Surface Acoustic Wave Nebulization-Mass Spectrometry as a New Tool to Investigate the Water Sensitivity Behavior of 20th Century Oil Paints

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DOI
10.1021/jasms.0c00272

Publication date
2021

Document Version
Final published version

Published in
Journal of the American Society for Mass Spectrometry

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Citation for published version (APA):

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Surface Acoustic Wave Nebulization—Mass Spectrometry as a New Tool to Investigate the Water Sensitivity Behavior of 20th Century Oil Paints

Alina Astefanei, Klaas Jan van den Berg,* Aviva Burnstock, and Garry Corthals

ABSTRACT: The sensitive surfaces of many unvarnished 20th century oil paintings are of great concern for conservators and collection keepers. They may show degradation problems such as paint delamination, dripping, and soft and sticky paint and pose challenges for cleaning due to solvent sensitivity. We report for the first time the use of an innovative ambient ionization technique, surface acoustic wave nebulization—mass spectrometry (SAWN—MS), for the identification and characterization of fatty acids, dicarboxylic species and glycerides in water-sensitive modern oil paints. The composition of 10 relevant Winsor and Newton 1964—1965 paint swatches that present different degrees of water sensitivity and two paint samples from a painting by the British artist Francis Bacon were studied. Principal component analysis was used for SAWN—MS data classification. Electrospray ionization (ESI)—MS was used as control method, specifically to compare the obtained ratios of markers of interest by the two ionization techniques. The results obtained by both ESI—MS and SAWN—MS are correlated and discussed in a broader context including the information on the oil media obtained by gas chromatography (GC—MS) and also on the inorganic materials and salts characterized using a combination of methods in previous reports on samples from the same manufacturer. SAWN—MS was found to be a suitable tool for the determination of soluble organic constituents present in the paints. The method provides an indication of the level of oxidation and hydrolysis of the paint film by monitoring specific markers such as free palmitic and stearic acids, azelaic acid, monoacylglycerols, and diacylglycerols. The data showed that a higher level of water sensitivity coupled with a high level of oxidation and hydrolysis is linked to higher dicarboxylic acid, diacyl- and triacylglyceride content and lower levels of short chain fatty acids. The data obtained by SAWN—MS provided a good correlation between the monitored species and the degree of water sensitivity.

KEYWORDS: surface acoustic wave nebulization, mass spectrometry, water sensitive modern oil paints, case studies

1. INTRODUCTION

Modern 20th and 21st century oil paintings often show deterioration phenomena that are different from those observed in paintings from previous centuries. The paintings may present problems such as water sensitivity, delamination, blooming, paint exudation, sticky paint that accumulates dirt, insufficient drying, and even paint liquefaction. This poses challenges for conservators as conventional conservation treatments such as surface cleaning, that usually employ solvents on cotton swabs in combination with some mechanical action, cannot be applied. The causes of the observed problems have been found to be linked to a low degree of cross-linking of the oils used, such as linseed, poppy, and safflower oils. Furthermore, the lack of heavy and alkali-earth metals in modern pigments leading to a poorly developed polymeric network with increased polarity. The drying and aging of oil paint involves 3 key processes: (i)
The complexity and the composition and drying behavior of modern oil paints presents a challenge for analysis, and necessitates the use of a combination of different analytical methods. The most commonly used analytical techniques to study oil artists' oil paints are gas chromatography (GC)–MS, pyrolysis-GC–MS,8,15 and direct temperature time-resolved MS (DT-MS).4 These methods are not sufficient to investigate some of the degradation phenomena observed in modern oil paints, including key information about the degree of hydrolysis of oil paints. They require relatively large samples, chemical derivatization, high temperatures, and/or high ionization energies, leading to loss of information due to extensive fragmentation of the compounds both in the derivatization and analysis step. It is not possible to infer from the results of analysis whether detected fragments are due to the analytical technique or due to degradation of the paint. More recently, direct infusion electrospray-MS has proven to be more suitable for determining the degree of oxidation and hydrolysis.20 A correlation between the degree of water sensitivity of paints has been hypothesized based on analysis of the ratios of fatty acids, diacyl- and triacyl-glycerides (DAGs and TAGs) using atmospheric pressure ionization (API)-MS techniques.11

Advances in high-resolution mass spectrometry has favored the use of ambient MS for analysis of samples from a range of cultural materials.21–24 Small samples can be analyzed with minimal preparation, reducing the risk of analyte degradation or modification. Surface acoustic wave nebulization-mass spectrometry (SAWN–MS) has the ability to detect and characterize a wide range of molecules and data acquisition is fast. Furthermore, among ambient MS techniques, SAWN has showed to be a softer ionization technique compared to ESI, maintaining the structural integrity of labile compounds, difficult to ionize by other techniques.25–27 SAWN has also been successfully coupled with liquid chromatography and paper-based delivery methods for the analysis of protein digest and drugs in human blood samples.26,28 Within the field of cultural heritage, we have recently reported the advantages of using this technique for the identification of synthetic dyes in textile fibers.21

The present study presents the first application of SAWN–MS for the analysis of organic molecules from a set of naturally aged Winsor and Newton (W&N) oil paints (1964–1965) that presented different degrees of water sensitivity. Samples from water sensitive areas from Figure in Landscape, by Francis Bacon (dated 1945, Tate Gallery London) (Figure 1S) and the W&N samples analyzed in this study were known to contain magnesium carbonate that is a marker for W&N paints.14,15 PCA was used for data interpretation. Information on the type of oil, metal composition and the presence of fillers, additives and extenders in the paint samples analyzed here were carried out in

**Figure 1.** (a) Diagram of possible reactions of glycerides in an oil paint, based on the chemical reactions that are occurring in the drying and aging of the paint film (courtesy of André van den Doel). (b) Reaction scheme for the formation of azeleic acid in triglycerides.
previous studies. ESI–MS analysis was also performed in this work and the results are discussed in the context of the interpretation of the data acquired using SAWN–MS.

2. EXPERIMENTAL SECTION

2.1. Samples. Samples from ten representative. Winsor & Newton “student quality” oil paint swatches prepared by the manufacturer between December 1964 and January 1965 as part of quality control including drying time tests were included in this study. The surfaces of many of these paints have shown different degrees of sensitivity to traditional cleaning procedures that were evaluated using cotton swabs and deionized water in a previous study. Sensitivity was based on the average number that were evaluated using cotton swabs and deionized water in an aqueous solvents, whereas the areas containing white are not the water sensitivity phenomena of modern oil paints. 

Two samples from Figure in a Landscape (1945), by Francis Bacon from the Tate Gallery, London (inv.nr. N05941), were included in the present study. The samples were taken from blue and red passages of paint (Figure 1S) and were analyzed using SAWN–MS for comparison to the W&N samples. A sample of blue paint was described by the conservator at Tate as instantly water sensitive (upon touching with a damp cotton swab), while the second sample of red paint was moderately water sensitive (after an unspecified number of swab rolls). These samples are also included in Table 1. Figure in a Landscape were painted in oil on canvas in the 1940s, measures 144.8 cm by 128.3 cm, and is also included in Table 1.

2.2. Sampling and Sample Preparation. For the W&N paint swatches, sampling was done by scraping the surface of the paint with a metallic surgical knife and collected with a spatula. The stock solutions were made by dissolving 1 mg of bulk paint sample in 1 mL of ethanol for 1 h in the dark and at room temperature and afterward sonicated for 15 min. The obtained colored solutions were then centrifuged at 3000 rpm at 20 °C for 5 min, and the supernatant was collected and stored for analysis. The samples from Figure in a Landscape were collected by Cooper et al. as part of a previous study and were re-examined here. The minute samples were solubilized in 20 μL of ethanol, sonicated, and centrifuged similarly to the procedure used for the W&N paint samples.

2.3. Mass Spectrometry. All experiments were conducted on a high-resolution mass spectrometer, a triple TOF 5600+ mass spectrometer (AB SCIEX, Concord, ON).

SAWN–MS. A SAWN device from DEURION (Seattle, WA) was used. A detailed description of the setup is included in a previous report.

The SAWN chip was placed 1 cm below and at 1 cm distance from the MS inlet with the delay zone, where the liquid sample is placed, centered under the MS orifice so that the aerosols are guided inside the MS orifice. The chip was operated by a software installed on an android tablet connected to an electronic box. For each acquisition, the SAW was regulated by applying 3–4 W in continuous mode. For each analysis, a total volume of 10 μL sample was on loaded dropwise (1 μL at the time) on the chip for 1 min. The order of the analyzed samples was randomized to prevent bias. The SAWN chip was cleaned before each new sample and blanks of ethanol have been performed before and after each run. The interface heater temperature was 150 °C, the inlet and outlet gas were set at 0 psi and the curtain gas to 10 psi. The mass spectra were acquired (m/z 100–1000) in negative ionization mode using multichannel acquisition (MCA) with an accumulation time of 3 s.

ESI–MS. For the ESI–MS measurements the data were acquired using a nanospray ion source. The ion source gas 1 value was set to 5 μL/min, ion source gas 2 was 0 μL/min, the curtain gas value was 30 psi, an ion-spray voltage of 2000 V, and an interface heater temperature of 150 °C. The flow rate of the syringe was set on 2 μL/min. The mass spectra were acquired (m/z 100–1000) in negative ionization mode. Peak view 2.0 software was used for data processing. In all measurements, the compounds have been identified based on their exact mass (within 2 ppm accuracy).

2.4. Data Analysis. Principal component analysis (PCA) on the covariance matrix was carried out using XLSTAT 2018.2 (Addinsoft). A set of 27 representative molecular ions corresponding to most significant extracted polar glycerides and fatty acids were monitored and selected for PCA analysis (Table 2). The 27 ions were selected based on previous studies and were identified based on their exact mass (accuracy <5 ppm). The intensity of the group of ions was normalized to the sum of all 27 ions, with the following groups: (1) short chain monocarboxylic acids (C6–C10); (2) free dicarboxylic acids (diC7–diC10); (3) monoacylglycerides of dicarboxylic acids (MAG (diC8,diC9)); (4) hydroxy-fatty acids (OH-C18 acids); (5) diglycerides containing suberic and/or azelaic acid (DAGs (2diC)); (5) diglycerides containing palmitic acid and diacids (DAG (P+diC)); (6) diglycerides containing stearic acid and diacids (DAG (S+diC)); (7) triacylglycerides containing azelaic acid (TAG (3diC9)); (8) free palmitic acid (P); (9) stearic acid (S) and oleic acid (O).

Table 1 also includes a short description of the composition of the paint samples made by W&N analyzed in this study as well as information on the pigments, extenders, additives, and binding media, previously obtained by SEM–EDX, ATR–FTIR, and GC–MS. According to the wet swab roll tests, all the paints showed sensitivity to swabbing excluding the whites. The level of water sensitivity increased in the following order: flake white (FW) and titanium white (TW) (none); cobalt blue tint (CB tint) (low); cobalt blue (CB), cobalt violet (CV), and chrome yellow (CY) (moderate); ultramarine blue (UB) and burnt sienna (BS) (sensitive); raw sienna (RS), and lamp black (LB) (highly sensitive). All the water-sensitive swatches contained magnesium carbonate as a filler, a known factor contributing to the water sensitivity phenomena of modern oil paints.

Barium sulfate was found in all the paint swatches except those showing a high water sensitivity (UB, BS, RS, and LB), which instead showed the presence of silicon-containing compounds. Si has also been found in CB tint and CV swatches. These may have been added as extenders, including clay and sand, or be present as part of the pigment composition (ultramarine, raw and burnt sienna).

Two samples from Figure in a Landscape (1945), by Francis Bacon from the Tate Gallery, London (inv.nr. N05941), were included in the present study. The samples were taken from blue and red passages of paint (Figure 1S) and were analyzed using SAWN–MS for comparison to the W&N samples. A sample of blue paint was described by the conservator at Tate as instantly water sensitive (upon touching with a damp cotton swab), while the second sample of red paint was moderately water sensitive (after an unspecified number of swab rolls). These samples are also included in Table 1. Figure in a Landscape were painted in oil on canvas in the 1940s, measures 144.8 cm by 128.3 cm, and is unvarnished, and the surface has a prominent texture with significant reworking and layering. Most of the colored paint passages in Figure in a Landscape were reported to be sensitive to aqueous solvents, whereas the areas containing white are not sensitive. Water-soluble magnesium sulfate heptahydrate salt (epsomite, MgSO4·7H2O) was found at the paint surface of the work, which has been found to be a degradation product of MgCO3 extender that was used by W&N.
### Table 1. Molecular Composition of Studied Paints

<table>
<thead>
<tr>
<th>swatch (pigment label)</th>
<th>composition as described in W&amp;N catalogue 1970</th>
<th>water sensitivity of paint surfaces</th>
<th>no. of swabs</th>
<th>SEM-EDX</th>
<th>ATR-FTIR</th>
<th>GC−MS</th>
<th>ESI−MS</th>
<th>SAWN−MS</th>
<th>conclusions (binder; pigments; additives)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flake white</strong> (FW)</td>
<td>carbonate of lead with small admixture of zinc to improve consistency, general working properties, maintenance of whiteness and to enable it to give clear tints with the colder colors. In refined safflower oil (Art no. 23H/9, Winton no. 19)</td>
<td>not sensitive</td>
<td>50</td>
<td>Pb, Zn, Ba, S</td>
<td>barium sulfate</td>
<td>P/S = 3.4; semidrying oil</td>
<td>P/S = 3.0; A/P = 0.2; DAG (P+A)/DAG(S+A) = 1.3</td>
<td>P/S = 3.0; A/P = 0.2; DAG (P+A)/DAG(S+A) = 1.5</td>
<td>Drying oil, unclear. ESI and SAWN indicate linseed oil with added poppy seed fatty acids (see text); lead white (lead carbonate) mixed with zinc oxide and extended with barium sulfate</td>
</tr>
<tr>
<td><strong>titanium white</strong> (TW)</td>
<td>titanium dioxide ground in (refined) safflower oil. Contains a little zinc oxide which helps to maintain whiteness (Art no. 244, Winton no. 40)</td>
<td>not sensitive (slight change in gloss when swabbed)</td>
<td>50</td>
<td>Ti, Zn, S, Ba</td>
<td>barium sulfates</td>
<td>P/S = 3.9; semidrying oil, stearates</td>
<td>P/S = 3.7; A/P = 0.3; DAG (P+A)/DAG(S+A) = 1.2</td>
<td>P/S = 3.0; A/P = 0.2; DAG (P+A)/DAG(S+A) = 1.5</td>
<td>Drying oil, unclear. ESI and SAWN indicate linseed oil with added poppy seed fatty acids (see text); titanium oxide mixed with zinc oxide extended with barium sulfate and zinc stearates</td>
</tr>
<tr>
<td><strong>cobalt blue</strong> (CB)</td>
<td>cobalt aluminate or cobalt phosphate containing some alumina (Art no. 203) or variety of ultramarine (Winton no. 15)</td>
<td>low (require mechanical actions)</td>
<td>40</td>
<td>Ba, Zn, Ca, Mg, Al, Si</td>
<td>barium sulfate, magnesium carbonate, silicates</td>
<td>NA</td>
<td>P/S = 3.4; A/P = 0.3; DAG (P+A)/DAG(S+A) = 3.5</td>
<td>P/S = 3.0; A/P = 0.4; DAG (P+A)/DAG(S+A) = 2.7</td>
<td>Unspecified drying oil; organic pigment. Extenders magnesium carbonate, barium sulfate and kaolin; Zn- and Ca-containing compounds</td>
</tr>
<tr>
<td><strong>cobalt violet</strong> (CV)</td>
<td>cobalt aluminate or cobalt phosphate containing some alumina (Art no. 229) or manganese phosphate (Winton no. 66)</td>
<td>moderate (mechanical action required)</td>
<td>23</td>
<td>Ba, S, Mg, Zn, Al, Si, Pb, Co on surface (low amount)</td>
<td>barium sulfate, magnesium carbonate,</td>
<td>NA</td>
<td>P/S = 2.0; A/P = 0.5; DAG (P+A)/DAG(S+A) = 1.6</td>
<td>P/S = 1.8; A/P = 0.5; DAG (P+A)/DAG(S+A) = 1.9</td>
<td>Poppy oil; cobalt aluminate; extenders: barium sulfate, magnesium carbonate and aluminum stearate; Zn- and Ca-containing compounds</td>
</tr>
<tr>
<td><strong>chrome yellow</strong> (CY)</td>
<td>normal chrome of lead (Art no. 112, Winton no. 13)</td>
<td>moderate</td>
<td>22</td>
<td>S, Pb, Cr, Mg, Al, Ba</td>
<td>barium sulfate, magnesium carbonate</td>
<td>NA</td>
<td>P/S = 3.0; A/P = 0.5; DAG (P+A)/DAG(S+A) = 3</td>
<td>P/S = 1.6; A/P = 0.5; DAG (P+A)/DAG(S+A) = 2.5</td>
<td>Safflower/poppoy seed oil; lead chromate, aluminum and magnesium compounds (possibly organic compounds—seen as inclusions in matrix). Extended with barium sulfate. Possibly kaolin and lead sulfate</td>
</tr>
<tr>
<td><strong>ultramarine</strong> (UB)</td>
<td>complex combination of silica, alumina, soda and silica (found in artists range no. 133 not found in Winton range)</td>
<td>sensitive</td>
<td>16</td>
<td>Al, Si, Na, Mg, S, K (Co, Zn)</td>
<td>silicates (ultramarine, magnesium carbonate)</td>
<td>P/S = 5.9; semidrying oil</td>
<td>P/S = 2.0; A/P = 1.0; DAG (P+A)/DAG(S+A) = 2.4</td>
<td>P/S = 2.0; A/P = 2.0; DAG (P+A)/DAG(S+A) = 2.1</td>
<td>A variety of synthetic ultramarine (sodium aluminate/silicate in unspecified drying oil—extended with magnesium carbonate or magnesium stearate and kaolin. Zirconium and cobalt salts added as driers. Aluminum soap, calcium carbonate/sulfate</td>
</tr>
<tr>
<td><strong>burnt sienna</strong> (BS)</td>
<td>calcined native earth containing ferric oxide (Art no. 103, Winton no. 2)</td>
<td>sensitive</td>
<td>12</td>
<td>Fe, Mg, Si</td>
<td>magnesium carbonate, silica</td>
<td>P/S = 3.4; semidrying oil</td>
<td>P/S = 1.7; A/P = 3.0; DAG (P+A)/DAG(S+A) = 2.1</td>
<td>P/S = 1.6; A/P = 4.0; DAG (P+A)/DAG(S+A) = 1</td>
<td>Linseed oil; iron oxide with magnesium carbonate and silica as extenders. Possible driers: cobalt and zirconium salts</td>
</tr>
<tr>
<td><strong>raw sienna</strong> (RS)</td>
<td>native earth containing ferric oxide (Art no. 128, Winton no. 34)</td>
<td>highly sensitive</td>
<td>9</td>
<td>Fe, Mg, Si (on surface)</td>
<td>magnesium carbonate, silica</td>
<td>P/S = 1.8; linseed oil</td>
<td>P/S = 1.4; A/P = 1.0; DAG (P+A)/DAG(S+A) = 1.7</td>
<td>P/S = 1.4; A/P = 1.0; DAG (P+A)/DAG(S+A) = 1.5</td>
<td>Linseed oil; iron oxide extended with magnesium carbonate and silica. Possible driers: cobalt and zirconium salts</td>
</tr>
<tr>
<td><strong>lamp black</strong> (LB)</td>
<td>not known</td>
<td>highly sensitive</td>
<td>6</td>
<td>Pb, Mg</td>
<td>magnesium carbonate, lead oxide, or acetate</td>
<td>NA</td>
<td>P/S = 1.4; A/P = 0.8; DAG (P+A)/DAG(S+A) = 2.4</td>
<td>P/S = 1.2; A/P = 1.0; DAG (P+A)/DAG(S+A) = 1.0</td>
<td>Linseed oil; organic black extended with magnesium carbonate; lead based drier.</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

3.1.1. Molecular Composition of Polar Fractions by SAWN–MS and ESI–MS. SAWN–MS and ESI–MS in negative ionization mode were used to gain molecular information on the extractable polar fractions such as dicarboxylic species, glycerides, and fatty acids. A total of 27 deprotonated molecules, \([M - H]^-\), were selected to be monitored in the obtained spectra as the most representative of the materials analyzed. The chemical identification, mass-to-charge ratio and molecular ion assignment of the monitored species are given in Table 2. As an example, Figure 2 shows the mass spectra obtained by SAWN–MS for a non-water-sensitive (FW) and a water-sensitive paint (UB). Significantly higher intensities of diacid species including suberic, azelaic, and sebacic acid (diC8-diC10) in the free form, in MAGs, DAGs, and TAGs, and higher amounts of extracted free azelaic acid (A) \((m/z 187)\) were observed for the sensitive samples.

<p>| Table 2. Monitored ([M - H]^-) Used for Data Analysis and Interpretation |
|-------------------------------|----------------|-----------------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>theoretical (m/z)</th>
<th>assignment</th>
<th>species name, abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>115,0764</td>
<td>([C_6H_{12}O_5H^-])</td>
<td>hexanoic acid, C6</td>
</tr>
<tr>
<td>129,0921</td>
<td>([C_7H_{14}O_5H^-])</td>
<td>heptanoic acid, C7</td>
</tr>
<tr>
<td>143,1077</td>
<td>([C_8H_{16}O_5H^-])</td>
<td>octanoic acid, C8</td>
</tr>
<tr>
<td>157,1234</td>
<td>([C_9H_{18}O_5H^-])</td>
<td>nonanoic acid, C9</td>
</tr>
<tr>
<td>159,0663</td>
<td>([C_{10}H_{20}O_5H^-])</td>
<td>heptanedioic acid (pimelic acid), diC7</td>
</tr>
<tr>
<td>171,1390</td>
<td>([C_{11}H_{22}O_5H^-])</td>
<td>decanoic acid, C10</td>
</tr>
<tr>
<td>173,0819</td>
<td>([C_{12}H_{24}O_5H^-])</td>
<td>octadecenoic acid (oleic acid) C18:1 (O)</td>
</tr>
<tr>
<td>187,0976</td>
<td>([C_{13}H_{26}O_5H^-])</td>
<td>nonanoic acid (arachidic acid), diC9 (A)</td>
</tr>
<tr>
<td>201,1132</td>
<td>([C_{14}H_{28}O_5H^-])</td>
<td>decanedioic acid (sebamic acid), diC10</td>
</tr>
<tr>
<td>247,1187</td>
<td>([C_{15}H_{30}O_5H^-])</td>
<td>diacid-MAG, MAG (dC8)</td>
</tr>
<tr>
<td>255,3395</td>
<td>([C_{17}H_{34}O_5H^-])</td>
<td>hexadecanoic acid (palmitic acid), C16 (P)</td>
</tr>
<tr>
<td>261,1344</td>
<td>([C_{18}H_{36}O_5H^-])</td>
<td>MAG of azelaic acid MAG (diC9)</td>
</tr>
<tr>
<td>281,2486</td>
<td>([C_{19}H_{38}O_5H^-])</td>
<td>octadecenoic acid (oleic acid) C18:1 (O)</td>
</tr>
<tr>
<td>283,2642</td>
<td>([C_{20}H_{40}O_5H^-])</td>
<td>octadecanoic acid (steaenic acid) C18:0 (S)</td>
</tr>
<tr>
<td>295,2278</td>
<td>([C_{21}H_{42}O_5H^-])</td>
<td>epoxy octadecanoic acid and/or hydroxy octadecadienoic acid, Epoxy-C18:1 and/or hydroxy C18:2</td>
</tr>
<tr>
<td>297,2435</td>
<td>([C_{22}H_{44}O_5H^-])</td>
<td>epoxy octadecanoic acid and/or hydroxy octadecenoic acid, Epoxy C18 or hydroxy-C18:1</td>
</tr>
<tr>
<td>315,2541</td>
<td>([C_{23}H_{46}O_5H^-])</td>
<td>dihydroxy octadecanoic acid, dihydroxy-C18:1</td>
</tr>
<tr>
<td>329,2490</td>
<td>([C_{24}H_{48}O_5H^-])</td>
<td>trihydroxy octadecanoic acid and/or dihydroxy epoxy octadecanoic acid, Trihydroxy-C18:1</td>
</tr>
<tr>
<td>403,1974</td>
<td>([C_{26}H_{54}O_5H^-])</td>
<td>DAG of 2x octadecanoid acid, DAG (2diC8)</td>
</tr>
<tr>
<td>417,2130</td>
<td>([C_{27}H_{56}O_5H^-])</td>
<td>DAG of octadecanoid acid and nonanedioic acid, DAG (diC8 + diC9)</td>
</tr>
<tr>
<td>431,2287</td>
<td>([C_{28}H_{58}O_5H^-])</td>
<td>DAG of 2x nonanedioic acid DAG, (2diC9)</td>
</tr>
<tr>
<td>471,3237</td>
<td>([C_{29}H_{60}O_5H^-])</td>
<td>DAG of hexadecanoic acid and heptanedioic acid, DAG (C16 + diC7)</td>
</tr>
<tr>
<td>485,3120</td>
<td>([C_{30}H_{62}O_5H^-])</td>
<td>DAG of hexadecanoic acid and octandioic acid DAG (C16 + diC8)</td>
</tr>
<tr>
<td>499,3276</td>
<td>([C_{31}H_{64}O_5H^-])</td>
<td>DAG of hexadecanoic acid and nonanedioic acid, DAG (C16 + diC9)</td>
</tr>
<tr>
<td>525,3433</td>
<td>([C_{32}H_{66}O_5H^-])</td>
<td>DAG of octadecanoic acid and nonanedioic acid, DAG (C18:1 + diC9)</td>
</tr>
<tr>
<td>527,3589</td>
<td>([C_{33}H_{68}O_5H^-])</td>
<td>DAG of octadecanoic acid and nonanedioic acid, DAG (C18 + diC9)</td>
</tr>
<tr>
<td>601,3229</td>
<td>([C_{35}H_{76}O_5H^-])</td>
<td>TAG of 3x nonanedioic acid, TAG(diC9)</td>
</tr>
</tbody>
</table>
compared to the nonsensitive paints. The nonsensitive paints showed higher amounts of short chain monocarboxylic acids, C6−C10 (m/z 115 to 171), higher amounts of (poly)hydroxy C18:0, C18:1, and C18:2 acids (m/z 295, 297, 315, and 329), and differences in the ratios between the C16 (P), C18:0 (S), and C18:1 (O) fatty acids were noted. These findings are in agreement with previous reports on water-sensitive paint surfaces from different brands and periods.11,32

Azelaic acid and other diacids are correlated with water sensitivity and are formed in paint films via the oxidation of unsaturated fatty acids. They derive from the binding oil or from other oils which are added mostly in the form of free fatty acids (FFAs) or as metal stearates. Azelaic acid is also used in the manufacture of alkyd paint and also as a plasticizer in polymer and industrial paint production.33 Among other manufacturers, W&N have acknowledged the use of FA derived from stearine or drying oils in the manufacture of their oil artist’s and alkyd paints.34

To obtain an indication on the level of oxidation and hydrolysis of the paint film, the ratios between azelaic and palmitic acid (A/P, indicates the level of oxidation)35 and azelaic acid and the azelaic acid monoacylglycerol (A/MAG(A), that

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**Figure 2.** SAWN−MS spectra of two W&N paint swatches (a) flake white (black trace, not water sensitive) and (b) ultramarine (blue trace, high water sensitivity).

**Figure 3.** PCA scatter plot of the analyzed W&N paint swatches; PCA component 1 versus PCA component 2 scores, with 69, 89% total variance and the corresponding loading plot (m/z of labeled ions are assigned in Table 2).
indicates the level of hydrolysis) were calculated from the ESI–MS and SAWN–MS results.\textsuperscript{11,12} The values obtained are compared in Table 1. The ratios are also presented; these reflect the ratio of the stable fatty acids, which in turn may give an indication of the type of lipid present.\textsuperscript{36} Since different fractions of lipids and metal soap extenders may be present especially in modern paints, this ratio is of limited value, although fractionation of the paint samples may give better insight.\textsuperscript{37} The content of P can be considered relatively stable and independent of the reactivity of the oil paint after application, whereas the A content is dependent on the degree of oxidation of the unsaturated fatty acid moieties in the oil fraction (Figure 1b).

The results for the non-water-sensitive paints presented a relatively low degree of oxidation and hydrolysis as indicated by the total azelaic acid content (A/P and A/MAG(A)), while water-sensitive paints presented varying degrees of oxidation and hydrolysis. The paint swatches presenting non-moderate water sensitivity (FW, TW, CB tint, CB, CV, CY) showed A/P values and A/MAG(A) values below 1, with the exception of CY that showed a higher level of hydrolysis with a A/MAG(A) value of 2. The samples from the paint swatches that showed higher water sensitivity (UB, RS, BS, and LB) presented a higher degree of oxidation (A/P ≥ 1) and hydrolysis (A/MAG(A) ≥ 2). The BS paint swatch has shown the highest degree of oxidation (A/P = 3) and together with UB the highest degree of hydrolysis (A/MAG(A) = 3).

3.1.2. Principal Component Analysis (PCA). The PCA plots (Figure 3) illustrate the results of W&N samples based on 27 monitored molecular ions. The clustering of the results correlates with the sensitivity noted from the swab tests. Four main clusters are visible as follows: on the left side of the PCA is a cluster that includes the nonsensitive white samples (FW and TW), the low water sensitivity (CB tint) is positioned between the whites and the cluster containing swatches of moderate sensitivity (CB, CV, and CY) and on the right of the PCA the highly sensitive swatches are clustered together (UB, RS, BS, and LB). The non-water-sensitive swatches cluster at negative values of PC1 and PC2, which relates mainly to the monocarboxylic acid content (C6–C10). Cobalt blue tint is not correlated to the PC2, and its position in the plot indicates a lower correlation with the C6–C10 monocarboxylic fatty acids. The moderately sensitive swatches (CB, CV, and CY) are clustered at positive PC2 values, and show a stronger correlation with the DAGs of stearic, oleic and azelaic acid, the TAG of azelaic acid, and free palmitic and stearic acid, and correlated to a lesser extend with the short chain monocarboxylic acids, oleic and hydroxy-C18 acids. The water sensitive swatches (UB, RS, BS, and LB), mostly cluster toward more positive values of PC1 which is associated with a higher relative amount of diacid containing species (diC7–diC10) and to some extent with MAGs of diC8–diC9 (negative PC2) and RS and LB are positioned toward positive values of PC2 being more correlated with diC7–diC10 and the DAGs of diacids species.

Based on this information, we can conclude that the sensitive and highly water sensitivity swatches contain higher amounts of extractable diacids compared to the moderate to low and the non-water-sensitive swatches. These results agree with a previous report on W&N Artists’ Oil Color swatches (1945 to 2003), in which the authors report a strong correlation with the presence of high amounts of diacids for water-sensitive swatches and the presence of higher amounts of monocarboxylic acids in the analyzed non-water-sensitive swatches.\textsuperscript{14} The loadings PCA plots show that the two groups, the short chain monocarboxylic acids (C6–C10) and the diacid containing species (diC7–diC10), products of oxidation of the binding medium, are negatively correlated. This was also observed by Lee et al.\textsuperscript{11} who suggested that this might be due to a preferential saponification of diacids over monocarboxylic acids.

3.1.3. Pigment Type and the Correlation to Water Sensitivity. It is known that heavy metals or alkali earth metals present in pigments and driers may form metal soaps with the acidic moieties released in the paint film. Paints containing heavy metals are insoluble, and materials containing heavy metals may contribute to the stability of the paint film by forming an ionomer-like network,\textsuperscript{16,37} and as a consequence the paint is less likely to be water sensitive.\textsuperscript{11,12} The white paint samples examined in this study that contained lead white mixed with zinc oxide and zinc oxide mixed with titanium oxide, respectively, were not water sensitive. Interestingly, in the same study, lead was also found in the CV, CY (moderate water sensitivity), and LB (high water sensitivity) paint swatches but not as pigment and in such low concentrations that this has not prevented the formation of water sensitivity.\textsuperscript{11,12,31}

Of all the paint samples presenting high water sensitivity, the sample taken from LB showed lower levels of oxidation, as observed herein in both ESI and SAWN–MS data, than the results from the highly sensitive paint samples (with the exception of RS; A/P ratios = 1, Table 1). It is known that the organic blacks, are much less water sensitive. In the present measurements, this is reflected by a relatively low diacid content, which can be explained by the fact that organic blacks are radical scavengers,\textsuperscript{38} that suppress the midchain oxidation.

CB tint (low water sensitivity) and CB (moderate water sensitivity) both contain Zn extenders while the CV and CY swatch (moderate water sensitivity) and LB contain traces of Pb. The rest of the paint swatches do not contain traceable amounts of metals that can react to insoluble metal soaps, such as Pb and Zn and have shown a higher level of water sensitivity. These paints contain metals as Al, Mg, Fe, and Na instead, which do not contribute to their solvent sensitivity.

3.1.4. Differences between Cobalt Blue Tint and Cobalt Blue Paints. Although in the 1970 W&N catalogue the same description is given for both cobalt blue and cobalt blue tint oil paints, their degree of sensitivity is different and has been shown by Silvester\textsuperscript{29} to have a different elemental composition (Table 1 and Figure 3). For the two paints, the pigment type is the same description is given for both cobalt blue and cobalt blue tint oil paints, their degree of sensitivity is different and has been shown by Silvester\textsuperscript{29} to have a different elemental composition (Table 1 and Figure 3). For the two paints, the pigment type is different, with cobalt aluminate found in the cobalt blue paint whereas the cobalt blue tint paint contains an unidentified organic pigment.\textsuperscript{29} Figure 3 shows the difference in composition of the blue paints reflected in the markers identified using SAWN analysis by PC2, characterized by different combinations of DAGs (C18, C18:1+diC9) and DAGS (C16+diCx) free palmitic and stearic acid, TAG (3diC9). Both samples were found to contain a semidrying oil (nonyellowing oil).\textsuperscript{39} The P/S peak abundance ratios calculated from the SAWN- and ESI–MS data, are around both in the FAA and in the glycerides which is around 3.0 which could indicate a semidrying oil such as safflower or poppyseed oil.

3.1.5. Lipids. All of the paints contained either semidrying or drying oils (commonly poppy seed and linseed, respectively). Refined linseed oil was used in W&N paints throughout, and poppyseed oil was used until the late 1960s when it was replaced by safflower oil, with some possible addition of beeswax or paraffin.\textsuperscript{34,39} In these oils, the acid value needs to be increased\textsuperscript{40} for a good dispersion and wetting of pigments. For this, free fatty acids...
acids from poppy oil (and later safflower) were used by W&N. It is not known what the proportion of FFAs was added to oil paints manufactured by W&N in the 1960s; however, it has been reported that excessive amounts of FFAs (>5%) from nondrying oils and the use of semi- or nondrying oils as the binder can contribute to water sensitivity or surface tackiness of oil paints. Table 1 includes the ratios of the extracted palmitic and stearic acids (P/S) both in the free form and contained in the DAGs are given. For comparison of ESI−MS and SAWN−MS, the calculated DAG (P+A)/DAG (S+A) indicates the ratio of P and S from the lipid fraction only, whereas the P/S ratio of the free fatty acids relates to the extracted free fatty acids that were added originally plus the FFAs hydrolyzed from the lipids. Comparing the P/S ratio of the free fatty acids and that present as glyceride gives an indication of the used oil type and the presence of added stearates. While both ratios matched were generally similar using both ionization techniques, the results for flake white and titanium white the lipids P/S ratios were significantly lower than the FFA P/S ratios. This could be explained by the addition of FFAs with a higher P/S content ratio than the lipid used. This could match previous statements that W&N used free fatty acids from poppyseed oil which has a relatively high P/S ratio compared to other lipids and soaps used in oil paints. The results from the analysis of the other samples showed no significant trends.

The calculated P/S values extracted from the ESI−MS and SAWN−MS data are in agreement with each other with one exception, CY (see Table 1). For CY, a lower P/S value was obtained by SAWN−MS (P/S = 1.6) compared to ESI−MS (P/S = 3). P/S values above 3 were obtained for the non-, low, and moderately water-sensitive samples and values below 2 were obtained for the highly sensitive paints. In several cases, the calculated P/S peak abundance ratios are significantly lower than the values obtained with GC−MS. The observed differences may be attributed to the completely different types of ionization. The P/S values obtained by electron impact ionization of separated analytes by GC−MS are distinct than the calculated P/S peak abundance ratios by SAWN−MS.

3.2. Samples from Figure in Landscape. Previous analysis performed on the samples examined in the present study revealed the presence of magnesium carbonate indicative of W&N paints and the presence of organic pigments. The red sample included a synthetic organic red pigment and a red lake, Prussian blue, and titanium white, and Prussian blue and a combination of phthalocyanine blue were detected in the blue paint sample. Beeswax was found in both samples and also carnauba wax in the red paint sample, which were typically used as a thickener by W&N manufacturers. For comparison, the SAWN−MS spectra of the two samples are shown in Figure 2S. The P/S, A/P, and A/MAG(A) values have been calculated from the results. Relatively similar P/S values were obtained (0.5-sample A and 0.6-sample B), but the A/P and A/MAG(A) values were significantly higher for sample B (A/P = 1, A/MAG(A) = 1) compared to sample A (A/P = 0.3, A/MAG(A) = 0.8), indicating a higher degree of oxidation and hydrolysis for sample B.

The PCA results obtained by including the SAWN−MS data from sample A and B together with the 10 samples taken from the W&N swatches were plotted using PCA are given in Figure 4. The plot shows that samples A and B fall close by their corresponding water sensitivity groups of the W&N paint samples. Sample A clusters closer to the W&N swatches that have shown moderate sensitivity. It is positioned at positive values of PC2 and has no contribution of PC1 component or presents equal amounts of short-chain monoacids and diacid...
This paper reports for the first time the use of SAWN−MS, a fast ambient ionization technique coupled with high-resolution mass spectrometry to study the fatty acids and lipid composition of oil paints. The PCA results showed a good correlation with four clusters grouping samples according to their degree of water sensitivity. The non-water-sensitive paint samples clustered at negative values of PC1 and PC2, which relates mainly to their monocarboxylic acid content (C6−C10). The position of CB10 in the PCA plot showed a lower correlation with the C6−C10 monocarboxylic fatty acids. The moderately sensitive swatches showed a stronger correlation with the DAGs of diCx and of C16+diCx. These observations are in agreement with the A/MAG(A) calculated from the SAWN−MS data. The values were significantly higher for the most water sensitive sample, indicative of a higher degree of oxidation and hydrolysis of the oil media. In the PCA plot, the less sensitive sample from the painting was clustered closer to the W&N swatches with moderate water sensitivity and the position in the plot indicated equal amounts of short-chain monoacids and diacid species. The most water sensitive sample from the painting was positioned in the PCA plot closer to the more sensitive swatches and showing a stronger correlation with high levels of diacids (diC7–diC10) and to some extent with the DAGs of diCx and of C16+diCx. These observations are in agreement with the A/P and A/MAG(A) values that point to a higher degree of oxidation and hydrolysis for the more sensitive sample.

SAWN−MS proved to be a suitable tool to study fatty acids and lipid composition in oil paint samples from works of art. An attractive feature, and especially appropriate for analysis of objects of cultural heritage from which samples are limited, is the uniquely soft ionization mechanism, which eliminates the necessity for high temperature or DC voltage applied during ionization. This reduces the uncertainty about whether the observed degradation products were already present in the sample or may have formed during the analysis. Additionally, this technique allows microsampling and involves a simple sample preparation, and the results are obtained within 1 min. As a next step, the efficiency of this technique to identify markers of interest by using wet swab sampling on the paint surface instead of scraping should be evaluated.

■ CONCLUSIONS

This paper reports for the first time the use of SAWN−MS, a fast ambient ionization technique coupled with high-resolution mass spectrometry to study the fatty acids and lipid composition of oil paints. The PCA results showed a good correlation with four clusters grouping samples according to their degree of water sensitivity. The non-water-sensitive paint samples clustered at negative values of PC1 and PC2, which relates mainly to their monocarboxylic acid content (C6−C10). The position of CB10 in the PCA plot showed a lower correlation with the C6−C10 monocarboxylic fatty acids. The moderately sensitive swatches showed a stronger correlation with the DAGs of diCx and of C16+diCx. These observations are in agreement with the A/MAG(A) calculated from the SAWN−MS data. The values were significantly higher for the most water sensitive sample, indicative of a higher degree of oxidation and hydrolysis of the oil media. In the PCA plot, the less sensitive sample from the painting was clustered closer to the W&N swatches with moderate water sensitivity and the position in the plot indicated equal amounts of short-chain monoacids and diacid species. The most water sensitive sample from the painting was positioned in the PCA plot closer to the more sensitive swatches and showing a stronger correlation with high levels of diacids (diC7–diC10) and to some extent with the DAGs of diCx and of C16+diCx. These observations are in agreement with the A/P and A/MAG(A) values that point to a higher degree of oxidation and hydrolysis for the more sensitive sample.

SAWN−MS proved to be a suitable tool to study fatty acids and lipid composition in oil paint samples from works of art. An attractive feature, and especially appropriate for analysis of objects of cultural heritage from which samples are limited, is the uniquely soft ionization mechanism, which eliminates the necessity for high temperature or DC voltage applied during ionization. This reduces the uncertainty about whether the observed degradation products were already present in the sample or may have formed during the analysis. Additionally, this technique allows microsampling and involves a simple sample preparation, and the results are obtained within 1 min. As a next step, the efficiency of this technique to identify markers of interest by using wet swab sampling on the paint surface instead of scraping should be evaluated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jasms.0c00272.

Illustration of Figure in a Landscape by F. Bacon: (a) diagonal white lines indicate areas of water sensitivity and (b) sampling sites (PDF)

SAWN−MS spectra of two samples from Figure in a Landscape, F. Bacon (a) sample A (moderate water sensitivity) and (b) sample B (high water sensitivity) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Klaas Jan van den Berg — Cultural Heritage Agency of The Netherlands (RCE), 1071 ZC Amsterdam, Netherlands; Conservation and Restoration, Faculty for the Humanities, University of Amsterdam, 1071 DV Amsterdam, Netherlands; orcid.org/0000-0002-8145-1262; Phone: +31334217176; Email: K.van.den.Berg@cultureel Erfgoed.nl

Authors

Alina Astefanei — Van ’t Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, 1098 XH Amsterdam, Netherlands; Centre of Analytical Sciences Amsterdam, 1098 XH Amsterdam, The Netherlands; orcid.org/0000-0001-8550-5726

Aviva Burnstock — Courtauld Institute of Art, London WC2R 0RN, United Kingdom

Garry Corthals — Van ’t Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, 1098 XH Amsterdam, Netherlands; Centre of Analytical Sciences Amsterdam, 1098 XH Amsterdam, The Netherlands; orcid.org/0000-0001-9423-5596

Complete contact information is available at: https://pubs.acs.org/10.1021/jasms.0c00272

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge Samantha Miller (Colorado State University) for her help with preliminary studies on using SAWN−MS for oil paints analysis and Dr. Bronwyn Ormsby and Dr. Joyce Townsend (Tate) for the samples from the Figure in a Landscape painting by Francis Bacon.

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