

Identification of synthetic organic pigments (SOPs) used in modern artist's paints with Secondary Ion Mass Spectrometry with MeV ions

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ABSTRACT: This work reports on the first systematic study using Secondary Ion Mass Spectrometry with MeV ions (MeV-SIMS) for the analysis of synthetic organic pigments (SOPs) that can be usually found in modern and contemporary art paints. In order to prove the applicability of the method to different chemical classes of SOPs, 17 pigments were selected for the analyses. The focus was on blue and green phthalocyanines, yellow and red (naphthol AS) azo pigments, red quinacridone, anthraquinone, and diketopyrrolo-pyrrole pigments. Since there are no reference spectra available for this technique, pure pigment powders were measured first to create a database. Simple two-component paint systems were also prepared for testing purposes by mixing synthetic organic pigments with alkyd and acrylic binders. Commercial paints that contain the SOPs with identical C.I. numbers as in the prepared two-component samples were analyzed. All pigments were successfully identified in commercial products in the MeV-SIMS mass spectra through molecular and larger specific fragment ion peaks. The main advantages of MeV-SIMS over other techniques used in SOPs identification, like pyrolysis gas chromatography mass spectrometry (Py-GC/MS), direct-temperature resolved mass spectrometry (DTMS) and laser desorption ionization mass spectrometry (LDIMS) can be summarized as follows: i) pigments and binders can be detected simultaneously in the same mass spectrum acquired over a short measurement time (up to 500 s) ii) only small sample flakes are required for the measurements, which are analyzed without any chemical treatment prior to the analyses, iii) samples are not consumed during the analyses and can be reused for other measurements, e.g. multi-elemental analysis by other ion beam analysis (IBA) techniques, such as particle-induced X-ray emission (PIXE). Compared to e.g. Raman spectroscopy, the significant benefit of MeV-SIMS is the exact identification of the SOPs in the paints even if pigments of similar structures are measured.

Synthetic organic pigments (SOPs) were introduced into the paint market during the 20th century and were commonly used in modern and contemporary art paints. Due to SOPs' complex but similar chemical structures¹, analytical methods that can provide information on the molecular composition are necessary for their identification and distinguishing among different chemical classes. Many well-known mass spectrometry techniques such as pyrolysis gas chromatography mass spectrometry (Py-GC/MS), direct-temperature resolved mass spectrometry (DTMS)², laser desorption ionization mass spectrometry (LDIMS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) using primary ions in keV range etc. have been well established in the analysis of paint materials in the field of cultural heritage³. However, in most cases, the paint samples must be chemically treated prior to the analysis and are consumed in order to allow the exact identification of the SOPs, or, as in the Py-GC/MS, pigments of the same chemical class may produce identical pyrograms, thus limiting the identification of a particular SOP.

Secondary ion mass spectrometry with ion excitation in the keV energy range (keV-SIMS) and time-of-flight mass separation (ToF) is a widely used analytical technique for

surface characterizations in materials science, such as semiconductors and polymers⁴. Further applications are reported in the studies of biological samples^{5,6}. In the field of cultural heritage this method was applied by different research groups mainly for the study of inorganic materials, such as corroded metal artefacts⁷⁻⁹, and ancient and weathered medieval glasses^{10,11}. Keune et al.¹² described the application of ToF-SIMS for the analysis of historical paintings. Not only used for depth profiling of inorganics, due to the high lateral resolution, ToF-SIMS is becoming also more and more important for chemical imaging of surfaces^{13,14}. As far as the authors know, no systematic studies were published up to now on ToF-SIMS analysis of synthetic organic materials applied in modern and contemporary paints. Vercammen et al.¹⁵ analyzed UV-curable acrylate-based multilayers containing synthetic organic pigments, which are of interest for industrial inkjet printing.

MeV-SIMS is a successor of plasma desorption mass spectrometry (PDMS) which uses MeV primary ions emitted from the radioactive decay of ²⁵²Cf and was developed in 1974 by Torgerson et al.¹⁶. Nowadays MeV ions produced in electrostatic accelerators are applied instead of fission fragments for the excitation, and this method is already

implemented in several ion beam laboratories in the world^{17–21}. While keV-SIMS is described by “collision cascade” and energy transfer from the primary ions to the surface through nuclear collisions, in case of MeV ions electronic sputtering is the dominant process, causing desorption of larger intact organic molecules from the sample surface and leading to secondary molecular ion yields up to three orders of magnitude higher compared to keV-SIMS. A systematic study comparing secondary molecular yields from MeV monomer ion with the keV cluster ion ToF-SIMS was done by Jones et al.²².

We have demonstrated already that MeV-SIMS can be successfully used for the identification and imaging of modern paint materials²³, forensics^{24,25} and biological samples²⁶. Matjačić et al.²⁷ demonstrated that MeV-SIMS can be performed under the ambient conditions, which could allow the non-destructive analysis of the modern and contemporary

artworks, e.g. paintings, when sampling is not allowed or in cases when the analyzing material is not vacuum compatible. Contrary to other TOF-SIMS techniques, MeV-SIMS is not as limited by the choice of the primary ion beam type and energy, thus each experiment can be individually optimized. In this work MeV-SIMS reference mass spectra of selected SOPs (in powder form), SOPs in self-made alkyd and acrylic paints as well as in commercial tube paints are presented.

EXPERIMENTAL SECTION

Pure Pigment Samples

Pigments analyzed by MeV-SIMS are summarized in Table 1, and the chemical structures of pigment classes presented in Figure 1 (designed in ACD/ChemSketch (Freeware) 2019.1.2, Advanced Chemistry Development, Inc. Canada). All pigments were provided by Kremer Pigmente (Germany), except PY74, a product of Sochim Pigmenti (Italy).

Table 1. Pigment powders analyzed with MeV-SIMS. C.I. = Color Index

Pigment C.I. generic name	Pigment C.I. number	Pigment class	Color	Chemical formula	Molecular weight (g/mol)
PB15:1	74160	Cu phthalocyanine	Deep intense blue with a red undertone	C ₃₂ H ₁₆ CuN ₈ , stabilized with 0.5–1 Cl	611.52
PB15:3	74160		Deep intense blue with a green undertone	C ₃₂ H ₁₆ CuN ₈	576.11
PB15:6	74160		Reddish blue	C ₃₂ H ₁₆ CuN ₈	576.11
PG7	74260		Green with a blue undertone	C ₃₂ Cl ₁₆ CuN ₈	1127.15
PG36	74265	Metal-free phthalocyanine	Green with a yellow undertone	C ₃₂ Br ₆ Cl ₁₀ CuN ₈	1393.85
PB16	74110		Intense blue-green with a red undertone	C ₃₂ H ₁₈ N ₈	514.58
PY3	11710	Monoazo	Bright yellow	C ₁₆ H ₁₂ Cl ₂ N ₄ O ₄	395.22
PY74	11741		Warm yellow	C ₁₈ H ₁₈ N ₄ O ₆	386.40
PV19	73900	Quinacridone	Bright rose violet	C ₂₀ H ₁₂ N ₂ O ₂	312.34
PR122	73915		Rich pinkish violet	C ₂₂ H ₁₆ N ₂ O ₂	340.40
PR112	12370	Naphthol AS	Light warm red	C ₂₄ H ₁₆ Cl ₃ N ₃ O ₂	484.78
PR170	12475		Warm red	C ₂₆ H ₂₂ N ₄ O ₄	454.52
PR177	65300	Anthraquinone	Vivid red with a blue undertone	C ₂₈ H ₁₆ N ₂ O ₄	444.46
PO73	561170	Diketopyrrolo-Pyrrole (DPP)	Bright warm orange	C ₂₆ H ₂₈ N ₂ O ₂	400.56
PR254	56110		Mid-range red	C ₁₈ H ₁₀ Cl ₂ N ₂ O ₂	357.20
PR255	561050		Bright scarlet red	C ₁₈ H ₁₂ N ₂ O ₂	288.32
PR264	561300		Dark deep red with a violet undertone	C ₃₀ H ₂₀ N ₂ O ₂	440.52

Two-component Paint Samples

Two-component paint systems were prepared as mock-ups. Paint layers as well as pure binding media were cast on the microscope glass slides. The pigment powders from Table 1 were mixed in different ratios (depending on the pigment) with pure binder (as supplied), in order to obtain a pasty texture. As binders, alkyd resin medium 4 (with phthalic anhydride and

pentaerythritol as main constituents, product of LUKAS, Germany) and acrylic binder Plextol D 498 (p(nBA/MMA) copolymer, product of Kremer Pigmente GmbH & Co KG, Germany) were used. The thickness of wet paint layers was approximately 150 μm. Mock-ups were dried at room temperature for two weeks. Afterward the samples were stored in boxes in dark conditions for two months before the analyses.

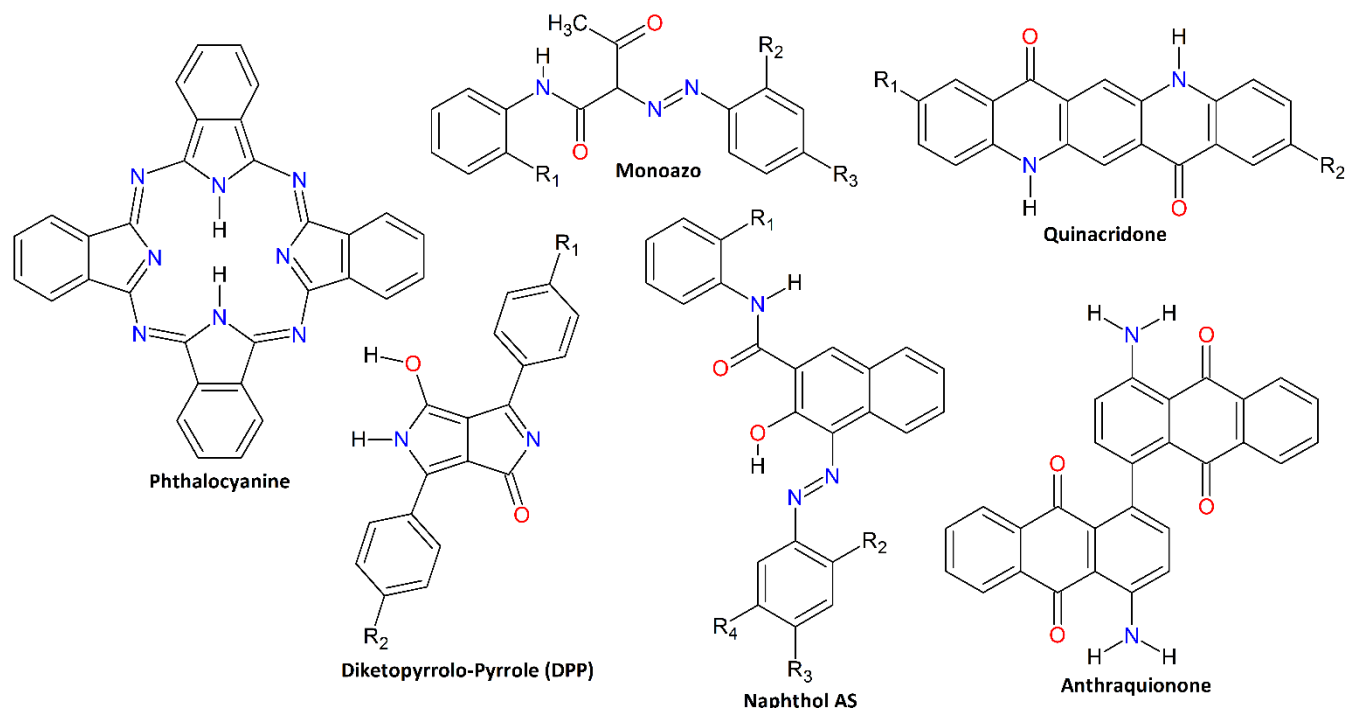


Figure 1. Structures of analyzed synthetic organic pigments (chemical classes)

Commercially Available Tube Paints

Since the contemporary artists use mostly commercially available tube paints and do not prepare the paints themselves, a limited number of commercial paints was chosen with criteria to contain the SOPs with identical C.I. number as the ones used for the pure pigments and two-component mock-up analyses. Commercial paints are usually complex mixtures containing not only pigments and binders but also different additives (fillers, surfactants, stabilizers, etc.), which are added for lowering the production costs, or to improve the physical and chemical properties of the paints. The chosen paints were cast on glass slides and dried at room temperature under the same conditions as described for two-component mock-ups. All alkyd containing commercial tube paints used in the present study were Winsor & Newton products, W&N Griffin Alkyd line: Phthalo Blue PB15, Phthalo Green PG7, Winsor Lemon PY3, and Permanent Rose PV19. Acrylic tube paints were commercial products of Winsor & Newton, UK, W&N Artists Acrylic line: Phthalo Blue (Red shade) PB15:1, Phthalo Green (Blue shade) PG7, Lemon Yellow PY3, Permanent Rose PV19, Naphthol Red Light PR112, Quinacridone Violet PR122, Pyrrole Red PR254, and Pyrrole Red Light PR255, one product of Schmincke, Germany, Academic line: PB15:3, and two products of LUKAS, Germany, Lukas Pastos line: PB15:6 and PB16.

Measurements

Analyses were performed using a ToF-SIMS spectrometer for secondary ion mass spectrometry with MeV primary ions installed at the heavy ion microbeam beamline at the Ruđer Bošković Institute, Croatia. Details about the setup can be found in Tadić et al.¹⁸. The sample surface was oriented under 45° towards the incident beam and secondary molecular ions were extracted from the sample by extractor tip that was positioned perpendicular to the sample surface at a distance of 10 mm. Due to the sample surface roughness, extraction angle was optimized for each performed measurement to achieve the maximum in the secondary molecular ion yield. Measurements

were carried out using a pulsed 5 MeV Si⁴⁺ primary ion beam assuring that the number of heavy ions on the sample was less than 1000 ions/s and therefore no ion beam induced damage of the sample was expected. The beam spot on the target was focused to 10×10 μm² and the beam was scanned across a 100×100 μm² sample area. During the measurements the vacuum in the analysis chamber was kept between 10⁻⁶ and 10⁻⁷ mbar. The sample was held at a potential of +5 kV or -5 kV corresponding to positive or negative ion mode, respectively. A Multi-Stop TDC Data Acquisition System in a heavy deflection start mode was used with 100 μs time between two heavy ion pulses (duration of 4 ns). All experimental and data acquisition parameters were controlled with the SPECTOR software package^{18,28,29}.

Small flakes of two-component and commercial paint samples were taken with a stainless-steel scalpel from the glass slides and pressed with a flat and clean aluminum plate into the indium surface (99.99% in tear drops, provided by Alpha Aesar, USA). Pure pigment powders were pressed directly into pure indium. This procedure was fast and simple, it allowed to obtain a flat surface and to minimize the topological effects which can change the extraction field for the secondary molecular ions. Two to three spots per sample were analyzed with a measuring time up to 500 s, depending on the sample. For most of the samples, MeV-SIMS spectra were recorded in a positive ion mode except for those containing pure acrylic resin Plextol D 498.

Data Treatment and Interpretation

Due to different sample geometries (shapes, heights), small variations in the effective extraction field between the paint sample surface and the extractor can exist thus changing the energy of secondary ions (desorbed molecules). Therefore, it was necessary to perform mass calibration of each spectrum individually. A routine procedure using Matlab software (Version 2011) was developed for identification of well-established low mass ions H⁺, H₂⁺ etc. and easily assigned C_xH_y⁺ fragments for the first stage of the mass calibration. Molecule

fragments with higher masses known from literature, obtained with other MS techniques (see paragraph below), were selected for final calibration. Sample surface roughness is the reason why mass resolution of the presented spectra is far from ideal, $M/\Delta M \sim 500$, which was published in the work of Tadić et al.¹⁸. Thus, all identified mass peaks are presented with the accompanied FWHM in the Supporting Information (SI). The mMass – Open Source Mass Spectrometry Tool was used for spectra analysis, version 5.5.0³⁰. For the spectra comparison, base peak normalization was employed.

As presently there is no database for the MeV-SIMS spectra of polymers or SOPs, the measured data (spectra) were compared with the mass spectra found in literature, obtained with other mass spectrometry techniques on the same material group. Therefore, the m/z values published from the Py-GC/MS^{31–35}, DTMS³⁶, LDIMS^{36,37}, keV-SIMS database from SurfaceSpectra (Static SIMS Library 4), and fast atom bombardment mass spectrometry (FABMS)³⁸ were used as well as from other sources^{39–41}.

RESULTS AND DISCUSSION

Analysis of the Pure Pigment Powders

The MeV-SIMS spectra of blue phthalocyanine pigment powders (PB16 metal-free, and the three forms of PB15 copper-containing pigment: PB15:1 α -form, PB15:3 β -form, and PB15:6 ϵ -form) are presented in Figure 2, with the characteristic peaks and the corresponding peak widths (FWHM) listed in the SI, Table S-1. All pigments were identified through their molecular ion peaks as well as several main fragment ions. The three main peaks of the PB15:3 and PB15:6 pigments can be identified as the molecular $[M]^{+\bullet}$ and protonated molecular ions $[MH]^+$ (m/z 575/576), copper benzene-1,2-dicarbonitrile fragment ion (m/z 191/193)^{30,31}, and the stable isotopes of Cu^+ at m/z 63 and 65. Lower intensity fragment ions were observed at m/z 152/154 $[C_7H_5Cu]^+$, 165/167 $[C_7H_4CuN]^+$, 102/103 and 128/129, these being the metal-free analogues to 165 and 191 fragments, respectively. Having identical mass spectra, PB15:3 and PB15:6 pigments cannot be distinguished by MeV-SIMS. The mass spectrum of PB15:1 pigment showed the same m/z peaks as found in PB15:3 and PB15:6 spectra, but with an additional lower intensity peak at m/z 609/611. This molecular ion peak is present due to the stabilization of copper phthalocyanine with 0.5–1 chlorine atom per molecule, which enables differentiation of the PB15:1 pigment from both PB15:3 and PB15:6 polymorphs by MeV-SIMS²³. In the case of metal-free phthalocyanine PB16, the molecular ion peak was observed at m/z 514 and the main fragment ions at m/z values 103, 114/115, and 129 as in PB15:1, PB15:3, and PB15:6 mass spectra, but with much higher relative intensities (Figure 2).

Mass spectra of the green phthalocyanine pigments PG7 and PG36 are given in Figure 3, and the main fragments (m/z with peaks' FWHM) listed in Table S-1 of the SI. For the PG7 pigment the molecular ion peak was detected at m/z 1127, indicating that this is a fully chlorinated form with 16 Cl atoms substituted on the phthalocyanine ring. Several peaks at lower m/z , from 1092 to 915, correspond to either loss of one to six Cl atoms from the parent molecule, or could indicate the presence of incompletely substituted phthalocyanine during the PG7 production process. The most intensive peak in the spectrum was Cu^+ ion fragment at m/z 63 and 65. Fragment ions detected at m/z values 264–270 $[C_8Cl_4N_2]^{+\bullet}$, 292–295 $[C_8Cl_3CuN_2]^+$ and 328–331 $[C_8HCl_4CuN_2]^+$ were expected as they are analogous to those found in PB15 pigment spectra (the dicyanitrile

fragments). The obtained results in this work are in good agreement with the published data from the Py-GC/MS analysis of PG7 in acrylic paints^{31,34,36,42}. The pure PG36 mass spectrum showed a series of molecular ion peaks of similar but relatively low intensities, from m/z 1839 to 992, depending on the ratio of Br and Cl substituted on phthalocyanine. The EDI-MS analysis of PG36 was reported by Kudaka et al.⁴³. The peak at m/z 1127 was also observed, probably corresponding to 16 Cl atoms on the phthalocyanine molecule (as in PG7), as well as the non-fully substituted chlorinated structures at m/z 1058 ($n(Cl)=14$), and 992 ($n(Cl)=12$).

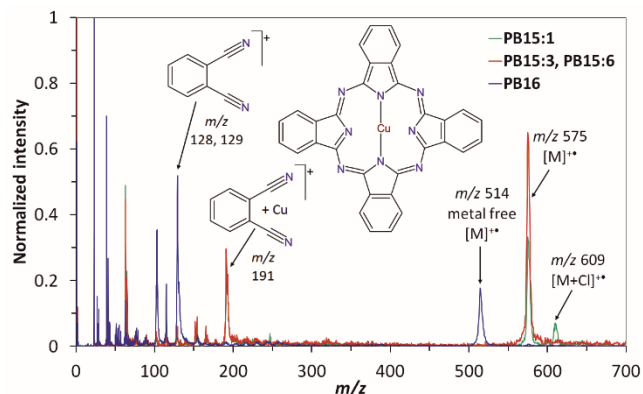


Figure 2. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the blue phthalocyanine pigment powders (PB15:1 Cl stabilized α -form, PB15:3 β -form, PB15:6 ϵ -form, and PB16 metal-free) measured on indium

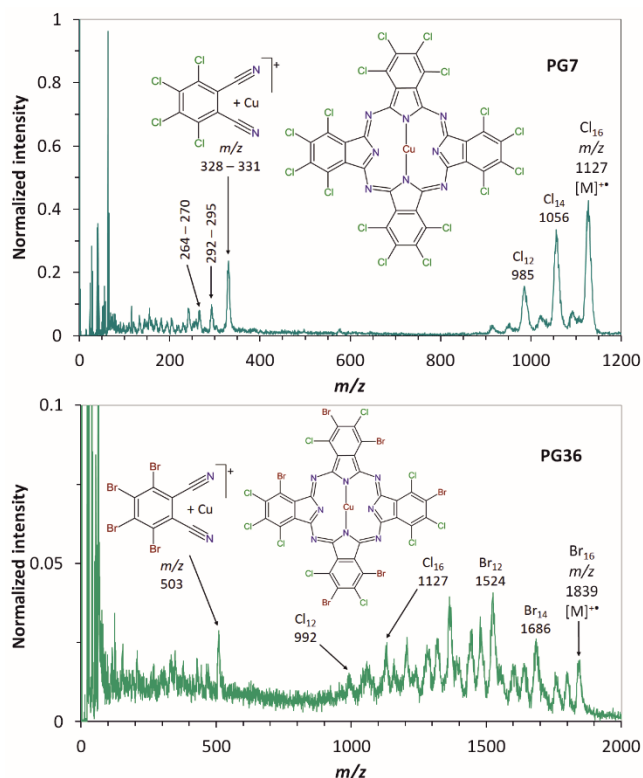


Figure 3. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the green copper phthalocyanine pigment powders PG7 (top) and PG36 (bottom) measured on indium

The characteristic peaks of the mass spectra of the yellow azo pigments, PY3 and PY74, are summarized in Table S-2 of the SI, and the spectra shown in Figure 4. The molecular and protonated molecular ions were observed in the PY3 mass spectrum (m/z 394/395), followed by a lower peak at m/z 378, due to O radical loss ($M - 16$) from the parent molecule. The peak at m/z 127/129 (o-chloroaniline fragment ion) dominated the spectrum (Figure 4)^{31,44}. The fragment ion corresponding to its loss from the parent molecule, due to amide bond cleavage, was also detected with good intensity at m/z 268/270, along with the fragment ion at m/z 171/173 from the azo bond cleavage³⁶. Similar intensity fragments at m/z 154/156 [C_7H_5NOCl]⁺ and 111/113 [C_6H_4Cl]⁺ were also observed. In the PY74 mass spectrum the high intensity molecular and protonated molecular ions at m/z 386/387 were detected (Figure 4). The fragment ion at m/z 123 (o-methoxyaniline ion) dominated the spectrum as was the case for the analogue fragment in PY3 pigment mass spectrum (o-chloroaniline ion). Rearrangement of the azo bond lead to the fragment formation detected at m/z 168 (2-methoxy-4-nitroaniline ion). The characteristic 1-methoxy-3-nitrobenzene fragment ion was detected at m/z 152³⁶.

Summary of the mass spectra of violet (PV19), red (PR112, PR122, PR170, PR177, PR254, PR255 and PR264) and orange (PO73) pigments is also given in Table S-2 of the SI. Molecular ions, molecular ions in protonated and/or deprotonated forms were detected with good intensities for all analyzed pigments.

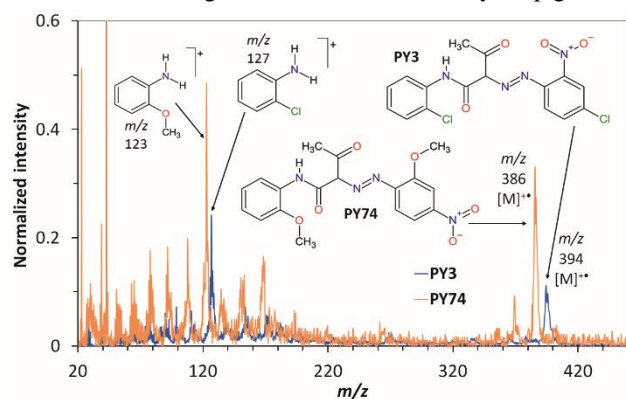


Figure 4. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the yellow monoazo pigment powders PY3 and PY74 measured on indium

The quinacridone pigment PV19 spectrum showed characteristic peaks at m/z 312, 295, 284 and 256, corresponding to the molecular ion and the loss of OH, CO and 2CO fragments from the parent molecule, respectively (Figure 5). The methyl substituted quinacridone pigment PR122 showed an identical mass spectrum up to m/z 312, this m/z corresponding to the loss of two methyl groups from the pigment molecule (Figure 5). The protonated molecular ion peak at m/z 341 dominated the spectrum⁴⁵, followed by a fragment ion at m/z 325/326 due to the loss of one methyl group from the ring. A molecular dimer was also observed at m/z 680–682. The anthraquinone PR177 pigment mass spectrum showed a series of peaks below the deprotonated molecular and molecular ion peaks (m/z 443/444), corresponding to similar fragmentation patterns as in quinacridone pigments (see Table S-2 of the SI). The observed peaks primarily correspond to sequential loss of CO and NH_2 radicals from the parent molecule.

The Naphthol AS pigments, PR112 and PR170, had relatively overlapping mass spectra in the mass region below

m/z 200 (Figure 6). Fragment ion of PR112 at m/z 377/379, that dominated the spectrum, corresponds to the larger fragment formed in the amide bond cleavage. The smaller corresponding fragment (o-methylaniline ion) was also detected at m/z 106/107. Products of the azo bond cleavage were probably also detected, where the unidentified peak at m/z 286–289 could correspond to the larger fragment being formed. The main observed fragment ion in the PR170 mass spectrum was at m/z 318, also due to the amide bond cleavage. The smaller corresponding fragment ion, 2-ethoxyaniline ion, was visible at m/z 136 as well.

The analyzed diketopyrrolo-pyrrole pigments (PR254, PR255, PR264 and PO73) all showed similar fragmentation patterns (Table S-2 of the SI). For PR254 pigment the highest peaks were observed at m/z 115 and 138/140, the latter corresponding to 4-chlorobenzonitrile ion formation (Figure 7). The unidentified 115-mass fragment was also detected in the PR255 spectrum, indicating that this could be a product from aldehyde fragment rearrangement observed in both spectra (m/z 130), but probable chlorobenzene ion formation cannot be ruled out for the chlorinated PR254 structure (m/z 111, 113). Indium ion detection at m/z 113, 115 may also be possible. The dominant fragment in the PR255 mass spectrum was the protonated benzonitrile ion at m/z 104. The main observed peaks of PR264 and PO73 are listed and described in Table S-2 of the SI, with molecular ions being dominant in the spectra.

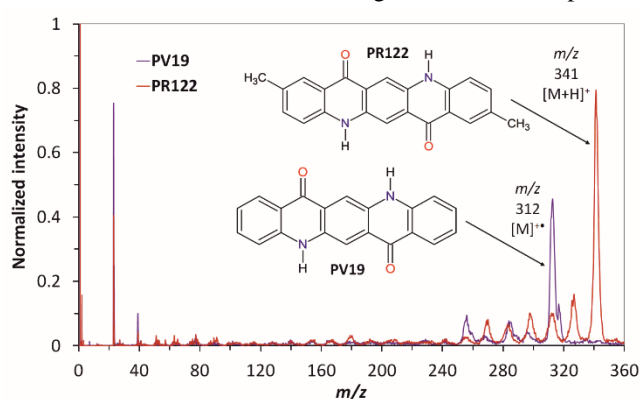


Figure 5. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the violet and red quinacridone pigment powders PV19 and PR122 measured on indium

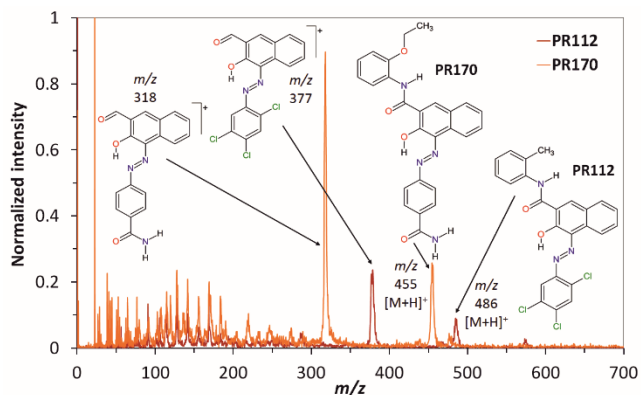


Figure 6. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the red naphthol AS pigment powders PR112 and PR170 measured on indium

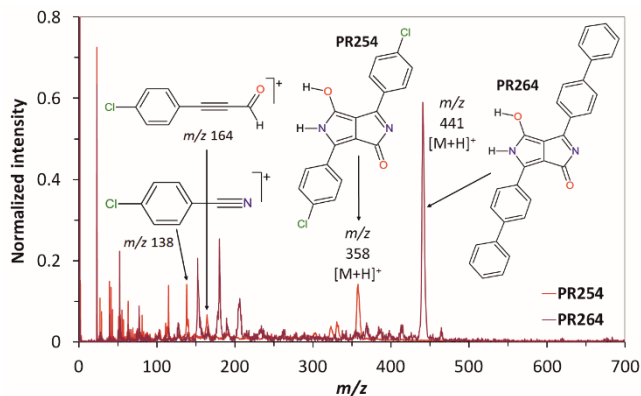


Figure 7. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of the red diketopyrrolo-pyrrole pigment powders PR254 and PR264 measured on indium

Analysis of Pure Alkyd and Acrylic Binders

Alkyd resins used as binders in commercial paints are condensation polymers of polyhydric alcohols, polybasic acids and unsaturated fatty acids³³. The mass spectrum of the alkyd binder Alkyd resin medium 4 is presented in Figure 8. In the lower mass region a series of hydrocarbon fragment ions, such as m/z 43 [C_3H_7]⁺, m/z 55 [C_4H_7]⁺, 57 [C_4H_9]⁺, and m/z 77 [C_6H_5]⁺ were detected. [$\text{C}_5\text{H}_7\text{O}$]⁺ ion fragment at m/z 83 is probably originating from pentaerythritol³³, the alcohol part of the alkyd resin. As reported in the literature³³, the results of the Py-GC/MS measurements of the same product showed the presence of azelaic (2C9:0), palmitic (C16:0), oleic (C18:1), linoleic (C18:2), and stearic (C18:0) acids. Peaks of the phthalic anhydride at m/z 148, and singly protonated phthalic anhydride at m/z 149, were detected. The fragment ion at m/z 105, due to the loss of CO_2 from the protonated phthalic anhydride, was also detected and is dominating the spectrum. Peaks at m/z 73, 147, 206, 221 and 281 indicate the presence of PDMS contaminant²³ (polydimethylsiloxane, a polymer present in the carbon tape that is usually used for sample mounting in the laboratory, indicating possible cross contamination of the sample).

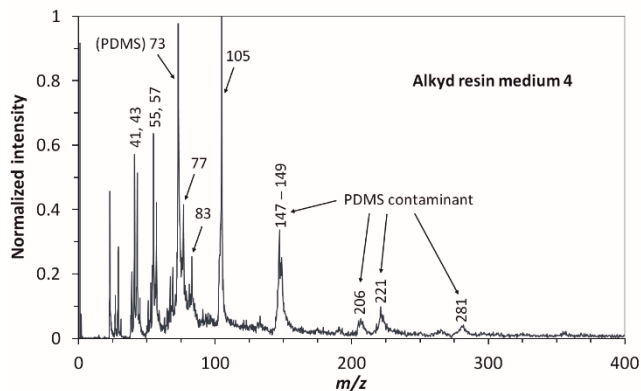


Figure 8. MeV-SIMS spectrum (5 MeV Si^{4+} , positive ion mode) of alkyd binder Alkyd resin medium 4 (LUKAS) measured on indium

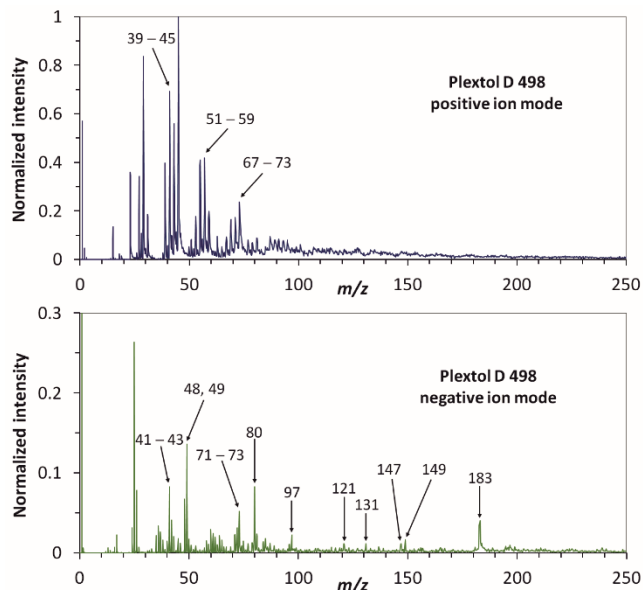


Figure 9. MeV-SIMS spectra (5 MeV Si^{4+}) of pure acrylic binder Plextol D 498 in positive (top) and negative (bottom) ion mode measured on indium

As reported by Pintus and Schreiner⁴⁶ with Py-GC/MS, the acrylic binder Plextol D 498 is a co-emulsion of poly(butyl acrylate/methyl methacrylate), a p(nBA/MMA) copolymer that most of today's acrylic emulsion paints are based on. In the MeV-SIMS spectrum of the pure Plextol D 498 molecular ions of MMA (m/z 100) and nBA (m/z 128) monomers were detected only with very low intensities in the positive ion mode. Therefore, we applied also the negative ion mode where m/z 73, 80, 97, 121, 131, 147, 149, and 183 were detected. Spectra obtained in positive and negative ion modes with 5 MeV Si^{4+} ion beam are presented in Figure 9.

Identification of SOPs in the Commercial Tube Paints

The obtained MeV-SIMS results on the commercial tube paints (alkyd and acrylic) are summarized in Table S-3 of the SI. In order to avoid repetitive presentation of the results, the spectra of two-component mock-ups are not shown. The two-component mock-ups were analyzed only for comparison purposes and are mentioned here when necessary.

For the four selected commercial alkyd paints (PB15, PG7, PY3 and PV19) the SOPs' characteristic peaks could be identified in all MeV-SIMS spectra. These signals had significantly lower intensities when compared to the pure pigments' spectra and were in good agreement with those obtained for two-component mock-ups. An example of a real sample mass spectrum is presented in Figure 10 for the W&N Phthalo Blue alkyd paint. Due to the m/z 576 and 609 molecular peaks, the chlorine containing PB15:1 could be identified in the commercial product labeled only as PB15. Confirming results were obtained with Raman spectroscopy on the same sample by Anghelone et al.⁴⁷. On the other hand, in the PG7 containing paints, the molecular and fragment ions at m/z values around 1000 were not detected, both in commercial and two-component mock-up samples. This may be a result of low pigment concentrations in the samples, especially in the commercial tube paint, in combination with lower sensitivity for masses larger than 1000 amu. Additionally, the binder can act as a blocking agent when mixed with the pigment and consequently decrease the ionization yield. The alkyd specific peaks were clearly identified in all the alkyd paints mass spectra

at m/z 43, 55, 57, 83, 105 and 148/149 but the presence of PDMS contaminant was also detected in some cases at m/z 73, 147, 206, 221 and 281. This could be expected since the samples were prepared in the same working environment as in other experiments done at the same beamline, where carbon tape is commonly used, indicating that delicate sample handling is necessary to prevent any cross-contamination.

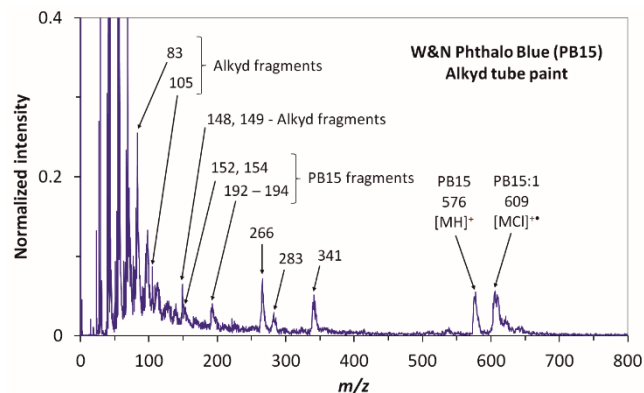


Figure 10. MeV-SIMS spectrum (5 MeV Si^{4+} , positive ion mode) of W&N alkyd tube paint “Phthalo Blue” with PB15 measured on indium

The SOPs’ characteristic peaks in the mass spectra of the investigated commercial acrylic tube paints analyzed by MeV-SIMS are also presented in Table S-3 of the SI. The molecular ions and characteristic fragments were detected for all analyzed paints (except for PG7 containing sample, as mentioned above), again with significantly lower intensities than in pure pigment spectra. An example of mass spectra of W&N acrylic tube paints with PR254 and PR255 is given in Figure 11. The same decrease in intensities of the characteristic peaks was observed for the two-component mock-ups, especially for the already mentioned PG7 pigment, indicating that the sensitivity of the present set up could be modified to meet the needs of molecular identification of SOPs with higher molecular weights and at concentrations available in commercial paints. In the low mass region of the mass spectra the characteristic peaks of the acrylic binder (m/z 39–45, 51–59, 67–73) were detected in all spectra (in positive ion mode) with high intensities.

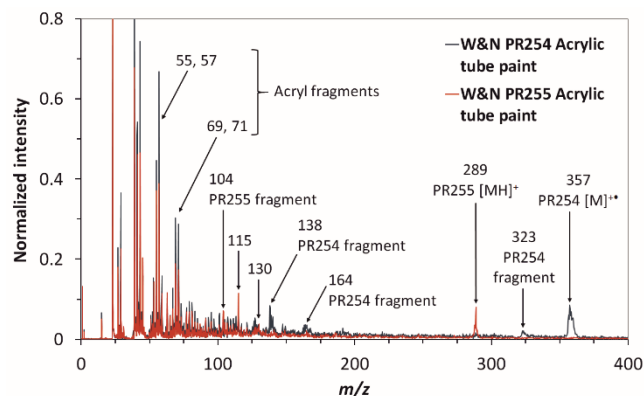


Figure 11. MeV-SIMS spectra (5 MeV Si^{4+} , positive ion mode) of W&N acrylic tube paints “Pyrrole Red” with PR254 and “Pyrrole Red Light” with PR255 measured on indium

CONCLUSION

This work presents the first reference MeV-SIMS spectra of 17 synthetic organic pigments (SOPs) and two types of binders, alkyd and acrylic, which are usually found in modern and contemporary art paints. All measurements were carried out in

positive ion mode, except in the analysis of pure acrylic binder, where negative ion mode proved to be more efficient. The results show that MeV-SIMS is a straightforward technique for the identification and characterization of SOPs in pigment powder form, as well as in self-made or in commercially available paints. Molecular ions (in some cases protonated and/or deprotonated) and larger fragment ions were detected for all investigated pigments, thus enabling a simple interpretation of the mass spectra. Additionally, no sample preparation or treatment was necessary before the measurements, nor was the sample consumed during the analysis. Spectra collection time was short as well, up to 500 s per spectrum. A clear identification and differentiation of SOPs was possible by this technique, including some polymorphic analogues (PB15:1 and PB15:3/PB15:6). The suitability of MeV-SIMS for identification of SOPs in the selected alkyd and acrylic commercial tube paints was also evaluated, showing that these pigments and binding media can be unambiguously identified in a single mass spectrum. With the current MeV-SIMS sensitivity and the concentrations of SOPs in commercial paints, the molecular ion peaks of molecular weights higher than 1000 amu could not be detected. Overall, we have shown that MeV-SIMS is a powerful technique in confirmation of SOPs molecular structure and that it could be used in combination or as an addition to other analytical tools in the field of cultural heritage, e.g. Py-GC/MS, DTMS or Raman spectroscopy, especially when sample preservation for complementary measurements is desired (e.g. for multi-elemental analysis by other ion beam analysis (IBA) techniques, such as particle-induced X-ray emission (PIXE)), or when small sample sizes are available for analysis.

ASSOCIATED CONTENT

Supporting Information

Supplementary Material Available: A listing of Tables containing MeV-SIMS spectral data/characterization of the analyzed SOPs (5 pages) is available as Supporting Information. Current ordering information is found on any masthead page.

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Notes

The authors declare no competing financial interest.

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Samples pressed
into pure indium

No chemical
treatment

