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A novel approach for high selective micro-sampling of organic painting materials by Er:YAG laser ablation

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Abstract

A new approach for sampling micro-amounts of mainly organic materials from thin layers of a painting is described. A pulsed Er:YAG laser system operating at 2.94 μm was used for collecting ablate materials. The experimental ablation conditions optimised on reference paint layer samples resulted in using laser energy lower than 20 mJ at 15 pulses/s (pps) assisted by water/ethanol mixtures. The ablate materials condensed on glass coverslips were characterised by Fourier transformed infrared spectrometry (FT-IR) and gas chromatography-mass spectrometry (GC-MS) procedures. The results showed that the laser energy did not significantly degrade the ablate organic material collected which can be successfully identified. The procedure, tested and calibrated on reference paint layer specimens, was applied for the sampling and characterisation of two old paintings. The presence of overpaintings consisting of egg and Venice turpentine in one case, and of “beverone” over a varnish (linseed oil and Venice turpentine) in the other one was highlighted. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Laser micro-sampling; Organic binders; FT-IR and GC-MS analysis; Paintings

1. Research aims

A painting is made up of several paint layers of thickness ranging between 5 and 40 μm which are difficult to collect selectively. When a characterisation of the organic matter is needed, sampling is a particularly difficult analytical step since organic matter is present in small percentages with respect to inorganic matter (pigments, ground, etc.). During the tests on the evaluation of a new Er:YAG laser system ($\lambda = 2.94 \mu\text{m}$) for cleaning paintings, many materials were ablated from the paint surface. In such cases, being able to collect the ablate material is a precise and selective sampling which would be a definite improvement on traditional methods based on mechanical tools. The main aims of this research were:

- to collect reproducible samples of the ablate material under optimised experimental conditions;
- to characterise the collected organic materials by means of sensitive analytical techniques, such as FT-IR and GC-MS;

- to check any changes in the matter composition induced by pulsed laser energy;
- to identify binders and varnishes in the ablate material from different paint layers.

Reaching these objectives entailed devising a powerful and innovative sampling method with limited invasivity in agreement with conservation guidelines.

2. Introduction

The characterisation of organic materials is one of the most difficult steps in the study of paintings [1]. Organic substances used as binders, adhesives or coatings are widespread in all the paint layers; moreover ageing and pollution processes may have strongly altered their original composition giving rise to products that are not easy to identify [2]. These factors make the work of modern restorers particularly difficult. In fact, before deciding on what conservation techniques to employ, they need accurate information on the organic and also the inorganic compounds employed both in the original painting and in any overpaintings due to subsequent restorations. While inor-

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59 ganic compounds can be determined quite easily with
60 non-invasive spectrometric techniques or just by taking
61 microscopical amounts of samples, organic compounds
62 entail collecting relatively large heterogeneous samples
63 (0.5–1 mg) whose content of organic compounds does not
64 exceed 200 µg. The collection of lower amounts often
65 hampers the identification of the organic media. Since
66 painting materials are present in a layered form with a
67 thickness of a few micrometers, a selective collection by
68 mechanical samplers is very difficult, and often the sample
69 includes materials from adjacent layers, thus affecting the
70 interpretation of the results. There is thus the need to have
71 a sampling methodology that can selectively collect organic
72 material from the different thin paint layers, to reduce the
73 invasivity of the procedure and to obtain sufficient material
74 to be analysed giving reliable results.

75 This paper describes a new sampling method based on
76 the recovery of ablated materials on a glass coverslip after
77 the paint surface has been radiated with a pulsed Er:YAG
78 laser operating at 2.94 µm [3]. Reference paint layer speci-
79 mens were employed to test and calibrate the overall
80 procedure. The material collected at different laser energies
81 and in the absence or presence of some wetting agents were
82 characterised by applying analytical procedures based on
83 FT-IR and GC-MS [4–6]. Comparisons between the pro-
84 posed method and the scalpel sampling method highlight
85 the potential of pulsed Er:YAG laser sampling. The opti-
86 mised experimental condition found allowed the sampling
87 of old paintings. In particular, the results related to samples
88 from a 17th century canvas copy of Caravaggio's "Christ
89 crowned with thorns", and a 13th century panel "Virgin with
90 Child" (Anonymous) under restoration at Opificio delle
91 Pietre Dure in Florence (Italian Ministry of Cultural Heri-
92 tage) are reported and discussed.

93 3. Materials and methods

94 3.1. Reference paint layer specimens

95 A large series of reference standards simulating the
96 layering of easel paintings was prepared at Opificio dell
97 Pietre Dure according to well-known traditional recipes.

Part of a series (E1, E2, E3, E4 specimens), consisting of 89 98
types of painting, especially prepared and aged to test out 99
Er:Yag laser cleaning [7], was used for checking the 100
sampling method. 101

Another series of reference samples (LSV, DV), consti- 102
tuted of thin layers of pure materials on glass tiles, prepared 103
in the framework of an Italian National research project 104
"Safeguard of Cultural Heritage" [8], was also utilised for 105
testing and calibrating the sampling procedure. Table 1 106
reports the sample name and the composition of the analy- 107
sed specimens together with the mean thickness of the 108
surface layer. 109

Analyses were performed on dried and wetted samples. 110
The wetting agents were deionised water with 2% surfactant 111
(Tween 20), 50:50 (v/v) water/ethanol mixture and white 112
spirit (a hydrocarbon mixture with 5% glycerol), named, 113
respectively, U, U1 and U2. 114

3.2. Old painting samples 115

The samples of paintings which are under restoration at 116
the Laboratories of OPD in Florence were collected from: 117

(1) a 17th century canvas copy of Caravaggio's "Christ 118
crowned with thorns" (five repeated samples at 13 mJ laser 119
energy with wetting agent U1); 120

(2) a 13th century panel "Virgin with Child" by Anony- 121
mous (one sample from the brown ground at 4 mJ laser 122
energy, three repeated samples from the green curtain at 20 123
energy with wetting agent U1 and two samples from the 124
same area at 10 and 20 mJ laser energy with wetting agent 125
U1). 126

Samplings were performed with scalpels along with the 127
laser procedure in the same areas. According to the restor- 128
ers, these paintings presented thick overpaintings, patinas 129
and varnishes. 130

3.3. Laser equipment and sampling procedure 131

A "Conservator 2940[®]" model Er:YAG laser by Schwartz 132
Electro-Optics (Orlando, FL, USA) operating at a wave- 133
length of 2.94 µm was used [3]. The laser impact zone has 134
an area of about 1 mm². The laser pulse rate was set to 135
15 pulses/s (pps); each laser pulse delivered a variable 136

Table 1
Sample name and characteristics of reference paint layer specimens

Sample name	Support	Ground layer	Paint layer	Surface layer	Composition thickness ^a (µm)
E1	Inert ceramic	Gypsum/animal glue (1:15)	Yellow ochre/lead white in whole egg tempera	Whole egg tempera	12
E2	Inert ceramic	Gypsum/animal glue (1:15)	Yellow ochre/lead white in whole egg tempera	Dammar resin	12
E3	Inert ceramic	Gypsum/animal glue (1:15)	Yellow ochre/lead white in whole egg tempera	Burnt umber/linseed oil	25
E4	Inert ceramic	Gypsum/animal glue (1:15)	Yellow ochre/lead white in whole egg tempera	Burnt umber/linseed oil on mastic resin	25
LSV	Glass	None	None	Linseed oil/sandrac	–
DV	Glass	None	None	Dammar	–

^a The mean thickness of the surface layers was estimated by examining cross-section from the reference samples using an optical microscope.

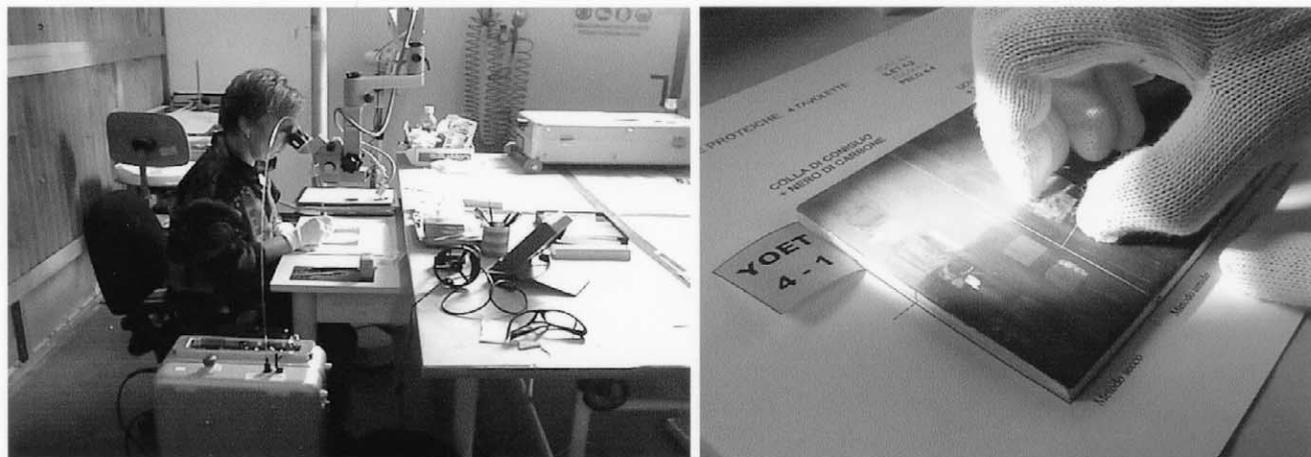


Fig. 1. The laser sampling method.

137 energy to the target ranging between 5 and 50 mJ. A silver
138 coated hollow glass waveguide tube (1 mm i.d. 1.5 m
139 length), whose end part looks like a pen, delivered the light
140 to the target.

141 A large set of microscope glass coverslips (15 × 15 mm),
142 used as sampling devices, was cleaned by washing with
143 deionised water, methanol and acetone, dried in an oven and
144 stored in cleaned tray boxes avoiding any contact with
145 organic substances. Cotton gloves were used to handle the
146 sampling devices. These were placed on the painting, and
147 after laser impact, the ablated material condensed on the
148 glass, thus giving the opportunity to collect the surface paint
149 material for chromatographic and spectroscopic analyses
150 (Fig. 1). Samplings on the specimens (described in Table 1)
151 and on old paintings were performed at the following laser
152 working conditions:

- 153 • a single pass at variable energies of 4, 10, 12, 13, 13.5,
154 15, 20, 30, 45 mJ;
- 155 • multiple passes at a fixed energy of 10, 13, 20 mJ re-
156 peating up to five times the treatment in the same area;
- 157 • a single pass at a fixed energy of 10, 12, 13, 15, 45 mJ
158 with the wetting agents U, U1 and U2.

159 3.4. Apparatus

160 The following instrumentations were used:

161 (1) A 5890 Series II gas-chromatograph (Hewlett Pack-
162 ard, Palo Alto, CA, USA) coupled with a quadrupole mass
163 spectrometric detector mod. 5971A (electron impact 70 eV,
164 ion source temperature 180 °C, interface temperature
165 280 °C).

166 (2) A "Trace gas-chromatograph 2000" (Thermo Quest,
167 USA) coupled with a quadrupole ion trap mass analyser
168 Polaris Q.

169 (3) A Perkin-Elmer 1725× FT-IR spectrophotometer, a
170 DMCS detector, an X-Y-Z micrometric sample holder for a
171 1.5 mm diameter pellets, KBr (Schilling spectroscopic
172 grade). Spectra collection and calculations were made with
173 PE Spectrum software (release 2.1).

3.5. Analytical procedure 174

3.5.1. GC-MS analysis 175

176 The glass sampling device with the ablate material was
177 inserted into a vial, covered with ammonia solution 2.5 M
178 and sonicated for 3 h. The ammonia extracts were analysed
179 for the amino acid content and the residue for the neutral
180 and acidic organic compound content according to a well-
181 established analytical procedure [4–6], that has been slightly
182 modified.

183 Chromatographic separation was performed on a chemi-
184 cally bonded fused silica capillary column HP-5 MS
185 (Hewlett Packard) and Rtx-5MS (Thermo Quest, USA).

3.5.2. FT-IR analysis 186

187 The glass sampling device with the ablate material was
188 gently scraped with a scalpel, the recovered material was
189 admixed with about 5 mg of KBr in a mortar, milled and
190 pressed to form 1.5 mm diameter micro-pellets.

4. Results and discussion 191

192 The FT-IR spectra of the ablated materials from the
193 reference paint layer specimens in all the working condi-
194 tions used were very similar to those of the material directly
195 sampled with a scalpel. Except a small shift of carbonyl and
196 double bonds stretching bands in reference specimens
197 containing oil and dammar varnish, no important modifica-
198 tion seems to have occurred during laser radiation. This is
199 highlighted in Fig. 2, where spectra for the E2 specimen
200 collected with the two sampling methods are compared.
201 Generally speaking, a bulk sample is obtained by using the
202 scalpel sampling method which means that traces of the
203 background binders may interfere with the absorption of the
204 compounds of the outer paint film as shown in Fig. 2. On the
205 other hand, the Er:YAG laser, under controlled conditions,
206 removes a very thin layer of the paint film thus reducing the

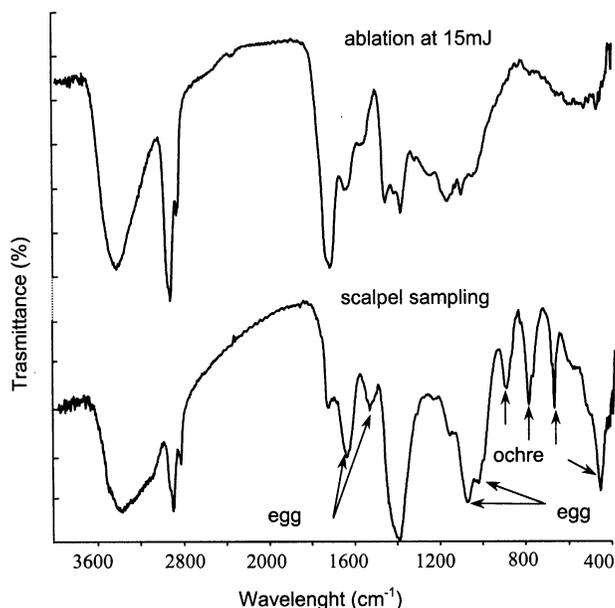


Fig. 2. FTIR spectra of the ablate material from E1 specimen at 15 mJ laser energy, and of a sample collected with scalpel. Egg and yellow ochre absorptions from background are highlighted.

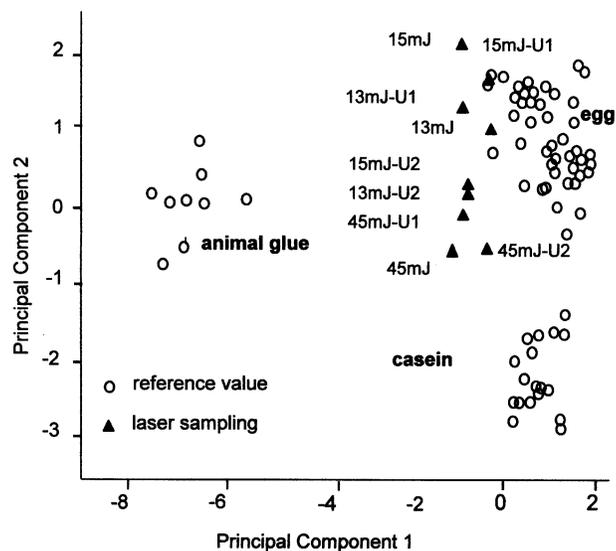


Fig. 3. Principal component analysis of the relative amino acid percentage contents of the ablate material from E1 specimen at various laser energies (13, 15 and 45 mJ) in the absence and presence of wetting agents U1 and U2.

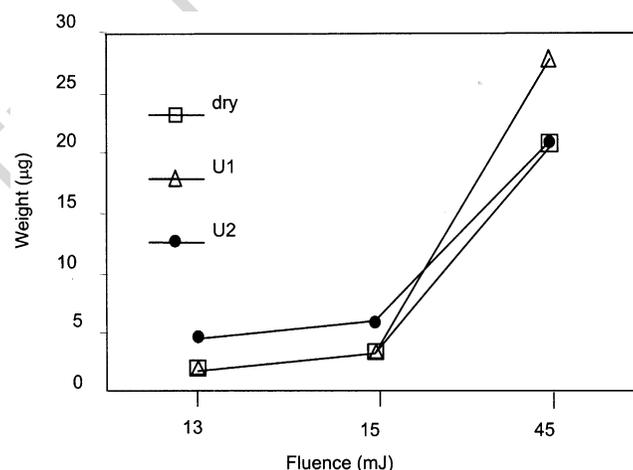


Fig. 4. Dependence of total amounts (μg) of recovered amino acids from the ablation of E1 specimen on various laser energies (13, 15 and 45 mJ) in the absence (dry) and presence of wetting agents U1 and U2.

207 above interference and simplifying the identification of the
208 ablate paint layer.

209 A deeper inspection of the ablate material was obtained
210 by GC-MS analysis. The chromatograms for all the analy-
211 sed samples showed that the binders and varnishes present
212 in the specimens were selectively recovered and identified,
213 in particular:

214 • *Proteinaceous media*. The ablate samples from E1
215 specimen exhibited an amino acid pattern quite similar
216 to the one expected both in the presence and absence of
217 wetting agents. The increase in the laser energy up to
218 45 mJ caused a loss of nearly 50% of serine (the
219 simplest hydroxy amino acid) and an increase in
220 proline and glutamic acid contents. The identification
221 of the protein obtained by applying principal compo-
222 nent analysis to the relative amino acid percentage
223 contents of each sample (Fig. 3) showed that the egg
224 protein is recognised for all the experimental condi-
225 tions, though the 45 mJ samples are slightly shifted
226 from the egg cluster. The increase in laser power also
227 led to a general increase in the total amount of
228 proteinaceous matter recovered, as shown in Fig. 4. The
229 use of U1 wetting agent seems to favour the removal of
230 the surface paint layer.

231 • *Lipids*. The fatty acid profile of linseed oil and of egg
232 was, respectively, found in all the lipidic ablate material
233 from LSV, E1 and E3 specimens for all the experimen-
234 tal conditions tested. Cholesterol and cholestanes were
235 also detected in specimens containing egg. The increase
236 in laser power increased the total amount of fatty acids
237 recovered. Specifically, removing dicarboxylic acids
238 seems more efficient than removing triglyceride units
239 containing monocarboxylic acids, as shown in Fig. 5.

240 Polar wetting agents such as U and U1 seem to enhance
241 this effect probably because they dissolve polar free
242 dicarboxylic acids entrapped in the three-dimensional
243 cross-linked polymer structure, thus facilitating their
244 removal from the paint. Provided laser energies lower
245 than 15 mJ are employed for sampling, these results
246 highlight that it is still possible to identify the lipidic
247 matter. In fact, as reported in Table 2, ratio values of
248 palmitic to stearic acid (P/S), of azelaic to palmitic acid
249 (A/P) and the sum of dicarboxylic acids (ΣD) agree
250 with those reported in the literature for linseed oil and
251 egg [1,4].

252 • *Natural resins*. The ablate matter from LSV specim-
253 ens containing sandarac resin showed the distribution of
254 pimaric, sandaracopimaric, isopimaric acid and to-

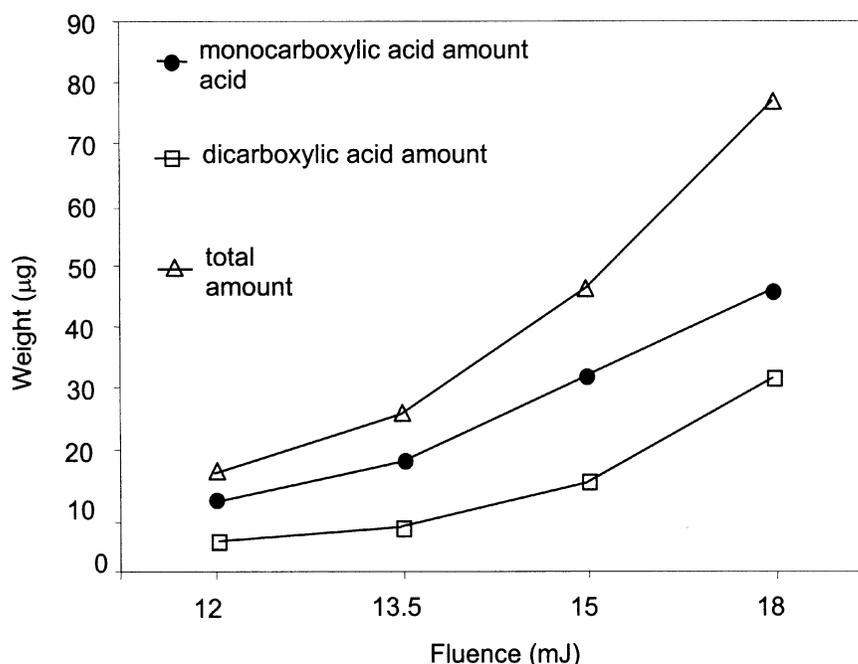


Fig. 5. Dependence of amounts (μg) of recovered dicarboxylic acids (sum of azelaic, suberic and sebacic acid contents), monocarboxylic acids (sum of lauric, myristic, palmitic, stearic and oleic acid contents) and total acidic amount from the ablation of LSV specimens on various laser energies (12, 13.5, 15 and 18 mJ) in the absence of wetting agents.

Table 2

Mean values of palmitic to stearic acid (P/S) and azelaic to palmitic acid (A/P) ratio values and the sum of dicarboxylic acids (ΣD) for the lipidic material ablated from reference paint layer specimens in the absence and presence of wetting agents at different laser energies

Sample name	Laser energy (mJ)	P/S	A/P	ΣD
LSV	10, 12, 13.5, 15, 18	1.0	1.0	30
E1	13, 15, 45	2.4	<0.05	0.9
E3	13	1.8	1.0	32
	40	2.1	1.4	45
	45	1.7	1.8	50
E4	13	1.5	1.1	31
	40	1.6	2.5	62
	45	2.1	2.4	65
Linseed oil ^a		1.5	1.1	29
Egg ^a		2.2	<0.1	3

^a Literature mean values⁴.

mean thickness of 25 μm . The overpainting was removed with a single pass at 45 mJ laser energy using U1 as a wetting agent. In 12 repeated experiments of ablation, only in one case was a trace of moronic acid (marker of mastic) of the underlying resin detected. The reproducibility of the overall proposed method was tested by sampling six times the E3 specimen with a single pass at a laser energy of 45 mJ with a U1 wetting agent. The amount of each fatty acid of the linseed oil film, determined in the ablates, ranged between 1 and 70 μg with a variance (CV) of 25–35%. Considering that the analytical procedure alone has a relative standard deviation of 15–20%, the uncertainty introduced by the sampling procedure would seem to be acceptably low. All these evidences highlighted that the best sampling conditions to employ are a laser energy lower than 20 mJ, and a water/ethanol mixture as a wetting agent: in these conditions, the ablate areas of about 100 mm^2 contained maximally 80 μg of organic material.

Since Er:YAG laser operates at 2.94 μm , it mainly interacts with $-\text{OH}$ groups [3]. Polar compounds such as dicarboxylic acids strongly adsorb the radiation and are easily ejected from the surface. Polar wetting solvents help the ablation mechanism as shown by the experimental results obtained on reference paint layer specimens. In fact, the sampling exploits a complex mechanism of material transfer from the surface [9]. The thermal effect due to the radiation absorption produces an increase in temperature and pressure which facilitates the vaporisation and gas expansion in micro-bubbles on the surface. The removal of material may follow several mechanisms: steam distillation, sublimation, explosion and mechanical transport. Since

tarolone with no significant changes in any of the experimental conditions tested: chromatograms obtained for materials from scalpel and laser sampling are basically identical as shown in Fig. 6. As far as the ablate dammar resin is concerned, the neutral and acidic terpenoid compounds determined allowed its identification on the basis of the presence of shoreic and ursonic acids, α and β amyrone. A mean ratio value of 9 between shoreic and ursonic acids was found; α and β amyrone contents seem to increase with the laser energy.

The selectivity of sampling was checked on E4 specimens, which consist of three layers: the ground, a mastic resin varnish layer with a mean thickness of 12 μm and an overpainting consisting of Burnt umber in linseed oil with a

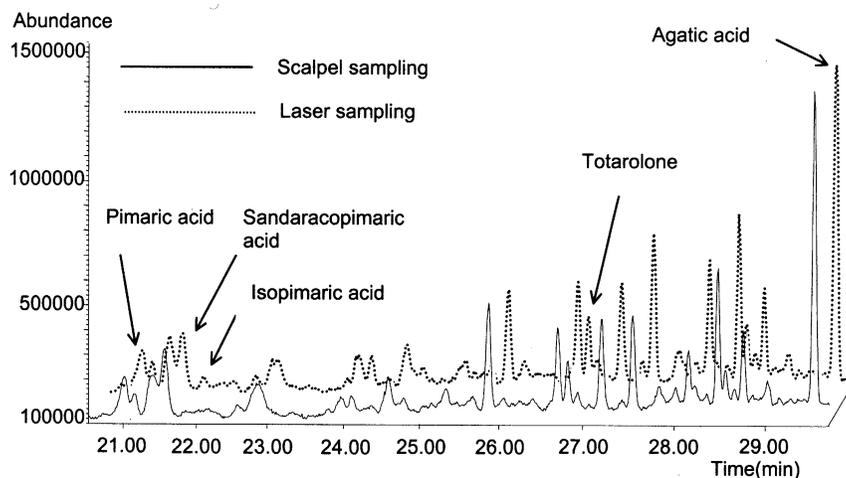


Fig. 6. Chromatograms acquired in the total ion current for LSV specimens sampled with scalpel (—) and laser (.....) methods. The identified peaks of sandarac resin are named in the figure.

301 compounds due to pyrolysis or to chemical transformation
 302 have not been observed in the ablate materials, significant
 303 photo-decomposition phenomena do not seem to occur
 304 during irradiation, thus avoiding doubts in the identification
 305 of the main components of a paint.

306 The encouraging results achieved with the reference
 307 paint layer specimens, seemed to suggest that the above
 308 sampling method could be applied to panel and canvas easel
 309 paintings. A copy of one of Caravaggio's canvases and a
 310 13th century panel were tested by applying the sampling to
 311 characterise in the former case a thick overpainting and in
 312 the latter some thin patinas and varnishes. In the first case,
 313 the results showed that the ablate matter did not contain
 314 drying oil and highlighted the presence of a protein and a
 315 terpenic resin. The medium of the overpainting was con-
 316 sisted above all of egg tempera identified by PCA analysis
 317 (Fig. 7) and Venice turpentine, showed by the presence of
 318 large amounts of 7-oxo-dehydroabiatic (54.9%), dehydroabi-

etic (23.0%) and di-dehydroabiatic (22.1%). To assess the
 319 depth of the overpainting, five samplings at 13 mJ laser
 320 energy were performed on the same area. In Fig. 7, the
 321 statistical treatment of amino acid data highlights that all the
 322 ablates belong to the egg cluster; moreover the presence of
 323 Venice turpentine was always observed showing the same
 324 terpenoid percentage profile. The thinning of the overpaint-
 325 ing corresponds to a lower and lower amount of protein
 326 recovered after each sampling; in particular in the fifth
 327 sample, the amino acids were revealed at the detection limit
 328 of the analytical method. This sampling method not only
 329 allows the identification of the medium, but by removing
 330 layers selectively, it also provides data on how to safely use
 331 the laser in restoration cleaning. In the above case, a sixth
 332 laser pass for cleaning would be dangerous since it might
 333 remove the paint binder.
 334

335 Concerning the panel "Virgin with Child", the analyses
 336 showed a widespread presence of animal glue, along with
 337 traces of Venice turpentine and egg protein. Fig. 8 shows the
 338 amino acid patterns for samples collected by mechanical
 339 and laser methods. Using a single pass at 4 mJ laser energy
 340 removes just a very thin layer which is clearly mainly made
 341

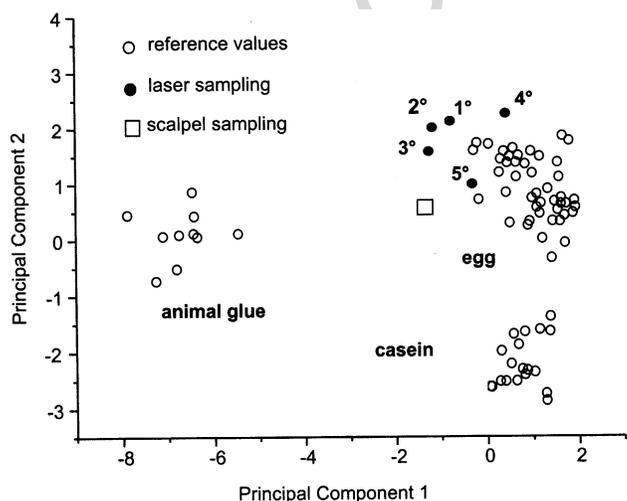


Fig. 7. Principal component analysis of the relative amino acid percentage contents of the ablate material from "Christ crowned with thorns" at 13 mJ laser energy in the presence of wetting agent U1 (●) and of a sample collected with a scalpel (◻).

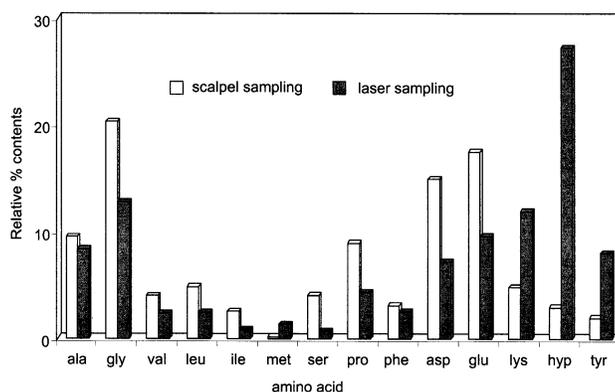


Fig. 8. Comparison between the profiles of amino acid percentage contents of the ablate material from "Virgin with Child" at 4 mJ laser energy and that from the material collected with a scalpel.

up of animal glue with only a trace of egg (confirmed by the presence of cholesterol) weighing 2.6 μg (as a sum of amino acid contents). The matter collected by the scalpel sampling contains several substances which also come from the substrate where the binder was egg. In fact, the amino acid weighed 9.9 μg (sample size was about 400 μg) and the amino acid profile resulted as a mixture of egg and collagen and was difficult to identify. Thus, the mechanical sampling method hampers the correct identification of substances in single layers. Moreover, the ablate samples from the green curtain of the painting exhibited $P/S = 1.0$, $A/P = 1.7$ and $\Sigma D = 50$ which, according to the values shown in Table 2, suggest the presence of linseed oil. All these results may indicate the use of a brightening mixture known as "beverone" which is spread over the whole surface in a very thin layer in addition to a typical varnish consisting of Venice turpentine and linseed oil. In fact, in further samplings operated at one 20 mJ pass laser energy, beverone was no longer found, confirming that laser ablation is able to draw out selectively very thin films.

5. Conclusions

The organic compound compositions which constitute paint layers were not affected by the laser energy in the ablation. In both reference paint layer specimens and in the old paintings, the organic compounds before the laser ablation and in the ablate material were found to nearly coincide. This means that Er:YAG laser equipment with threshold conditions of energies lower than 20 mJ at 15 pps assisted by wetting polar agents such as water/ethanol mixture (U1), can be safely used for selectively collecting thin layers from paintings. This allows the binders and varnishes in the painting to be correctly identified. The procedure is quite simple and fast. Moreover, since the Er:YAG laser acts mainly on hydroxyl groups, polar organic materials, which generally increase as a painting ages [2,10], absorb the laser pulsed energy, with a small thermal effect limited to the surroundings of polar molecules. The use of water polar wetting agents which are adsorbed on the paint layer favours the thermal effect, which in turns induces the evaporation of water molecules from the surface. This heating effect leads to an enrichment of organic substances in the ablate mainly through steam distillation; in any case, other mechanisms such as sublimation, explosion and mechanical transport occur at the same time [11]. The result is to obtain a pre-concentration of the analytical sample for each paint layer present: the ablation for areas of about 100 mm² is able to collect a maximum of 80 μg of organic substance in the optimised experimental conditions. This result could not be achieved using traditional mechanical samplers, unless large amounts of material were collected. Thus, from the point of view of conservation, this sampling method has limited invasive effects, and therefore its use is

advisable for works of art whenever an analysis of organic materials needs to be carried out.

Finally, since this sampling method offers a unique chance to study the effects between IR radiation and material transformation, more studies are in progress in order to correlate the reactivity of other -OH containing molecules used in paintings.

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