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Evaluation of the “added value” of SIMS: A mass spectrometric and spectroscopic study of an unusual Naples yellow oil paint reconstruction

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ABSTRACT

Naples yellow-containing oil paints aged under natural and artificial conditions were investigated as model systems to evaluate the potential of secondary ion mass spectrometry (SIMS) when used in combination with other mass spectrometric and spectroscopic analytical methods. Although the advantage of SIMS is the simultaneous detection of organic and inorganic components and their spatial distribution, the methodology has limitations in compound sensitivity and shows bias towards certain constituents. Gas chromatography–mass spectrometry (GC/MS) shows dicarboxylic fatty acids to be main components in the paint, but SIMS detects these compounds poorly. Electrospray ionisation mass spectrometry (ESI-MS) shows a broad range of glyceryl derivatives of mono- and dicarboxylic fatty acids (mono-, di- and triglyceride derivatives), while SIMS only detects the mono- and diglycerides of the monocarboxylic acids. Compared to SIMS, direct temperature-resolved mass spectrometry (DTMS) offers greater insight into how the various constituents are incorporated into the paint film, but SIMS data supports the information provided by Fourier transform infrared (FTIR) on metal soap formation. The surface sensitivity of SIMS is an advantage for probing paint constituent distributions and was exploited to examine variations in the composition of the top and bottom of a paint film, and the spatial correlation between metal and fatty acid composition in metal soap aggregates. Disadvantages of SIMS are the low yields and matrix dependency of the organic species in the paint matrix. Application of an ultra-thin gold coating overcomes this, and enhances the organic secondary ion yields leading to more accurate spatial distribution.

1. Introduction

Secondary ion mass spectrometry (SIMS) is well established for the analytical surface characterisation of materials such as polymers and semiconductors [1]. In the field of cultural heritage, the application of SIMS has shown itself to be useful, for example, depth profiling and/or imaging studies of inorganic materials such as deteriorated glass and corroded metals objects and has provided relevant information regarding provenance, treatment and preservation of valuable artefacts [2–10]. A few publications have also illustrated the potential of SIMS to be used for the characterization of organic components in works of art e.g., molecular species in the wool used for tapestries [11] or the identification of proteins, starch, urate salt and lipids on African wooden statuettes [12]. SIMS can also be a very useful tool for the identification and localisation of binding medium components, pigments and their degradation products in oil paintings from the 15th to 20th century [13–22]. Comparative studies of various preparatory grounds from paintings by Van Gogh have shown that SIMS data can be processed by principal component analysis (PCA) and related image analysis techniques [23].

The advantage of SIMS applied to these heterogeneous, complex and sometimes multilayered paint samples derived from painted works of art is that the nature and distribution of organic and inorganic components can be studied simultaneously in a single sample in one analytical run. The mass spectral information obtained is highly informative about both the material composition in the cross-section and its spatial distribution. Furthermore, as static SIMS probes only the upper atomic layers of the surface, no structural damage is visible and the same sample can be used for other imaging techniques like Fourier transform infrared (FTIR) microscopy, Raman microscopy and scanning electron microscopy (SEM).

The application of SIMS to historical paintings research is relatively new and it is therefore important to evaluate the analytical information it can provide and compare the data obtained

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with that from complementary mass spectrometric and spectroscopic analytical techniques. When used as an analytical MS tool, SIMS can be used to identify organic and inorganic components and the analytical data compared with information obtained from using more established analytical techniques including gas chromatography–mass spectrometry (GC/MS), electrospray ionisation mass spectrometry (ESI-MS), direct temperature-resolved mass spectrometry (DTMS) and FTIR microscopy to determine the additional information ("added value") it can offer. Further, when used in the imaging mode, SIMS provides information on the spatial distribution of components. Imaging SIMS data can be compared with data obtained using light microscopy (visible and ultraviolet (UV) fluorescence), imaging FTIR microscopy and SEM combined with elemental (SEM-EDX) mapping to determine in what way SIMS adds additional information.

To evaluate the unique potential of SIMS for the study of oil paints, a Naples yellow-containing linseed oil paint reconstruction aged in a laboratory environment (naturally aged) and under accelerated aged conditions (artificially aged) was selected as a case study. The drying of oil paint films is a complex process involving a number of competing bond-forming and degradative reactions and pigment–oil interactions, which in the longer term, influence the visual, chemical and physical properties of the mature oil paint film. Previous studies suggest that when oil paint films are exposed to high light levels at elevated (>50%) relative humidity (RH), an unusually high proportion of photolytically induced cleavage of the fatty acid side-chains occurs during the early drying stage [24], as well as hydrolysis of the ester linkages in the oil triglycerides [25–27]. These reactions generate high quantities of shorter-chain scission products and a reduced degree of polymerisation, reducing the coherence of the films and even re-liquification of a non-pigmented drying oil film [24]. Although the artificially aged paint samples are not directly comparable with mature oil paint systems aged under natural conditions, they can yield information regarding the drying and ageing of oil paint and the occurrence of pigment–medium interactions including the formation of metal soaps. The modern Naples yellow pigment used in the paint reconstruction was found, unexpectedly, to contain zinc oxide and a lead-chloride-containing compound in addition to the Naples yellow (lead antimonate) pigment. While this makes the reconstruction atypical of historic paint films pigmented with Naples yellow, our case study is interesting as it illustrates zinc soap aggregate formation in zinc oxide-containing paint films in a relatively short period of time under conditions of high light intensity and high relative humidity. Zinc and lead soap aggregates are found in many oil paintings from the 13th to 20th century containing zinc- or lead-based pigments or additives [28–33].

2. Experimental

2.1. Samples

Naples yellow ($Pb_2Sb_2O_7$)-containing linseed oil paint reconstructions were prepared and artificially aged [24]. The analytical results from reconstructions aged at an RH of 51% and 90% are compared. Naples yellow Light pigment (no. z512, A.P. Fitzpatrick Fine Art Materials, London) was ground with Kremer cold-pressed linseed oil and applied to a Teflon support. Once the films were touch dry, they were placed in sealed enclosures maintained at different RH (51% [$Mg(NO_3)_2$] and 90% [$BaCl_2$]) using saturated salt solutions. The enclosures were then placed in a light box providing an illuminance of up to 22,000 lux. The light-ageing equipment and experimental set-up are detailed elsewhere [24]. A control film was placed next to a window and allowed to age in the laboratory environment. The samples were aged for 2 years.

2.2. Paint cross-section

Paint samples were embedded in polyester resin (Polypol) and dry polished with Micro-mesh® polishing cloths (final step 12,000 mesh) (Scientific Instruments Services Inc., MN).

2.3. SIMS

The static SIMS experiments were performed on a Physical Electronics (Eden Prairie, MN) TRIFT-II time-of-flight SIMS (TOF-SIMS). The surfaces of the naturally and artificially (90% RH) aged paint samples were scanned with a 15 keV primary ion beam from an $^{115}In^+$ liquid metal ion gun. The pulsed beam was compressed (bunched) to ~1 ns for paint films to obtain a good mass resolution and non-bunched with a pulse length of 20 ns for paint cross-sections to acquire a good spatial resolution. These experiments were performed in positive and negative ion mode with 600 pA beam current using a total primary ion dose of 1.0×10^{12} ions/cm^2. The primary ion beam rasters over a 150 μm × 150 μm sample area, which is divided into 256 × 256 pixels. All measurements were charge compensated with electrons pulsed in between the primary ion beam pulses. A non-magnetic stainless steel plate with slits (1 mm) was placed on top of the sample to prevent large variations in the extraction field over the large insulation surface area of the sample.

A glass plate is taken on which double-sided tape is attached. On top of the double-sided tape the paint chip is positioned. Depending on the orientation of the paint film (face-up or face-down) the top or bottom of the paint film can be analyzed. The paint cross-sections (150 mm × 50 mm × 3 mm) were rinsed in hexane to reduce contamination with silicones.

A 2 nm layer of gold was sputter coated on the sample surface using a Quorum Technologies (Newhaven, East Sussex, U.K.) SC7640 sputter coater equipped with a FT7607 quartz crystal microbalance stage and a FT7690 film thickness monitor.

2.4. GC/MS

The naturally and artificially (51% RH) aged paint samples were treated with 5 μL of 5% methanolic *m*-(trifluoromethyl) phenyltrimethylammonium hydroxide (TMTFTH), sealed and heated at ~70 °C for ~5 h. Thermolytic methylation was accomplished, under moderate conditions, upon injection into the GC (injection port 270 °C). A second set of samples were treated with 10 μL neat bis-*N*,*O*-trimethylsilyl trifluoroacetamide (BSTFA), sealed and heated at ~60 °C for ~30 min. Each sample was centrifuged before 1 μL of the supernatant was withdrawn and injected. Analysis was carried out on a Trio 2000 quadrupole mass spectrometer coupled to a Hewlett-Packard 5890 Series II gas chromatograph. The latter was operated with a 30 m × 0.32 mm bore BPX5-coated silica capillary column with 1 μm film thickness (5% phenyl (equiv.) polysilphenylene-siloxane stationary phase), injector temperature 250 °C, helium carrier, column head pressure 48 kPa, splitless mode, column programme: 70 °C for 1 min followed by ramping at 10 °C/min to 300 °C held for 105 min, with a line temperature 290 °C. Mass spectrometer conditions: 70 eV electron impact, source temperature 210 °C, scan range 40–600 Da, scan time 1 s, interscan time 0.1 s.

2.5. ESI-MS

Naturally and artificially (51% RH) aged paint samples were prepared by ethanol extract or full hydrolysis. The paint samples were weighed (400–600 μg) into 1 mL tapered vials. Extraction: 100 μL ethanol was added with tridecanoic and tetradecanedioic acids as internal standards. The samples were extracted for 18 h under ambient conditions. Hydrolysis: a 0.1 M ethanolic NaOH solution with tridecanoic and tetradecanedioic acids as internal standards was added to the samples. The hydrolysis took place in an oven held at about 80 °C for 1.5 h. Each solution was shaken and centrifuged after extraction or hydrolysis. The extract or hydrolysate was subsequently transferred to a vial containing cation exchange resin (DOWEX HCR-W2 ion-exchange resin, Sigma–Aldrich) and left for 30 min to remove pigment-derived cations. The supernatant solution was removed from the resin and transferred to a new vial. Ethanolic ammonium acetate was added until a final concentration of 10 mM ammonium acetate was achieved. An aliquot of 1 μL of the solution was analysed on a QToF2 instrument (Micromass Wythenshawe, U.K.) in the positive and negative mode (for the extracts) and negative mode (for the hydrolysates). Mass spectrometer conditions: capillary voltage: 2 kV, cone voltage: 10 V, collision energy: 10 eV, TOF: 9.1 kV and the detector was set at 2150 V in the positive mode and 2300 V in the negative mode.

2.6. DTMS

Naturally and artificially (90% RH) aged paint samples (5–10 μg) were ground in 15–25 μL ethanol. 1–2 μL aliquots of this solution were placed on the Pt/Rh filament of a direct insertion probe for in-source analysis. DTMS experiments were carried out on a JEOL JMS SX-102 double focussing mass spectrometer (B/E). The filament (Pt/Rh 9:1; 100 μm) was heated at a rate of 0.5 A/min to an end temperature of about 800 °C. Ions were generated by electron ionisation (EI) (16 eV) in an ionisation chamber kept at 190 °C, accelerated to 8 kV, analysed from m/z 20 to 1000 (about 1 s cycle time) and post-accelerated to 10 kV.

2.7. FTIR microscopy

Naturally and artificially (90% RH) aged paint samples were placed between the windows of a Spectra-Tech micro-compression diamond cell. Spectra were acquired in transmission mode using a Nicolet 5700 Series FTIR spectrometer with a NicPlan infrared microscope, fitted with a MCT Type A detector.

3. Results and discussion

3.1. Light microscopy

The artificially aged paint samples aged under 51% or 90% RH have a lumpy surface morphology while the surface of the naturally aged paint sample is still smooth. Under UV illumination strongly bluish-fluorescent spots (diameter ~ 50 μm) are visible at the surface of the artificially aged paint film (Fig. 1A). Under the same light conditions the surface of the naturally aged paint sample showed, besides the strongly bluish-fluorescent spots (diameter ~20 μm), many tiny yellow/greenish-fluorescent spots (Fig. 1B). The strongly bluish-fluorescent spots are attributed to zinc soap aggregates and the tiny yellow/greenish-fluorescent spots to residual zinc oxide particles from the pigment. In cross-section, the naturally aged paint shows a higher fluorescence in the upper compared to the lower part of the paint layer (Fig. 1C). In the cross-section from the artificially aged paint sample large fluorescent areas are visible throughout the layer (Fig. 1D).

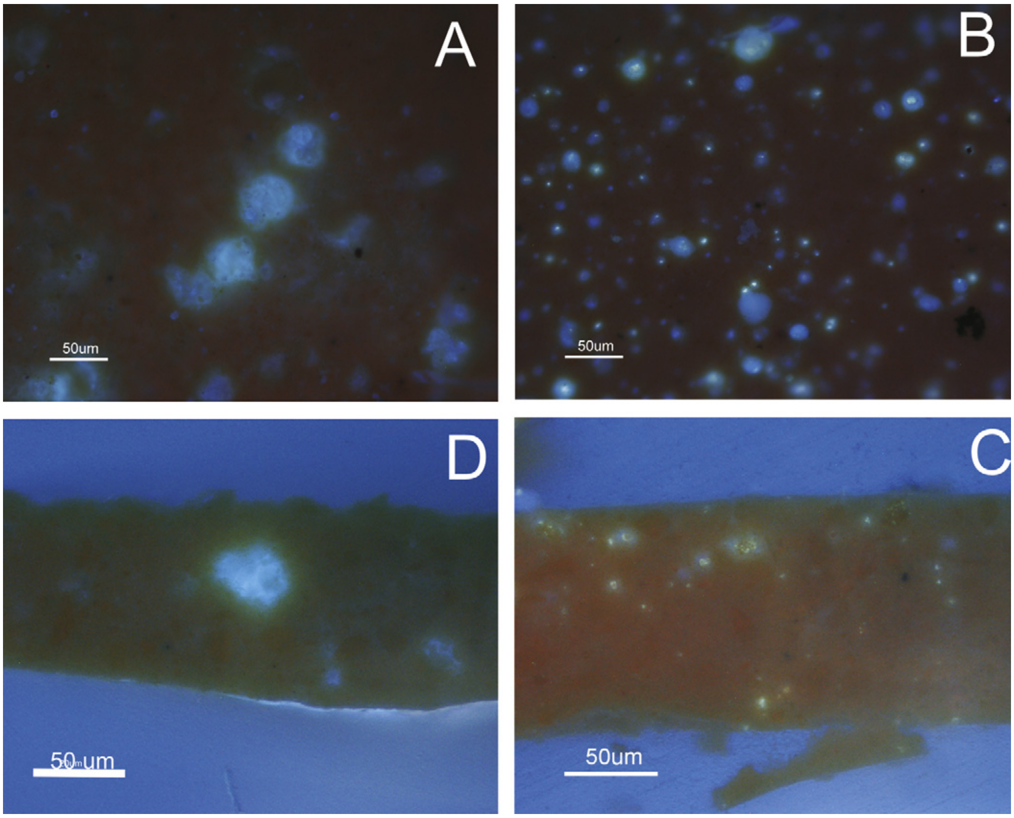

Fig. 1. Light microscopic image (under UV illumination) of Naples yellow-containing oil paint film aged under natural and artificial (90% RH) conditions: (A) surface of artificially aged paint film, (B) naturally aged paint film; (C) paint cross-sections of naturally aged paint film and (D) artificially aged paint film.

3.2. SIMS

Peaks due to oil components in the positive and negative ion spectra are identified with the use of reference materials described elsewhere [34].

3.2.1. SIMS measurements on the surface of the naturally and artificially aged paint films: positive ion mode

The positive ion SIMS spectra of the top surface of the artificially and naturally aged paint films show the characteristic fragment peaks of triacylglycerol esters (TAGs) at *m*/*z* 551, 579 and 607 (ions of diacylglyceryls with palmitic and stearic acids), *m*/*z* 313 and 341 (ions of monoacylglyceryls of palmitic and stearic acid), and *m*/*z* 239 and 267 (acylium ions of palmitic and stearic acid originating from free or ester-bound fatty acid moieties) (Fig. 2A and B). The secondary ion yields of free fatty acids i.e., palmitic and stearic acid (protonated monocarboxylic fatty acids (monoacids) at *m*/*z* 257 and *m*/*z* 285) are very low in both samples (not indicated in Fig. 2A and B). Peaks representative of mono- and diacylglycerols containing one or two oleic acids (*m*/*z* 339, 577, 603 and 605) and oxidized forms of the same components (*m*/*z* 355, 593 and 621) are found in the spectrum of the naturally aged paint film (Fig. 2A). These unsaturated and oxidized fatty acid-containing components very much reduced in the SIMS spectrum of the artificially aged paint sample (Fig. 2B). Overall, the results indicate that the oxidation, network-forming and degradation processes in the artificially aged paint system are in a more advanced stage compared to the naturally aged paint system.

The most intense peaks seen in the positive ion SIMS spectra are the lead isotope peaks (*m*/*z* 206–208; this spectral region is not shown). In the spectrum of the artificially aged paint film, lead soaps of palmitic and stearic acids and the acylium ion of azelaic acid, at *m*/*z* 461–463, *m*/*z* 489–491 and *m*/*z* 375–377, respectively, are detected in low intensities (Fig. 2B).

3.2.2. SIMS measurements on the surface of the naturally and artificially aged paint films: negative ion mode

The negative ion SIMS spectra of the top side of the surface of the artificially and naturally aged paint films show two dominant negative ions peaks at *m*/*z* 255 and 283 corresponding to deprotonated palmitic and stearic acids, respectively (Fig. 3A–C). These ions originate from free, ester- or metal-bound fatty acid moieties [18,34]. The detected aliphatic chain fragment ions of fatty acids (*m*/*z* 99, 113, 127, 141, 155, 169, 183, 197) are marked with an asterisk in Fig. 3. The spectrum of the naturally aged paint sample shows the presence of ions of deprotonated oleic acid and deprotonated oxidized oleic and stearic acids at *m*/*z* 281, 295 and 297, respectively. Deprotonated oleic acid and its oxidized form have very low ion yields in the spectrum of the artificially aged sample. The relative intensity of oleic acid compared to stearic acid is much lower on the topside of the film than on the bottom side of the film (Fig. 3A and B). This illustrates that the top of the film, which is directly exposed to light, oxygen and moisture, is in a more advanced stage of ageing than the bottom side of the film, which has been more protected from the atmosphere.

Peaks in the spectrum of the naturally aged paint sample are observed at *m*/*z* 143, 157 and 171 that can be attributed to deprotonated octanoic, nonanoic and decanoic acid. The peak at *m*/*z* 187 is attributed to deprotonated dicarboxylic acid (diacid), azelaic acid (Fig. 3A and B). These short chain fatty and diacids are known oxidation and degradation products of aged oil paints [25]. The absence of these peaks in the artificially aged sample may suggest evaporation of the smaller fatty acids from the paint system and/or trapping of the diacids by metals within the paint system (Fig. 3C). Unfortunately, SIMS is not a suitable technique for the detection of such diacid soaps because, even if one carboxylic acid group is released by the impacting primary ion, the second carboxylic group can still remain attached to the network in its carboxylate soap form and is not fully ionised. Additional negative ions characteristic of oil paint are observed at *m*/*z* 311 and 339 (corresponding to monoacylglycerol esters of palmitic and stearic acids; Fig. 3C).

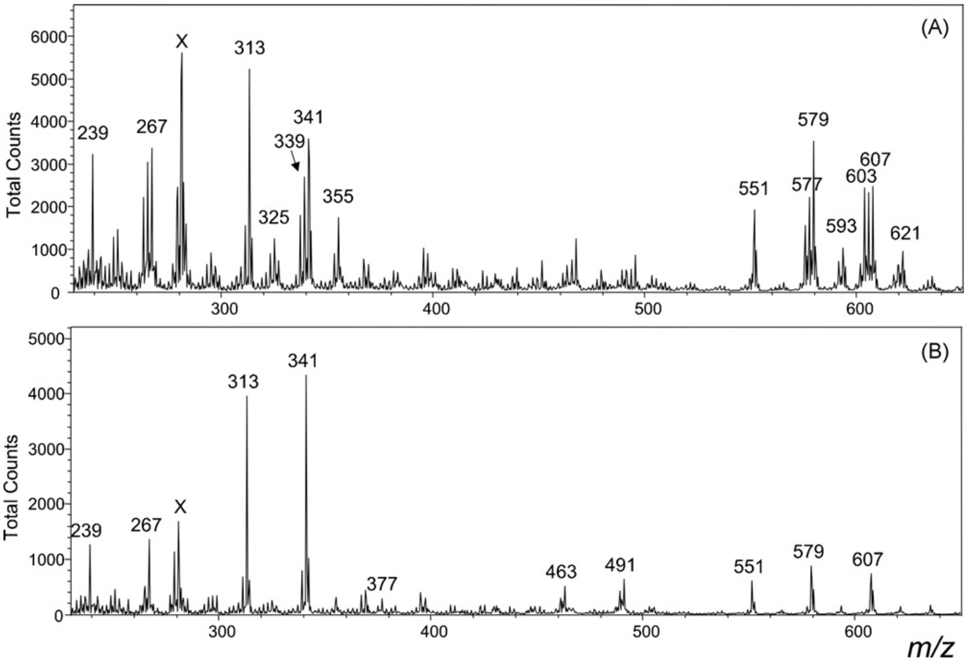

Fig. 2. SIMS spectra in positive ion mode (mass range *m*/*z* 230–650) of the top side of the Naples yellow-containing oil paint film: (A) naturally aged and (B) artificially aged (90% RH) (X = poly(dimethyl siloxane) contamination).

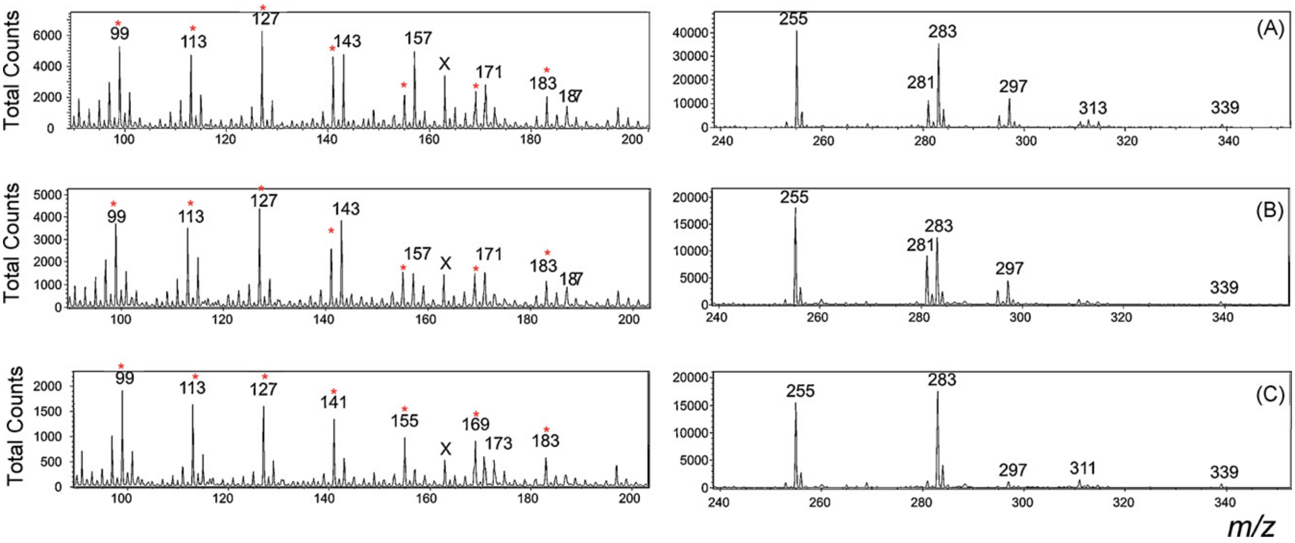

Fig. 3. SIMS spectra in negative ion mode (mass range m/z 90–205 and 240–350) of the film of Naples yellow-containing oil paint sample: (A) naturally aged topside, (B) bottom side of the film, and (C) artificially aged topside of the film.

3.2.3. *Imaging SIMS of the paint cross-section of the naturally aged paint sample: positive and negative ion mode*

The total ion current map and the spatial distribution of lead (m/z 206–208), antimony (m/z 121), zinc (m/z 64) and chloride (m/z 35) within the naturally aged paint sample is plotted in Fig. 4A–E. Organic secondary ions representative of the oil medium with sufficient yields to plot their spatial distribution are deprotonated (F) azelaic (m/z 187), (G) palmitic (m/z 255), (H) oleic (m/z 281) and (I) stearic acids (m/z 283) (Fig. 4F–I). Antimony from Naples yellow (Fig. 4C) is homogenously distributed and corresponds with part of the distribution of lead (Fig. 4B), with the exception of the lead in particulate 'hot' spots. These 'hot' spots in the lead map correlate with the 'hot' spots in the chloride map (Fig. 4E), pointing to a lead-chloride-containing compound being present in the original pigment mixture (a result confirmed with a SEM-EDX study of the pure pigment used for these paint films). Zinc is present in the areas where secondary ion yields of lead and antimony are absent or low (Fig. 4D). The few zinc 'hot' spots in Fig. 4D might be indicative of intact zinc oxide particles, a result also suggested by its fluorescence under UV illumination in light microscopy and confirmed when the pure pigment was examined by SEM-EDX. The organic secondary ions representative of the oil medium are detected throughout the paint matrix with relative higher yields of monoacids at the bottom of the paint film (Fig. 4F–I). The reduced secondary ion yields of monoacids towards the surface of the paint film are due to evaporation of monoacids from the paint surface.

3.2.4. *Imaging SIMS of the paint cross-section of the artificially aged paint sample with and without a gold coating: positive and negative ion mode*

The spatial distribution of lead, antimony, zinc, chloride, deprotonated palmitic and stearic acids and the lead soap of palmitic acid in the cross-section of the artificially aged paint are plotted in Fig. 5A–H. The middle of the paint cross-section contains a zinc soap aggregate. This aggregate fluoresces strongly under UV illumination (Fig. 1D) and the backscattered electron image illustrates that the aggregate does not contain any pigment particles (Fig. 5I). Lead and antimony are distributed around this aggregate (Fig. 5B and C), while zinc is present inside the aggregate (Fig. 5D). Very low amounts of lead and chloride (Fig. 5E) are detected in an area inside the zinc-containing aggregate. This area corresponds with the lighter grey area in the backscattered electron image (Fig. 5I). 'Hot' spots of lead in the paint matrix again correlate with 'hot' spots of chloride. Palmitic and stearic acids are detected in the paint matrix but not in the aggregate (Fig. 5F and G).

Based on previous research using SIMS, high secondary ion yields for fatty acids (negative ion mode) are typically observed inside lead-containing aggregates in oil paint films [19]. These studies have shown a direct spatial correlation between fatty acids and lead, with a higher proportion of both fatty acids and lead being present in the aggregate compared to the paint matrix. Zinc soap aggregates are expected to show similar properties to lead soap aggregates, but experience gained from the examination of a wide range of paint samples has shown that lead is unusual in enhancing the secondary ion yield of fatty acids in a paint film (both within aggregates and the paint matrix) and that for other metal soap aggregates such correlations cannot be directly established.

Coating paint samples with a layer of gold has been shown to improve the yield of organic components and to overcome matrix effects within samples [35]. When the cross-section was coated with a 2 nm layer of gold, the distribution of lead, antimony, zinc and chloride was unaffected (not shown), while the fatty acids could now be detected inside the zinc soap-containing mass as well (Fig. 5J–K). A relatively higher amount of fatty acids in the aggregate compared to the paint matrix is in agreement with previous studies of paints [19].

3.3. *GC/MS*

GC/MS analysis enables the detection of fatty acids and various degradation and oxidation products formed by hydrolytic and auto-oxidation processes in oil paint. The microsamples analysed do not allow the acquisition of spatially resolved information. On the other hand when two different derivatization reagents are used, speciation of the mode of occurrence of the fatty acids is possible. TMTFTH methylates the ester-, metal-bound and free fatty acids (E + M + F), whereas BSTFA reacts with metal-bound and free acid groups (M + F) and leaves the ester-bound species intact.

In the TMTFTH-GC/MS single ion chromatogram (cross-scan for m/z 74) of the naturally and artificially aged paint films (Fig. 6A and B) the main components of the binding media include the methyl esters of the short and long chain saturated fatty acids (nr. 1, 10, 11,

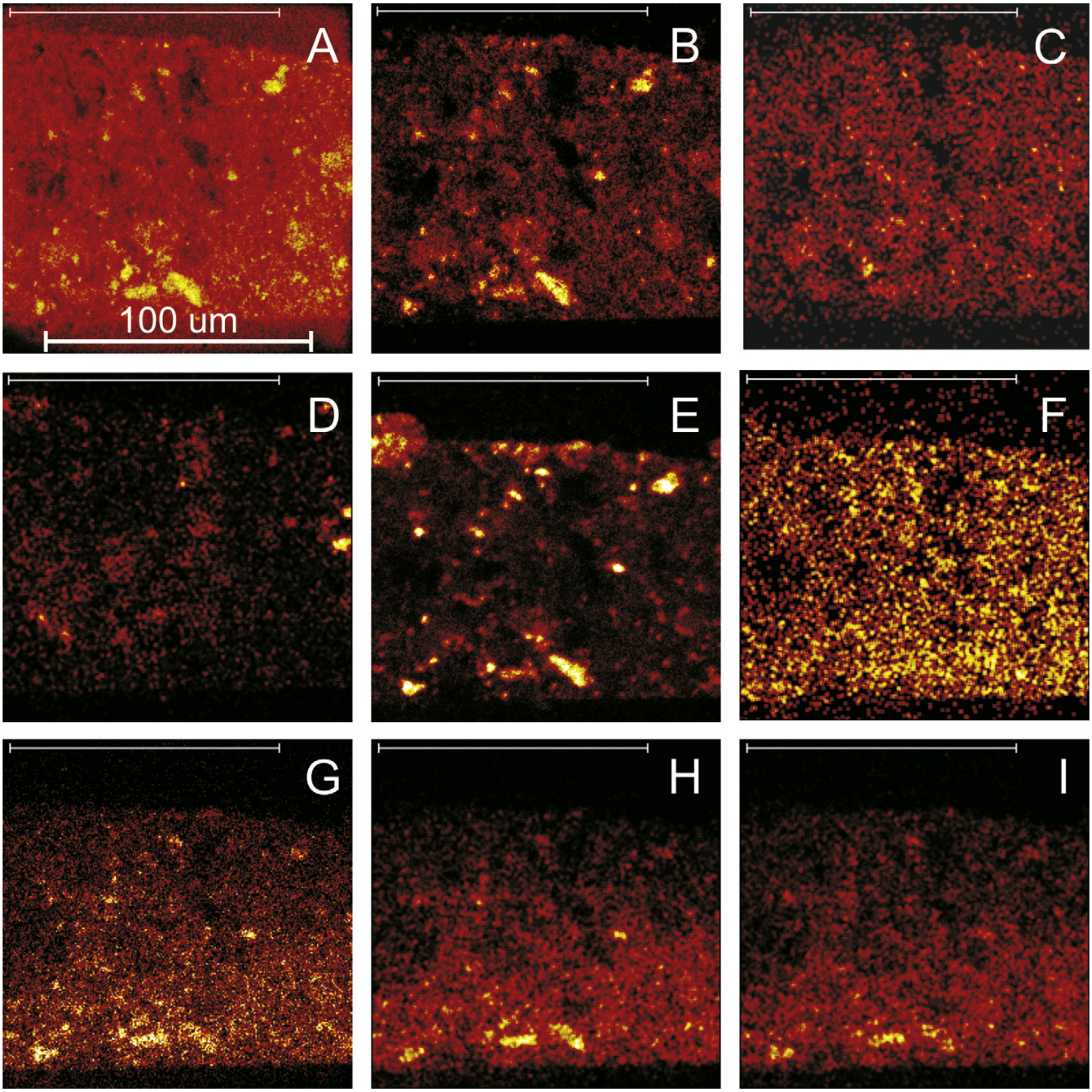

Fig. 4. SIMS image of a paint cross-sections of naturally aged Naples yellow-containing oil paint showing the spatial distribution of (A) the total positive ions (TIC), (B) lead, (C) antimony, (D) zinc (all positive ion mode) and as negative ions (E) chloride, and the deprotonated (F) azelaic, (G) palmitic, (H) oleic and (I) stearic acids.

12, 13, 15 in Fig. 6), dimethyl esters of diacids (nr. 2, 4, 7, 8, 9 in Fig. 6), and traces of methyl esters of unsaturated (nr. 14 in Fig. 6) and oxidised C18 fatty acids (nr. 16 in Fig. 6). The TMTFTH-GC/MS total ion chromatogram of the artificially aged paint sample also shows peaks for dimethyl esters of 4-oxo-dialkanoic acids and methyl esters of 2-oxotetrahydrofuryl-4-*n*-alkanoic acids (chromatogram not shown). These compounds are formed under the artificial ageing conditions. In comparison to the artificially aged sample, the naturally aged paint sample contains a relatively higher abundance of oleic acid (nr. 14 in Fig. 6A), epoxidised oleic acid (nr. 16 in Fig. 6A) and several oxidized small chain fatty acids (nr. 3, 5, 6 in Fig. 6A).

In the BSTFA-GC/MS single ion chromatogram (cross-scan for m/z 73) of the naturally and artificially aged paint films (Fig. 7A and B) the main components of the binding media are trimethylsilyl esters of diacids (nr. 1, 2, 4, 6, 7, 8, 9, 10 in Fig. 7), trimethylsilyl esters of long chain saturated fatty acids (nr. 12, 16 in Fig. 7), trimethylsilyl esters of unsaturated C18 fatty acid (nr. 15 in Fig. 7). Other components identified include trimethylsilyl esters of glycerol (nr. 3 in Fig. 7), the trimethylsilyl ester of monoacylglycerols containing heptanedioic acid (nr. 14 in Fig. 7), octanedioic acid (nr. 15 in Fig. 7), and nonanedioic acid (nr. 17 in Fig. 7). A higher abundance of metal-bound or free small chain diacids is observed in the artificially aged paint sample compared to the naturally aged paint sample, indicating a higher degree of oxidation and hydrolysis. This is expected for such a film exposed under these conditions; high levels of light and humidity promote oxidative and hydrolytic processes. As seen with TMTFTH, the naturally aged paint sample contains a higher abundance of oleic acid compared to the artificially aged one.

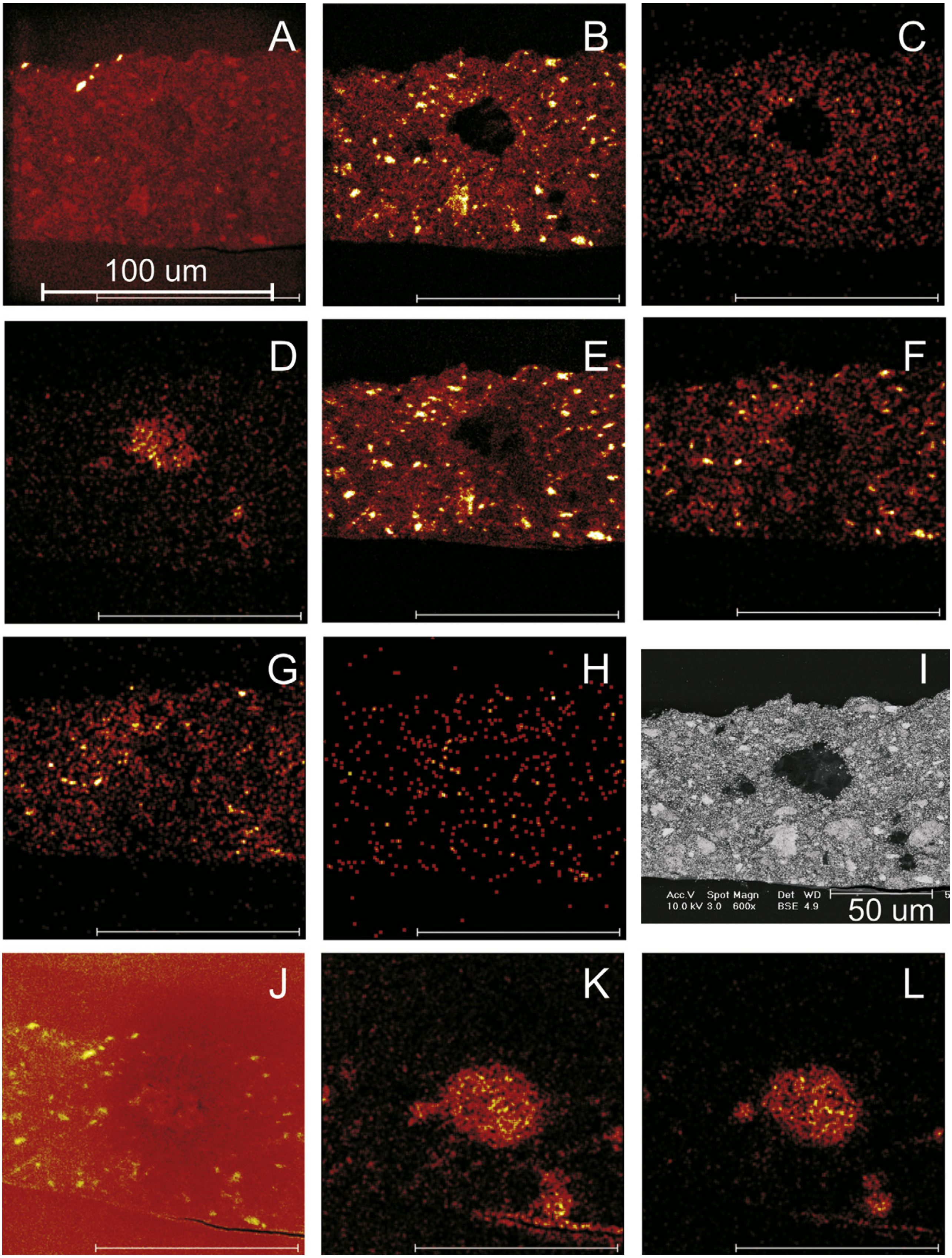

Fig. 5. SIMS image (without a gold coating) of a paint cross-section of the artificially aged Naples yellow-containing oil paint showing the spatial distribution of (A) the total positive ions (TIC), (B) lead, (C) antimony, (D) zinc (all positive ion mode) and in the negative ion mode (E) chloride and the deprotonated ions of (F) palmitic, and (G) stearic acid. The lead soap of palmitic acid is shown in positive ion mode (H). (I) shows the SEM backscattered electron image. The SIMS image of the same paint cross-section covered with a 2 nm thick gold coating shows the spatial distribution of (J) the total negative ions (TIC), deprotonated negative ions of (K) palmitic and (L) stearic acid.

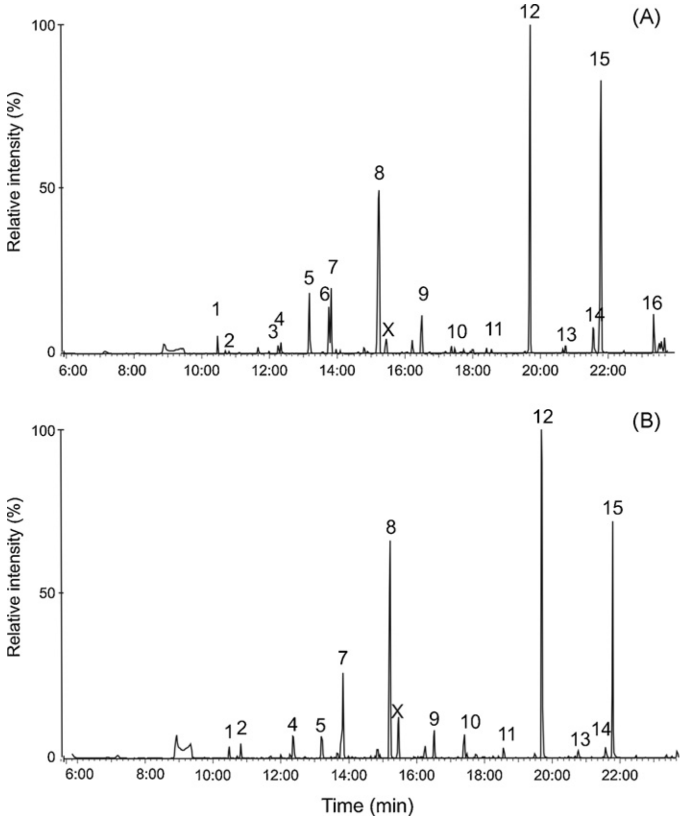

Fig. 6. TMTFTH-GC/MS single ion chromatogram (*m*/*z* 74) of the naturally aged paint sample (A) and artificially aged (51% RH) paint sample (B). Main components detected are (1) nonanoic acid methyl ester, (2) hexanedioic acid dimethyl ester, (3) 8-oxo-octanoic acid methyl ester, (4) heptanedioic acid dimethyl ester, (5) 8-hydroxy-octanoic acid methyl ester, (6) 1,2,4-trioxolane-2-octanoic acid methyl ester, (7) octanedioic acid dimethyl ester, (8) nonanedioic acid dimethyl ester, (9) decanedioic acid dimethyl ester, (10) tetradecanoic acid methyl ester, (11) pentadecanoic acid methyl ester, (12) hexadecanoic acid methyl ester, (13) heptadecanoic acid methyl ester, (14) octadecenoic acid methyl ester, (15) octadecanoic acid methyl ester, (16) 3-octyl-oxiraneoctanoic acid methyl ester.

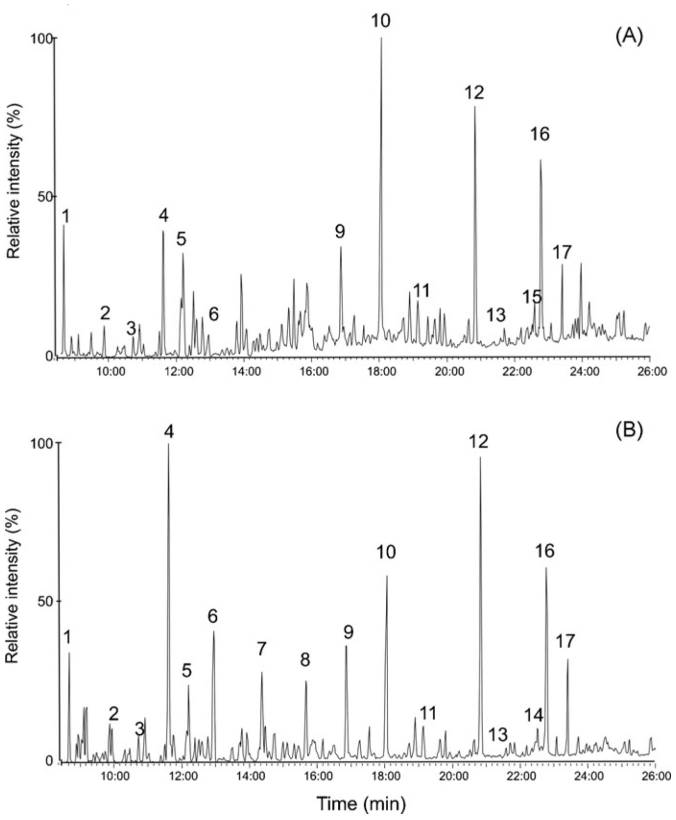

Fig. 7. BSTFA-GC/MS single ion chromatogram (*m*/*z* 73) of the naturally aged paint sample (A) and artificially aged (51% RH) paint sample (B). Main components detected are (1) ethanedioic acid trimethylsilyl ester, (2) propanedioic acid trimethylsilyl ester, (3) 1,2,3-propanetriol 3-trimethylsilyl ester, (4) butanoic acid trimethylsilyl ester, (5) 2-hydroxyheptranoic acid 2 trimethylsilyl ester, (6) pentanoic acid trimethylsilyl ester, (7) hexanedioic acid trimethylsilyl ester, (8) heptanedioic acid trimethylsilyl ester, (9) octanedioic acid trimethylsilyl ester, (10) nonanedioic acid trimethylsilyl ester, (11) decanedioic acid trimethylsilyl ester, (12) hexadecanoic acid trimethylsilyl ester, (13) monoacylglycerol containing heptanedioic acid trimethylsilyl ester, (14) monoacylglycerol containing octanedioic acid trimethylsilyl ester, (15) octadecenoic acid trimethylsilyl ester, (16) octadecanoic acid trimethylsilyl ester, (17) monoacylglycerol containing nonanedioic acid trimethylsilyl ester.

3.4. *ESI-MS*

ESI-MS gives semi-quantitative information about (un) saturated mono- and diacids in the negative mode, and mono-, di- and triacylglycerols with (un)saturated mono- and diacids in the positive mode. In negative ion mode, the ethanol extracts of the paint films were investigated (free or alkali metal-bound acids detected), as well as their hydrolysates (all hydrolysable acids detected). The compounds identified under these conditions are comparable to those observed with GC/MS. The percentage of the total amount of extractable mono- and diacids in both the samples were calculated. The relative amount of mono- and diacids obtained from the extracted samples is divided by the relative amount of mono- and diacids obtained from the hydrolysed samples using tridecanoic acid and tetradecanedioic acid as internal standard. The extractable proportion of mono- and diacids is not the same for both ageing conditions (Fig. 8A). The artificially aged paint film has the largest extractable fraction of mono- and diacids. Twice as much azelaic and stearic acid is extracted from the artificially aged paint film, while three times as much palmitic acid is extracted compared to the naturally aged paint film. This indicates a higher degree of hydrolysis for the artificially aged paint film with a selective higher rate of hydrolysis for palmitic acid.

An indication of the degree of hydrolysis of an oil film is also obtained from the positive ion data for an ethanol extract of the paint films scaled to *m*/*z* 688. Triacylglycerols with one diacid and two monoacids, and with two diacids and one monoacid dominate the positive ion ESI-spectrum of the naturally aged paint sample (Fig. 8B). However in the artificially aged paint sample triacylglycerols with one diacid and two monoacids are low in abundance while diacylglycerols with two diacids, with one diacid and one monoacid, and triacylglycerols with two diacids and one monoacid are more prominent (Fig. 8C). The difference between the two paint systems is a higher degree of ester-bound diacids and a lower degree of ester-bound monoacids in the artificially aged paint. In general, the artificially aged paint has a higher degree of hydrolysis of the ester-bound fatty acids.

3.5. *DTMS*

DTMS allows a physical separation of the paint components by gradual heating of the sample. The temperature at which constituents are released is related to the type of compound and the way it is incorporated in the paint matrix. Detailed interpretation of the different components can be found elsewhere [25]. The DTMS spectra of both naturally and artificially aged paint films

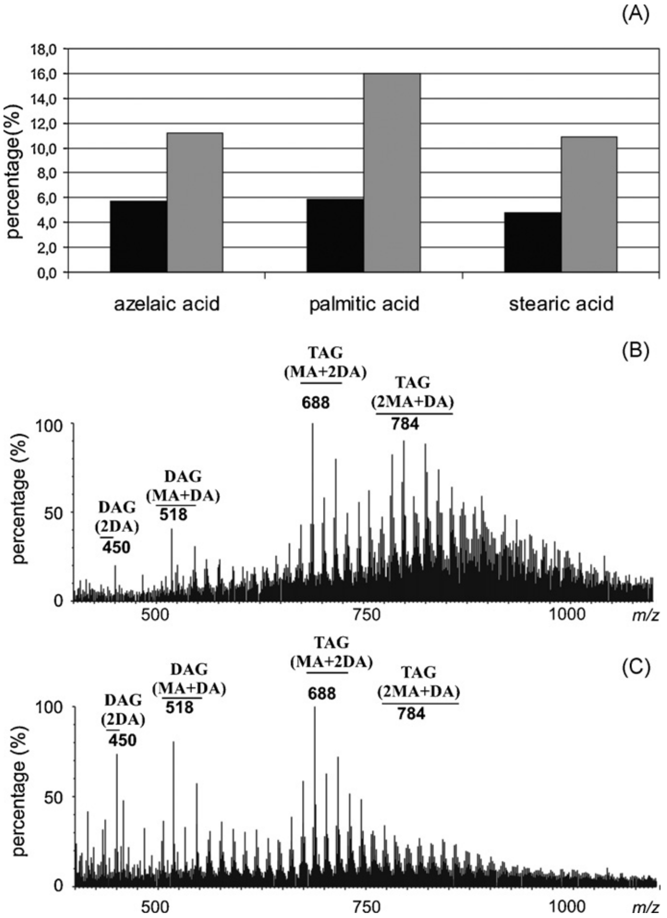

Fig. 8. Percentage of the total amount of azelaic, palmitic and stearic acids that can be extracted with ethanol from naturally (black) and artificially (grey) aged paint sample (A). Part of positive ESI-spectrum of naturally (B) and artificially aged (51% RH) paint extracts (C): *m*/*z* 450 diacylglycerol with two azelaic acid moieties; *m*/*z* 518 diacylglycerol with one azelaic and one palmitic acid moiety; *m*/*z* 688 triacylglycerol with two azelaic acids and one palmitic acid moiety; *m*/*z* 784 triacylglycerol with one azelaic acid, one palmitic and one stearic acid moiety.

show the presence of (un)saturated mono- and diacids, mono- and diacylglycerols, a cross-linked paint network and inorganic components. The total ion chromatogram can be divided into five separate temperature-dependent "events": a very volatile fraction (A), a volatile (sequestered) fraction (B), a more highly bound fraction (C), a pyrolysed fraction (D) and a high temperature fraction (E). During event A, mainly free fatty acids are released, while during event B, ester-bound fatty acids (that are thermally easy to hydrolyse) are released. During event C, ester- and metal-bound fatty acids are detected. The release of further ester-bound fatty acids during this higher temperature event implies that a proportion of such acids are more integrated within the paint matrix. During event D, thermally altered cross-linked network fragments are released. Any fatty acids released during this event are highly integrated into the paint network. During event E, inorganic components from the network or pigment particles can also be detected as CO_2 (carbonates), SO_2 (sulphates and reduced metals (lead, zinc, copper and cadmium)).

During events A and B low intensities of free and ester-bound fatty acid moieties are detected in both paint samples (Fig. 9B and C). The molecular ions of palmitic and stearic acid are detected at *m*/*z* 256 and 284, respectively, with minor electron ionisation chain fragments at *m*/*z* 185, 171, 129, 73 and the γ-H-rearrangement ion *m*/*z* 60. The acylium ions of the palmitic and stearic moieties (*m*/*z* 239 and 267, respectively) in these events are indicative of ester-bound fatty acids.

The molecular ions of palmitic and stearic acids, which are indicative of free, ester- or metal-bound fatty acid modes, predominate in event C of both DTMS spectra (Fig. 9D). In this temperature range metal- and/or ester-bound monoacids within a cross-linked oil network can easily absorb a proton from their environment and therefore be detected as the molecular ions of palmitic and stearic acids. In both spectra acylium ions of palmitic and stearic moieties (*m*/*z* 239 and 267, respectively), the corresponding monoacylglycerides (*m*/*z* 313, 341) and diacylglycerides (*m*/*z* 550, 578, 606) and fragments characteristic of diacids (*m*/*z* 84, 98, 124, 138, 152) are also observed. A small amount of lead is detected in both spectra suggesting the presence of "organic" lead (from lead carboxylates for example). Evidence for lead soaps of diacids (*m*/*z* 348, 349, 350 resulting from decarboxylation of azelaic acid) is found in the DTMS spectrum of the artificially aged paint sample. No evidence for lead soaps of monoacids was found in this spectrum.

The DTMS spectrum of event D of both paints is dominated by inorganic ions of antimony and oxygen (Sb_3O_4 at *m*/*z* 427, 429, 431, 433, Sb_4 at *m*/*z* 484, 486, 488, 490, 492 and Sb_4O_6 at *m*/*z* 580, 582, 584, 586, 588) (Fig. 9E). Markers for the cross-linked oil network, e.g., *m*/*z* 91 or *m*/*z* 105 (representative of aromatic compounds) are relatively low in the spectra and are most likely suppressed by the inorganic components. Lead (*m*/*z* 206–208) derived from the Naples yellow pigment dominates in event E (Fig. 9F). The main difference between both paint films by DTMS is the presence of a relatively higher abundance of lead-bound diacids in the artificially aged paint sample compared to the naturally aged one (not shown).

3.6. FTIR

Transmission FTIR was used to detect the presence of metal carboxylates in the naturally and artificially aged Naples yellow-containing paints (Fig. 10). The metal carboxylate bands are more intense in the artificially aged paint sample compared to the ester carbonyl band at 1710 cm^{-1}. Based on the band position, zinc carboxylates are identified in both samples. However, the peak shapes of the metal carboxylate vibrations are relatively broad compared to spectra of pure metal soaps and do not have a Gaussian band shape. This can be interpreted as a mixture of zinc and lead mono- and diacid carboxylates leading to superimposed bands and/or the incorporation of the metal carboxylates in a more complex chemical or physical environment leading to broadening of the carboxylate vibrations.

4. Discussion

An overview of the characterization of Naples yellow-containing oil paint reconstructions with SIMS, light microscopy, GC/MS, ESI-MS, DTMS and FTIR is given in Table 1. The results of measurements of these reconstructions with the various mass spectrometric and spectroscopic techniques illustrate the chemical changes in the oil paint caused by the accelerated ageing conditions. The SIMS results show that the naturally aged paint system still contains unsaturated and oxidized fatty acids and has a relatively higher relative abundance of ester-bound fatty acids, which is in agreement with the outcome of GC/MS and ESI-MS studies. SIMS can also be used to detect different stages of ageing in a single paint film by analysing the top and bottom side of the paint film. This comparison can only be obtained with this technique.

SIMS provides information about cross-linked oil paint as well as its degree of hydrolysis upon ageing by the detection of varying proportions of fatty acid moieties, e.g., mono- and diacylglycerols,

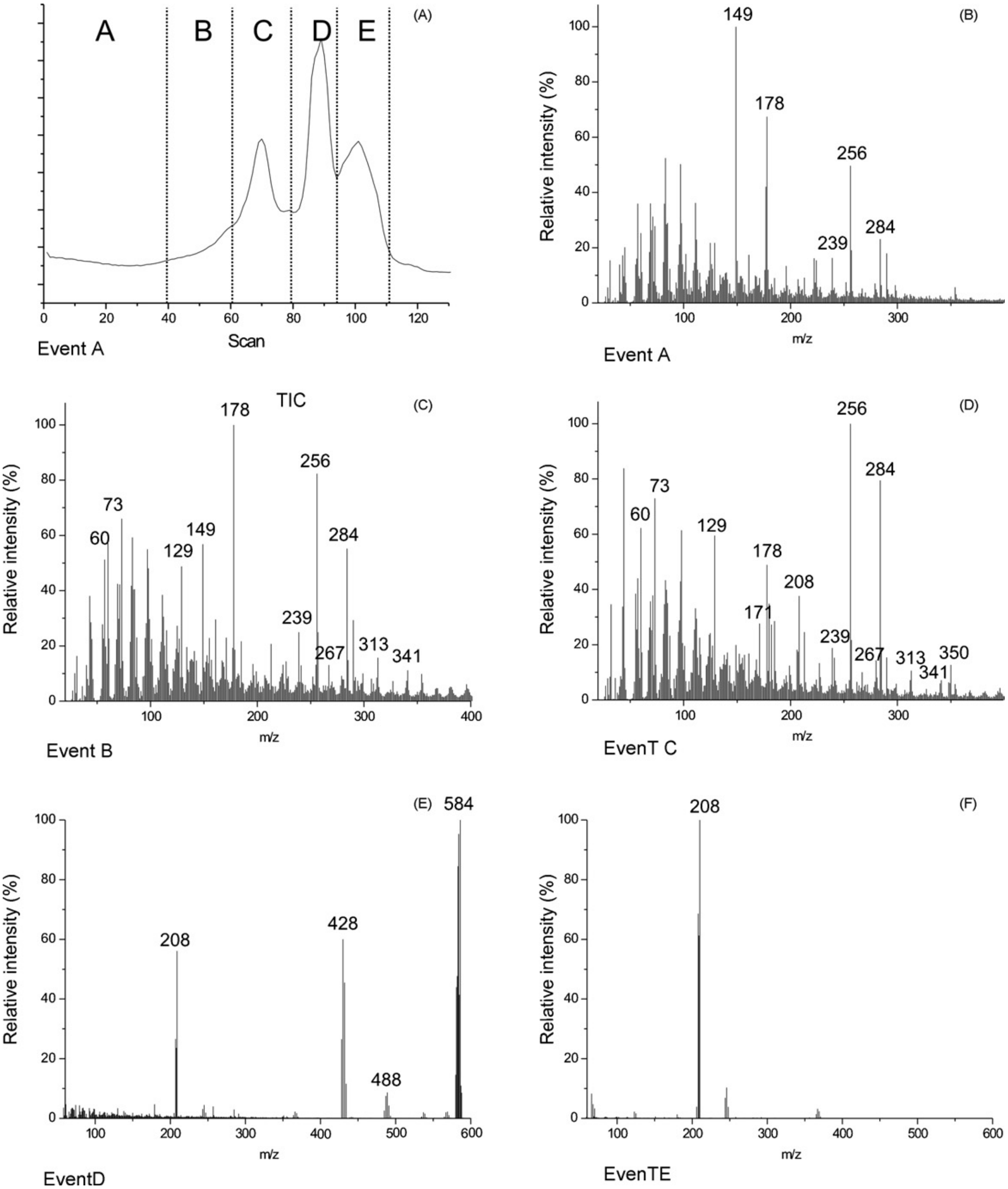

Fig. 9. DTMS spectra of artificially aged paint sample (A) total ion current; (B) event A at scan 5–40; (C) event B at scan 40–60; (D) event C at scans 60–80; (E) event D at scans 80–95; (F) event E at scans 95–110. The peak at *m*/*z* 149 is representative of phthalates and is present due to contamination from the experimental set-up. The significance of *m*/*z* 178 is unknown.

ester- and/or metal-bound fatty acids (i.e., acylium ions of fatty acids and metal fatty acids salts) and free fatty acids. The relative amount of diacylglycerols is higher compared to the monoacylglycerols in the naturally aged paint. This points to an increase in the degree of hydrolysis upon artificial ageing. ESI-MS supports these observations with the triacylglycerols less prominent in the artificially aged paint than in the naturally aged paint. ESI-MS detects mono-, di- and triacylglycerols with various mono- and/or diacids; this large variety of di- and monoacid-containing acylglycerols is not observed in the SIMS spectra. In contrast to reference compounds, triacylglycerols and diacid-containing compounds in a paint matrix are not stable under the SIMS ionization conditions. BSTFA-GC/MS and DTMS also provide information on fatty acids moieties and network components, but hardly any difference between naturally and artificially aged paint films is observed with these techniques. In contrast to SIMS, BSTFA-GC/MS detects monoacylglycerols of diacids. The types of fatty acid moieties formed and detected with DTMS are similar to the ones detected with SIMS. However, the single ion temperature profiles of the DTMS data give extra information about the incorporation of components in the paint system. In DTMS, the single ion temperature profile of mass fragments at *m*/*z* 91 and 105 (from alkylbenzenes) illustrate a release of these fragments at high temperatures. This can be interpreted as aromatic components released by thermal rearrangement of the polymeric oil network. By contrast, in the SIMS spectra, secondary ions with a mass below 100 are mostly not very characteristic and represent alkyl fragment ions resulting from carbon chain scission.

SIMS provides limited information on oxidation and degradation products in the paint systems. TMTFTH- and BSTFA-GC/MS and ESI-MS are more informative, showing diacids (C2–C10) as main components in the paint system, particularly after ageing. These components are not observed in the SIMS spectra as the ionisation conditions of SIMS are not favourable for the analysis of diacids.

SIMS does, however, detect three short chain fatty acids (C8, C9 and C10) formed as result of the ageing of the oil paint, in the naturally aged sample. TMTFTH-GC/MS supports the presence of these short chain fatty acids. After accelerated ageing, these short chain fatty acids cannot be detected in significant amounts by SIMS or by TMTFTH-GC/MS, presumably because they have evaporated from the paint system. Other types of oxidation or degradation products, like 2-oxotetrahydrofuryl-4-*n*-alkanoic acids, identified with GC/MS are not found in the SIMS spectra. This may be mostly linked to the relative abundance of such components.

SIMS as well as DTMS provides information on metal-bound fatty acids. Both techniques characterize lead-azelaic acid salts in the paint after artificial ageing, while SIMS also indicates the presence of lead soaps of palmitic and stearic acids in this sample. By contrast, FTIR microscopy indicated a predominance of zinc soaps

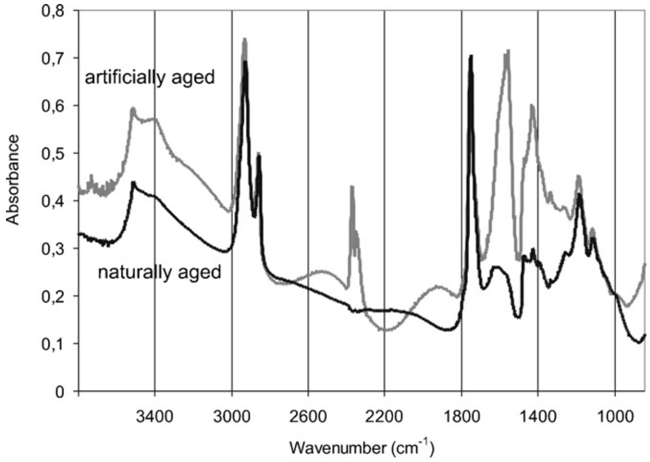

Fig. 10. Transmission FTIR spectra of Naples yellow-containing oil paint film aged under natural (black line) and artificial (90% RH) (grey line) ageing conditions.

Table 1
Overview of the features of Naples yellow-containing oil paint reconstructions analysed with SIMS, light microscopy, GC/MS, ESI-MS, DTMS and FTIR.

Analytical technique	Information obtained from Naples yellow-containing oil paint reconstruction		Remarks
	Naturally aged (NA)	Artificially aged (AA)	
SIMS	(Un)saturated FA's, small chain smaller FA's, azelaic acid, mono- and diacylglycerols of (un)saturated and/or oxidized FA's, lead, zinc, chloride, antimony.	Saturated FA's mono- and diacylglycerols of saturated FA's, lead soaps of azelaic, palmitic and stearic acid, lead, zinc, chloride, antimony.	Topside of the *NA* paint layer is in a more advance stage of ageing compared to the bottom side.
	Pb map (partially) overlays with Sb and Cl maps but is unrelated to Zn map. FA's are associated with paint matrix.	Pb map (partially) overlays with Sb and Cl maps and unrelated with Zn map. FA's are associated with zinc aggregates and paint matrix.	*AA higher degree of hydrolysis*
LM	*Surface*: bluish- and tiny yellow/greenish-fluorescent spots.	*Surface*: lumpy, many large bluish fluorescent spots.	Bluish fluorescent areas are attributed to zinc soaps and yellow/greenish spot to residual zinc oxide.
	Cross-section: upper part of paint layer shows a higher bluish fluorescence.	*Cross-section*: large bluish fluorescent aggregates.	*AA higher degree of saponification*
TMTFTH-GC/MS	(Un)saturated and/or oxidized FA's, dicarboxylic acids, small chain smaller FA's.	(Un)saturated and/or oxidized FA's, dicarboxylic acids.	A higher abundance of diacids is observed in the artificially aged paint sample. *AA higher degree of oxidation*
BSTFA-GC/MS	(Un)saturated and/or oxidized FA's, dicarboxylic acids C4-10 (diC4–10), glycerol, monoacylglycerol of mono- and diacids.	(Un)saturated and/or oxidized FA's, dicarboxylic acids C4-10 (diC4–10), glycerol, monoacylglycerol of mono- and diacids.	A higher abundance of diacids is observed in the artificially aged paint sample. *AA higher degree of oxidation*
ESI-MS	(Un)saturated mono- and di-carboxylic acids and various mono-, di- and triacylglycerols with (un)saturated, mono- and dicarboxylic acids.	(Un)saturated mono- and di-carboxylic acids and various mono-, di- and triacylglycerols with (un)saturated, mono- and dicarboxylic acids.	Compared to the *NA* sample the AA sample has a relatively larger portion of EtOH-extractable di- and monoacids. *AA* paint has a higher degree of hydrolysis of ester-bound fatty acids. *AA higher degree of hydrolysis*
DTMS	(Un)saturated FA's, mono- and diacylglycerides of palmitic and stearic acid, lead.	(Un)saturated FA's, mono- and diacylglycerides of palmitic and stearic acid, lead-azelaic acid salt, lead.	
FTIR	Zinc carboxylates (and lead carboxylates) (weak/medium intensity).	Zinc carboxylates (and lead carboxylates) (very strong intensity).	Metal carboxylate band is asymmetric, possibly lead carboxylates present. *AA higher degree of saponification*

FA, monocarboxylic fatty acid; NA, naturally aged; AA, artificially aged.

in both samples, particularly in the artificially aged one. SIMS and DTMS analyses of pure zinc stearate demonstrate that these techniques are not able to detect its molecular ion. The presence of zinc soaps cannot therefore be identified with SIMS and DTMS, and FTIR is the most suitable technique to obtain information about the presence of a wide range of metal carboxylates in a paint system. However, the spatial resolved information obtained with SIMS (with gold coating) is suggestive of the presence of zinc soaps because zinc, palmitic and stearic acids are all detected inside the aggregates.

The presence of zinc oxide in the Naples yellow pigment leads to the formation of zinc soaps in the pigmented oil paint reconstructions, with a relatively higher concentration of zinc soaps found in the artificially aged paint sample. The zinc soaps aggregate, indirectly visualized by light microscopy and SIMS (with gold coating), causes the lumpy surface morphology. Lead soaps are also detected with SIMS, DTMS and FTIR. These are likely to originate from the lead-chloride-containing compound as low amounts of lead and chloride are detected inside the zinc-containing aggregate with SIMS.

In general, the combined results of the range of analytical techniques used reveal that the artificially aged paint system is in a more advanced stage of ageing with a higher degree of hydrolysis and a higher state of oxidation. The artificial ageing conditions, with high levels of light and humidity, promote saponification and metal soap formation/aggregation in these Naples yellow-containing paint reconstructions. The pigment itself however is stable and unaffected. The reactive components are the additional constituents of zinc oxide and a lead-chloride compound.

5. Conclusion

This study evaluates the potential of SIMS as an analytical tool to study oil-containing paint samples. SIMS provides combined organic and inorganic information about the oil paint composition. The SIMS molecular signature also provides speciation information. Uniquely it gives spatially resolved information about the composition of the upper atomic layers of a surface and can be applied to compare the composition of the top and bottom of a paint film (where limitations in oxygen availability can lead to differences in composition).

The SIMS analysis shows characteristic peaks for oil paint constituents, which are confirmed by GC/MS, ESI-MS, DTMS and FTIR. However, SIMS has some limitations because the diacids, shown to be major components of the oil paint film by GC/MS are only detected with SIMS in low yields. Similarly, ESI-MS demonstrates the presence of a broad range of mono-, di- and triacylglycerols esterified with mono- and diacids are present, while SIMS only detects the less polar mono- and diacylglycerols with palmitic and/or stearic acids. SIMS is only able to provide fairly non-specific information about the polymeric oil paint network, but clearer evidence for its presence is provided by DTMS. FTIR is very informative about the presence and composition of metal carboxylates. By contrast, while lead soaps can be characterized and localized with SIMS, zinc soaps are unstable under SIMS ionization. Indirect evidence for zinc soap can be obtained using SIMS after application of an ultra-thin gold coating, showing the spatial correlation of fatty acids and zinc inside metal soap aggregates. It is essential to use a range of various analytical techniques in combination to obtain a clearer understanding about the different aspects of the chemistry of the pigmented oil paint systems. In this perspective, SIMS is a useful tool to visualize certain paint constituents derived from pigment and medium, but to obtain a “complete” picture of the chemical composition of the paint system additional analytical techniques are required.

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