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Micro-Raman and FTIR investigations on paint samples from the outdoor sculpture „*Vrata“,* 1984 by Branko Ruzic

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1. Introduction

Two samples (BR-1 and BR-3, *Table 1*) were taken by Dr. Sagita Mirjam Sunara (University of Split) and Mag. Neven Peko (Gradski muzej Sisak) from the outdoor sculpture “Vrata“, painted steel, 1984 by B. Ruzic and provided for the analyses. For comparison, two further samples from the pipe construction supports (BR-2 and GMS-1, *Table 1*), should be analysed.

Table 1 summarises the descriptions of the samples provided and the requested information expected by scientific analysis.

Sample	Description	Information requested
BR-1	Sample fragments from the front side of the sculpture containing two layers: *Orange-red base coat paint* and *black top coat paint*	Identification of pigments and binders in both layers
BR-2	Sample fragments from the pipe construction supporting the sculpture on the backside: *reddish-brown base coat*	Identification of pigment(s) and the binder
BR-3	Sample fragments from the backside of the sculpture containing two layers: *Orange-red base coat paint* and *black top coat paint*	Identification of pigments and the binders in both layers, comparison of the results with the sample BR-1
GMS-1	Sample from the pipe construction inside “Gradski muzej Sisak” containing two layers: *Red base coat paint* and *grey paint layer*	Identification of pigment(s) and binders, comparison of the results with the sample BR-2

Table 1: Samples provided for analyses.

Figures 1-4 (Photo documentation provided by Dr. S. M. Sunara) show the outdoor sculpture “Vrata” and the sampling positions. *Figure 5* depicts the pipe construction shown in the permanent exhibition in Gradski muzej Sisak.

Figure 1: Front side of the outdoor sculpture “Vrata”, condition 2016. *(Photo provided by Dr. S.M. Sunara)*

Figure 2: Outdoor sculpture “Vrata” with the sampling position for **BR-1**. *(2019, Photos provided by Dr. S. M. Sunara)*

Figure 3: Outdoor sculpture “Vrata” with the sampling position for **BR-2**. *(2019, Photos provided by Dr. S. M. Sunara)*

Figure 4: Outdoor sculpture “Vrata” with the sampling position for **BR-3**. *(2019, Photos provided by Dr. S. M. Sunara)*

Figure 5: Sample GMS-1 was taken from the pipe construction, shown in permanent exhibition in the Gradski muzej Sisak. *(2019, Photos provided by Dr. S. M. Sunara)*

2. Analytical methods

The investigations were carried out using µ-Raman spectroscopy and Fourier Transform Infrared spectroscopy (FTIR) in order to determine the pigments and binders in the samples mentioned above.

2.1 µ-Raman spectroscopy

For the analyses a LabRAM Aramis (Horiba Jobin Yvon) instrument was available. The instrument is equipped with 3 lasers (532, 632.8, and 785 nm), a confocal microscope coupled to a 460-mm focal length spectrograph with different diffraction gratings and a Peltier cooled CCD camera as detector. Such set-up of the Raman instrument is optimized for analysis of pigments.

In order to determine the pigments, the measurements were performed with 632.8 nm and 785 nm lasers, using 10x, 50x LWD (long working distance), or 100x objective and 600 gr/mm grating. The laser power and the measuring time were adapted depending on the sample analysed. The range of acquisition was between 150 and 1800 cm^{-1}. At least two different positions on the sample were analysed with both lasers. In the case of pigment grains in the paint showing different colors, several grains were analysed.

For qualitative evaluation the measured spectra were compared with spectra of the Raman database of the Institute (ISTA).

The results of the Raman measurements carried out on all samples are summarised in Chapter 3 (*Table 2*). One has to keep in mind that, when using the µ-Raman instrument mentioned above, the analysing spot is about 1-2 micrometers or less in diameter.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

All measurements were performed in transmission mode using the LUMOS FTIR microscope (Bruker Optics, Germany) and a diamond cell (Spectra Tech Inc., USA). Therefore, small particles taken of each paint layer were pressed between two diamond crystals of the diamond cell in order to get flat surface. The FTIR instrument is equipped with a MCT detector and spectra were acquired in the range between 450 cm^{-1} and 4000 cm^{-1} with a resolution of 4 cm^{-1}. Depending on the results, between 3 and 5 spots per sample were analysed. The spectra were evaluated by comparison to reference spectra of the IRUG database[1] (Version 2000) and the FTIR pigment database of the Institute (ISTA).

FTIR analyses were carried out in order to get the information about binders in the paint samples and in particular cases also about the pigments (*see Table 2, Chapter 3*).

3. Results and conclusion

Samples BR-1, BR-2, and BR-3:

By means of *µ*-Raman spectroscopy the pigments ***iron oxide*** *(Fe_2O_3)* and ***calcite*** (*$CaCO_3$* as extender), were determined in all orange-red or reddish-brown layers (base coats, *Table 2*) in the samples BR-1, BR-2, and BR-3. On these samples no lead-based pigments were identified. In layers mentioned above, both paler and darker areas were analysed showing the only difference in the contents of calcite. Paler areas contain more calcite than darker orange-red areas. In the black layers of the samples BR-1 and BR-3 ***carbon black*** *(C)* was identified.

The FTIR spectra acquired in all layers of the samples BR-1, BR-2, and BR-3 showed the biggest similarity to the reference spectra of alkyd paints. Thus, alkyd resin can be assumed as binder in the paints used in these samples. In addition to the alkyd binder also calcite (chalk) was determined by FTIR in all 3 samples. Small

[1] http://www.irug.org/search-spectral-database

amounts of chalk were found by FTIR also in the black layers of the samples BR-1 and BR-3.

Sample GMS-1:

Raman spectra acquired in the red layer of the sample GMS-1 showed the presence of ***chrome red*** *($PbCrO_4$)* and a red synthetic organic pigment of the ß-Naphthol class. The best comparison of the Raman spectra with reference spectra of the database was achieved with the pigment ***pigment red 3*** *(PR3).* In Raman spectra of the grey layer of this sample ***titanium white*** *(TiO_2, rutile)* and ***calcite*** *($CaCO_3$)* were determined.

In the FTIR spectra of the red layer of the sample alkyd was identified as binder and again calcite (chalk) used probably as extender. In the grey layer, the FTIR showed again the presence of the alkyd binder.

All results of the *µ*-Raman and FTIR investigations are summarized in the *Table 2:*

Sample	**Description**	**µ-Raman Spectroscopy** ***Pigments***	**FTIR** ***Binder/ Pigment***
BR-1	*Orange-red base coat paint with white grains* *black top coat paint*	***Iron oxide*** (Fe_2O_3), *Calcite* ($CaCO_3$) ***Carbon black*** (C)	***Alkyd*** */ Calcite* ($CaCO_3$) ***Alkyd*** */ traces of Calcite* ($CaCO_3$)
BR-2	*reddish-brown base coat*	***Iron oxide*** (Fe_2O_3), *Calcite* ($CaCO_3$)	***Alkyd*** */ Calcite* ($CaCO_3$)
BR-3	*Orange-red base coat paint with white grains* *black top coat paint*	***Iron oxide*** (Fe_2O_3), *Calcite* ($CaCO_3$) ***Carbon black*** (C)	***Alkyd*** */ Calcite* ($CaCO_3$) ***Alkyd*** */ traces of Calcite* ($CaCO_3$)
GMS-1	*Red base coat paint* *Grey paint layer*	Synthetic organic pigment (SOP) of the **ß-Naphthol** class, probably ***Pigment Red 3*** (PR3), ***Chrome red*** ($PbCrO_4$) ***Titanium white*** (TiO_2, rutile), ***Calcite*** ($CaCO_3$)	***Alkyd*** */ Calcite* ($CaCO_3$) ***Alkyd*** */ Calcite* ($CaCO_3$)

Table 2: Results of the µ-Raman and FTIR measurements performed on the samples from the outdoor sculpture “Vrata”

As can be concluded, in the red sample GMS-1, which was analysed for comparison purposes with samples BR-1, BR-2, and BR-3, there are no similarities concerning the pigments in alkyd paints. Thus, different alkyd paint was used for the outdoor sculpture “Vrata” and the pipe construction from the permanent exhibition placed in the Gradski muzej Sisak.