INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 10, Issue 2, April-June 2019: 249-256 www.ijcs.uaic.ro

A PROCEDURE FOR COMBINING THE REMOVAL AND THE IDENTIFICATION OF A PATINA ON A 15TH CENTURY BYZANTINE ICON

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Abstract

In our paper, we report a workflow, which combines cleaning procedures and Gas Chromatography Mass Spectrometry (GC-MS) for the removal and the identification of a patina from a byzantine 15th century icon representing the Virgin and Child. Our strategy suggest a convenient interaction between restoration procedures and analytical methodologies aimed at the cleaning of the surface of the artwork and the identification of unknown compounds responsible for its alteration. These informations can be very useful not only to return the colors to their original brightness but to reconstruct the story of the icon too.

***Keywords**: Patina; GC-MS; Solvent cleaning; Cultural heritage*

Introduction

Chemical and physical damages caused by air pollution, the action of living microorganisms as well as ritual habits, are the main responsible for artworks deterioration [1-4]. Moreover, some painting techniques and/or restoration procedures can be responsible for darkening effects on painted surfaces [5, 6]. Very often, patinas (which darken the colors, affecting the original image created by the artist), are among the main issues.

Many artists used to apply a film of natural varnishes as a protective at the end of their work; at the same time trials to revitalize colors were already performed in 1700/1800, during that period in fact, the use of a mixture of wax, linseed oils and honey (known as "*beverone"*) [7] was a very common. As centuries went by, these films turned into dark layers affecting the painting itself because of darkening effect [8].

Nowadays, one of the priority tasks for restorers is to remove and identify these patinas in order to give the original color back to the artwork and eventually identify some paintings procedures or later restorations.

The removal is often preceded by cleaning assays to test the efficacy of different solvents with diverse polarities [9]. During the last ten years, solvents thickened with appropriate chemicals such as cellulose polymers (Klucel G) as long as gels derived from polyacrylic acid (Carbopol, Pemulens), have been widespread to vehicle the active cleaning components to the surface, thus avoiding the diffusion of liquids on painted surfaces [10-12].

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Once removed, the identification of the patina components can be very useful for the conservation and the collection of historical informations about the artwork.

As for the identification, in this study we used a gas chromatography/mass spectrometry based methodology [13, 14], a wide spread methodology in Fine Arts and Restoration fields used to identify shellac, Arabic gums, and other natural compounds used by artists [15]. Thanks to this technique, we could separate and identify the components of a very complex mixtures of natural compounds such as the one extracted from the surface of the artwork under investigation.

However, sampling procedures represent the limiting step for the above-mentioned analytical methodology. In order to preserve the integrity of an artwork, restorers strongly discourage the removal of pieces for diagnostic purposes, even if relatively small. To this aim, many efforts have been performed to develop non-invasive and micro invasive sampling procedures [16-18].

In this paper, we present a case of study where we used thickened solvent cleaning procedures directly coupled with mass spectrometry. In our workflow, we combined cleaning steps to the sampling ones. In fact, we directly analyzed thickened benzyl alcohol used for varnish removal, thus obtaining a molecular profile of the patina removed from the painted surface. Taking advantage of the high resolution, sensitivity and reproducibility of mass spectrometry methodologies, we could identify the composition of the patina.

Our workflow was used on a wooden 15th century byzantine icon (described in Materials and Methods section) representing the Virgin and Child. The table, showed a brownish patina, which clearly modified the original colors chosen by the artist to depict the figure. The aim of our work was to remove the dark layer from the surface of the icon and to identify it. The painting technique used for the realization of such artwork involves the final use of an "olifa" varnish as a protective layer [19], however the putative co-presence of other kind of varnishes related to some effort to renew color brightness connected to previous restorations might be responsible for the darkening effect.

Materials and Methods

Artwork description

The artwork analyzed in this study is a classic byzantine devotional icon. The stylistic connotations indicate a probable dating within the fifteenth century. The painting was published in the catalog "The art collection of the Pagliara Foundation" by *A. Caputi* and *M.T. Penta*, with an attribution of "an unknown artist of the end of the fifteenth century" [16]. The iconographic recognition attests it as the *Mother of God Hodegetria* with a slight variation in the three-quarter position of the Head of the Child [20].

It belongs to the group of so-called "greek" icons because of its liturgical use and for the color chosen for the *maphorion* of the *Virgin*, (the female mantle used in Byzantium to cover the head and the tunic; in the Byzantine iconography, the *maphorion* of the Mother of God in purple red indicates her royal dignity). Thanks to some documentation and to the stylistic features, we could attribute the artwork to the "bottega binzantina-cretese". The Cretan school, or better known as the "Post-Byzantine", was a pictorial school born on the island of Crete, a colony of the Venice between 1204 and 1669. Thanks to the political situation, it soon became the Christian artistic center of production of icons of Greek matrix from the fifteenth to the seventeenth century, because of the ever-increasing demand for icons in Europe. In this environment, a particular pictorial style developed which was characterized, both by tradition and by the Byzantine and Latin movements. At the end of the fifteenth century, the Cretan artists created a distinct style of icon painting, characterized by precise contours, a modulation of the complexion obtained under dark and thick browns, a greater highlighting of the cheeks of the faces, the bright colors of the garments with a geometric design of the folds, all with a composition of the picture more balanced or clear images, thin bodies, linear curtains and restrained movements [18, 20, 21].

Cleaning procedure

For the removal of the dark layer from the painting, after the usual cleaning test phase, the best solvent resulted to be benzyl alcohol, which was thickened with Klucel G. The mixture used was the following: 4g of Klucel G in 100mL of benzyl alcohol, the solution was stirred for about 20min. The solution was applied to the area to be cleaned for 90 seconds using a soft bristle brush and then removed from the pictorial surface by a spatula. The surface was finally rinsed with a white spirit solution.

Chemical derivatization and GC-MS analysis

An aliquot (100μL) of the removed solution was dried under vacuum and directly submitted to trimethylsilylilation in 200μL of N,O-bis-(trimethylsilyl)-acetamide (TMS) at 90°C for 45 min. The sample was dried down under nitrogen, dissolved in 50μL of hexane and centrifuged. The hexane supernatant (1/50) was used for the GC-MS analysis.

GC-MS analyses were performed on an ISQ-QD quadrupole mass spectrometer (Thermo Fisher scientific) equipped with a TRACE™ 1300 Gas Chromatograph using a Zebron ZB-5HT Inferno (5%-Phenyl-95%-Dimethylpolysiloxane) fused silica capillary column (Column 30m x 0.32mm x 0.10μm) from Phenomenex.

The injection temperature was 250°C, the oven temperature was held at 70°C for 2min and then increased to 230°C at 20°C/min, increasing to 240°C at 20°C/min and finally to 270°C at 20°C/min and held for 3 min. Electron Ionization mass spectra were recorded by continuous quadrupole scanning at 70eV ionization energy, in the mass range of m/z 30-800.

x

Table 1. Chemical species identified by GC-MS

RT	Compound	Fragment Ions Used For Identification	Area (% of total)
10.11	3-methyladipic acid	41-43-55-59-83-114	0.07
10.9	suberic acid	74-138-69-97-43	0.12
11.14	alpha-linoleic	45-55-67-73-75-79-93-108	0.08
12.15	adipic acid methyl propil ester	43-55-56-87-11-114-129-143	0.13
15.72	deoxiribofuranose	59-73-77-303-304-305	3.44
16.96	miristic acid	41-43-45-57-69-74-75-87-143	0.66
17.16	benzoic acid 3,5 di tert butil 4-hydroxy methyl ester	57-91-103-111-117-233-249-250-264	0.19
17.9	levoglucosan	45-73-75-103-129-147-204-217	1.70
18.7	galactose	73-75-116-117-129-133-147-204	2.36
19.9	glucose	73-75-116-117-129-133-147-204	0.80
20.13	palmitic acid	41-43-57-69-74-75-87-143	4.94
21.04	derivate auleritic acid	73-75-117-129-317-299	0.95
21.33	N-acetylglucoseamine	73-75-116-117-129-133-147-204	0.81
21.7	10,18- bisnorabieta-8,11,13-triene	55-128-129-141-143-144-157-227-228-242	3.95
21.85	4, 6, 8 (14)-cholestatriene	41-44-55-366	1.64
22.21	N-acetylgalactosamine	73-75-116-117-129-133-147-204	8.46
22.45	stearic acid	41-43-55-57-74-75-87	4.12
23.07	5- beta-podocarpa, 8,11,13-trien-16 oic acid	115-117-128-129-131-141-143-197-198-257	2.56
23.42	laccijalaric acid	73-75-117-129-408	6.95
23.94	isopimaric acid	41-43-55-73-75-81-109-241-256-257	5.68
24.75	16-hydroxyhexadecan-9-enoic acid	73-75-117-129-217-383-414	14.33
24.99	abiet-8-en-18-oic acid	41-91-95-105-135-187-243-289-304	2.04
25.15	dehydro abietic acid	41-43-73-75-171-173-239-240-255-357	8.54
25.76	emodin	73-355-385-456-471-486	13.39
26.81	oxo dehydro abietic	187-213-253-254-269-313-328-329	4.76
28.4	cinamine acetate	43-343	4.00
28.9	jalaric acid	73-75-117-129-378-391	1.18
30.4	tricotyl trimellitate	43-57-70-71-113-193-305	2.12

Mass spectra assignment was generally based on the direct match with the spectra of NIST library, if the correlation match index was higher than 95%, the identification was considered reliable. As for unknown analytes, the identification was performed by extraction of molecular and fragment ions and comparison with the ones of standard compounds.

As a control sample, we used benzyl alcohol thickened with Klucel G not applied to the pictorial surface and subject to the same chemical treatment as the sample.

Results

The 15th century byzantine icon representing *the Mother of God Hodegetria* was initially covered by a patina (Fig. 1) which was responsible for an overall darkening effect. The main goal of our work was to return the image to its original colour and, at the same time, to identify the nature of the patina.

The use of benzyl alcohol thickened with Klucel G clearly proved to be an effective method to return the icon its original colors. As in fact shown in Figure 2 after 90 seconds of application, the patina was completely removed and the image show a brighter set of colours especially if compared to the areas where it was not applied yet.

Fig. 1. Icon before cleaning procedure

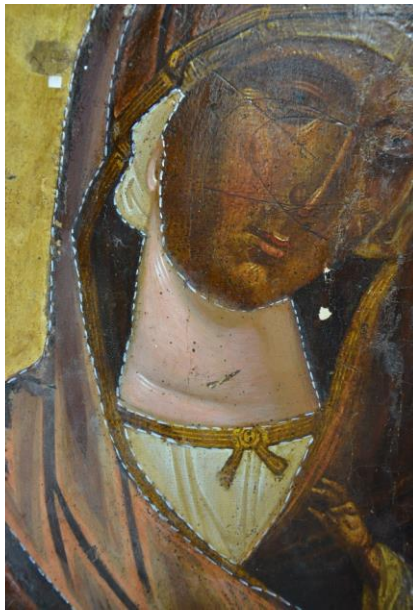

Fig. 2. Comparison of different areas of the icon before and after cleaning procedure

In order to obtain more details on the painting techniques used for the icon and eventually on some restoration attempts, we identified the nature of the patina. To this aim, the brownish solution after cleaning tests, which is usually discarded, was instead analysed by GC-MS (along with a “control sample” as described in the Materials and Methods section).

The sample after derivatization and extraction was injected in the GC-MS (as reported in Materials and Methods). Results are summarized in Table 1 and the total ion chromatogram (TIC) is reported in Figure 3.

The profile of identified molecules shows a considerable heterogeneity, we could in fact detect, among the others, fatty acids, monosaccharides and terpenes, which were all circumstantial evidence for the presence of a very complex sample.

As for fatty acids, we identified alpha-linolenic, palmitic and stearic acid; even if the co-presence of these three fatty acids is quite common in many biological matrices, it is in perfect agreement with literature data showing their co-presence in linseed oil used for "olifa" varnish preparation [22].

At the same time, we could identify some chemical markers for the presence of shellac. Among these Emodin (Fig. 4), an anthraquinone sinthesized by an octaketide precursor in insects especially *Eriococcus* species [23], and characterized by an orange colour [24], considered to be highly diagnostic for the presence of the resin.

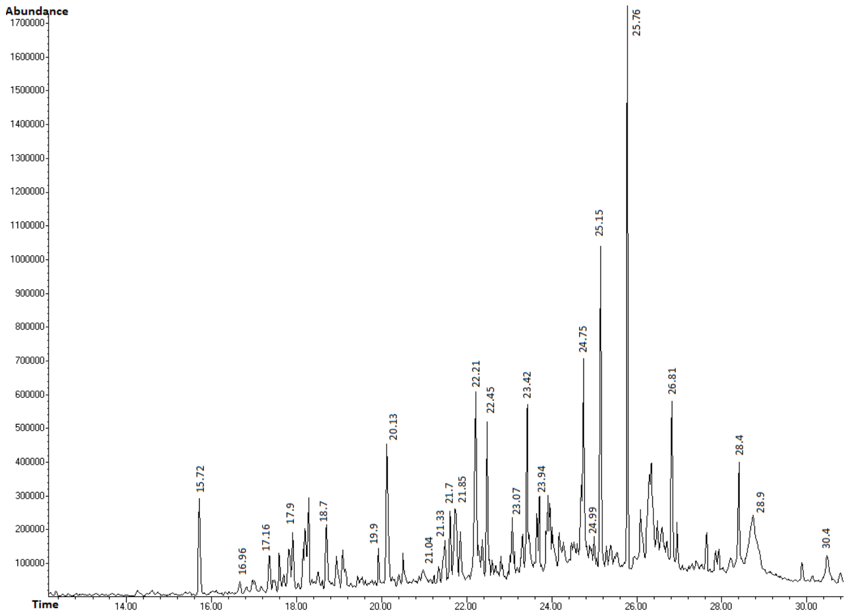

Fig. 3. The chromatogram (total ion current) obtained

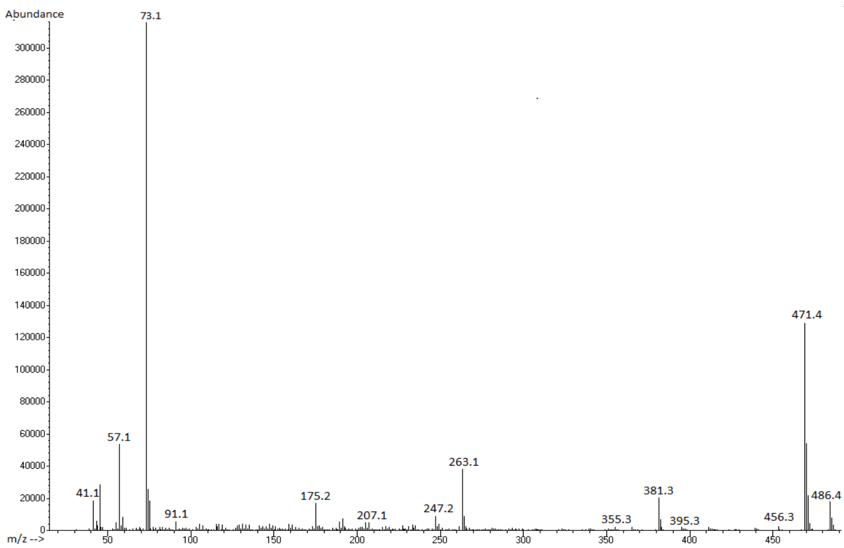

Fig. 4. EI fragmentation spectra used for the identification of Emodin

Finally, the identification of some sesquiterpenoids such as jalaric and laccijalaric acids represent the final evidence [25-30] that the patina removed from the icon was shellac.

Conclusions

The analytical methodology presented in our paper resulted to be very effective and returned interesting results useful, in our case of study, for the direct identification of a patina affecting the original colours of a 15^{th} century icon [31, 32].

The combination of solvent cleaning procedures with mass spectrometry methodologies described, represent a very powerful tool not only for restoration processes but also to collect more informations about artworks (including painting techniques and putative restorations trials) thus allowing the comparison of data with historical sources.

Thanks to our approach, we could remove the dark patina from the surface of the icon thus returning the colours and the golden background to their original brightness. Furthermore, thanks to the analytical power of mass spectrometry (coupled to gas chromatography), we could identify some of the chemical markers of the "olifa" varnish originally used by the artist who realized the icon and, at the same time, we could unambiguously identify the presence of shellac, connected to some more recent restoration intervention.

Acknowledgements

The authors would like to thank Regione Campania for the financial support (POR Campania FESR 2007 – 2013)

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Received: May 20, 2018
Accepted: May 22, 2019