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The use of various X-ray fluorescence analysis modalities for the investigation of historical paintings: The case study on the Late Gothic panel painting

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ABSTRACT

The presence of heavy chemical elements in old pigments is possible to identify in historical paintings using X-ray fluorescence analysis (XRF). This is a non-destructive analytical method frequently used in examination of objects that require in situ analysis, where it is necessary to avoid damaging the object by taking samples. Different modalities are available, such as microanalysis, scanning selected areas, or depth profiling techniques. Surface scanning is particularly profitable since 2D element distribution maps are much more understandable than the results of individual analyses. Information on the layered structure of the painting can be also obtained by handheld portable systems. Results presented in our paper combine 2D element distribution maps obtained by scanning analysis, and depth profiling using conventional XRF. The latter is very suitable for objects of art, as it can be evaluated from data measured with portable XRF device. Depth profiling by conventional XRF is based on the differences in X-ray absorption in paint layers.

The XRF technique was applied for analysis of panel paintings of the Master of the St George Altarpiece who was active in Prague in the 1470s and 1480s. The results were evaluated by taking micro-samples and performing a material analysis.

1. Introduction

There are several X-ray fluorescence techniques that are beneficial in investigation of paintings. The simplest XRF technique involves analyzing a selected area of a painting with a handheld portable system. Additionally to a point element composition, a new approach allows us to record information on the stratified structure of the painting and the depth profile can be predicted. The depth of the layer can be described by $K\alpha/K\beta$ ratio of an element; i.e. lower ratio indicates deeper position (Frahm and Doonan, 2013). Depth profiling that uses $K\alpha/K\beta$ technique is based on the differences in X-ray absorption in paint layers (Trojek et al., 2007). This kind of analysis is easy to perform, though it only provides information about the elemental composition of an individual spot. The analyzed area is usually only a few millimeters in diameter. Next important non-destructive technique that was used was XRF 2D scanning. This modality is well established and often used in painting examination (Alfeld et al., 2013).

In our paper, the XRF analysis results of three triangular retables (one both-sided) from the Altarpiece from Kadaň (Retables, called from

Kadaň, Prague, ca. 1470, tempera, wood, 176×75 cm, The National Gallery in Prague, Inv. Nos. O 7033–7035, Pešina (1950) and Fajt and Chlumská (2014)) are presented. The results were combined and evaluated by the material analysis (pigments and materials of gilding). Confocal XRF is not considered here since it is mainly associated with immobile devices.

2. Background

2.1. Depth profiling

Information on depth distribution can be obtained by means of the $K\alpha/K\beta$ technique with or without Monte Carlo (MC) simulations (Trojek et al., 2007) and the theory of the method was overviewed in Trojek and Čechák (2007). The $K\alpha/K\beta$ technique is considered a classical application of XRF, there is no need to use any extensive instrumentation, e.g. X-ray optics in confocal configuration, for the measurement and the application remains simple. The arrangement of the measurement is as follows. A divergent and relatively wide X-ray

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beam is aimed at a large area of the specimen; the depth information is then the average depth from this given area of layer. The principle resides in the different absorption coefficients for the $K\alpha$ and $K\beta$ lines (Chantler et al., 2005; Trojek et al., 2007). For elements deposited on the surface, the emitted X-rays are only slightly affected by absorption in the specimen. If an element is present at some depth in the specimen, its characteristic radiation has to penetrate through a thick layer of the matrix and the characteristic X-ray fluxes are significantly changed.

In this case the $K\alpha/K\beta$ ratio is reduced because the linear attenuation coefficient for $K\alpha$ line is higher than for $K\beta$ in low Z matrix (Trojek et al., 2008). However, additionally to this effect, the theoretical $K\alpha/K\beta$ intensity ratio (Markowitz, 2002) is also changed by self-absorption and it is dependent on the thickness of the layer (absolute intensity of characteristic line, concentration of the element). Therefore, the $K\alpha/K\beta$ diagrams, displaying $K\alpha/K\beta$ ratio versus $K\alpha$ intensity, are preferable than solely $K\alpha/K\beta$ ratio (Trojek et al., 2008).

These $K\alpha/K\beta$ diagrams are useful as a calibration tool for depth calculation of the layer. For each duplet of X-ray characteristic lines energies one separate diagram has to be created. Diagrams are constructed from absolute count rates or their normalized values where point [1;1] means uncovered saturated (thick) layer of an element. Then two dependences of characteristic X-ray lines ratio on the intensity of one X-ray line have to be determined. The first stays for self-absorption (thin to thick layer of single element material) and the second stays for saturated layer of an element covered by layers of another element (i.e. aluminum). This could be done by experiments and analytical computation or by Monte Carlo simulation. While diagram with normalized values can be obtained by calculations with or without any experimental results, the construction of the diagram with absolute count rates requires an analysis of at least one reference material containing the given element. In the cases of both calculations, the measurement geometry and setup parameters (incident and take-off angles, anode material, voltage, filters) has to be implemented from the experiment while linear attenuation coefficients and densities are implemented from tabular data (i.e. Chantler et al., 2005).

For the saturated layer covered by another element, the dependence of the covering layer thickness on the relative characteristic X-ray line intensity (attenuation) can be expressed approximately by logarithmic function. Then the dependence of characteristic X-ray lines ratio on the intensity of one X-ray line for saturated layer of an element covered by layers of another element can be shifted for different thicknesses of the measured element layer (using the dependence for self-absorption). So, from these diagrams the thickness of the single element layer and its depth (in single element matrix) can be calculated. Actual depth of the layer and concentration of the measured element can be also obtained when the composition of the covering layer (matrix) and its density is determined. More about construction of calibration diagrams (by Monte Carlo simulation) was presented in Trojek et al. (2008) and calibration diagrams for historic pigments composition are in the scope of our future work. The $K\alpha/K\beta$ diagram cannot provide us with detailed depth concentration profiles of individual elements. However, this quite simple determination of the mean depth of an element in an analyzed area and its amount (thickness of a single elemental layer) in this depth could be beneficial for correct interpretation of XRF analysis of objects with possible layered structure.

An example of the dependence of mass attenuation coefficient on energy in chalk and lead white is shown in Fig. 1 (Solé et al., 2007), which can be important if a brightening upper layer is added to the top of the painting. These white pigments are part of the layer that must be penetrated by characteristic lines of measured element in some depth (for example, copper in blue pigment azurite). Recently, the effects of covering layer composition was investigated and discussed in Bártořová et al., in press. It has been demonstrated that a calibration diagram for a certain element is almost matrix independent. Still, it must be also taken into account that another element, which is presented with an absorption edge between these two lines ($K\alpha$, $K\beta$), can cause an

increase of the examined ratio. Then the $K\beta$ line can be absorbed to a greater extent than the $K\alpha$ line. As for the different matrices, combination of these effects may occur.

The method based on $K\alpha/K\beta$ ratio was successfully applied to identification of pigment layers in illuminated manuscripts (Trojek et al., 2010) and paintings (Trojek and Trojková, 2015), thickness measurement of coated Ni on brass (Karimi et al., 2009), and recognition of gold and gilding (Trojek and Hložek, 2012). However, in above mentioned papers, the presented results didn't implement the advanced method using $K\alpha/K\beta$ diagrams that utilizes both $K\alpha/K\beta$ ratio and $K\alpha$ intensity.

2.2. Scanning XRF analysis

One of the laboratory XRF options is mapping of the surface distribution of present elements. The procedure of this technique consists in scanning a selected area of a sample with a narrow X-ray beam and acquiring hundreds or thousands of individual X-ray fluorescence spectra from different points of the sample. The spectra can be then evaluated and variations in surface distribution (concentration) of measurable elements can be drawn. Surface scanning requires samples with smooth and plane surface because roughness or any curvature of a sample causes changes in measured X-ray intensities and it is difficult to distinguish whether the differences in X-ray intensities are related to heterogeneous distributions of elements or influenced by disturbing effects (Trojek et al., 2010). Such maps, displaying the differences in detected $K\alpha$ (or $L\alpha$) count rate of an element, can be also affected by variable depth distribution of an element. Therefore, we decided to present the $K\alpha/K\beta$ map in this article to visualize the laying of paint layers.

3. Material and methods

3.1. X-ray fluorescence analysis

The handheld XRF device NITON XL3t GOLDD+ containing a mini X-ray source (X-ray tube) with a silver anode was used. The induced radiation in a sample was detected by an integrated large area silicon drift detector with the minimal spot size of 8 mm in diameter. For the measurement we used four different setups of measurement conditions, we present results from three of them. The measurement conditions with the name of the setup (as it is provided by manufacturer) are presented in Table 1. The name of each setup reflects the intended range of measured elements (main, low, light atomic number Z). For reaching of the requested measurement stability, the tripod stand was used. Each data point was measured twice in order to have more reliable results. All spectra that are presented in our paper and all computed ratios (excluding the Cu $K\alpha$ /Cu $K\beta$ ratio 2D map) were obtained by this handheld portable XRF device.

Spectra processing was mainly performed by PyMca software (Solé et al., 2007) except from Pb M X-ray characteristic lines which were fitted using QtiPlot software (Vasilef, 2013). Due to the large volume of measured data, batch mode was used in PyMCA software. The peak areas of X-ray characteristic lines Ca $K\alpha$ (KL3a, 3.690 keV) and Ca $K\beta$ (KM3b, 4.013 keV) were fitted from spectra obtained in 'low' setup (see Table 1). Pb $L\alpha$ (L3M4 – 10.450 keV, L3M5 – 10.551 keV) lines were fitted from spectra obtained in 'main' setup (Table 1). Peak areas were determined using pseudo-Voigt function (linear combination of Gaussian and Lorentzian curve). The polynomial continuum of 5th order was used and background was computed using sensitive non-linear iterative clipping peak (SNIP) method. Fit algorithm also included possibility of stripping, two escape peaks, pile-up effect and scattering peaks.

In QtiPlot software areas of X-ray characteristic lines Pb M (M4N6 – 2.444 keV, M5N7 – 2.347 keV) were determined from spectra obtained in 'light' setup (Table 1). Fitting of M lines in PyMCA software didn't show results with sufficient χ^2 value and neither it was suitable for

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