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Analytical procedure for characterization of medieval wall-paintings by X-ray fluorescence spectrometry, laser ablation inductively coupled plasma mass spectrometry and Raman spectroscopy☆

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Analytical procedure for the comprehensive chemical characterization of samples from medieval Nubian wall-paintings by means of portable X-ray fluorescence (pXRF), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and Raman spectroscopy (RS) was proposed in this work. The procedure was used for elemental and molecular investigations of samples from archeological excavations in Nubia (modern southern Egypt and northern Sudan). Numerous remains of churches with painted decorations dated back to the 7th–14th century were excavated in the region of medieval kingdoms of Nubia but many aspects of this art and its technology are still unknown. Samples from the selected archeological sites (Faras, Old Dongola and Banganarti) were analyzed in the form of transfers (n = 26), small fragments collected during the excavations (n = 35) and cross sections (n = 15). XRF was used to collect data about elemental composition, LA-ICPMS allowed mapping of selected elements, while RS was used to get the molecular information about the samples. The preliminary results indicated the usefulness of the proposed analytical procedure for distinguishing the substances, from both the surface and sub-surface domains of the wall-paintings. The possibility to identify raw materials from the wall-paintings will be used in the further systematic, archeometric studies devoted to the detailed comparison of various historic Nubian centers.

1. Introduction

Archeometric investigations of cultural heritage objects demand a deep understanding of a historical context of the monument as well as recognition of the general physic-chemical nature of the analyzed samples [1,2]. Microsampling, if allowed, should be done carefully because a selection of the sampling area is of utmost importance for the reliability of the final results. Multilayered archeological finds usually demand a detailed planning of research and individual development of the whole analytical procedure, therefore various analytical protocols can be found in the literature [3–6].

One of methods commonly used for determination of elemental composition of archeological finds is X-ray fluorescence spectrometry (XRF). Portable instrumentations became commercially available from the 1960s and then the number of its application in archeometry and conservation science has started to increase constantly due to possibility for in situ investigations [7,8]. XRF spectrometry enables non-invasive and non-destructive analyses, therefore it is often applied in the preliminary studies of the valuable historic objects. Sometimes the information provided by XRF is sufficient to solve specific chemical problems and the straightforward identification of various white pigments, can be a good example for such a case [9]. Lead white ($PbCO_3 \cdot Pb(OH)_2$) was used since antiquity, whereas zinc white (ZnO) was put into practice in 1834 and titanium white (TiO_2) in 1821, but it was not until 1921 that it was introduced for artistic purposes. The presence and popularity of these pigments can be linked with the specific time of their applications and as they can be easily distinguished from each other on the basis of their major elemental composition, they can give the assumption for identification of restoration and repaint areas over the investigated objects [10].

Far more often a collection of both: elemental and molecular data of the investigated object is needed to draw reliable, final conclusions about the original chemical nature and possible secondary changes of the artifact [11–21]. Laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy have proven to give the complete information

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about the investigated objects. LIBS provided the information about elemental composition, while RS allowed molecular fingerprinting of the samples, therefore it was concluded that these two methods together could be successfully used to identify raw materials of investigated item [12]. Depending on the acquiescence for mechanical sampling from objects the use of various instrumental methods can be included in the analytical scenario [13]. Although the identification of the same components is possible either directly from the monument or from the previously collected micro-samples, still the analysis of samples would allow more arbitrary investigations and a possible decision about sampling from cultural heritage objects would be an important issue of archeometric research.

This work concerns wall-paintings from the territory of medieval Nubia, where numerous remains of churches decorated with wall-paintings were excavated along the Nile river [22]. Nubian artists and architects established a unique formal art which is still studied by archeologists in respect of the iconography and technical detail. Some of the greatest ancient Nubian paintings were discovered in the Cathedral at Faras by a Polish expedition when the decision about building of Aswan High Dam was made [23]. The construction of Aswan High Dam changed the level of the water and a vast area of the region of the former medieval kingdoms of Nubia was flooded [24]. To prevent the cultural heritage of this region UNESCO organized the so-called Nubian Campaign and the discovery of the cathedral of the city of Faras which was repeatedly rebuilt and subsequently decorated with new layers of plasters and wall-paintings. This numerous collection of paintings can be dated to the 7th–14th century and was one of the greatest achievements of the archeological mission at that time [23]. Nearly 50% of the rescued wall-paintings were given to the National Museum in Warsaw as the gratitude for the help.

The wall-paintings from Faras were transported in the form of *transfers* and small fragments of murals which had been collected during the excavations. *Transfer* is a name given to big fragments of wall-paintings, which had been detached from the original locations and then mounted in special, moveable but stable constructions. According to the International Council on Monuments and Sites (ICOMOS): "detachment and transfer are dangerous, drastic and irreversible operations that severely affect the physical composition, material structure and esthetic characteristics of wall-paintings. These operations are, therefore, only justifiable in extreme cases when all options of in situ treatment are not viable" [25]. The use of transfer technique is now restricted to the exceptional cases where the only alternative is a total loss of the entire monument. Such the exceptional case concerned the situation of Faras which has been completely submerged by the water of Nasser Lake resulting from the Dam construction.

The interest in the Nubian archeology increased during the Nubian Rescue Campaign and promoted an interest of the Nubian culture. Studies of the iconography of Nubian wall-paintings are in progress, but detailed physic-chemical investigations of these materials have never been comprehensively carried out. The limited sources of historical textual evidence concerning the history of the Nubian kingdoms make many aspects of this art mysterious. In the case of the wall-paintings from Faras one can distinguish 3 main layers: (*i*) painting layer; (*ii*) lime whitewash or lime plaster and (*iii*) mud plaster. During the most intensive conservation works realized in the 60-ties of the XXth century no particular chemical analyses were carried out and the preventive treatments during the removing of the wall-paintings were established intuitively due to the lack of time. The written sources concerning the technology of Nubian wall-paintings are scarce and Nubiologists expect to complete the information about the chemical composition of the wall-paintings with the use of the modern analytical techniques. The evaluation of the influence of past conservation treatments onto the existing transfers would be interesting as well.

The general aim of this study was to elaborate analytical multi-instrumental procedure allowing to obtain chemical information about elemental and molecular composition of the raw materials of the Nubian wall-paintings. The comparison of various wall decorations was undertaken with attention to their original, structural inhomogeneity naturally reflected in the inhomogeneity of samples taken for analysis. Inhomogeneous samples can be studied with different analytical methods allowing for imaging of elemental distribution and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is one of them. LA-ICPMS with the limits of detection in the range of $\mu g\ g^{-1}$ allows for simultaneous collection of information about major and trace elements during imaging studies of solid materials of various matrixes [26–28].

In this work, apart from the bulk elemental XRF analysis, elemental mapping of cross-sections by LA-ICPMS was proposed as a fast method allowing to access chemical information about heterogeneous samples and to support the selection of areas for RS measurements.

2. Materials and methods

2.1. Instrumentation

p-XRF (portable X-Ray fluorescence spectrometry) was used during the elemental analysis of transfers and selected fragments of wall-paintings. The Bruker TRACER III-SD Handheld Portable XRF (X-ray fluorescence) spectrometer was operated with 40 kV and 11.1 μA, the fluorescence spectra were always collected during the constant time of 60 s, with the use of the vacuum set-up.

LA-ICPMS (laser ablation inductively coupled plasma mass spectrometry): an inductively coupled plasma mass spectrometer Perkin Elmer NexION 300 equipped with the laser ablation system LSX-213 (CETAC, USA) was used. The laser ablation systems combine stable, environmentally sealed 213 nm UV lasers (Nd-YAG, solid state) with a high sampling efficiency, variable 1 to 20 Hz pulse repetition rate and maximum energy up to 5 $mJ\cdot puls^{-1}$. All experiments were performed using Ar as the carrier gas. Home-made, open ablation cell was used within this study [28] with an effective volume of c.a. $v = 4.5\ cm^3$. Instrumental settings and data acquisition parameters are given in Table 1.

RS (Raman spectroscopy): Raman spectra were collected on the dispersive Raman spectrometer Nicolet Almega equipped in an Olympus

Table 1
Instrumental settings and data acquisition parameters.

Laser ablation characteristics and settings	
LA system	LSX-213
Wavelength, nm	213
Pulse duration, ns	5
Energy, mJ	5.0
Beam diameter, μm	25
Pulse repetition rate, Hz	4
Multiple line scan	15
ICP-MS characteristics and settings	
RF Power, W	1050
Neb. gas flow rate, L min^{-1}	1.04
Carrier gas	Ar
ICP-MS data acquisition parameters	
Scanning mode	Peak hopping
Readings	1
Replicates	7252
Sweeps	1
Dwell time, ms	5
Pre-integration time, s	30
Integration time, s	1204
Isotopes monitored	^{12}C, ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{32}S, ^{35}Cl, ^{39}K, ^{42}Ca, ^{49}Ti, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{65}Cu, ^{66}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{137}Ba, ^{139}La, ^{178}Hf, ^{202}Hg, ^{207}Pb, ^{232}Th, ^{238}U