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Synchrotron-based scanning macro-X-ray fluorescence applied to fragments of Roman mural paintings

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ABSTRACT

Roman wall fragments dating from 2nd and 3rd centuries AD, from two sites of the Roman province of Germania Superior, near the present day towns of Wössingen (Baden-Württemberg) and Mülheim-Kärlich (Rheinland-Pfalz), were analyzed with synchrotron-based scanning macro-X-ray fluorescence (SR-MA-XRF) at the FLUO beamline (ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology). Lead, iron, copper, calcium, potassium, among other elements, were detected and are correlated with red, blue, yellow and green pigments. In the fragments from Mülheim-Kärlich, red has high correlation with Pb (red lead pigment), Fe and Ca were detected in 2 different hues of yellow respectively, and Cu is correlated with the blue pigment. The green pigment investigated in the Wössingen's fragments has high correlation with Fe and K, indicating the use of green earth, and the red pigment is correlated with iron, indicating the use of the red ochre. Synchrotron-based scanning macro-X-ray fluorescence applied in fragments of wall paintings has shown to be a fast, non-destructive and effective technique in the identification and discrimination of the pigments, plaster, different layers and impurities in paintings through the 2D elemental distribution.

1. Introduction

During the Roman Empire, decoration of houses and public buildings with wall paintings was commonplace. The quality of the painting depended on the social status of the house's owner or on the function of the building. The culture of the wall paintings started around 200 BC and spread throughout Roman Empire; this technology was well established and is described by the Roman architect Vitruvius in “Ten books of Architecture”, written around 15 BC [1].

Most of the mural paintings have been discovered in the last centuries. Few of these paintings are still intact in panel forms [2], but most of the archeological artifacts are in form of fragments. Indeed, analyses at these sites have only been made possible due to advances in analysis methods and measurement technology [3,4,5,6] in the last 50 years. For this progress, several combinations of techniques have been used in the analyses of wall paintings to identify and characterize the pigments, plaster, mortar and aggregates used. The knowledge of these materials can give information about the lifestyle of a community. The study of pigments can help answer questions about the use and source of these pigments, the importance of a certain building within a town, and even perhaps the trade inside the Roman Empire with the town and individuals. Pigments from Roman mural paintings have been widely studied, but in many areas of the old Empire, buildings are continually being found, as in the region of the Province of Germania Superior (part of current Germany, France and Switzerland).

The analyses are unique depending on site and involve many new and established techniques. Some experiments are performed directly on the mural painting panels (in situ) without any sample preparation using handheld equipment [2]. In others, it is allowed to prepare samples by cross-sectioning [7] or scratching [3,5], but it is obvious that such invasive sample preparation needs to be avoided. Such complicated preparation is however needed for various different destructive and non-destructive analysis techniques, such as optical microscopy, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy equipped with energy-dispersive spectrometry (SEM-EDS) and X-ray diffraction (XRD) [3,5]. Analyses of such artifacts are obviously more difficult when no sample preparation is possible and require reliable calculations and robust methodology, but equally with complicated sample preparation, care is needed not to compromise the results. An analytical approach without sample preparation minimizes the risk of damage to a priceless object.

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Table 1
Information about the fragments and analyzed areas.

Site	Number of fragments/ number of analyzed areas	Number of analyzed areas by each color	Shown in the paper (colors)
Mülheim-Kärlich “Im Depot” (MUEK)	3 fragments/ 21 analyzed areas	Red: 17 Yellow: 15 Blue: 15	MUEK1- A1 MUEK1-A2 (red, yellow, blue)
Wössingen (WOES)	13 fragments/ 51 analyzed areas	Red: 34 Yellow:16 Blue: 6 Green: 18 White: 41	WOES1-A1 (white, green) WOES2-A1 (red, white)

Techniques with which one can measure only limited number of points are usually used, and this can lead to errors which a more detailed analysis would avoid. The paintings were typically made in a complicated process using pigments (produced by minerals, and containing impurities) with plaster and aggregates layers, and all these elements can have a large influence in the analysis. A scanning technique allows the researcher to observe more details about the sample and helps to distinguish between the elements from the pigments, their impurities, and the plaster and aggregates contributions.

Synchrotron-based scanning macro-X-ray fluorescence technique (MA-XRF) has been used over the years in the analysis of fossils and paintings in canvas. In these paintings, MA-XRF has proven suitable for identification of pigments and detection of hidden features in the paintings [8]. The application of synchrotron-based scanning macro-X-ray fluorescence in fragments of mural paintings has not yet been performed. Due to the rough and curved surface of many mural paintings, it is technically difficult and inefficient to scan (at the moment) the entire fragment at once; however, it is effective to scan smaller (around 1 cm × 1 cm) smooth areas. In this paper, it is demonstrated that MA-XRF applied to fragments of mural painting allows characterization of the regions of each color, producing maps of the elements present with short acquisition time. Details of the pigments and impurities or aggregates are observed in such maps. MA-XRF is an alternative analysis of fragments of wall paintings and requires no sample preparation; the elements of each pigment used in the paintings are identified. The results of the analyses of the pigments of fragments from a Roman rural villa near to contemporary Wössingen and a villa rustica “Im Depot” close to today's Mülheim-Kärlich are presented.

2. Materials and methods

2.1. Samples

Roman mural paintings were created with the fixation of the pigments in the damp plaster through chemical reaction. The evaporating water from the damp plaster brings forward the setting lime to the surface, forming a thin transparent layer of $CaCO_3$ under the pigments. This process is responsible for the conservation of the pigments in the wall paintings even almost 2000 years after the painting was created [9].

Roman mural painting fragments from the *Frigidarium* (part of the Baths) of the Roman villa of Mülheim-Kärlich “Im Depot” and a room from the Roman villa of Wössingen (both from the Roman province of Germania Superior) are being studied. The Mülheim-Kärlich's (MUEK) fragments date from the Severan Dynasty (195–235 AD); they were uncovered in 1983 and are kept by the Generaldirektion Kulturelles Erbe (GDKE), Koblenz, Germany [10]. The fragments from Wössingen (WOES) are dated between the middle of the 2nd century AD and 260 AD; they were uncovered in 1966 and are kept by the Badisches Landesmuseum Karlsruhe, Karlsruhe, Germany [11]. The mural painting fragments, sized about 3–10 cm of length and width, and 1–3 cm of thickness, have well-preserved pigments (green, red, blue, and yellow) (Fig. 2a and Fig. 5a). Information about the fragments and analyzed areas are listed in Table 1.

In order to avoid modification of the fragments, no sample preparation was performed. Clamps, glue or tape, etc., are not suitable for fixing the delicate fragments. Instead, embedding the samples in very fine sand ensures a gentle fixation, which is reliable as far as acceleration forces are kept sufficiently low. Since direct contact of sand and fragments had to be omitted as well, we placed thin polypropylene foil between the sample and a box filled with fine sand, which we placed on the sample positioner. Selected regions with relatively comparable flat surfaces and different pigments were chosen for the analyses with synchrotron-based scanning macro-X-ray fluorescence microscopy (MA-XRF) in order to identify the pigments and the distribution of them in the painting.

2.2. Experimental

Synchrotron-based scanning macro-X-ray fluorescence (MA-XRF) experiments were carried out at the FLUO beamline at the ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology (KIT), Germany. X-ray fluorescence technique provides qualitative and quantitative elemental information about the sample, and in the 2D mode, lateral distribution of the elements. Broadband synchrotron radiation with 6.2 keV critical energy was generated by a 1.5 T bending magnet and was monochromatized using a double multilayer monochromator (W-Si multilayers with 2.7 nm period) to provide 31 keV (above Sb K-edge) X-ray radiation within a 0.2 keV bandwidth [12]. Slits restricted the beam size to 100 μm × 100 μm in horizontal and vertical direction. The experiments were performed in air with the samples positioned 45° in relation to the source and the detector. The distance detector sample was 0.6 cm in order to avoid any collision, unfortunately likewise limiting soft X-ray sensitivity and impeding the detection of elements with atomic number lower than sulfur. The X-ray photons

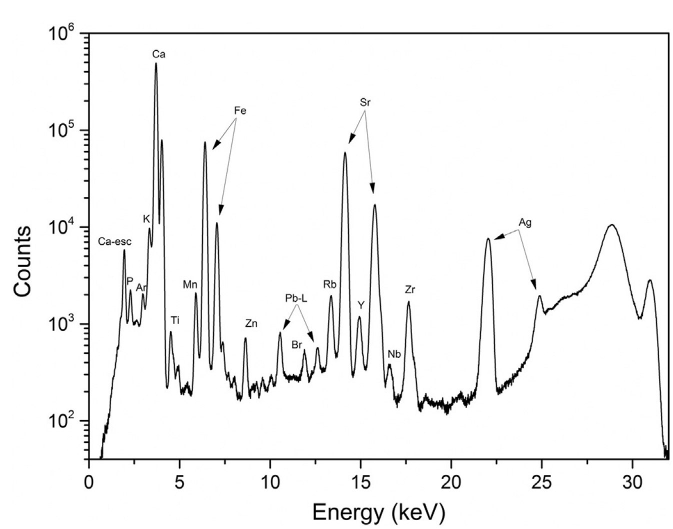

Fig. 1. Sum spectrum of the analysis of the pigments present in the WOES1-A1. The sum spectrum corresponds to the sum of spectra from each point scanned.