

# AN INTEGRATED APPROACH TO THE STUDY OF RI DE POMME, A PAINTING BY JULIAN SCHNABEL

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#### Abstract

The painting Ri de Pomme (1988) by American artist Julian Schnabel was recently subjected to an extensive and disputed restoration with polyvinyl acetate (PVAc) paints. To characterize and locate on the painting the materials used in the original and in the repainted areas, we employed several spectroscopic and chromatographic techniques. Fibre Optics Reflectance Spectroscopy (FORS), Micro-Raman, Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) and Gas Chromatography/Mass Spectrometry (GC/MS) were used. The original and restoration paint layers were differentiated by a preliminary FORS survey. The pigments were studied with Micro-Raman and the oil binder was characterized by GC/MS. Moreover, the support of the painting, a weathered tarpaulin, was characterized by Py-GC/MS.

**Keywords:** Julian Schnabel; Pyrolysis-Gas Chromatography/Mass Spectrometry; Gas Chromatography/Mass Spectrometry; Fibre Optics Reflectance Spectroscopy; Contemporary Art/

#### Introduction

*Ri de Pomme* is a large scale painting by artist Julian Schnabel, dating 1988 and presently owned by the Luigi Pecci Center for Contemporary Art of Prato (Italy). Julian Schnabel (October 26, 1951, New York, USA) is an American artist, screenwriter and filmmaker. He was one of a number of international painters - including David Salle in the United States, Georg Baselitz and Anselm Kiefer in Germany, and Francesco Clemente in Italy - to emerge in the late 1970s, whose bold expressive style was termed Neo-Expressionist. Schnabel's art is characterized by the use of eclectic historical images to create highly personal and allusive works [1]. He was first acknowledged for canvases whose painting surface was built up of shattered crockery, called "plate paintings". He has often used unconventional supports such as black velvet, cardboards and weathered tarpaulins and his paintings frequently have massive dimensions.

The object of our study, the painting *Ri de Pomme*, is painted on an aged tarpaulin, which is an old military equipment with evident spots of dirt. The artist did not use any kind of

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preparatory layer and the colour is applied directly on the tarpaulin [2]. The painting has huge dimensions, measuring 488x488cm.

In 2002 the artwork underwent an extensive restoration and a re-painting that have almost completely covered the original colours. The restorer's notes report the use of Lefranc & Bourgeois polyvinyl acetate (PVAc) paints [3]. The intervention has been disputed by the owner, the Pecci Center, being considered too invasive.

In order to evaluate its present state of conservation, the painting was subjected to a diagnostic campaign aimed at characterizing both the original and non-original paint materials. In particular, we aimed at verifying the possibility to differentiate between the original colours and the vinyl ones employed during the restoration. This discrimination is crucial for a correct and selective removal of the vinyl colours, in order to bring the painting back to its original conditions. For the identification of the pigments, non-invasive Fibre Optics Reflectance Spectroscopy (FORS) and Micro-Raman were employed, while to identify the binder, both Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) and Gas Chromatography/Mass Spectrometry (GC/MS) were used.

Fibre Optics Reflectance Spectroscopy (FORS) is one of the most promising noninvasive techniques used in the field of Cultural Heritage [4-8], based on the use of optical fibres, which convey light upon the painting and then collect the light backscattered from the surface of the painting. Optical fibres allow the investigation of a wide range of the electromagnetic spectrum, from about 250nm up to about 11,000nm, and thus they cover the UV, Vis, near- and mid-IR ranges. FORS is a portable technique that allows in situ measurements. It is mainly employed for colour monitoring and for the identification of pigments by matching the spectra acquired on the paint surface with those in a suitable pigment database.

The Raman technique has proven highly effective in detecting a wide range of synthetic organic pigments in paints [9-13], but can be employed also for the analysis of binding media [14]. In some cases, fluorescence phenomena due to binding media or varnishes may prevent the identification. Some authors have thus proposed Fourier-Transform-Raman (FT-Raman) [15] and Surface-Enhanced Raman Spectroscopy (SERS) [16, 17] for the analysis of pigments.

With regard to micro-destructive techniques, chromatographic techniques coupled with Mass Spectrometry (MS) are probably the most important array of instruments extensively employed for the characterization of organic materials in works of art and archaeological materials. In the present work they were used for the analysis of polymers, synthetic pigments and oils [18].

#### Experimental

#### **Reference** materials

Three different commercial PVAc paints were analysed, namely Violet, Violet Blue and Egypt Violet from Flashe® (Lefranc & Bourgeois). The paints were purchased from Zecchi (Florence, Italy). Accordingly to the manufacturer, Violet paint contains the organic pigments PV23 and PR122, Violet Blue contains PV23 only, while PV23 and PB29 are the colouring materials in Egypt Violet, that also contains PW6 (titanium white). Reference paint mock-ups were prepared by casting commercial vinyl paints colours over glass slides. The products were left to dry for one month before testing.

### Sampling

A micro-invasive sampling was performed for Py-GC/MS and GC/MS analyses. Four paint samples - S1, S2, S3 and S4 - (< 0.1mg) were collected from the painting and one sample - S5 - from the tarpaulin support. All the paint samples were carefully collected from the edges

of the painting, where the original layers of paint were not interested by re-paintings. The samples were observed under an optical microscope prior to analysis. For three of the paint samples (S1, S2 and S3) it was not possible to separate the fibres of the tarpaulin from the paint layer. Sample S4 was in form of flakes and devoid of any fibre of the support.

Fibre Optics Reflectance Spectroscopy (FORS)

The FORS measurements were performed with a high performance CCD spectrophotometer model Prime X BTC621E (B&W Tek, Newark, DE, USA) in the 200-1000 nm range, equipped with FRP optical fibres (geometry  $0^{\circ}/0^{\circ}$ ) and a tungsten lamp as light source. The spectral resolution of the spectrophotometer was 10nm/pixel. BWSpec software was used for the data acquisition.

Micro-Raman

Micro-Raman measurements were carried out using a Renishaw RM 2000 spectrophotometer, coupled with an optical Leica DLML microscope, equipped with a NPLAN objective 50x. The laser source was a Helium-Neon laser with a wavelength of  $\lambda = 632.8$ nm and a laser power output at the objective of around 2mW. The spectrometer consists of a single grating monochromator (1200 lines mm<sup>-1</sup>), coupled with a CCD detector, a RenCam 578×400 pixels (22µm × 22µm) cooled by a Peltier-element. The spectral calibration of the instrument was performed on the 520.5cm<sup>-1</sup> band of a silicon wafer.

## Gas Chromatographic techniques

Reagents – Pyrolysis was performed in the presence of 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Sigma–Aldrich, USA) to obtain the on-line thermally assisted derivatisation of the pyrolysis products. The derivatisation agent used for the GC/MS analyses was N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (Sigma-Aldrich, USA). The fatty acids stock solution in acetone contained lauric (3.49mg/g), suberic (3.60mg/g of Su), azelaic (3.47mg/g of A), myristic (3.32mg/g of My), sebacic (3.25mg/g of Se), palmitic (3.70mg/g of P), oleic (4.94mg/g of O) and stearic (5.57mg/g of S) acids. Tridecanoic acid solution in isooctane, 151.4ppm, was used as derivatization internal standard. Hexadecane solution in isooctane, 200.4ppm, was used as injection internal standard. All acids and hexadecane, purity 99%, were purchased from Sigma-Aldrich (USA). The standard solutions were used to derive calibration curves.

Apparatus – Py-GC/MS was performed with a Pyroprobe pyrolizer 5000 (CDS Analytical, USA) coupled with a 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA), interfaced with a 5973 single quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The pyrolysis temperature program was: initial temperature 50°C, ramp of 20°C/ms up to final temperature of 600°C. The pyrolyser interface was set at 180°C, the transfer line at 300°C and the valve oven at 290°C. The GC injection port was kept at 180°C. The GC column used was an HP-5MS fused silica capillary column (5% diphenyl/95% dimethyl-polysiloxane, 30m x 0.25mm i.d., 0.25 $\mu$ m film thickness, J&W Scientific, Agilent Technologies, Palo Alto, CA, USA) with a deactivated silica precolumn (2m x 0.32mm i.d., J&W Scientific, Agilent Technologies, Palo Alto, CA, USA). The carrier gas was used in the constant flow mode (He, purity 99.995%) at 1 mL/min. Samples were injected in split mode (variable split ratio depending on the sample amount).

The chromatographic oven was programmed as follows:  $32^{\circ}$ C, isothermal for 10 min,  $10^{\circ}$ C/min up to  $280^{\circ}$ C, isothermal for 3 min,  $15^{\circ}$ C/min up to  $300^{\circ}$ C, isothermal for 30 min. Ions were generated by electron-impact (EI) ionization (electron energy 70 eV) in the ionisation chamber of the mass spectrometer and MS spectra were recorded in the range 50-800 m/z in TIC (total ion current) mode.

For the GC/MS analysis, the GC/MS apparatus, the column and the conditions used were the same of the Py-GC/MS analysis, except for the temperature programme. The GC/MS

chromatographic oven was programmed as follows: initial temperature 80°C, isothermal for 2 min, 10°C/min up to 200°C, isothermal for 3 min; 10°C/min up to 280°C, isothermal for 30 min. The MS spectra were recorded in the range 50-800m/z both in TIC (total ion current) and in SIM (single ion monitoring) mode. The selected ions for the SIM acquisition were lauric acid m/z 117-257; suberic acid m/z 169-303; azelaic acid m/z 149-317; myristic acid m/z 117-285; sebacic acid m/z 149-331; palmitic acid m/z 117-313; oleic acid m/z 117-339; stearic acid m/z 117-341.

The saponification of lipids was performed using a microwave oven model ETHOS One (High Performance Microwave Digestion System) Milestone (Sorisole, Bergamo, Italy).

Analytical Procedure - The GC/MS analytical procedure was derived from a previously published combined procedure [18, 19], slightly modified and adapted for the analysis of the lipid-resinous fraction only. About 1 mg of each sample is subjected to saponification assisted by microwaves with 300µL of KOH in ethanol (10% wt) at 80°C for 60 min. After saponification, the solution is diluted in bi-distilled water, and the unsaponifiable fraction is extracted in n-hexane (400 µL, three times). Subsequently, the residue of the n-hexane extraction is acidified with HCl (6 M) and then extracted with diethyl ether (400  $\mu$ L, three times). The two extracts, containing the organic acids and the neutral fraction, were admixed and subjected to derivatization with 20µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 50  $\mu$ L of *iso*octane (solvent), and 5  $\mu$ L of tridecanoic acid solution at 60°C for 30 min. Prior to injection, 100 µL of isooctane and 5µL of hexadecane solution were added. 2µL of the isooctane solution of derivatized neutral and acid compounds were then analysed by GC/MS. Mass spectral assignment was based on the direct match with the spectra of NIST 1.7 and Wiley 275 libraries and a library created by the authors on purpose. Comparisons with mass spectra of reference standards, when available, were made. In the absence of reference spectra, the peak assignment was based on mass spectra interpretation.

#### **Results and Discussion**

#### Fibre Optics Reflectance Spectroscopy (FORS)

The FORS technique is generally employed for the identification of painting materials by comparison with suitable archives or reference spectra. FORS is a non-invasive, portable, point-by-point technique and the analysis time is extremely short, thus allowing us to perform *in situ* measurements and to map the painted surface. This step was fundamental at the beginning of the diagnostic campaign, to guide a thoughtful and representative sampling.

Several FORS measurements were performed on *Ri de Pomme*: 18 spots on the front of the painting and 4 on the sides were examined. The map of the FORS measuring points on the front of the painting is shown in Figure 1.

Two different types of violet coloured areas are present on the painting, presenting two different FORS spectra, shown in Figure 2. The lighter shade of violet corresponds to the PVAc paint used during the restoration, while the darker violet underneath can be related to the original paint, that has been almost completely covered. The FORS technique allowed us to differentiate between the original and non-original paint layers. Nonetheless, the identification of the original pigments was complicated, since extensive FORS libraries of synthetic organic pigments are lacking. The identification of the original paint layer is extremely important, if a removal intervention of the vinyl invasive paint layers will be planned.

The FORS results were used to select the sampling areas on the edges of the painting where small spots still retained the original colour only.

Unfortunately the FORS spectra of the PVAc mock-up paints – an example is reported in Figure 1, box on the bottom right - were not completely comparable with those acquired on the

painting, most probably because the FORS spectrum corresponding to the non-original paint layer on the painting is in fact the combination of both the individual spectra of the original and of the re-painted layer.

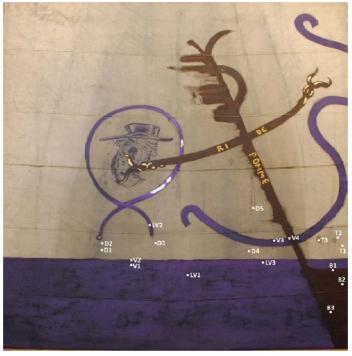
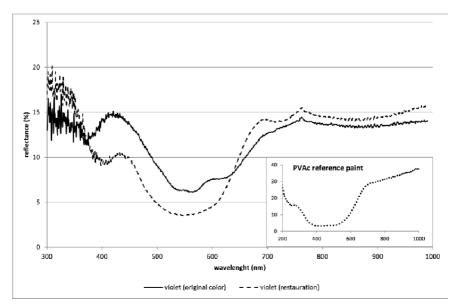
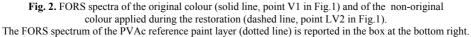


Fig. 1. *Ri de Pomme* by Julian Schnabel. The FORS measures are highlighted in white. D (drop), T (tarpaulin support), B (brown area), V (violet area), LV (light violet area).





#### Micro-Raman

Three paint samples from "*Ri de Pomme*" were analysed with Micro-Raman, together with the violet PVAc paints (Lefranc & Bourgeois) used during the restoration of the painting in 2002.

By comparing the Micro-Raman spectra with several libraries of pigments' spectra [12, 20, 21] it is possible to confirm that all the three Lefranc & Bourgeois violet paints contain PV23, dioxazine violet, a common synthetic organic pigment, as stated by the manufacturers. The three violet PVAc colours have the same Raman profile, thus the other pigments in the vinyl paints (PR122, PB29 and PW6) are not detectable, probably due to their very low amount. The spectrum of one of the PVAc colour ("Violet") is given in Figure 3 (spectrum A) as an example. None of the PVAc characteristic Raman frequencies [22] were detected in the spectra of the three Lefranc & Bourgeois vinyl paints, probably because the pigment is the component of the paint that contributes to the Raman spectrum to a greater extent.

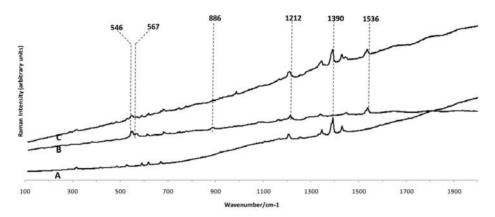


Fig. 3. Raman spectra of the PVAc colour containing PV23 (spectrum A), of sample S1 (spectrum B) and of sample S3 containing both the original paint layer and the PVAc resin layer (spectrum C). The band positions of the three spectra are listed in Table 1.

With regard to the paint samples, the Micro-Raman technique confirmed the distinction made by FORS between the original and the non-original layers of paint. The absorbance peaks of all the paint samples and their tentative attributions are listed in Table 1.

As expected from the preliminary survey, samples S1 and S2 did not show any of the characteristic PV23 peaks, thus these two paint samples contained the original paint and not the one used during the restoration. The spectrum of S2 is shown in Figure 3 (spectrum B). Unfortunately, no complete match was found in spectra libraries for the violet pigment in the original paint layer. Nonetheless, a partial match with the phthalocyanine pigments was found, based on the identification of the peaks at 1536, 1337 and 746cm<sup>-1</sup>, that are characteristic of this class of dyes. Moreover, the peaks at 1212, 775, 680cm<sup>-1</sup> were identified as characteristic of a green phthalocyanine by Aibéo et al [23] Thus, we hypothesized that the violet paint used by Schnabel contained a mixture of two or more pigments, one being a phthalocyanine pigment. The peak at 1443cm<sup>-1</sup> could be attributed to the binder, that is linseed oil [14], as highlighted by the GC/MS results discussed later on.

Interestingly, the Raman spectrum of the third paint sample S3 (spectrum C in Figure 3) shows some absorbance peaks detected in S1 and S2, and some others characteristic of PV23. Thus, S3 contains both the original paint and the vinyl one, juxtaposed during the re-painting. The absorbance peaks of sample S3 in common with PV23 are: 1441cm<sup>-1</sup>; 1430cm<sup>-1</sup>; 1390cm<sup>-1</sup> (most intense peak); 1344cm<sup>-1</sup>; 316cm<sup>-1</sup>. The absorbance peaks not attributable to PV23 and in common with samples S1 and S2 are: 1536cm<sup>-1</sup>; 986cm<sup>-1</sup>; 546cm<sup>-1</sup> and 567cm<sup>-1</sup>.

Paint samples S1 and S2	Paint sample S3	Attribution	
1536 (s)	1536 (m)	Phthalocyanine class	
1529(sh)		•	
1443 (m)		Linseed oil [14]	
	1430 (m)	PV23	
	1390 (s)	PV23	
	1344 (m)	PV23	
1337 (m)		Phthalocyanine class	
1212 (s)		Green phthalo? [23]	
1192 (sh)			
1080 (w)			
986 (w)	986 (w)		
886 (w)			
775 (w)	775 (w)	Green phthalo? [23]	
746 (m)		Phthalocyanine class	
680 (m)	680 (w)	Green phthalo? [23]	
613 (w)	613 (w)		
	589 (w)	PV23	
567 (m)	566 (w)		
546 (s)	547 (m)		
	316 (w)	PV23	

**Table 1.** Raman shifts  $(cm^{-1})$  observed in the spectra of paint samples S1, S2 and S3from *Ri de Pomme*, with the tentative attributions.

(s) strong, (m) medium, (w) weak, (sh) shoulder

### Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

We performed Py-GC/MS to obtain information on the original binding medium. Py-GC/MS analysis showed that the binder in the paint used by Schnabel is a lipid material. In the pyrograms of all the paint samples, peaks corresponding to mono- and di-carboxylic fatty acids are observed [24]. As an example, the pyrogram of the paint sample S4 is shown in Figure 4. The identified compounds are listed in Table 2. The pyrolysis profile shows azelaic acid as the main peak, suggesting the use of a siccative oil.

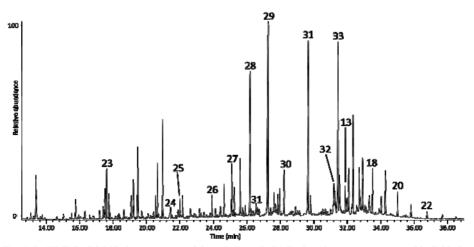


Fig. 4. Py(HMDS)-GC/MS chromatogram of the paint sample S4. Peak assignments are reported in Table 2.

We also applied Py-GC/MS to the analysis of the reference mock-ups prepared with the PVAc paints used during the restoration of the painting. In this case, we decided to work without the HMDS derivatising agent, in order to be able to identify the PVAc monomers, as described in the literature [25, 26]. The pyrograms obtained for the PVAc reference materials (an example of the "Violet" paint is shown in Fig. 5) are characterized by the acetic acid and benzene peaks (#1 and #2, respectively), produced *via* a side group elimination reaction pathway. Moreover, the distinctive profile of a versatate (VeoVa) plasticizer (peak #8) was detected. These results were in agreement with the literature [25-27]. None of the characteristic peaks of the PVAc resins were found in the paint samples, thus confirming that they were collected from the original layers.

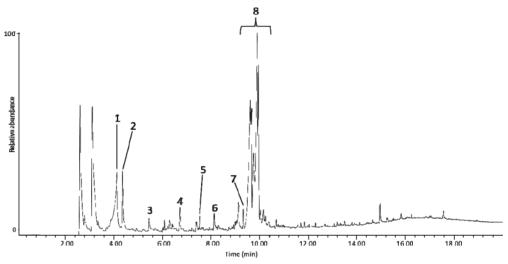


Fig. 5. Py-GC/MS chromatogram of the "Violet" PVAc paint (Lefranc & Bourgeois). 1. acetic acid; 2. benzene; 3. methyl benzene; 4. styrene; 5. phenylpropene; 6. 1H-indene; 7. azulene; 8. VeoVa plasticizers.

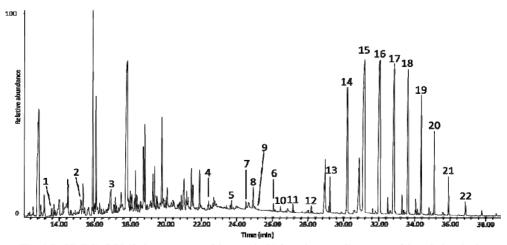


Fig. 6. Py(HMDS)-GC/MS chromatogram of the sample S5 from the tarpaulin support of the painting. Peak assignments are reported in Table 2.

We also analysed a sample collected from the support of the painting, constituted of a weathered tarpaulin. Saturated long-chain hydrocarbons are the most abundant peaks in the pyrogram (Figure 6). Moreover, peaks related to the pyrolysis of a cellulose-derived material are observed (levoglucosan, peak #10; dehydrated glucose, peak #8; 1,2,3-trihydroxybenezene, peak #7). These features are characteristic of a fabric made of cellulosic fibres [28] and waterproofed with a paraffin wax [29, 30].

Number	Retention time	Compound	
	(min)		
1	13,6	2-Ciclopenten-1-one, 2 methyl	
2	15,2	2-Furancarboxaldehyde, 5 methyl	
3	16,9	1,2-Cyclopentanedione, 3 methyl	
4	22,4	1-Tetradecene	
5	23,7	1-Pentadecene	
6	26	1-Heptadecene	
7	24,5	1,2,3-Trihydroxybenzene, 3TMS	
8	24,9	Dehydrated glucose, 2TMS	
9	25,1	1,2,4-Trihydroxybenzene, 3TMS	
10	26,4	Levoglucosan, TMS	
11	27,1	1-Octadecene	
12	28,1	1-Nonadecene	
13	29,2	Eicosane	
14	30,2	Heneicosane	
15	31,1	Docosane	
16	31,9	Tricosane	
17	32,8	Tetracosane	
18	33,5	Pentacosane	
19	34,3	Hexacosane	
20	35	Heptacosane	
21	35,9	Octacosane	
22	36,8	Nonacosane	
23	17,6	Hexanoic acid, TMS	
24	21,4	Succinic acid, 2TMS	
25	22	Nonanoic acid, TMS	
26	23,9	Adipic acid, 2TMS	
27	25,1	Pimelic acid, 2TMS	
28	26,2	Suberic acid, 2TMS	
29	27,3	Azelaic acid, 2TMS	
30	28,2	Sebacic acid, 2TMS	
31	29,7	Palmitic acid, TMS	
32	31,3	Oleic acid, TMS	
33	31,5	Stearic acid, TMS	
34	26,6	Acridine 1,2,3,4,5,6,7,8 octahydro	

 Table 1. Compounds identified in the pyrograms reported in Figures 4 and 6.

 The TMS abbreviation stands for trimethylsilyl esters and ethers.

## Gas Chromatography/Mass Spectrometry (GC/MS)

We performed GC/MS on the samples identified as the original paint layers thanks to the Raman analyses. The chromatogram of sample S1 is reported in Figure 7 as an example, and the compounds identified are listed in Table 3. All the paint samples show peaks due to mono- and di-carboxylic fatty acids, with azelaic acid as the most abundant [31], confirming that Schnabel

used a siccative oil. The amount of fatty acids was above the LOQ of the procedure  $(1.20 \ \mu g)$ . The long chain hydrocarbons in the GC/MS chromatograms derive from the tarpaulin support. The peak indicated with a star in the chromatogram in Figure 7 is attributed to the dibutyl phthalate, an ubiquitous contaminant, found also in our procedure blanks, not to be confused with the external plasticizer used in many PVAc formulations.

To obtain more detailed information about the siccative oil used by Schnabel, the relative abundances of five mono-carboxylic (lauric, myristic, palmitic oleic, stearic) and three di-carboxylic (suberic, azelaic, sebacic) fatty acids were taken into consideration. The ratio between palmitic and stearic acids (P/S) is generally used to determine the botanical origin of the oil [32, 33]. The sum of the di-carboxylic fatty acids ( $\Sigma D$ ) and the ratio between azelaic and palmitic acids (A/P) are useful parameters to evaluate the degree of oxidation of the oil. The values of these characteristic parameters for the paint samples collected from *Ri de Pomme* are reported in Table 4. The values of P/S and the high content of dicarboxilic acids results are compatible with linseed oil, or for linseed oil mixed with other siccative or semi-siccative oils used in modern oil-based paint media (P/S < 2; A/P > 1;  $\Sigma D > 40$ ) [32, 33].

number	<b>Retention time</b>	compound		
	(min)			
1	12,02	Hexadecane (IS1)		
2	12,65	Lauric acid, TMS		
3	13,22	Suberic acid, TMS		
4	13,73	Tridecanoic acid, TMS (IS2)		
5	14,29	Azelaic acid, 2TMS		
6	14,84	Miristic acid, TMS		
7	15,49	Sebacic acid, 2TMS		
8	17,89	Palmitic acid, TMS		
9	20,29	Oleic acid, TMS		
10	20,60	Stearic acid, TMS		
11	20,01	Docosane		
12	21,18	Tricosane		
13	22,24	Tetracosane		
14	23,18	Pentacosane		
15	24,05	Hexacosane		
16	24,88	Heptacosane		
17	25,69	Octacosane		
18	26,6	Nonacosane		
19	27,70	Triacontane		
20	28,97	Hentriacontane		

 Table 2. Compound identified in the GC/MS chromatogram reported in Figure 7.

 The TMS abbreviation stands for trimethylsilyl ester.

Table 3. Characteristic parameters of fatty acids calculated for the Ri de Pomme paint samples

Paint sample	P/S	A/P	∑D (%)	μg of FA
S1	1,1	4,9	75	2,3
<b>S2</b>	1,1	3,3	67,6	2,8
<b>S4</b>	1,2	1	36	2,7

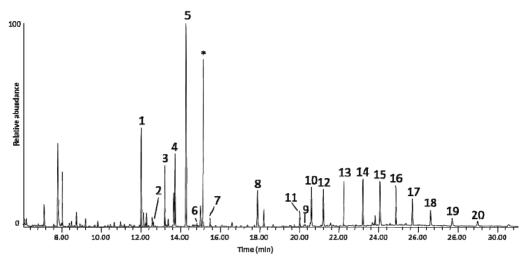


Fig. 7. GC/MS chromatogram of the paint sample S1. The \* indicate the peak of buthyl phthalate, an ubiquitous contaminant. Peak assignments are reported in Table 4.

#### Conclusions

The combination of non-invasive and micro-destructive spectroscopic and chromatographic techniques enabled the characterization of the paint materials used in both the original and in the restored areas. We first differentiated between the original colours used by Schnabel and the ones used during the restoration by means of non-invasive FORS survey, and confirmed our hypotheses by Micro-Raman technique. These two techniques give complementary information: on one hand, FORS is a non-invasive, portable technique and the analysis time is very short, thus allowing us to map the painted surface. On the other hand, Micro-Raman is a very suitable technique for the study of synthetic organic pigments, enabling us to identify the synthetic pigment of the vinyl colours, PV23, which was not the same pigment used by the artist. This helped us confirming if our paint samples were collected from the original layers of colour or from the restored areas. Moreover, we were able to identify the class of one of the synthetic pigments that constitute the original paint layer, the phthalocyanine class. We also performed Py-GC/MS and GC/MS to obtain information on the binder used by Schnabel. The chromatographic data revealed that the paint used by the artist contained siccative oil as binder, and the GC/MS quantitative analysis pointed out linseed oil as the most likely candidate, which could have been used pure, or mixed with other siccative or semisiccative oils. Moreover, no traces of synthetic polymers were found in the samples collected from the original paint layer. The Py-GC/MS analysis gave us information on the tarpaulin support, which turned out to be composed by a cellulosic material waterproofed with a paraffin wax.

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