Naturwissenschaften und Technologie in der Kunst
Institutsvorstand: o. Univ. Prof. Univ. Doz. Dipl. Ing. Dr. Manfred Schreiner
Akademie der Bildenden Künste, A-1010 Wien, Schillerplatz 3
Tel.: (+43) 1 58816 DW 8600 Fax: (+43) 1 58816 8699
www.ntk.akbild.ac.at; d.jembrih@akbild.ac.at

E-mail distribution list:

Dr. Iva Bogdanovic Radovic, Rudjer Boskovic Institute, Zagreb

Mag. Mirta Pavic, Museum of Contemporary Art in Zagreb

Doc. Sagita Mirjam Sunara, Umjetnička akademija Sveučilišta u Splitu

RESEARCH REPORT Nr. 2015/3

Outdoor sculpture *"Objekt II"* (1979) by Josip Diminić: μ-Raman analysis of 9 paint samples in the frame of UKF-project cooperation with RBI, Zagreb

DI Dr. Dubravka Jembrih-Simbürger

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1. Introduction

The sculpture “Objekt II” is one of 38 outdoor objects presented in the sculpture park in Sisak, Croatia. The sculptures were made between 1971 and 1990 by prominent sculptors who participated in the Sisak Ironworks Art Colony.

Before the conservation work was started, 9 paint samples (see Table 1) were taken from “Objekt II” (painted steel) and provided for the analysis by Mag. Mirta Pavic (Museum of Contemporary Art in Zagreb). These real samples were analysed additional to self-made mock-ups in the frame of the project “Study of modern paint materials and their stability using MeV SIMS and other analytical techniques”[1].

The Secondary Ion Mass Spectrometry with primary ions in the MeV range (MeV SIMS) is a novel method and their application for the identification and characterisation of synthetic organic pigments and binders in paints is presently under investigation in the framework of the UKF project.

In order to preselect the samples, which contain synthetic organic pigments and binders for MeV SIMS, first investigations were carried out using µ-Raman spectroscopy at the Institute of Science and Technology in Art, Academy of Fine Arts Vienna. By means of Raman spectroscopy inorganic and a number of organic pigments can be identified and distinguished from each other.

2. µ-Raman analysis

µ-Raman spectroscopy is a widely applied non-destructive method for the analysis of pigments and binding media in the samples/objects in the field of cultural heritage giving the molecular information about the sample material.

Compared to the Fourier Transform Infrared (FTIR) spectroscopy, high lateral resolution which can be achieved in Raman spectroscopy allows the non-destructive analysis of the particles down to 1 µm lateral resolution. Thus, very precise measurements can be performed on pigment grains of different colours and shapes which give spectra without overlapping bands of two or more components in the sample. Furthermore, several inorganic pigments widely used in paintings (e.g. cinnabar, cadmium yellow, zinc oxide, realgar, massicot/litharge etc.) don’t show IR spectra in the middle IR range, but they can be clearly identified due to their Raman spectra. Also the identification of inorganic, carbon based black pigments (e.g. charcoal, lamp black) can be easily performed by means of Raman spectroscopy.

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[1]Study of modern paint materials and their stability using MeV SIMS and other analytical techniques, the project is supported by the Unity through Knowledge Fund (UKF), Ministry of Science, Education, and Sports, Croatia.

For the analysis, Lab RAM Aramis (Horiba Jobin Yvon) instrument was used. The instrument is equipped with 3 lasers (532, 633, and 785 nm), a confocal microscope coupled to a 460-mm focal length spectrograph with different diffraction gratings and a pettier cooled CCD camera as detector.

Samples were placed into the Raman microscope and illuminated with a laser beam in visible (633 nm) and/or near infrared (785 nm) range. Scattered light is collected and sent through the spectrometer to obtain Raman spectrum of the sample. The general measuring conditions were: 50x LWD (long working distance) objective, ca. 0.12 to 15 mW laser power at the sample, a 600 gr/mm grating and a measuring time up to 3x40 s. The measuring conditions were changed (especially the laser power and measuring time) depending on the sample analysed.

3. Results and conclusion

The pigments determined by µ-Raman analyses are summarised in *Table 1:*

Table 1: Results of the µ-Raman measurements (*n.a. – not analysed)

Sample No.	**Colour of the surface paint**	**Ground layer** (orange)	**Pigments in the surface paint**
1	White	n.a.	TiO_2, rutile
2	blue-green, dark	n.a.	Prussian blue ($Fe_4[Fe(CN)_6]_3$) mixed with Chrome yellow ($PbCrO_4$)
3	pink/red	n.a.	Chrome red ($PbCrO_4$*PbO) + ?
4	Reddish	n.a.	Chrome red ($PbCrO_4$*PbO) + ?
5	Blue	sample without ground layer	Phthalocyanine PB15:x
	yellow (on blue)		Chrome yellow ($PbCrO_4$)
6	blue-green	Pb_3O_4	Prussian blue ($Fe_4[Fe(CN)_6]_3$) mixed with Chrome yellow ($PbCrO_4$)

7	yellow, dark	Pb_3O_4	Chrome yellow ($PbCrO_4$)
Sample No.	**Colour of the surface paint**	**Ground layer** (orange)	**Pigments in the surface paint**
8	Red	Pb_3O_4	Chrome red ($PbCrO_4$*PbO) + ?
9	yellow, dark	Pb_3O_4	Chrome yellow ($PbCrO_4$) and barite ($BaSO_4$)

As can be seen from the Tab.1, in **white paint layer** of the sample No. 1 titanium white (rutile) was used. In samples taken from **blue-green areas** Prussian blue ($Fe_4[Fe(CN)_6]_3$) mixed with chrome yellow ($PbCrO_4$) was determined by Raman spectroscopy.

All **red samples** (No. 3, 4, and 8) showed the same Raman spectra with the presence of chrome red ($PbCrO_4$*PbO). In the spectral region between 950 cm^{-1} and 1650 cm^{-1} a number of additional Raman peaks were measured which could not be identified with available Raman databases. Additionally, FTIR spectra of the red samples were measured, where only Alkyd binder could be determined.

In samples from **yellow paint areas** (No. 5 and 7) chrome yellow was clearly determined by Raman. In sample No. 9 showing yellow surface layer, additionally to chrome yellow barite ($BaSO_4$) was determined as white pigment. That means that a white pigment was added to yellow colour in order to produce pale yellow shade.

In the **blue surface layer** of the sample No. 5 a synthetic organic pigment, the blue phthalocyanine pigment PB 15:x was identified. Due to the presence of synthetic organic pigment only this sample will be investigated by MeV SIMS analysis which can give information about exact blue phthalocyanine pigment used in this paint area.

After investigation with µ-Raman conclusion is that MeV SIMS measurements will be carried out to identify the blue phthalocyanine pigment and to characterize alkyd binder in the sample No. 5. Those measurements will be performed in March 2015 at the Rudjer Boskovic Institute (RBI) in Zagreb.