 45 × 38 cm) was stored in the same conditions as the relief and therefore had similar type of contaminations.

Test samples: 3 Carrara marble samples (2 × 2 × 0.5 cm) polished with sandpaper of 40–20 micron grain size were used for testing the safety of developed cleaning mixture.

### Reagents for cleaning mixture development

Solvents of "reagent grade" qualification were used on the first stage of our study separately: methanol, ethanol, acetone, chloroform, *n*-hexane, 2-propanol, methylene chloride, cyclohexane, acetonitrile of "HPLC" qualification; acetyl chloride of "h" qualification, as well as the mixture of solvents (isopropanol, cyclohexane, methylene chloride, acetonitrile, 1:1:1:1).

Specially prepared targeted cleaning mixtures developed during our study, SMS-2A (alkali) and SMS-2N (neutral) are described in Table 1.

The 100% EDTA was included into the study for the comparison of effectiveness.

### Sample preparation

Sample preparation from the surface of exhibits was performed by qualified restorers of the museum.

Washings from the exhibits surface were collected with cotton swabs soaked with solvent or solvent mixture. (See Fig. 1 (below *samples S5-**) and Fig. 2) Several solvents with different chemical properties were used for

separate flushing of contaminants: methanol, ethanol, isopropanol, acetone, chloroform, hexane, cyclohexane, methylene chloride and acetonitrile. The best extraction results were observed in case of a 4-component mixture of solvents: isopropanol, cyclohexane, methylene chloride, acetonitrile. Therefore, further studies were carried out on the samples obtained using a quaternary mixture. It should be noted that we collected a few samples from the areas with the same visible pollutions to raise a concentration of the studied contaminants.

The cotton swabs with contaminants were desiccated in a natural way and then were used for studying the pollution composition by X-ray fluorescence analysis (XRF). After that, the contaminations were washed out from the swabs and concentrated through extraction. Extraction was performed with 5 ml of a 4-component mixture of solvents in the ultrasonic bath at 50 °C for 60 min. Then, the solvents were removed under a nitrogen stream at room temperature, and the residue was dissolved in 100 µl of chloroform or acetonitrile.

To study non-volatile fractions, we prepared methyl esters. The extracts in chloroform were subjected to acid hydrolysis and esterified with methanol. For this purpose, 200 µl of test extract in chloroform was placed into a glass ampoule, and 1 ml of methanol was added. Then, 50 µl of acetyl chloride was carefully added dropwise. The sealed ampoule was heated in an oven at 105 °C for 5 h, after that it was cooled to a room temperature, 1 ml of water and 1 ml of hexane were added, and the ampoule was shaken vigorously. After separating the layers, the upper (hexane) layer was separated and filtered through anhydrous sodium sulphate into an evaporating dish, and the solvent was removed at a room temperature. The residue was dissolved in 100 µl of chloroform.

**Table 1 Composition of cleaning mixtures SMS-2A and SMS-2 N**

| | Component name | Content, % SMS-2A | Content, % SMS-2N | Properties for cleaning |
|---|---|---|---|---|
| 1 | Ethylenediaminetetraacetic acid (EDTA) | 3.5 | 3.5 | Universal complexing agent. Binds calcium, magnesium and heavy metal ions |
| 2 | Oxyethylidenediphosphonic acid (HEDP) | 3.5 | 3.5 | Complexing agent |
| 3 | Sintanol DS-10 | 2 | 2 | Medium emulsifier, wetting agent |
| 4 | Oxyethylated nonylphenol (9-12 Neonol AF) | 2 | 2 | Non-ionic surfactant, low foam wetting agent, emulsifier |
| 5 | Sodium alkylbenzene sulfonate (Sulfonol) | 3.5 | 3.5 | Anionic surfactant |
| 6 | Sodium tripolyphosphate | 4 | 4 | Disinfector, bleach, increases washing ability |
| 7 | Polyethylene glycol (PEG 400) | 1 | 1 | Stabilizing and lubricating agent |
| 8 | Monoethanolamine | 2 | 2 | Organic solvent |
| 9 | Edaplan 490 | 1.5 | 1.5 | Emulsifier |
| 10 | Sodium hydroxide | 4 | 2 | Substance to achieve a given pH |
| 12 | Water | 73 | 75 | Base of cleaning mixture |

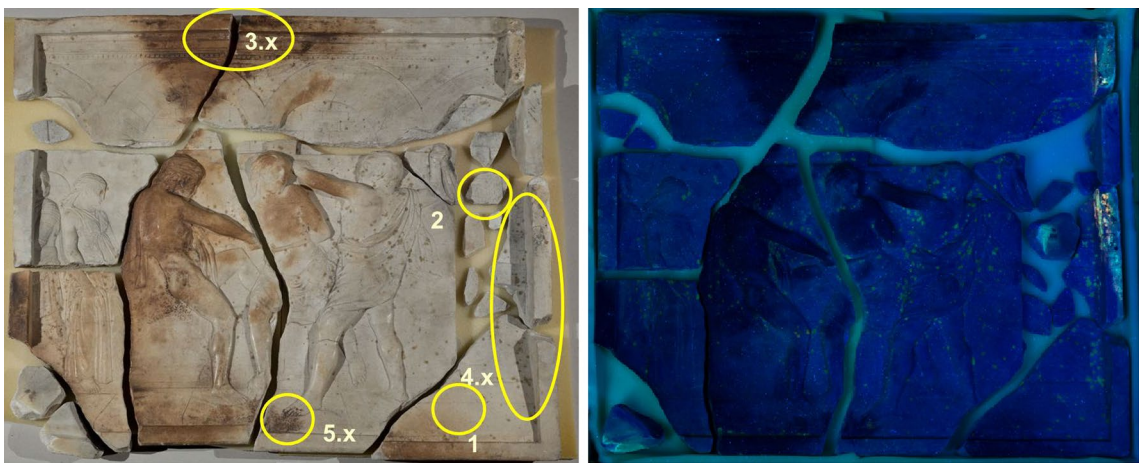


**Fig. 1** Relief sculpture "Flagellation of Christ" (S5). The view in visible and UV range with the sampling areas

**Fig. 2** Majolica "Madonna with Child in her arms" (S17). View in visible and UV range with the sampling areas

## Equipment and accessories

Chromatographic systems were used for pollutant identification: system 1 and system 2 with mass-spectrometry were used for gas chromatography-mass spectrometry (GC–MS) analyses of contaminant extracts from the cotton swabs, and system 3 was used to test the hypothesis about presence of beeswax in the contamination. IR spectrometer allowed us to refine the chemical composition of pollutants. X-ray fluorescence spectroscopy of washings allowed us to select lead and iron containing areas on the exhibit surface. Optical and scanning electron microscopy were used to control marble sample surface during the solvents testing.

### *Chromatographic system 1 (GC–MS)*

Gas chromatograph Crystal 5000.02 Chromatec with mass spectrometric detector ISQ Thermo Scientific. Chromatographic conditions: capillary column TR-5MS with the length of 30 m and the inner diameter of 0.25 mm; stationary phase film thickness was 0.25 μm. The initial temperature of the column thermostatic oven was 70 °C; temperature programming was 70 °C to 280 °C with the pace 10 °C/min. Samples were kept at the final temperature for 9 min. The carrier gas was helium, the flow rate was 1.2 ml/min, split ratio was 1:10. Injector temperature was 280 °C, interface detector temperature was 250 °C. Sample volume was 1 μl. Detection was performed in the scanning mode based on total ion current.

### *Chromatographic system 2 (GC–MS)*

Gas chromatograph HP 6890 with mass spectrometric detector MSD 5975 Agilent Technologies. Chromatographic conditions: capillary column DB-5 ms with the length of 30 m and the inner diameter of 0.25 mm; stationary phase film thickness was 0.25 μm. The initial temperature of the column thermostatic oven was 100 °C; temperature programming was 100 °C to 280 °C with the pace 15 °C/min. Samples were kept at the final temperature for 10 min. The carrier gas was helium, the flow rate was 1 ml/min, split ratio was 1:10. Injector temperature was 280 °C, interface detector temperature was 280 °C. Sample volume was 1 μl. Detection was performed in the scanning mode based on total ion current.

### *Chromatographic system 3 (GC)*

Gas chromatograph Bruker GC with the flame ionization detector on a capillary column VF-1 ms with the length of 15 m and the inner diameter of 0.32 mm; stationary phase film thickness was 0.25 μm. Temperature program of the column: initial temperature was 200 °C, then keeping for 5 min, raising the temperature up to 270 °C with the pace 10 °C/min and then keeping in isothermal mode for 38 min at 270 °C. Injector temperature was 270 °C. Detector temperature was 270 °C. The flow rate of the carrier gas (nitrogen) was 1 ml/min, split ratio was 1:10. Sample volume was 2 μl.

#### *Infra-red spectroscopy*

IR spectra of chloroform extracts were captured using Vertex 70 by Bruker in KBr sample cell at the optical path length of 0.63 mm.

#### *X-ray fluorescence analysis (XRF)*

Spectrophotometer of X-ray energies CEP-01 ElvaX Light. The analysis was performed using the reference-free method of fundamental parameters at voltage of 40 kV and current of 20 mA (X-ray tube: rhodium anode, beryllium window of 140 μm).

#### *UV light*

A wide-range UV lamp with a wavelength range of 190–380 nm was used.

#### *Optical microscopy*

Stemi 508 Carl Zeiss stereoscopic microscope with 100× magnification was used.

#### *Scanning electron microscopy (SEM)*

Scanning electron microscope Hitachi SU1510. Micrographs were taken under the following conditions: accelerating voltage: 5–7 kV, electron emission: 85–100 μA, magnification: 3000× and 300×, focal length varied depending on geometrical parameters of each sample.

## Results and discussions

The studied works of art were examined under ultraviolet light. Spots that glowed in the UV range were selected for further research as well as control areas without glowing (Figs. 1, 2). Preliminary XRF analysis revealed presence of compounds containing lead, probably of man-made origin, in that spots.

The areas 1 (S5-1) and 2 (S5-2) were used as a control samples because the surface in these areas was less contaminated. The areas 3 (S5-3.x) and 5 (S5-5.x) had dark contaminations, and area 4 (S5-4.x) had the greatest concentration of the spots which were luminescent under UV.

The areas of sampling for S17 were chosen based on their luminescence under UV and the contamination color in visible range.

The chromatograms of contamination extracts are shown in Fig. 3. Differences in the chromatograms show the variety of contaminant composition on the surface of the relief.

Mass spectra of certain compounds are shown in Fig. 4. The identification was carried out by comparing the mass spectra of compounds with the library of mass spectra (NIST 11 2011/EPA/NIH). Identification results are shown in Table 2.

As shown in Table 2, the main classes of identified organic compounds were: fatty alcohols and fatty acid esters. In one of the extracts from the surface of the bas-relief "Flagellation of Christ", squalene was found—an acyclic polyunsaturated liquid hydrocarbon (C30H50) in substantial quantities (up to 15%) that is part of human sebum [25, 26]. It could be trace of handling or touching, but we can't refine the time of its appearance.

Comparison of the data for the identification of detected compounds with the results of literature searches [27–29] allowed us to suggest that the extracts of organic contaminations from the surface of the bas-relief contained beeswax.

According to the literature [30, 31], the beeswax consists of 50 different chemical compounds, including esters (31–77%), free fatty acids (13–15%) and free fatty alcohols (2–3%). The main component of beeswax is myristin ($C_{16}H_{31}COOC_{31}H_{61}$) which is an ester of palmitic acid ($C_{15}H_{31}COOH$) and myricyl alcohol ($C_{31}H_{61}OH$). It is a very high boiling compound (more than 500 °C) with complex chromatographic conditions and it was not eluted from the column.

In order to test the hypothesis about presence of beeswax in the compounds of the contamination on the marble bas-relief, we used a shorter chromatographic column—VF-1ms with the length of 15 m.

The chromatogram of the extract of combined S 5-3 samples is shown in Fig. 5a.

For greater reliability, the transesterification of extracts was carried out with methyl alcohol. Thus, myricyl palmitate ester was converted into a low-boiling methyl ester of palmitic acid and myricyl alcohol. For a comparative qualitative analysis, a sample of modern beeswax was also subjected to treatment with methyl alcohol. The chromatogram of the sample extract S5-3 of contamination after methylation is shown in Fig. 5b. The following were identified in the chromatograms (Fig. 5): myricyl palmitate, methyl ester of palmitic acid and myricyl alcohol, which confirms the presence of the beeswax in the contaminants.

Gas chromatographic analysis of the washings from bas-relief areas with no naked-eye visible contaminations ("clean background") also revealed presence of the main components of beeswax. On this basis, it can be concluded that the wax was used as a coating for protecting marble bas-relief from harmful external effects.

It was evident that the identified compounds from the extracts of marble bas-relief contaminations (Table 2) contained esters of fatty alcohols and acetic acid. From the description of items presented for the restoration, it is known that they were found after a fire in the storage room. According to the literature [32, 33], the major product of thermal degradation of wood

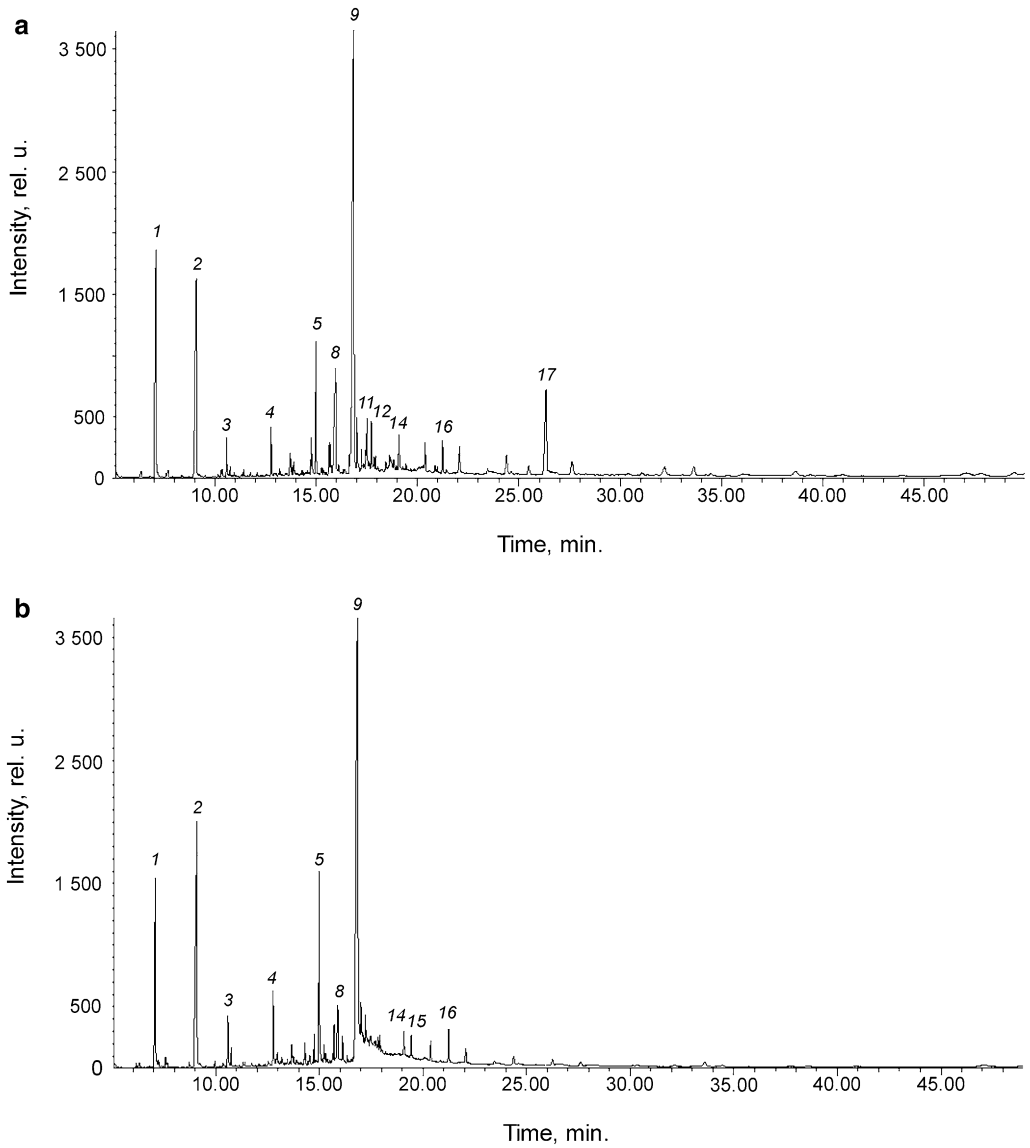


**Fig. 3** GC-MS chromatograms of extract contaminations from marble bas-relief (S5): **a** combined samples S5-3, **b** trial S5 6.1 (spots)

(pyrolysis under fire) is acetic acid. Based on this, it can be assumed that contaminants contained in the substance were formed by reaction of organic acids with a fatty wax wood pyrolysis product—acetic acid.

When investigating contaminations on the surface of the marble bas-relief, it can be seen that they have a focal localization. There are several large brown areas and also small brown spots. As noted above, these spots appeared as a result of a fire in the storage room.

According to the literature [34], wax melts at a temperature of 62–68 °C. Above 120 °C, the wax begins to evaporate due to the thermal degradation of some of its components, and at 300 °C the wax becomes flammable. Detection of wax in the contaminants on the surface of the bas-relief leads to the conclusion that the marble bas-relief had not been subjected to severe thermal stresses, and its structure had not been damaged. Brown spots of impurities formed by dripping or spraying liquid probably induced condensation of wood combustion products in a fire in the storage on a marble surface covered with wax.

It is also known that free fatty acid wax may interact with certain metals to form a coloured salt [35]. For example, when in contact with iron salts, wax acquires a brown color; with copper—green color; with dissolved zinc—dirty grey color.

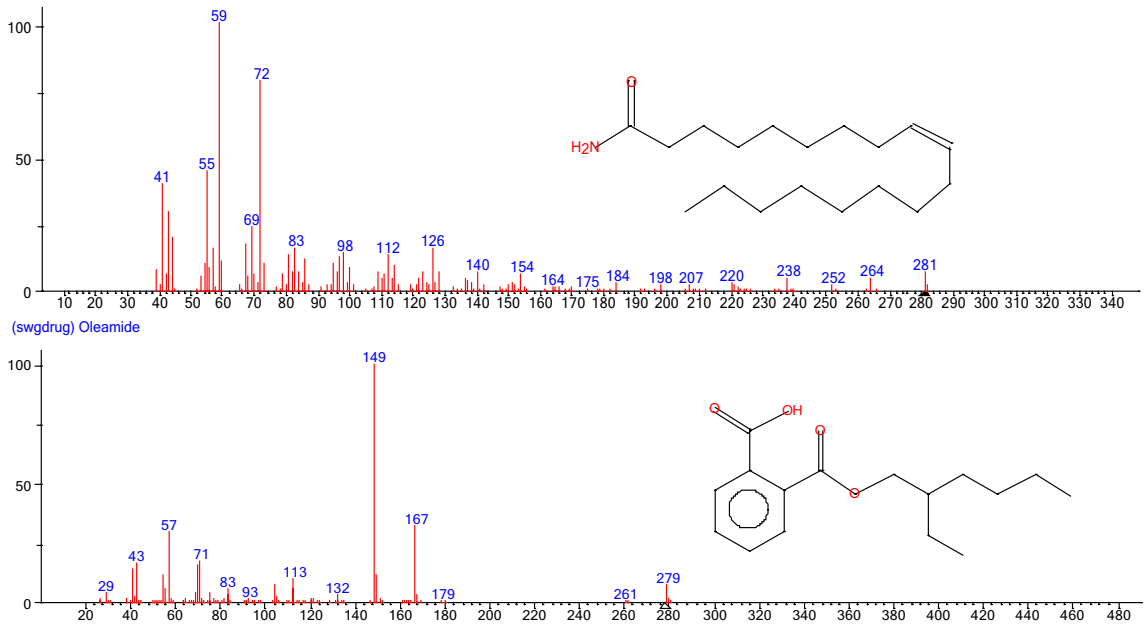


**Fig. 4** Examples of mass spectra obtained during analysis of washings from the surface of the bas-relief "Flagellation of Christ". **a** #14 and **b** #16 (see Table 2), respectively

**Table 2 Identified organic compounds**

| # | Organic compound | Quantity, % | | | | | Accuracy,% |
|---|---|---|---|---|---|---|---|
| | | Sample S5-3.x | Sample S5-4.x | Sample S5-5.1 | Sample S5-5.2 | Sample S5-1&S5-2 | |
| 1 | Ethanol, 2-phenoxy | 7.60 | 11.16 | 4.01 | 11.58 | 11.56 | 94 |
| 2 | 3-Methyl-3-Decen-2-one | 16.99 | 10.58 | 7.38 | 12.10 | 19.34 | 36 |
| 3 | 1-Tridecanol | 2.37 | 1.21 | 1.17 | 1.37 | – | 91 |
| 4 | Tetradecanoic acid | 0.88 | 1.08 | 0.31 | 0.38 | – | 98 |
| 5 | *n*-Pentadecanol | 6.97 | 3.71 | 3.57 | 4.25 | 3.62 | 91 |
| 7 | Palmitoleic acid | 0.72 | 1.12 | 0.51 | 0.42 | – | 90 |
| 8 | *n*-Hexadecanoic acid | 4.79 | 7.41 | 7.21 | 5.39 | – | 93 |
| 9 | 9-Tetradecen-1-ol, acetate | 38.91 | 33.25 | 28.85 | 33.58 | 31.26 | 87 |
| 10 | *n*-Heptadecanol-1 | 3.90 | 0.67 | 2.12 | 2.42 | – | 91 |
| 11 | 9-Octadecen-1-ol | 4.01 | 0.84 | | 1.46 | – | 99 |
| 12 | Linoleic acid ethyl ester | 1.46 | 1.67 | 5.43 | 2.37 | 8.37 | 91 |
| 13 | Isobutyl acid undeca-10-enyl ester | 3.90 | 1.67 | 4.35 | 1.42 | 12.14 | 74 |
| 14 | 9-Octadecenamide | 0.89 | 0.48 | 8.61 | 5.17 | – | 95 |
| 15 | 1-Octadecanal | 0.81 | 1.01 | 0.71 | 0.53 | – | 90 |
| 16 | Bis(2-ethylhexyl)phthalate | 1.40 | 1.06 | 1.41 | 1.04 | 3.62 | 90 |
| 17 | Squalene | – | 6.94 | – | – | – | 99 |

Therefore, it is likely that brown coloration of the test spots of contamination on the marble bas-relief is a consequence of action of some liquid condensate formed as a result of the fire. This liquid was probably aqueous solution or suspension containing iron salts (for example, rust). This suggestion was verified by positive results of the qualitative reaction for iron salts [36] in extract contaminants from a marble bas-relief with a solution of potassium ferricyanide because iron salts of fatty acids are soluble in the same solvents as wax, and also by XRF data.

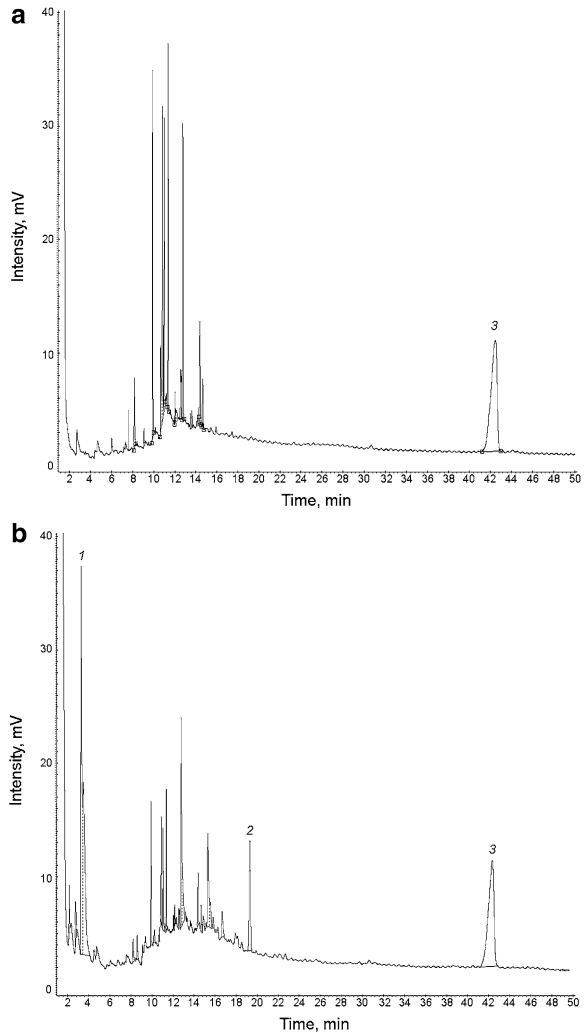


**Fig. 5** Chromatograms of extracts of combined sample specimens S5-3.x for marble bas-relief: **a** before methylation; **b** after methylation. 1—methyl ester of palmitic acid; 2—myricyl alcohol; 3—myricyl palmitate

Chromatographic analysis of washings from the surface of control exhibit, majolica "Madonna with Child in her arms" ("Madonna Friedrichshain") showed that they have an approximately identical composition of contaminants with marble bas-relief which were formed mainly due to condensation of pyrolysis products on their surfaces. The analysis of the contaminant washings from the majolica surface showed results similar to the ones obtained for the marble bas-relief with the exception of the difference due to the absence of beeswax components on the surface of majolica.

Contamination size on the majolica was less than on the marble bas-relief. It can be easily understood since, unlike marble, majolica has a smooth, non-porous surface, therefore, the adsorption of contaminants was not that high in this case. Marble, in turn, has a porous surface that facilitates adsorption of more contaminants. Moreover, marble was treated with beeswax which can also absorb organic pyrolysis products.

Analysis of XRF data of the washings from majolica surface showed that on the less-contaminated background of images, compounds were detected containing mainly copper and iron, while the spots glowed under the UV (Fig. 2) contained a large amount of lead, in some areas more than 50% by weight. We suppose that traces of lead and iron belong to the ammunition remains (of the Second World War) that appeared on the exhibits surface during the fire.

### Development of targeted clearing mixtures of detergent

Detergent compositions for targeted cleaning have been developed based on the obtained data. The results of GC and GC-MS analyses showed that the surface of the exhibits is contaminated with compounds containing fatty acids, fatty alcohols, esters and ethers. To remove them, it is necessary that they form soluble salts. To do this, saponifying components with reactivity with respect to impurities of different origin were mixed in a certain proportion to obtain targeted cleaning mixtures. Also the surfactants (tripolyphosphate) were added to the mixtures for contamination emulsification. Thus, the components complement each other and their combination forms a universal cleaning mixture composition capable of removing complex chemical composition:

- High washing capacity of EDTA and HEDP (#1 and #2, Table 1) for various salt depositions was the reason for including them to the mixtures. We took into account that EDTA-based detergent was very aggressive against marble surfaces according to Lauffenburger [37], so for this reason we minimized it concentration for SNS-2N and SNS-2A
- Sintanol and Neonol are highly effective non-ionic surfactants.
- Sulphonal is an effective ionic surfactant.
- Sodium tripolyphosphate helps emulsify fat on contaminated surfaces.
- Mono-ethanolamine is also a component of various detergents, allowing to proper remove certain types of contamination.
- Polyethylene glycol is known as universal solvent for many organic compounds.

The first stage of developed mixtures testing was performed on the control exhibit—majolica (S17). Its glazed surface has very strong resistance to chemical action and

low adhesion to contaminations. Therefore, the effectiveness of mixtures as solvents for the contaminants was tested on the majolica surface.

Effective removal of contaminations was performed with mixtures that were diluted with water in the volume ratio of 1:5 and then treated with a cotton swab soaked in the solution for the surface treatment. The mixtures were left on the surface for 6 min, then removed with a dry swab and cleaned with a swab soaked with distilled water.

The second stage of testing was evaluating the mixtures safety for marble surface. It was performed on the polished test marble sample. The test marble sample was treated with the cleaning mixtures developed by us. SEM microphotographs of this test sample (Fig. 6) before and after treatment allowed us to make conclusion on the nondestructive properties of these compositions SNS-2N and SNS-2A and their suitability for studying marble exhibits.

In the Fig. 6a, one can observe increase of the surface defects, which aligns with the conclusions in the article [37]. Meanwhile, the surfaces of the second and third test samples didn't change.

In the third stage, the mixtures were used for cleaning the darkest area on the marble bas-relief (on a fragment with area S5-3). The detergent compositions were applied to the sample with a cotton swab, up to a noticeable brightening observed on the marble surface due to reducing the amount of contamination between marble grains. Comparative efficiency of solvents and cleaning mixtures on a section of the marble bas-relief "Flagellation of Christ" is shown in Fig. 7. Treatment procedure was the same as for the tested marble samples with the exposure time of 2 min (Fig. 7a) and 6 min (Fig. 7b).

It can be seen that the alkaline mixture cleaned surface better than neutral (see Additional file 1 for details). Compared with the results of washing with EDTA-based detergent [37], the effectiveness of our mixture SNS-2A is lower under equal conditions of use. But since it is non-destructive (Fig. 6), it can be used repeatedly with minimal risk of damaging the decontaminated marble surface.

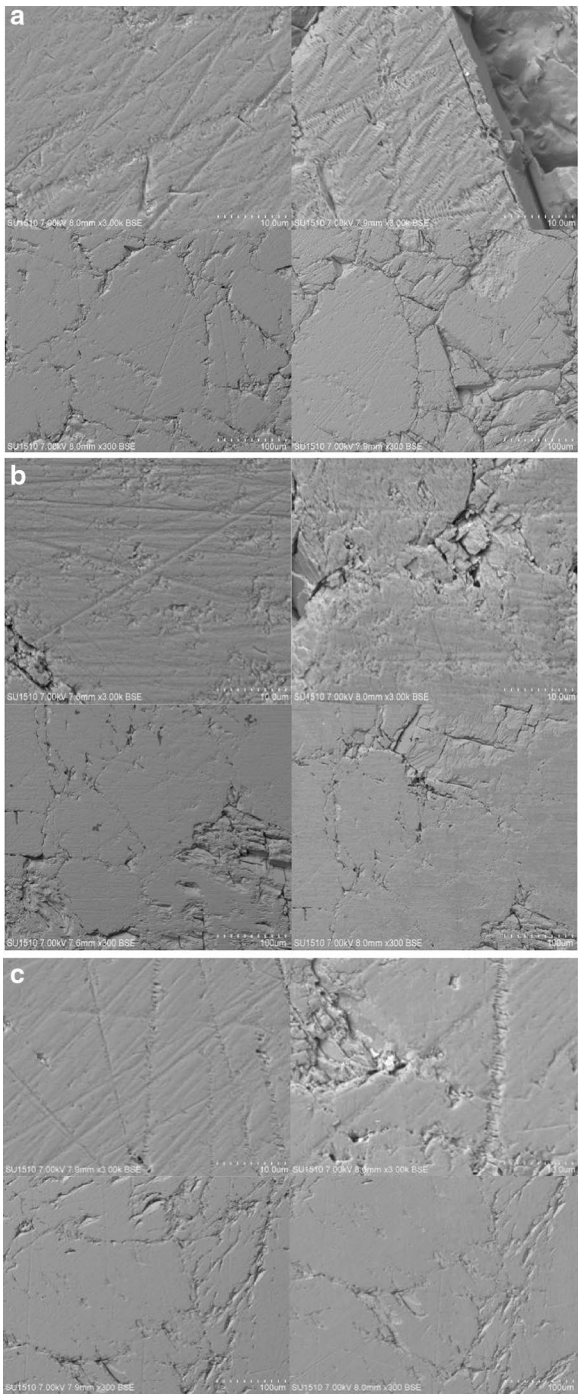


**Fig. 6** SEM microphotographs of the two different areas of the test marble samples: before (left side) and after (right side) treatment with **a** EDTA-based detergent prepared according to Lauffenburger [37], **b** neutral SNS-2N and **c** alkaline SNS-2A targeted cleaning mixtures

## Conclusions

The presented results show an individual approach to cultural heritage objects restoration in particular example—two contaminated museum exhibits: "Flagellation of Christ" (marble bas-relief) and "Madonna with Child in her arms" (majolica), covered by complex contaminants formed after the fire in the storage room.

Approximately 20 different organic compounds were identified in the contaminants: fatty alcohols, fatty acids and esters, including those containing lead and iron. It was found that the marble bas-relief was coated with beeswax which had not been subjected to strong thermal stress, but had absorbed pyrolysis products, probably traces of ammunition, wood impregnation or other products of man-made origin.

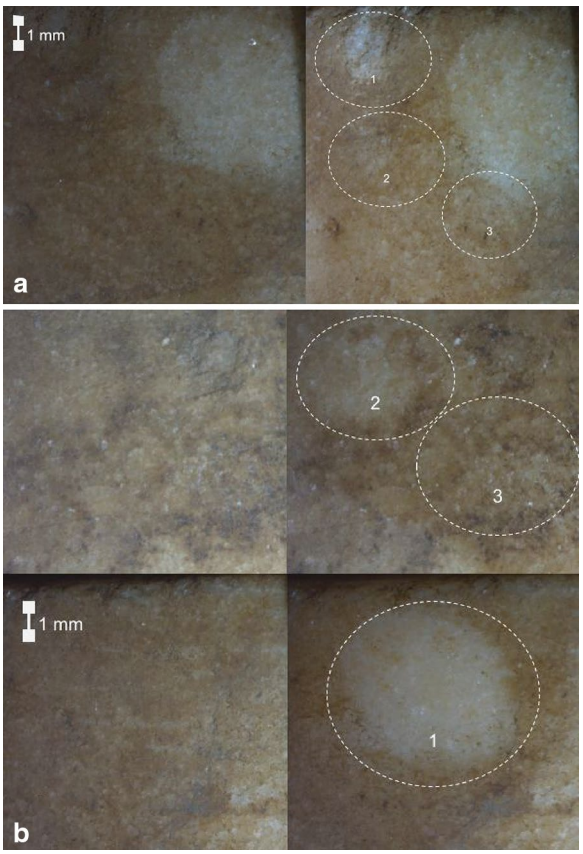


**Fig. 7** Comparative efficiency of solvents and detergents on a section of the marble bas-relief "Flagellation of Christ". **a** Area treated with detergents during 2 min; on the left side—the initial area before treatment, on the right side—the area after 2 min treatment; 1—EDTA-based detergent, 2—SMS-2A alkaline cleaning mixture, 3—SNS-2N neutral cleaning mixture, **b** area treated with detergents during 6 min; on the left side—the initial area before treatment, on the right side—the area after 2 min treatment; 1—EDTA-based detergent, 2—SNS-2A alkaline cleaning mixture, 3—SNS-2N neutral cleaning mixture

Based on the data about the surface contamination composition, targeted detergent compositions were developed as mixtures of different chelators (HEDP, EDTA, long-chain polyols, ethanolamines and non-ionic surfactants). We studied their safety on the test marble samples and their comparative effectiveness on the control exhibit "Madonna with Child in her arms" and on the darkest area of the marble bas-relief "Flagellation of Christ". It was found that the highest cleaning efficiency is achieved using an alkaline detergent composition.

Suggested cleaning mixtures are distinct from several cleaning methods for marble samples presented in the literature by their ability to selectively remove complex contaminants on the studied exhibits.

Our proposed scheme for the removal of such complex contaminations will be used for restoration of the exhibits of the Pushkin State Museum of Fine Arts with similar contaminations. This approach can compete with other forms of marble treatment in conservation practice especially for the cases of complex surface pollutants as such as [37–39].

## Supplementary information

**Supplementary information** accompanies this paper at https://doi.org/10.1186/s40494-019-0329-z.

**Additional file 1.** The results of testing different detergent compounds on the marble relief surface "The Flagellation of Christ" from Pushkin Museum of Fine Arts.

### Abbreviations

UV: ultraviolet; IR: infra-red; HPLC: high performance liquid chromatography; GC–MS: gas chromatography-mass spectrometry; EDTA: ethylenediaminetetraacetic acid; DTPA: diethylenetriaminepentaacetic acid; HEDP: oxyethylidenediphosphonic acid; PEG 400: polyethylene glycol; SEM: scanning electron microscopy; XRF: X-ray fluorescence.

### Acknowledgements

The authors are grateful to RFBR for their partial support of the study according To grant # 17-29-04100 (in the part of design of cleaning mixture), activity plan of NRC "Kurchatov Institute" (in the part of exhibits surface studies) and to Ministry of Science and Higher Education for their partially support of the study within the State assignment FSRC "Crystallography and Photonics" RAS (in the part of research methodology development).

### Authors' contributions

VMP interpreted gas chromatography–mass spectrometry results and was a major contributor in writing the manuscript. VMR chose the chemical reagents for preparing samples, analyzed their with XRF and SEM, and designed the cleaning mixtures. AVK analyzed the samples with gas chromatography. SKB studied samples with IR spectroscopy, gas chromatography-mass spectrometry. ASN tested the cleaning compounds on new marble samples. VAR prepared the washings from the exhibits and tested the developed cleaning mixtures on the exhibits. IVB interpreted the experimental data regarding the future conservation and restoration of the exhibits. EYT summarized the experimental results and was a major contributor in writing the manuscript. RAS designed the cleaning compounds. EBY designed the research program for studying the contaminated exhibits. MVK carried out general leadership of research collaboration of NRC "Kurchatov Institute" and Pushkin Museum of Fine Arts. All authors read and approved the final manuscript.

### Authors' information

Pozhidaev Viktor—Ph.D. in chemistry, chief specialist of the Department of Biotechnology and Bioenergy of the Center of NBICS-technologies of the NRC "Kurchatov Institute". Field of Interest: application of high-performance liquid chromatography, gas–liquid chromatography and mass spectrometry methods for studying organic fragments of remains in archaeological artifacts and museum exhibits.

Retivov Vasily—Ph.D. in chemistry, Head of Analytical Research Center of NRC "Kurchatov Institute" - IREA". Field of Interest: application of ICP-MS, ICP-AES, ESI–MS, high-performance liquid chromatography, gas–liquid chromatography and mass spectrometry methods for studying organic, bioorganic and inorganic materials.

Kamaev Andrey—leading engineer of the Center of NBICS-technologies of the NRC "Kurchatov Institute". Field of interest: use of high-performance liquid chromatography and mass spectrometry in the study of archaeological artifacts.

Belus Svetlana—researcher of Analytical Research Center of NRC "Kurchatov Institute" - IREA". Field of Interest: gas–liquid chromatography and mass spectrometry methods for studying organic, FTIR-spectroscopy.

Nartov Aleksandr—Junior Researcher of Analytical Research Center of NRC "Kurchatov Institute" - IREA"; postgraduate of The State University of Land Use Planning. Field of Interest: application of high-performance liquid chromatography, gas–liquid chromatography, mass spectrometry and microscopic methods for studying organic and bioorganic materials and for geoecology research.

Rastorguev Vasili—Ph.D. in Art History, Senior research fellow, curator of sculpture in the Pushkin State Museum of Fine Arts. Field of Interest: Medieval and Early Modern Sculpture, History of collections.

Borodin Igor—Head of the Pushkin State Museum's Department of conservation. Fields of Interest: studying historical technologies, developing methods for conservation-restoration of objects of organic.

Tereschenko Elena—Ph.D. in physics and mathematics, senior researcher of FSRC "Crystallography and Photonics" RAS, Deputy head of Laboratory "Natural Science Methods in Humanitarian Sciences" NRC "Kurchatov Institute". Field of Interest: structural studies of organic, bioorganic and inorganic materials using synchrotron radiation, elemental analysis, historical materials science.

Sandu Roman—Dr. habil., Deputy Director for Science of the NRC "Kurchatov Institute". Field of interest: materials science, analytical chemistry, chemical technology, technology of synthetic detergents, technology of paints and varnishes.

Yatsishina Ekaterina—Ph.D. in Philology, Deputy Director for Science of the NRC "Kurchatov Institute", Head of the Laboratory «Natural Science Methods in Humanitarian Sciences» (LNSMHS), Laureate of the Government of the Russian Federation Prize in the field of education. Field of interest: historical materials science, philosophy of natural science.

Kovalchuk Mikhail—Corresponding member of RAS, Professor, President NRC «Kurchatov Institute», Scientific Director of the FSRC "Crystallography and Photonics" RAS, Laureate of the State Prize of the Russian Federation in the field of science and technology and the Government of the Russian Federation in the field of education. Field of Interest: interdisciplinary research of materials, X-ray physics, development of synchrotron and neutron structural diagnostics techniques.

**Availability of data and materials**
All data generated or analyzed during this study are included in this published article.

**Competing interests**
The authors declare that they have no competing interests.

**Author details**
[1] National Research Centre «Kurchatov Institute», Moscow, Russia. [2] The Federal State Unitary Enterprise «Institute of Chemical Reagents and High Purity Chemical Substances», National Research Centre «Kurchatov Institute» (NRC «Kurchatov Institute» - IREA), Moscow, Russia. [3] The Pushkin State Museum of Fine Arts, Moscow, Russia. [4] Shubnikov Institute of Crystallography, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Moscow, Russia.

Received: 25 February 2019 Accepted: 18 October 2019
Published online: 02 November 2019

**References**

1. Toniolo L, Zerbi C, Bugini R. Black layers on historical architecture. Environ Sci Pollut Res Int. 2009;16(2):218–26.
2. Troiano F, et al. Successful combination of chemical and biological treatments for the cleaning of stone artworks. Int Biodeterior Biodegradation. 2013;85:294–304.
3. Gulotta D, et al. Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan. Herit Sci. 2014;2:6–19.
4. Ricci C, Miliani C, Brunetti B, Sgamellotti A. Non-invasive identification of surface materials on marble artifacts with fiber optic mid-FTIR reflectance spectroscopy. Talanta. 2006;69(5):1221–6.
5. Maravelaki-Kalaitzaki P. Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): characterization and origin. Anal Chim Acta. 2005;532(2):187–98.
6. Polo A, et al. Feasibility of removing surface deposits on stone using biological and chemical remediation methods. Environ Microbiol. 2010;60:1–14.
7. Pinna D, Galeotti M, Rizzo A. Brownish alterations on the marble statues in the church of Orsanmichele in Florence: what is their origin? Herit Sci. 2015;3:7.
8. Pinna D, et al. A follow-up on the analytical study of discolouration of the marble statues of Orsanmichele in Florence. Environ Sci Pollut Res. 2017;24:334–52.
9. Rampazzia L, et al. An interdisciplinary approach to a knowledge-based restoration: the dark alteration on Matera Cathedral (Italy). Appl Surf Sci. 2018;458:529–39.
10. Macchia A, et al. The Treatment of Iron-stained Marble: toward a "Green" Solution. Int J Conserv Sci. 2016;7(1):323–32.
11. Spile S, et al. Effective cleaning of rust stained marble. Herit Sci. 2016;4:12.
12. Cappitelli F, et al. Advantages of using microbial technology over traditional chemical technology in removal of black crusts from stone surfaces of historical monuments. Appl Environ Microbiol. 2007;73:5671–5.
13. Schottmüller, F. Die Italienischen und Spanischen Bildwerke der Renaissance und des Barock. Erster Band. Die Bilwerke in Stein, Holz, Ton und Wachs. Zweite Auflage. Berlin und Leipzig. p. 8, cat. 1979. 1933.
14. Schottmüller F. The Die italienischen und spanischen Bildwerke der Renaissance und des Barocks in Marmor, Ton in, Holz und Stuck. Berlin. P. 15, cat. 27. 1913.
15. Bode W. Denkmäler der Renaissance-Skulptur Toskanas. München: F.Bruckmann, 1892–1905. p. 21, Taf. 67.
16. Schubring P. Donatello. Des Meisters Werke in 277 Abbildungen. Stuttgart und Leipzig. p. 33, 195. 1907.
17. Venturi A. Storia dell'arte italiana. Vol. VI. La scultura del Quattrocento. Milan. p. 255–7. 1908.
18. Kaufmann H. Donatello. Eine Einführung in sein Bilden und Denken. Berlin. p. 59–61, 56, 148, 180, 215 note 179. 1935.
19. Schottmüller, F. Die Italienischen und Spanischen Bildwerke der Renaissance und des Barock. Erster Band. Die Bilwerke in Stein, Holz, Ton und Wachs. Zweite Auflage. Berlin und Leipzig. p. 24–25, cat. 143. 1933.
20. Marquand, A. Luca della Robbia. p. 160. 1914.
21. Gentilini, G. I Della Robbia e La scultura invetriata nel Rinascimento. Firenze. p. 102. 1992.
22. Venturi A. Storia dell'arte italiana. Vol. VI. La scultura del Quattrocento. Milan. p. 563. 1908.
23. Planiscig L. Luca della Robbia. Wien. p. 23, 35, ill. 78. 1940.
24. Pope-Hennessy, J. Luca della Robbia. Oxford. p. 62. 1980.
25. He H-P, Cai Y, Sun M, Corke H. Extraction and purification of Squalene from of Amaranthus grain. J Agric Food Chem. 2002;50:368–72.
26. Kelly GS. Squalene and the its' Potential clinical uses. Altern Med Rev. 1999;4:29–36.
27. Asperger A, Engewald W, Fabian G. Advances in the analysis of natural waxes provided by thermally assisted hydrolysis and methylation (THM) in combination with the GC/MS. J Anal Appl Pyrolysis. 1999;52:51–63.
28. Maia M, Nunes FM. Authentication of beeswax (Apis mellifera) by the high-temperature gas chromatography and chemometric analysis. Food Chem. 2013;136(2):961–8.
29. Bonaduce I, Colombini MP. Characterisation of beeswax in works of art by gas chromatography–mass-spectrometry and pyrolysis-mass-spectrometry procedures. J Chromatogr A. 2004;1028:297–306.
30. Vcelak V. Chemie und Technologie des Montanwaxes. Praga. p. 475. 1959.
31. Belkevich PI, Golovanov H. Wax and its technical counterparts. Minsk: Sci Equip; 1980. p. 176.
32. Kislitsin AH. Pyrolysis of wood: chemistry, kinetics, products, new processes. Moscow; 1990; p. 312
33. Ponomarev DA, Spitsyn AA, Piyalkin VN. Thermal methods to obtain liquid fuels and other products from wood. Russ J Gen Chem. 2012;82(5):1006–12.

34. GOST 21179-2000 Beeswax. Specifications.
35. Eccentrics VG. The technology of bee products. Moscow. 1979; p. 200.
36. Zolotov Y. Fundamentals of analytical chemistry. Moscow. p. 463. 2001.
37. Lauffenburger JA, Grissom CA, Charola AE. Changes in gloss of marble surfaces as a result of methylcellulose poulticing. Stud Conserv. 1992;37:155–64.
38. Pozo-Antonio JS, Montojo C, de Silanesc ML, de Rosario I, Rivas T. In situ evaluation by color spectrophotometry of cleaning and protective treatments in granitic Cultural Heritage. Int Biodeterior Biodegrad. 2017;123:251–61.
39. Melquiades FL, Appoloni CR, Andrello AC, Spagnuolo E. Non-destructive analytical techniques for the evaluation of cleaning and protection processes on white marble surfaces. J Cult Herit. 2019;37:54–62.

## Publisher's Note