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Identification and imaging of modern paints using Secondary Ion Mass Spectrometry with MeV ions

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Abstract

Secondary Ion Mass Spectrometry using MeV ion excitation was applied to analyse modern paint materials containing synthetic organic pigments and binders. It was demonstrated that synthetic organic pigments and binder components with molecular masses in the m/z range from 1 to 1200 could be identified in different paint samples with a high efficiency and in a single measurement. Different ways of mounting of mostly insulating paint samples were tested prior to the analysis in order to achieve the highest possible yield of pigment main molecular ions. As Time-of-Flight mass spectrometer for MeV Secondary Ion Mass Spectrometry is attached to the heavy ion microprobe, molecular imaging on cross-sections of small paint fragments was performed using focused ions. Due to the fact that molecules are extracted from the uppermost layer of the sample and to avoid surface contamination, the paint samples were not embedded in

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6 of cultural heritage.

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9 *Keywords:* MeV-SIMS, synthetic organic pigments, modern paints, heavy ion microprobe,
10 molecular imaging
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12 13 14 **1. Introduction** 15

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18 Due to the development of the modern industry in the 20th century a large variety of Synthetic
19 Organic Pigments (SOPs) and polymers was produced. Some of the polymers started to be used
20 as new binding media by the artists in the modern and contemporary art [1]. Nowadays synthetic
21 organic polymers are widely used binding media in artistic object, especially acrylic, vinyl and
22 alkyds. Whereas a huge amount of research is continuously focused on the investigations of art
23 objects from the earlier centuries, some researchers have moved recently their interest toward
24 studying of art works from the second half of the 20th century. Those studies are important to gain
25 information about the durability, usability and stability of modern paint materials [2].
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30 Ion Beam Analysis (IBA) techniques are often used for studying cultural heritage objects [3-5]
31 and among them Particle Induced X-ray Emission (PIXE) has been established as the most often
32 used one [6-8]. However, PIXE, as well as the standard IBA techniques do not give any
33 information about the molecular composition of the sample, which is important to distinguish
34 among different SOPs showing very similar molecular structures and polymers used as binders in
35 the modern paint materials. SOPs are typically studied with methods like Gas Chromatography
36 Mass Spectrometry (GC/MS), Pyrolysis-GC/MS, Fourier Transform Infrared (FTIR)
37 spectroscopy, Raman spectroscopy, Nuclear Magnetic Resonance (NMR), etc. [9-15]. Although
38 GC/MS and Py-GC/MS are the most important analytical techniques for routine analysis of
39 organic materials, both methods are based on separation of the mixture compounds before their
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4 identification with MS. In the case that polar compounds have to be identified even a chemical
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6 derivatization of the sample has to be done before the analysis [16,17]. FTIR and Raman
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8 spectroscopy that are today widely used for the identification of chemical compounds in artworks
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10 mainly due to the possibility of using portable instruments [18] are limited in determination of
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12 components in complex mixtures due to the overlapping bands in the measured spectra or due to
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14 the low concentrations of SOPs in the paints. Thus, sometimes only the class of the material can
15
16 be identified and not the exact molecular composition itself. Time-of-flight Secondary Ion Mass
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18 Spectrometry with keV ions (keV-ToF-SIMS) [19] is established in the cultural heritage for
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20 many years. It specifies the organic or inorganic surface composition with high spatial and mass
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22 resolution and has already been applied to the analysis of paints containing oil or tempera binders
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24 and traditional pigments [20-24]. Inspired by the progress of its keV energy primary ion
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26 counterpart, heavy MeV ion desorption [25,26] came back into the focus this time under a new
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28 name – MeV-SIMS [27-30]. The main difference between the two methods comes from the
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30 different interaction mechanism that keV and MeV ions have with the sample surface. In case of
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32 keV-SIMS, secondary molecular ions are ejected from the sample surface due to the dominant
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34 nuclear sputtering (collision cascade), while ejection of secondary molecular ions with MeV
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36 primary ions is a consequence of electronic sputtering mechanism that dominates the MeV ion
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38 energy deposition process and causes desorption of intact large secondary molecular ions. Several
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40 orders of magnitude larger yields as well as less fragmentation are expected for larger molecular
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42 masses when MeV ions are used for the excitation [30].
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53 Here we will demonstrate that the SIMS technique that employs MeV heavy ion excitation can
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55 be a method of choice for the identification of SOPs used in modern art objects. In the present
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57 work MeV-SIMS was applied for the identification of SOPs in the surface layer of the paints as
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59 well as for molecular imaging of pigments in the layered paint samples (non-embedded paint
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4 cross-sections). In order to show that very good results can be achieved even for the identification
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6 of very similar SOPs in the paints, paints containing characteristic phthalocyanine pigments such
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8 as copper phthalocyanine blue, Pigment Blue PB15:1 and PB15:3 (two different polymorphs),
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10 metal-free phthalocyanine PB16, and chlorinated copper phthalocyanine green Pigment Green
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12 PG7 were selected. To show the influence of different methods of mounting on the MeV-SIMS
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14 spectra, the red paint containing a red organic pigment belonging to the Naphthol AS class,
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16 Pigment Red PR112 is chosen.
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23 24 **2. Experimental**

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27 All measurements were performed in a high vacuum ($10^{-6} - 10^{-7}$ mbar) using MeV-SIMS setup
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29 with a Time-of-Flight (TOF) spectrometer at the RBI heavy ion microprobe, which is described
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31 in detail in Tadić et al. [31]. For the analysis of paint materials, focused 5 and 8 MeV Si ions
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33 were used. The typical beam lateral resolution was about $5 \times 5 \mu\text{m}^2$. Beam was scanned over
34
35 different sample areas (from $100 \times 100 \mu\text{m}^2$ for the identification of pigments to $1200 \times 1200 \mu\text{m}^2$
36
37 for the imaging of paint cross sections). The beam current in the pulsed mode was ~ 0.2 fA.
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39 Secondary molecular ions were steered towards the TOF by the +5 kV voltage applied to the
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41 sample holder. Multi-Stop TDC Data Acquisition System in the heavy ion deflection start mode
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43 was used with the 100 μs time between two heavy ion pulses (duration of 4 ns). All experimental
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45 parameters and data acquisition were controlled with the SPECTOR software [31,32].
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52 As this is the first application of the MeV-SIMS in the field of cultural heritage, the analyses
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54 were first carried out on the paints that were systematically prepared at the Institute of Science
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56 and Technology in Art, at the Academy of Fine Arts. For self-made paints different
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58 phthalocyanine blue (PB15:1, PB15:3 and PB16) phthalocyanine green (PG7) and Naphthol AS
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4 red (PR112) pigment powders were mixed with alkyd binder in order to get pasty consistence of
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6 the paint. These paints were then casted onto microscope glass slides with approximately 150 μm
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8 thick coating and dried for 2 weeks. All pigments were provided by Kremer Pigmente (Germany)
9
10 and the alkyd binder was Alkyd resin medium 4, a product of LUKAS (Germany). For the
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12 analysis, a small surface fragment from each sample was taken and put either on the conductive
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14 carbon tape or pressed directly into the pure indium metal surface. For reference spectra (not
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16 shown), all pigment powders were also prepared by pressing the pigment powder into pure In
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18 metal surface.
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24 To test imaging capabilities of our MeV-SIMS setup, two samples were used. First, self-made
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26 sample with two phthalocyanine blue pigments in alkyd binder was prepared on the glass slide.
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28 Therefore a layer of the alkyd paint containing PB15:1 was painted over the alkyd paint
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30 containing PB15:3. A cross-section was prepared by just cutting the sample and fixing it together
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32 with the glass between two In sheets. Thereafter a cross-section of the paint sample from the
33
34 outdoor sculpture “Plavi cvijet”(2000), made by Vjenceslav Richter (1917 – 2002) and belonging
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36 to the “Richter collection” from the Museum of Contemporary Art in Zagreb was measured. To
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38 prepare the cross-section, a paint flake was cut with a scalpel and fixed between two In plates. No
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40 embedding procedure of the samples in polymer resin was used in this study due to the fact that
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42 embedding and polishing is contaminating the surface layer of the sample and the scattering
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44 chamber was not equipped with an Ar gun, which is normally used in SIMS for cleaning surface
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46 contamination.
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3. Results and discussion

3.1. Different sample mountings

As MeV-SIMS has not been applied before for the analysis of modern paint samples it was important to determine the best possible mounting procedure for the pigment/paint samples. According to the present instrument setup, positive secondary molecular ions were extracted from the sample kept at +5 kV using an acceleration potential difference between the sample surface and a grounded extractor. Therefore it was not possible to use directly pigments/paints casted on the insulating glass slides due to the fact that homogeneous extraction electric field as well as no sample charging cannot be ensured. First small paint fragments were put onto conductive carbon tape attached to the Si wafer. This way of mounting did not work well for all analysed paints with pigments from different pigment classes, especially for paints with red pigments where no high mass peaks were observed in the mass spectrum. A further problem found in the spectra collected from the samples mounted on the carbon tape was that in all spectra peaks characteristic for PDMS (polydimethylsiloxane) were detected. PDMS is a well-known surface contaminant coming from the carbon tape glue (which was clearly visible in the mass spectrum from C tape, not shown here). Therefore, another sample mounting procedure was used which consisted of pressing the very small sample fragment into the pure indium metal. First, pure indium (99.9% Alpha Aesar indium shot, tear drop) was pressed to obtain flat surface and then a paint fragment was gently pushed into it with a help of a flat and clean aluminium plate. Using this method a good extraction field was ensured for the secondary molecular ions of all classes of pigments analysed and no PDMS contamination was present in the spectra.

Fig. 1 shows mass spectra of the same alkyd paint with PR112 (Naphthol AS, $[M+H]^+$ at m/z 484.0) mounted on the carbon tape (black) and on indium (red). From the figure it can be seen

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4 that for the sample mounted on indium the main peak at m/z 484.0 and the fragment ions at m/z
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6 378.0 and 106.1, which are characteristic for this pigment, are clearly seen compared to the
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8 sample fixed on the Si wafer with carbon tape where those peaks are not seen at all. The peaks at
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10 m/z 105.0 and 149.0 are fragments from the alkyd binder. Also for the sample mounted on C
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12 tape, PDMS peaks with m/z 147, 207, 221, 281 were detected which are not present in the case
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14 when the sample is mounted directly on In. This clearly indicates that handling and mounting of
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16 samples is crucial for extracting intact molecular ions from the sample surface.
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24 **3.2. Identification of SOPs in paints**

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27 In Fig.2 the MeV-SIMS spectra (m/z range between 100 and 700) for three different blue
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29 phthalocyanine pigments in alkyd paint were presented. PB16 is metal-free phthalocyanine
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31 showing the main molecular peak $[M]^+$ at m/z 514.2 and a fragment ion $[C_8H_5N_2]^+$ at m/z 129.0
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33 (black line). Both, PB15:3 and PB15:1 are copper containing (Cu-Pc's) phthalocyanine pigments,
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35 showing the main molecular peaks $[M]^+$ at m/z 575.1 (blue and red line). As PB15:1 is chlorine
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37 stabilized PB15 pigment which contains 0.5-1 Cl atoms per molecule[1], PB15:1 has an
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39 additional $[M]^+$ at m/z 609.0 (molecule is containing 1 Cl atom) compared to PB15:3. The mass
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41 difference between two peaks is 34 not 35 due to the fact that when molecule is containing Cl, 1
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43 H from the phthalocyanine ring is substituted by Cl. This feature can be used to distinguish the
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45 PB15:3 from chlorine stabilized PB15:1. Learner [9] reported also the presence of chlorine
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47 stabilized blue Cu-phthalocyanine in some artistic paints. Additionally, in both paints,
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49 phthalocyanine (Pc) fragment ion $[C_8H_5CuN_2]^+$ at m/z 192.0 (red line) belonging to PB15:3 and
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51 PB15:1 is clearly seen.
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4 The alkyd binder used in this study is an orthophthalic based alkyd, the polyalcohol part is
5 pentaerythritol (not glycerol). This is confirmed by Py-GC/MS measurements of the samples
6 reported here. Further peaks shown in the Fig.2 are corresponding to the protonated phthalic
7 anhydride at m/z 149.0 and the fragment ion at m/z 105.0 resulting from the loss of CO_2 from
8 protonated phthalic anhydride, which is a mass signature of this alkyd binder type. This
9 demonstrates that pigments as well as binder can be identified in a single spectrum in only one
10 measurement. A great advantage of the MeV-SIMS over other mass spectrometry techniques
11 used for the identification of SOPs in paints, such as Py-GC/MS, is that the molecular ion peak
12 and larger fragment ions are obtained, enabling a straightforward identification without
13 consuming or destroying the sample during analysis and without any chemical sample treatment
14 step priory to the analysis. Thus samples still remain for analyses with complementary methods.
15 As already mentioned, Raman and FTIR analyses with the possibility to be employed in a non-
16 invasive way are often limited by paint matrix (e.g. paint mixtures, low pigment concentrations),
17 making exact identification or distinguishing between PB15:3 and chlorinated PB15:1 pigments
18 in paints not always possible.
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43 As demonstrated in Fig.3, mass spectra for PG7 pigment powder, phthalocyanine green, with
44 main molecular peak $[\text{M}]^+$ at m/z 1127.2, (depending on chlorination, in this case it is fully
45 chlorinated PG7 with 16 Cl) obtained using 5 MeV Si^{4+} ions, collection time $t=173$ s and ion
46 current $I=0.16$ fA. Main molecular peak $[\text{M}]^+$ as well as several peaks corresponding to the lower
47 numbers of Cl atoms per molecule can be clearly seen. This proves that pigments with masses
48 above m/z 1000 can be also detected through main molecular peaks in short collection time and
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4 with very low ion currents which can be important when sample damage by ion beam should be
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6 avoided.
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11 Summarised, the big advantages of the MeV-SIMS can be clearly pointed out: MeV-SIMS
12 gives the exact identification of the synthetic organic pigments (SOPs) in paints. The alkyd
13 binder is identified as well in the same spectrum, meaning in only one analysis. Usually, to get
14 comparable information multi-analytical approach is used such as Raman spectroscopy, applied
15 to identify SOPs, and FTIR for the identification of the binders in the paints. In many cases also
16 additional Py-GC/MS or different MS based measurements (e.g. DTMS, Direct Temperature-
17 Resolved Mass spectrometry [33]) are necessary to provide exact identification of SOPs.
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30 ***3.3. Imaging of paint cross sections*** 31

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33 In many cases it is of great importance when analysing paint samples from art objects to see
34 how the detected pigments and/or binders are distributed in different layers of the paint. This can
35 give information about painting technology, which can further support dating of the objects or
36 support the conservators in their work on objects.
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43 To test ability of the method for molecular imaging in different paint layers, two-layered paint
44 with two phthalocyanine blue pigments in alkyd binder was used (PB15:1 and PB15:3 containing
45 paint on microscope glass slide). In Fig. 4 the sample is turned through 90 degrees, thus the
46 PB15:1 containing paint is shown on the left side of the images, followed by the PB15:3
47 containing paint on the right). Mass m/z at 575.1 as described earlier, which is characteristic peak
48 for both, PB15:1 and PB15:3 is clearly distributed in both paint layers. The difference between
49 this two pigments is due to peak at m/z at 609.0 attributed to Cl stabilized PB15:1 and this peak is
50 clearly present only in left layer, where PB15:1 is mixed with alkyd. Resulting maps are showing
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4 a) overlay of three signals coming from alkyd (red, m/z 105.0), PB15:1 and PB15:3 (blue, 575.1),
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6 and PB15:1 (green, m/z 609.0), b) m/z 105.0 (alkyd), c) m/z 575.1, and d) m/z 609.0. Total
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8 scanned area is 1.2×1.1 mm². For the measurements 8 MeV Si⁴⁺ ions were used (detection in
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10 positive ion mode).
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15 The next example in Fig. 5 presents the application of MeV-SIMS for the identification of
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17 synthetic organic pigments in the real sample taken from the outdoor sculpture “Plavi cvijet”
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19 (2000). The sample shows dark blue colour and is analysed on the front side, which was exposed
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21 to the environmental conditions. As can be seen, the blue phthalocyanine pigment PB15:3 (m/z
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23 575.1) and the weak signal from the pigment violet PV23 (m/z 589.5) was detected by MeV-
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25 SIMS as well as the alkyd binder in the paint (peaks at m/z 105 and 149). It is important to
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27 mention that sample was not treated or cleaned in any way and therefore signals from both
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29 pigments PB15:3 and PV23 were probably weak due to fact that surface of the sample was
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31 exposed to the environmental conditions and that MeV SIMS is detecting molecules from the
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33 uppermost layer of the sample.
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39 To confirm existence of both pigments PB15:3 and PV23 as well as to see their depth
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41 distribution, cross-section was prepared by cutting the sample by scalpel and fixing freshly
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43 prepared cross section between two In sheets without any polishing. Fig. 6 shows 2D maps of
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45 selected mass peaks obtained on cross section from the sample “Plavi cvijet”. Surface of the
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47 sample is on the right side. Total scanned area was 175µm×145µm. For the measurements 8 MeV
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49 Si⁴⁺ ions were used. Fig. 6 shows: a) overlay of three signals corresponding to alkyd (red),
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51 PB15:3 (blue) ,and PV23 (green), b) single map for alkyd m/z 105.0, c) single map for PB15:3
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53 m/z 575.1, and d) single map for PV23 m/z 589.5. As obtained in Fig. 6, both pigments are
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55 distributed in the whole analysed area of the dark blue paint layer and no layered structure was
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4 found. It seems that measured area on the right of the image is slightly richer in the binder, which
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6 is most probably due to the inhomogeneous extraction field caused by the sample surface
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8 morphology (sample was not polished).
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10 11 12 13 14 **4. Conclusions**

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18 The present work describes the first application of the MeV-SIMS method for cultural heritage
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20 studies, namely for the identification of SOPs and binders in modern and contemporary paint. We
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22 have shown that different SOPs could be easily identified together with the alkyd binder in a
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24 single measurement. We have also demonstrated that with MeV-SIMS and a focused heavy ion
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26 beam, molecular imaging at the micrometer level can be achieved. Using molecular ions and
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28 large fragments of blue phthalocyanine pigments showing similar molecular structure can be
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30 quickly distinguished between each other in paint layers. Further, different SOPs were identified
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32 in a real sample from an outdoor sculpture, even though such samples usually show much more
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34 stronger ageing than paintings usually shown in museums.
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40 MeV-SIMS presents very promising features important for the study of cultural heritage such
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42 as: high molecular yields for intact high mass secondary molecular ions obtained with currents
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44 three orders of magnitude lower than the ones used for other microprobe IBA techniques
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46 (important for valuable and sensitive cultural heritage samples) and short measurement time.
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48 Furthermore, this type of MeV-SIMS with a ToF spectrometer could be introduced at low cost in
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50 any heavy ion IBA setup. Thus, MeV-SIMS investigations of modern and contemporary
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52 paintings can be added as a new application field for accelerator based analytical techniques.
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23 Schreiner.
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4 Figure Caption:
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8 Fig. 1. Comparison of the MeV-SIMS mass spectra of the alkyd paint containing red pigment
9 PR112 mounted on carbon tape (black) and pressed into indium (red). Both measurements were
10 done using 5 MeV Si⁴⁺ ions in a positive ion mode.
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15 Fig. 2. MeV-SIMS spectra of self-made paints containing different blue phthalocyanine pigments
16 in the alkyd binder measured with 5 MeV Si⁴⁺, positive ion mode. Main molecular peaks of the
17 metal-free (PB16, black line), metal-containing (PB15:3, blue line) and chlorine stabilized metal-
18 containing (PB15:1, red line) pigments are clearly separated. Alkyd binder is identified through
19 peaks at m/z 149.0 and 105.0.
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26 Fig. 3. MeV-SIMS spectra for PG7 (phthalocyanine green) obtained using 5 MeV Si⁴⁺ ions in a
27 positive ion mode, collection time t=173 s and ion current I=0.16 fA. Main molecular peak at m/z
28 1127.2 as well as several peaks corresponding to the lower numbers of Cl atoms per molecule can
29 be clearly seen.
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37 Fig. 4. 2D-molecular maps taken on the cross-section of the alkyd paint containing PB15:1 (layer
38 on the left side) painted over the layer of alkyd paint containing PB 15:3 (right side). a) Overlay
39 of three signals coming from alkyd (red), PB15:1+PB15:3 (blue) and PB15:1 (green), b) m/z
40 105.0, c) m/z 575.1 and d) m/z 609.0. Scan size is 1.2×1.1 mm².
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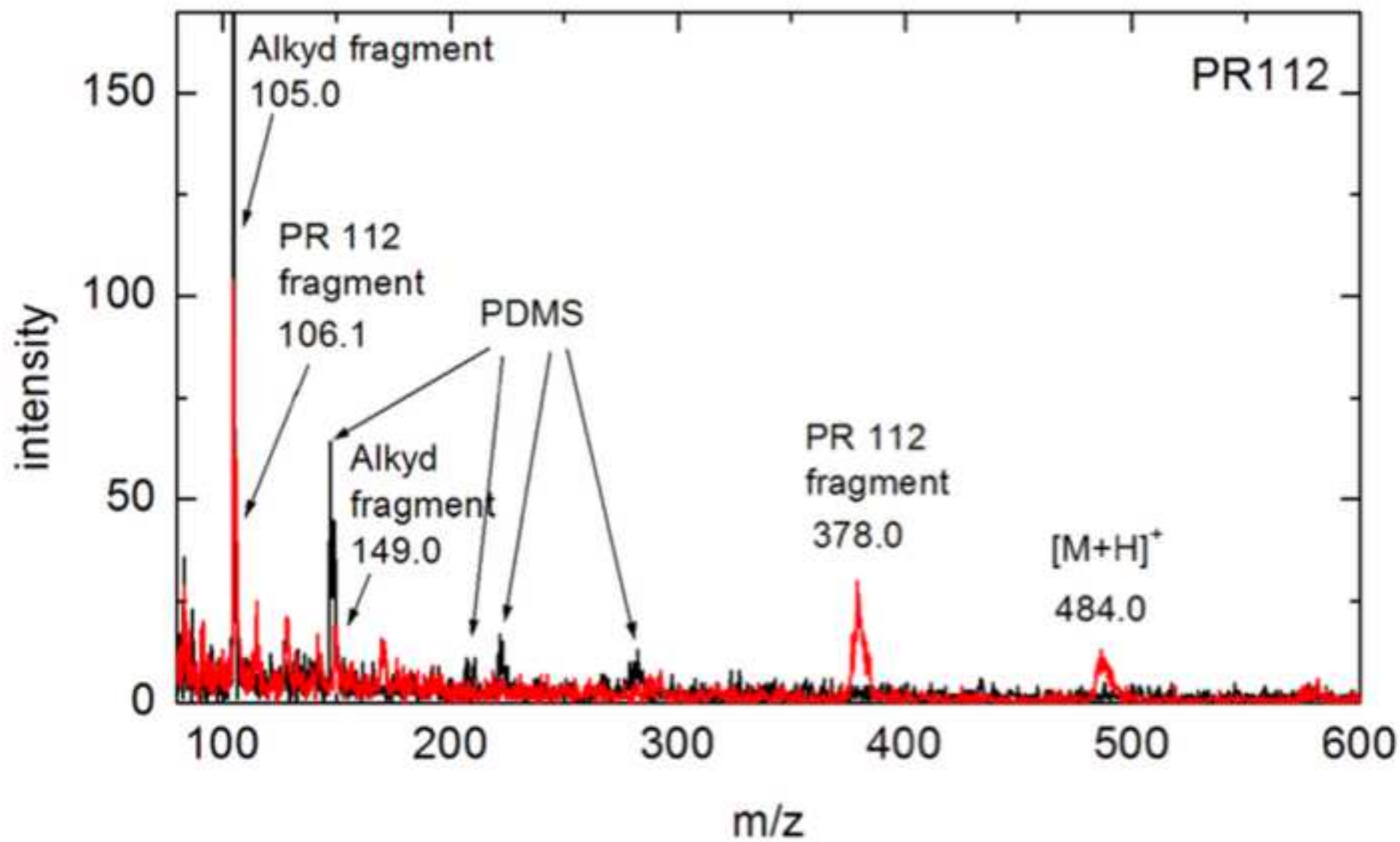
46 Fig. 5. MeV-SIMS spectrum taken from the front side of the dark blue sample “Plavi cvijet”
47 (2000). 5 MeV Si⁴⁺ ions, detection in positive ion mode.
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54 Fig. 6. 2D-molecular maps of the cross-section of the sample “Plavi cvijet” (2000): a) overlay of
55 alkyd signal (red), PB15:3 (blue), and PV23 (green), b) single map of alkyd signal, c) signal map
56 of PB15:3 signal and d) single map of PV23 corresponding signal. Surface of the sample is on the
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right. Total scanned area is 175 μm x 145 μm . For the measurements 8 MeV Si^{4+} ions were used, detection in positive ion mode.

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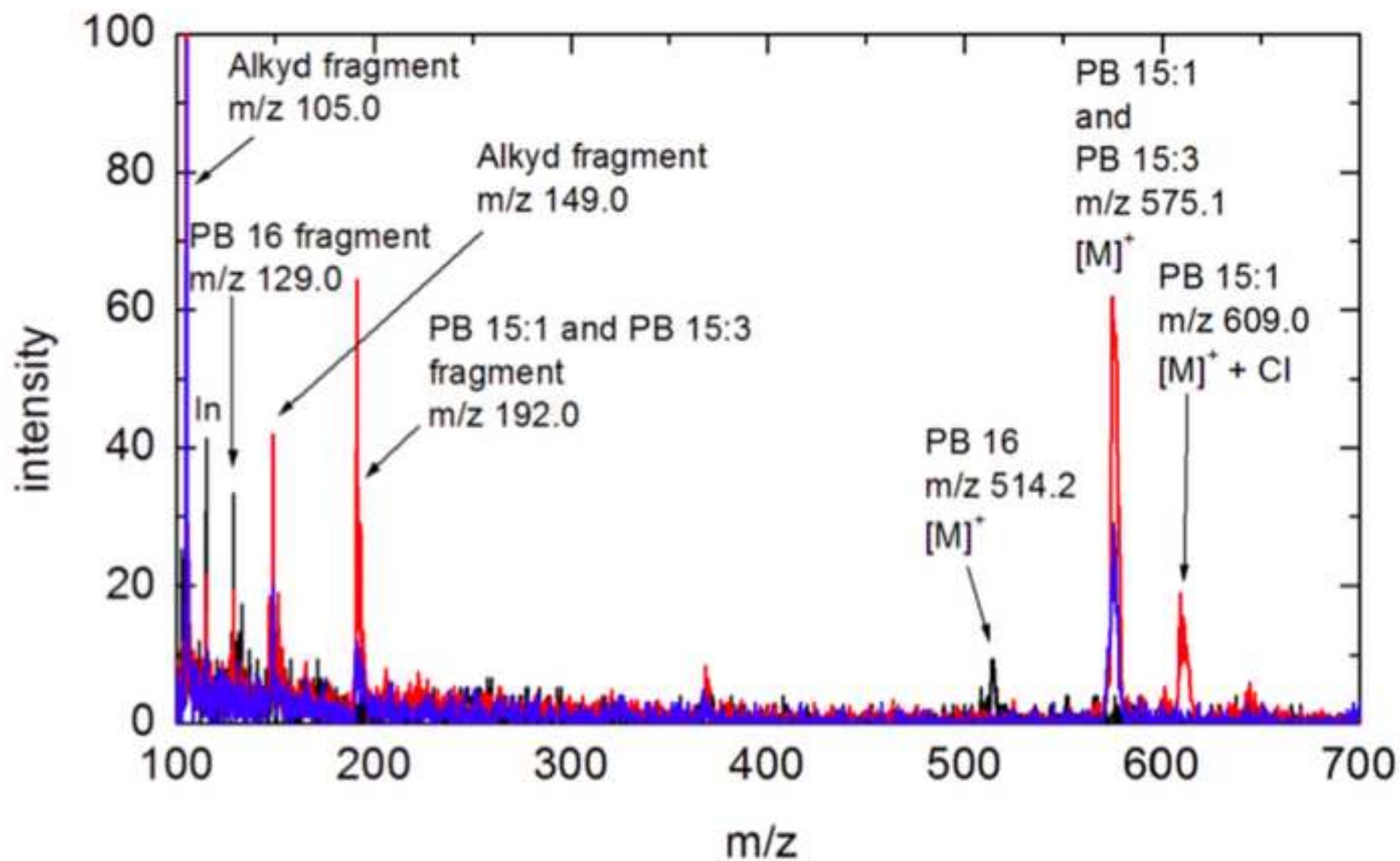
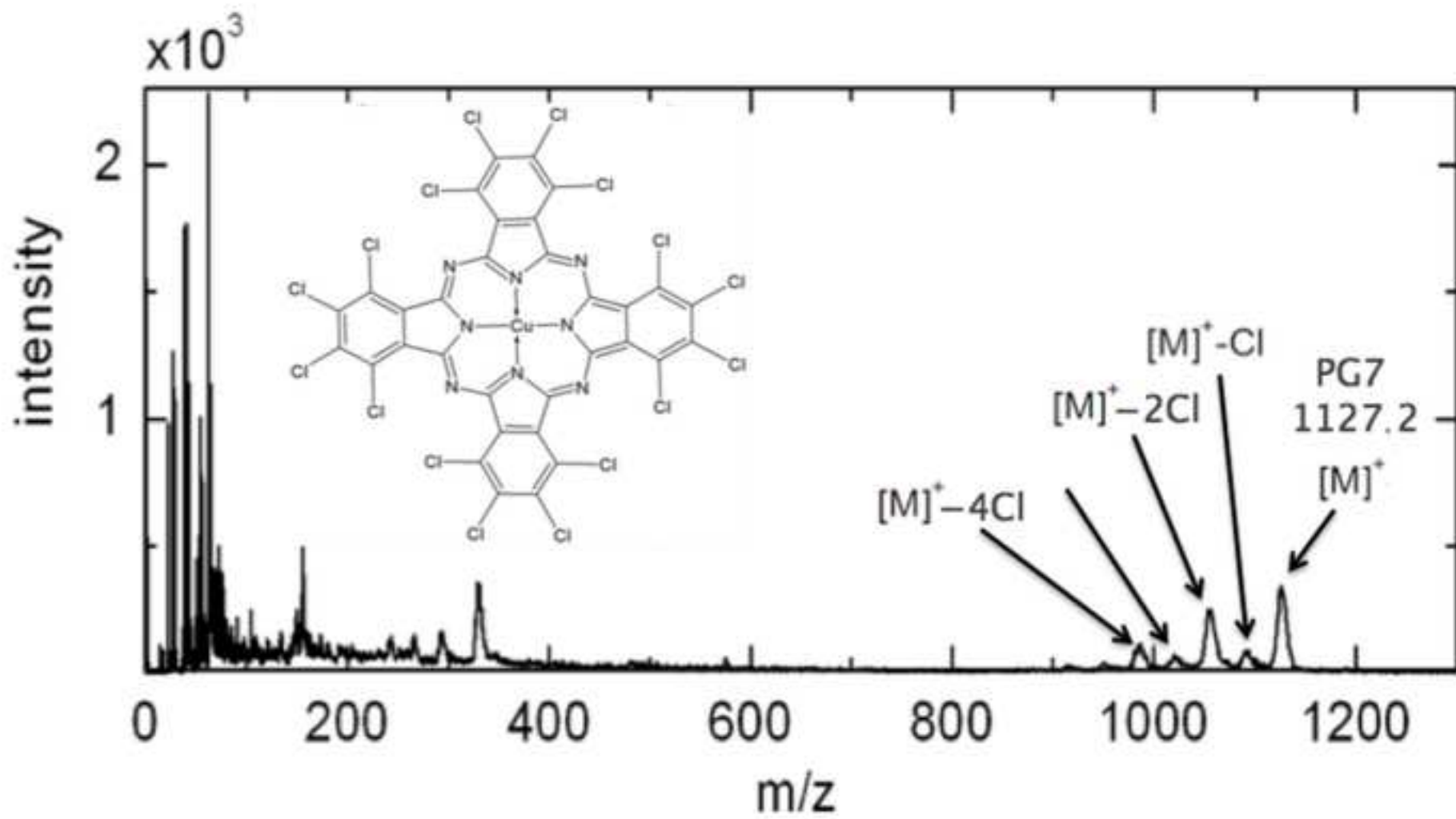
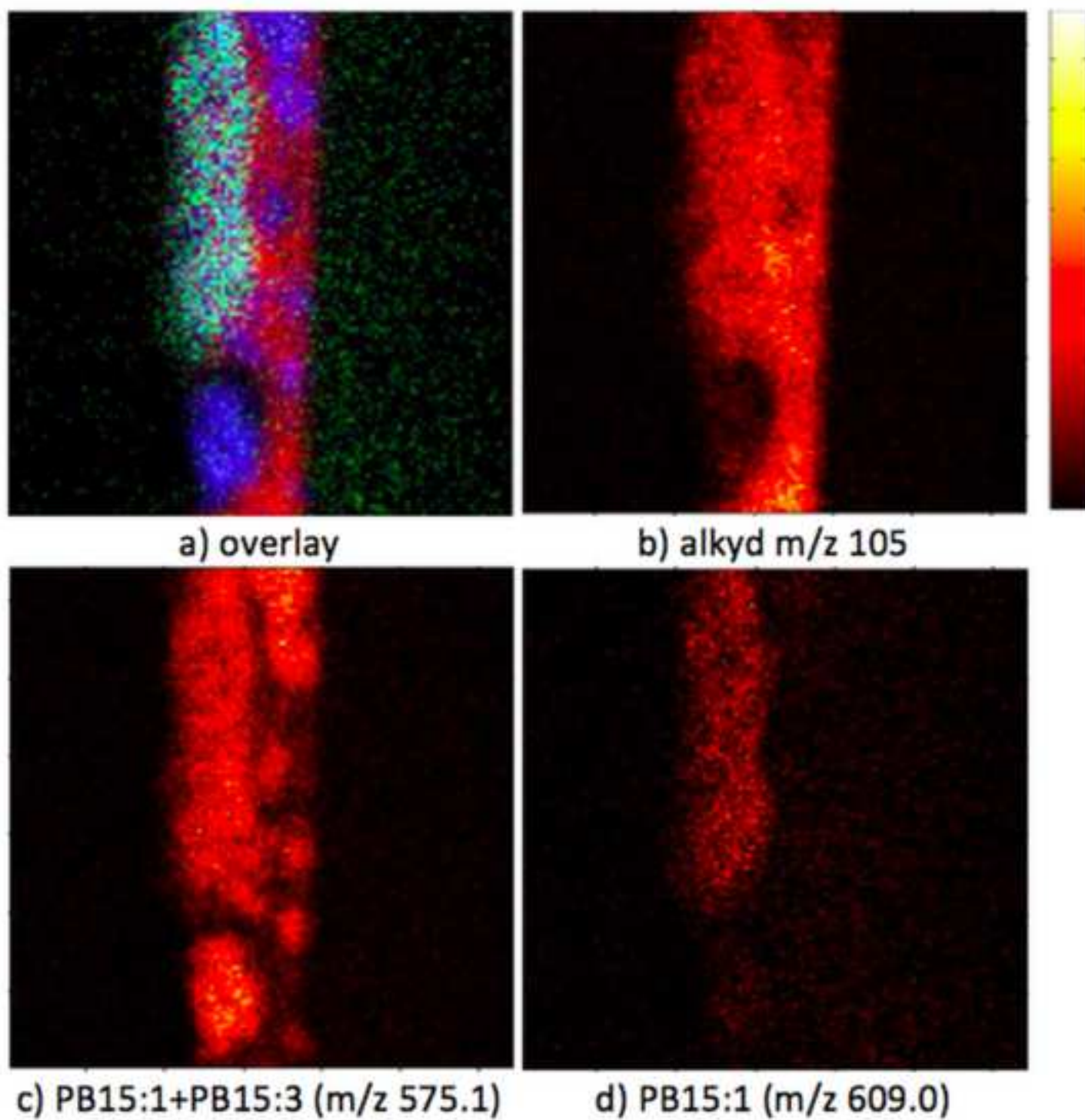


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