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Micro-Raman and FTIR investigations on 5 paint samples taken from the outdoor sculpture „*Cvijet*“ – *(Flower,* 1980, Vera Fischer)

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1. Introduction

Five samples (see *Table 1 and Figures 1 and 2*) were taken from the outdoor sculpture “Cvijet“, (“Flower” 1980, by V. Fischer) belonging to the Sisak Steelworks Sculpture Park (Croatia) and provided for the analyses by Dr. Sagita Mirjam Sunara (University of Split).

Table 1 summarizes the descriptions of the samples provided and the requested information about the samples.

Sample	Description	Information requested
13_b1	Large sample containing two layers of the topcoat at the inner surface.	Identification of pigments and binders in both layers.
13_c2	Big sample containing the upper of the two layers of primer, one part of the surface is discoloured.	Identification of pigments and the binder in the layer, analysis on both sides of the flake. Nature of the changes in the discoloured part?
13_a3	Scratched sample flakes	Identification of pigments and the binder.
13_b4	Sample containing possibly two layers of the top coat	Identification of pigments and binders in both layers, analysis on both sides of the flake.
13_c5	Scratched sample of the lower of the two layers of topcoat (they might contain particles of metal substrate)	Identification of pigments and the binder.

Table 1: Samples provided for analyses. This information is partly taken from the “Sample submission form” prepared by Dr. S. M. Sunara.

The *Figures 1* and *2* (Photo documentation provided by Dr. S. M. Sunara) show the object from the west and the east including the sampling positions.

Vera Fischer, *Flower*, Sisak Steelworks Sculpture Park – view from the west

Figure 1: Outdoor sculpture “Flower” with sampling positions. *(Photo: Dr. S. M. Sunara)*

Vera Fischer, *Flower*, Sisak Steelworks Sculpture Park – view from the east

Figure 2: Outdoor sculpture “Flower” with sampling positions. *(Photo: Dr. S. M. Sunara)*

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

2. Analytical methods

2.1 µ-Raman spectroscopy

For the analyses 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 a set-up of the Raman instrument is optimized for analysis of pigments.

In order to determine the pigments in the paint samples the measurements were performed with 632.8 nm and 785 nm lasers, 50x LWD (long working distance) 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 2000 cm^{-1}. At least two different positions on the sample were analysed with both lasers.

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

The results of the Raman measurements carried out on all samples are summarised in the Chapter 3 (*Table 2*). The sample 13_c5 is very dark and contains mostly metal particles, thus no position on the sample could be found to obtain Raman spectra of the paint flakes. One has to keep in mind that when using the Raman instrument mentioned above, the analysing spot is about 1-2 micrometer in diameter. Thus, the Raman spectra of all positions selected only showed the peaks related to the components of the steel.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Measurements of the samples 13_a3 and 13_c5 (scratched samples from the surface) were performed in transmission mode using the FTIR-microscope (Perkin Elmer instrument Spectrum 2000, Germany) and a diamond cell (Spectra Tech Inc., USA). Therefore, small particles of each sample were pressed between two diamond crystals of the diamond cell in order to get flat surface.

The sample flakes of the samples 13_b1, 13_b4, and 13_c2 were analysed by ATR-FTIR (Attenuated Total Reflection-FTIR) on both sides. These measurements were carried out with the LUMOS instrument (Bruker Optics, Germany).
Both FTIR instruments are equipped with MCT detectors and spectra were acquired in the range between 4500 and 450 cm^{-1} and 580 cm^{-1} with a resolution of 4 cm^{-1}. Depending on the results, between 3 and 6 spots per sample were analysed. The

spectra were evaluated by comparison to reference spectra from the IRUG database[1] (Version 2000) and FTIR pigment database of the Institute (ISTA).

FTIR analyses were carried out in order to get the information about binders in paint samples and in particular cases (sample 13_c5 and 13_b4) also additional information about pigments could be gained (see Table 2, Chapter 3).

3. Results and conclusion

By means of *µ*-Raman spectroscopy the pigments lead chrome yellow, iron oxide, and titan white (rutile) were determined in the pale paint layer of the sample **13_b1**. In the dark layer of the same sample lead chrome yellow, iron oxide, zinc white and carbon black were identified. The FTIR spectra of both layers showed the biggest similarity to the reference spectra of alkyd paints. Thus, alkyd resin can be assumed as binder in both layers of the sample 13_b1.

In the Raman spectra of both surface parts (discoloured and orange paint) of the sample **13_c2** the same pigments could be detected: lead chrome yellow, iron oxide, chalk and barite. Relatively to the lead chrome yellow and iron oxide, the content of white pigments chalk and barite was higher in the discoloured area. This could explain the paler colour of this area. FTIR spectra of both, discoloured and orange parts of the surface showed again the biggest similarity to reference spectra of alkyd paints.

In the sample **13_a3** (lower primer layer) lead chrome yellow and barite were identified by Raman spectroscopy, whereas in FTIR spectra alkyd resin was identified as binder.

In the upper blue paint of the sample **13_b4** the pigment phthalocyanine blue (PB15:x) was determined. The best comparison of the Raman spectra with reference spectra from the database was achieved with the pigments PB15:1 and PB15:3. Both pigments have the same chemical composition; the difference is only in 1 chlorine atom in the structure, which could not be distinguished in the spectra acquired on the sample. By means of FTIR alkyd could be determined as binder in the paint.

The pigment phthalocyanine blue (PB15:x) was also detected in the Raman spectra of the lower blue paint layer of this sample. Additionally, the FTIR spectra clearly showed the presence of chalk, which was not detected by the Raman analysis. This is probably due the small analysing spot used in the setup of the Raman instrument compared to FTIR (measuring spots are usually in the range between 50 and 100 µm). Again, the best comparison of FTIR spectra was achieved with alkyd resin, which might be used as binder also in this sample.

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

As already mentioned, the Raman spectra of the scratched flakes of the sample **13_c5** didn`t give any information about pigments, only compounds related to the steel could be detected. In the FTIR spectra of the sample flakes the blue pigment Prussian blue was identified as well as 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***
13_b1	***Pale side***	*Lead chrome yellow* ($PbCrO_4$), *Iron oxide* (Fe_2O_3), *Titanium white* (TiO_2, Rutile)	*Alkyd*
	Dark side of the flake from the inner surface	*Lead chrome yellow* ($PbCrO_4$), *Iron oxide* (Fe_2O_3), *Zinc white* (ZnO), *Carbon black* (C)	*Alkyd*
13_c2	***Discoloured part** of the surface*	*Lead chrome yellow* ($PbCrO_4$), *Iron oxide* (Fe_2O_3), higher content of white pigments *Chalk* ($CaCO_3$) and *Barite* ($BaSO_4$) detected than in the intact orange surface	*Alkyd*
	Orange surface of the sample from the inner surface	*Lead chrome yellow* ($PbCrO_4$), *Iron oxide* (Fe_2O_3), *Chalk* ($CaCO_3$), *Barite* ($BaSO_4$)	*Alkyd*
13_a3	***Scratched sample*** (lower primer layer)	*Lead chrome yellow* ($PbCrO_4$), *Barite* ($BaSO_4$)	*Alkyd*
13_b4	***Upper blue paint layer*** (bright colour)	*Phthalocyanine blue* (PB 15:x)	*Alkyd*
	Lower blue paint layer	*Phthalocyanine blue* (PB 15:x)	*Alkyd/ Chalk* ($CaCO_3$)
13_c5	***Dark particles of paint layer*** on metal substrate	No results	*Alkyd/ Prussian blue* $Fe_4[Fe(CN)_6]_3$

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