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Investigation of color layers of Bohemian panel paintings by confocal micro-XRF analysis

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ABSTRACT

Confocal micro X-ray fluorescence spectroscopy (confocal micro-XRF) has recently become a significant instrumental method for analyses of cultural heritage as it provides depth-resolved information on elemental distribution of the investigated samples. This work describes results of confocal micro-XRF analyses of paint layers of two Bohemian panel paintings from the half of the 15th century that are part of the collections of the National Gallery in Prague. All the measurements were performed using a table top confocal micro-XRF setup designed at the Czech Technical University in Prague. A depth-profiling was used for investigation of red and blue paint layers in order to compare the composition and structure of the used pigments. Obtained results were compared with findings from the material survey on the sample taken from the painting Assumpta from Deštná (ca 1450, inv. no. O 724) to verify their origin in the same workshop. Confocal micro-XRF provides satisfactory data to specify the art workshop.

1. Introduction and research aim

Confocal micro X-ray fluorescence analysis (confocal micro-XRF) is a promising instrumental method for a non-destructive investigation of stratified samples. Unlike the conventional XRF, the confocal micro-XRF enables acquiring depth-resolved information on elemental composition of analyzed objects. The confocal micro-XRF setup contains two X-ray optics. The first one in the excitation channel focuses the primary X-rays from the source (either synchrotron or X-ray tube). The second lens (in front of the detector) collects the characteristic X-rays. The two optics are placed in such a configuration that their focal spots are overlapping. As a result, a small volume (called confocal volume) is created which represents the probing volume of the confocal micro-XRF setup. Depth-resolved elemental composition can be obtained by scanning the sample with the confocal volume perpendicularly to its surface (depth-profiling). Thus, it is possible to distinguish single layers in multilayered samples in a non-destructive way.

Due to its properties, confocal micro-XRF has become a useful technique for the study of cultural heritage, especially historical paintings. Since 2003, when the first application of confocal micro-XRF was published (Kanngießer et al., 2003), several authors have demonstrated the advantageous utilization of this technique in paint layers analyses. Woll et al. (2006) constructed a confocal X-ray fluorescence microscope at the CHESS synchrotron radiation facility in order to obtain elemental depth profiles of historical paintings. At the Beijing Synchrotron Radiation Facility, Wei et al. (2008) performed confocal micro-XRF analysis of a faux bamboo painting of the Forbidden City in Beijing. The results revealed a stratified structure of the paint and indicated that the painting was probably restored in the past. In 2005, Kanngießer et al. (2005) were the first to show that it is feasible to perform confocal micro-XRF of paint layers also with a laboratory setup using an X-ray tube. Reiche et al. (2012) applied a laboratory-based confocal micro-XRF spectrometer to the non-invasive study of Renaissance paintings from the Louvre collection. In the paper of Sun et al. (2014), it was suggested that the confocal micro-XRF spectrometer can be also used for a non-destructive analysis of paint layers of vehicles as a criminal evidence in traffic accidents. Nakano et al. (2016) analyzed the replica sample of Daubigny's Garden painting by Vincent van Gogh with the confocal micro-XRF spectrometer developed at the Osaka City University and visualized a hidden drawing beneath the surface. Laclavetine et al. (2016) recently published analyses of experimental paint multilayers performed with a new mobile confocal micro-XRF system designed at the University of Seville.

One of the most important benefits of the confocal micro-XRF analysis of paint layers is the possibility to find out the elemental composition and structure of the layers without taking samples from the

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painting. Moreover, the identification of the used pigments sometimes enables determination of the author of the painting and alternatively can provide information for truth or falsehood judgement. In some cases, just making the elemental analysis of the paint layers may be inconclusive because various authors may have used the same pigments. But, unravelling also the structure of the layers may lead to a clear identification of the particular author or his workshop (Šefců et al., 2015).

This paper presents results of some of the first confocal micro-XRF analyses of historical paintings performed with a new laboratory confocal micro-XRF setup that has been recently constructed at the Czech Technical University in Prague (Trojek et al., 2017). A depth-profiling technique was used for examination of two Bohemian panel paintings from the half of the 15th century that belong to the collections of the National Gallery in Prague. The aim of the study was to determine the composition and structure of the used pigments in order to attribute the origin of the paintings to a particular workshop.

2. Experimental

2.1. Description of the laboratory confocal micro-XRF setup

The laboratory confocal micro-XRF device was constructed at the Czech Technical University in Prague for the purpose of in-situ analyses of paintings, see Fig. 1. The device is equipped with X-Beam® Superflux PF (a compact source of exciting radiation produced by the XOS company) which consists of an air-cooled X-ray tube (Mo target, 50 W) and focusing polycapillary lens attached to the X-ray tube. The focusing polycapillary lens has a focal spot size of 15 μm (FWHM) at 17.4 keV with a working distance (output focal distance) of 4 mm and intensity gain of 3000 (compared to a pinhole collimator of the same size, 100 mm from the source). The input focal distance (IFD) of the focusing lens is 20 mm. The secondary lens is a polycapillary collimating optics manufactured by XOS as well. The collimating optics has the IFD of 3.5 mm and the input focal spot size of 20 μm (FWHM) at 17.4 keV. The characteristic radiation is detected with FAST SDD™ detector (Amptek, active area: 25 mm^2, energy resolution: 125 eV at 5.9 keV). The collimating optics is placed in front of the entrance window of the detector on a motorized x-y-z stage, which allows to quickly adjust the confocal arrangement or alternatively to switch the setup from confocal to the micro-XRF configuration. All the components mentioned above are mounted on a movable metallic board and the whole confocal micro-XRF setup is placed inside a glass shielding box to reduce the dose rates

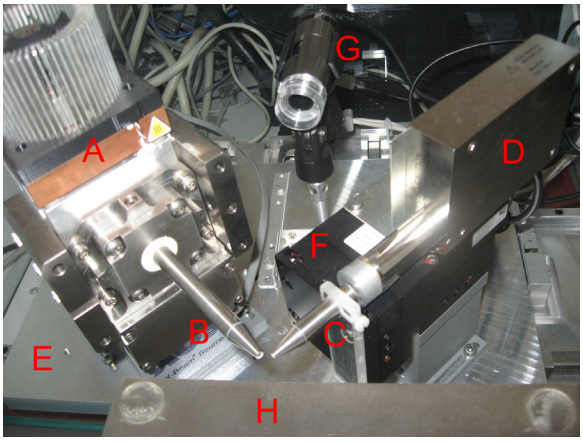

Fig. 1. A photograph of the confocal micro-XRF device depicting its main components: A – X-ray tube, B – polycapillary focusing optics, C – polycapillary collimating optics, D – detector, E – metallic board for the setup movement, F – motorized x-y-z stage for the collimating optics, G – microscopic camera for the sample observation, H – removable platform for measurements of small samples.

to the natural background level. A more detailed description of the confocal micro-XRF device can be found elsewhere (Trojek et al., 2017).

2.2. Depth resolution of the confocal micro-XRF setup

Depth resolution of the confocal micro-XRF setup is determined by the size of the probing volume depending on the focal spot sizes of the used polycapillary lenses. The size of the probing volume of the laboratory confocal micro-XRF device was characterized by depth profiling of a set of thin foils with a thickness of about 5 μm: Ti, Cr, Fe, Ni, Cu, and Pb. With the depth step of 5 μm, the foils were scanned through the confocal volume perpendicularly to their surface. The depth profiles of the foils were measured at the voltage of 50 kV and current of 1 mA. Measurement life time was 60 s at each step. For every foil, five such depth scans were measured. Depth-profiling of the foil with such a small thickness compared to the size of the probing volume (and thus with a negligible self-absorption) results in a depth profile that can be fitted with a Gaussian function, see inset in Fig. 2. Depth resolution of the confocal micro-XRF setup at a particular energy is then expressed as the FWHM value of this Gaussian shaped depth profile (Laclavetine et al., 2016). The results (Fig. 2) clearly show the expected decrease of the depth resolution with increasing energy of characteristic X-rays. This is a known effect resulting from the energy dependence of the critical angle of total reflection (Mantouvalou et al., 2014). The uncertainties of the depth resolution measurement are expressed as a standard deviation of the mean value of FWHM obtained from the five depth scans of each of the foils. From Fig. 2 it can be seen that the depth resolution of the confocal micro-XRF setup ranges from (46 ± 2) μm at K_α(Ti) to (27 ± 2) μm at L_α(Pb).

2.3. Depth profiling of unknown multilayered samples

Contrary to thin elemental foils with negligible self-absorption, depth profiling of thick multilayered samples is more complex due to X-ray interfering effects that occur within the mass of the sample. To the most important matrix effects influencing the amount of detected signal belong the absorption of primary and fluorescence X-rays in the sample and secondary enhancement. The intensity of absorption effect evidently increases with depth and affects primarily the depth profiles of low fluorescence energies. Sometimes, the absorption effect makes it even impossible to detect some elements that are too deep below the surface or have too low energy of fluorescence radiation. Another effect modifying the shape of the depth profile is the size of the probing volume. The depth profile increases gradually and the steepness of the growing part is given by the size of the probing volume and so by the depth resolution of the confocal XRF setup. The probing volume is smaller for higher fluorescence energies (as can be seen from Fig. 2), which results in a steeper rise and fall of the depth profile.

All the effects mentioned above cause distortion of the original concentration profile of a particular element, which complicates the evaluation of the confocal micro-XRF data. It follows from the above that the deformation of the depth profile increases with decreasing fluorescence energy. A more detailed description of these effects in relation to quantitative confocal micro-XRF can be found in the paper of Mantouvalou et al. (2012).

The quantitative evaluation of the depth profiles obtained from confocal micro-XRF consists in reconstruction of layers' thicknesses and concentrations of present elements. Because of the complicated matrix effects description in confocal geometry, the quantification of the depth profiles is a demanding task, especially in the case of polychromatic excitation. But in the context of our study, even the qualitative evaluation of the depth profiles (i.e. determining the composition and sequence of the color layers and estimating their thickness) brings valuable information for the investigation of medieval paintings.