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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 the resin as is usually done when imaging of paint samples using different techniques in the field of cultural heritage.

1. Introduction

Due to the development of the modern industry in the 20th century a large variety of Synthetic Organic Pigments (SOPs) and polymers was produced. Some of the polymers started to be used as new binding media by the artists in the modern and contemporary art [1]. Nowadays synthetic organic polymers are widely used binding media in artistic object, especially acrylic, vinyl and alkyds. Whereas a huge amount of research is continuously focused on the investigations of art objects from the earlier centuries, some researchers have moved recently their interest toward studying of art works from the second half of the 20th century. Those studies are important to gain information about the durability, usability and stability of modern paint materials [2].

Ion Beam Analysis (IBA) techniques are often used for studying cultural heritage objects [3–5] and among them Particle Induced X-ray Emission (PIXE) has been established as the most often used one [6–8]. However, PIXE, as well as the standard IBA techniques do not give any information about the molecular composition of the sample, which is important to distinguish among different SOPs showing very similar molecular structures and polymers used as binders in the modern paint materials. SOPs are typically studied with methods like Gas Chromatography Mass Spectrometry (GC/MS), Pyrolysis-GC/MS, Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy, Nuclear Magnetic Resonance (NMR), etc. [9–15]. Although GC/MS and Py-GC/MS are the most important analytical techniques for routine analysis of organic materials, both methods are based on separation of the mixture compounds before their identification with MS. In the case that polar compounds have to be identified even a chemical derivatization of the sample has to be done before the analysis [16,17]. FTIR and Raman spectroscopy that are today widely used for the identification of chemical compounds in artworks mainly due to the possibility of using portable instruments [18] are limited in determination of components in complex mixtures due to the overlapping bands in the measured spectra or due to the low concentrations of SOPs in the paints. Thus, sometimes only the class of the material can be identified and not the exact molecular composition itself. Time-of-flight Secondary Ion Mass Spectrometry with keV ions (keV-ToF-SIMS) [19] is established in the cultural heritage for many years. It specifies the organic or inorganic surface composition with high spatial and mass resolution and has already been applied to the analysis of paints containing oil or tempera binders and traditional pigments [20–24]. Inspired by the progress of its

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keV energy primary ion counterpart, heavy MeV ion desorption [25,26] came back into the focus this time under a new name – MeV-SIMS [27–30]. The main difference between the two methods comes from the different interaction mechanism that keV and MeV ions have with the sample surface. In case of keV-SIMS, secondary molecular ions are ejected from the sample surface due to the dominant nuclear sputtering (collision cascade), while ejection of secondary molecular ions with MeV primary ions is a consequence of electronic sputtering mechanism that dominates the MeV ion energy deposition process and causes desorption of intact large secondary molecular ions. Several orders of magnitude larger yields as well as less fragmentation are expected for larger molecular masses when MeV ions are used for the excitation [30].

Here we will demonstrate that the SIMS technique that employs MeV heavy ion excitation can be a method of choice for the identification of SOPs used in modern art objects. In the present work MeV-SIMS was applied for the identification of SOPs in the surface layer of the paints as well as for molecular imaging of pigments in the layered paint samples (non-embedded paint cross-sections). In order to show that very good results can be achieved even for the identification of very similar SOPs in the paints, paints containing characteristic phthalocyanine pigments such as copper phthalocyanine blue, Pigment Blue PB15:1 and PB15:3 (two different polymorphs), metal-free phthalocyanine PB16, and chlorinated copper phthalocyanine green Pigment Green PG7 were selected. To show the influence of different methods of mounting on the MeV-SIMS spectra, the red paint containing a red organic pigment belonging to the Naphthol AS class, Pigment Red PR112 is chosen.

2. Experimental

All measurements were performed in a high vacuum (10^{-6}–10^{-7} mbar) using MeV-SIMS setup with a Time-of-Flight (TOF) spectrometer at the RBI heavy ion microprobe, which is described in detail in Tadić et al. [31]. For the analysis of paint materials, focused 5 and 8 MeV Si ions were used. The typical beam lateral resolution was about $5 \times 5\ \mu m^2$. Beam was scanned over different sample areas (from $100 \times 100\ \mu m^2$ for the identification of pigments to $1200 \times 1200\ \mu m^2$ for the imaging of paint cross sections). The beam current in the pulsed mode was ~0.2 fA. Secondary molecular ions were steered towards the TOF by the +5 kV voltage applied to the sample holder. Multi-Stop TDC Data Acquisition System in the heavy ion deflection start mode was used with the 100 μs time between two heavy ion pulses (duration of 4 ns). All experimental parameters and data acquisition were controlled with the SPECTOR software [31,32].

As this is the first application of the MeV-SIMS in the field of cultural heritage, the analyses were first carried out on the paints that were systematically prepared at the Institute of Science and Technology in Art, at the Academy of Fine Arts. For self-made paints different phthalocyanine blue (PB15:1, PB15:3 and PB16) phthalocyanine green (PG7) and Naphthol AS red (PR112) pigment powders were mixed with alkyd binder in order to get pasty consistence of the paint. These paints were then casted onto microscope glass slides with approximately 150 μm thick coating and dried for 2 weeks. All pigments were provided by Kremer Pigmente (Germany) and the alkyd binder was Alkyd resin medium 4, a product of LUKAS (Germany). For the analysis, a small surface fragment from each sample was taken and put either on the conductive carbon tape or pressed directly into the pure indium metal surface. For reference spectra (not shown), all pigment powders were also prepared by pressing the pigment powder into pure In metal surface.

To test imaging capabilities of our MeV-SIMS setup, two samples were used. First, self-made sample with two phthalocyanine blue pigments in alkyd binder was prepared on the glass slide. Therefore a layer of the alkyd paint containing PB15:1 was painted over the alkyd paint containing PB15:3. A cross-section was prepared by just cutting the sample and fixing it together with the glass between two In sheets. Thereafter a cross-section of the paint sample from the outdoor sculpture ‘‘Plavi cvijet” (2000), made by Vjenceslav Richter (1917–2002) and belonging to the ‘‘Richter collection” from the Museum of Contemporary Art in Zagreb was measured. To prepare the cross-section, a paint flake was cut with a scalpel and fixed between two In plates. No embedding procedure of the samples in polymer resin was used in this study due to the fact that embedding and polishing is contaminating the surface layer of the sample and the scattering chamber was not equipped with an Ar gun, which is normally used in SIMS for cleaning surface contamination.

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

3.2. Identification of SOPs in paints

In Fig. 2 the MeV-SIMS spectra (m/z range between 100 and 700) for three different blue phthalocyanine pigments in alkyd

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