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Identification of forgeries in historical enamels by combining the non-destructive scanning XRF imaging and alpha-PIXE portable techniques

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ABSTRACT

Particle induced X-ray emission performed with alpha particles (alpha-PIXE) and scanning X-ray fluorescence (XRF) imaging have been used for the non-invasive investigation of three enameled artworks dated back to the XI–XII century AD. The attribution of the three objects has been performed based on art historical considerations even if an analytical investigation was never applied to confirm their authenticity.
The alpha-PIXE technique allowed to determine the compositional pattern of the glass matrix in the three artworks; the XRF imaging performed by scanning the sample surface allowed to obtain the signature of opacifying and coloring agents.
The high concentration values of Pb in the glass matrix as well as the extensive use of chemical components based on Cr, Zn, and As, questioned the authenticity of the three artworks and postponed their manufacturing dating from the XVIII century AD. The application of a matrix factorization analysis to the XRF data allowed highlighting the chemical associations among Cd, Se, Ba and Zn, indicating the use of a modern cadmium lithopone in the red decorations. The analytical results obtained during the investigation suggest a classification of the three objects as modern copies.

1. Introduction

The scientific investigation of cultural heritage and archeological materials provides useful information for their knowledge and preservation. When the analysis is performed on artworks, it is often mandatory to operate with non-destructive and mobile instruments. In general, X-ray based techniques fulfill the above requirements; several examples of their application for the analysis of cultural objects are published in the scientific literature [1–7].

In many analytical cases, the chemical elements in a sample present a spatial distribution and a heterogeneous composition. Consequently, the analysis requires the combination of analytical techniques with a high spatial resolution and a multi-elemental sensitivity.

An interesting case concerns the analysis of historical enamels in a metal support that can present decorative motif in a wide range of colors and with dimensions down to the millimeter scale. Usually, enamels are fragile and the sampling is often not possible. Consequently, their investigation with a non-invasive approach is mandatory.

Enamels are manufactured by applying a paste of a colored powdered glass in a metal. The firing at high temperature induces the melting of the glass and its adhesion to the metal substrate.

A first evidence of the use of enamels for decorating metals dates back in the second millennium BC [8]. Because of the jewel-like appearance, the enameling art knew its golden age during the medieval time where enamels were used for embellishing religious items [9,10].

The enamels manufactured in the medieval period were based on an alkali silica glass [11–13]. The former component of the glass matrix consisted of a siliceous sand containing impurities of aluminum oxide (Al_2O_3), calcite ($CaCO_3$), magnesium oxide (MgO), and iron oxides.

During heating in the furnace, calcite transforms to calcium oxide (CaO). The main stabilizers of the glass are Al_2O_3, CaO and MgO.

Metal alkali oxides (Na_2O and K_2O) were the fluxing agents. During antiquity, the main source of sodium (Na) was natron ($Na_2CO_3 \cdot 10H_2O$). Afterwards, both Na and potassium (K) could be obtained from the ash of plants. The relative compositional ratio of these components changed

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during the different historical periods depending on the availability of sources for their procurement.

Lead oxides were also ingredients of the vitreous matrix; during the medieval period, they were used mainly for the production of some colored glasses and with a concentration not exceeding 20% by weight. The use of lead (Pb) as a stabilizer and/or for imparting high brilliance to the glass is post-medieval.

The presence of iron oxides in the former component could induce in the glass a tint with a shade depending on the iron (Fe) oxidation state. This unintentional color (frequently a bluish tint due to the presence of Fe(II)) could be controlled by using manganese dioxide (MnO_2) or antimony pentoxide (Sb_2O_5) and by operating the firing at the most appropriate atmosphere in the furnace [14]. Heating in an oxidizing atmosphere induces Fe(II) to transform to Fe(III) presenting a yellowish color. This shade was balanced by a purple tint provided by the presence of Mn(III) introduced by a phase transformation of MnO_2 during heating in the molten glass matrix. On the contrary, the use of a reducing atmosphere could be used to compensate the impurity of Fe(III). A similar effect was obtained with Sb_2O_5.

The most common opacifiers were stannic oxide (SnO_2) and lead tin oxide (Pb_2SnO_4). Their use was replaced by lead arsenate ($As_4O_{16}Pb_3$) starting from the XVIII century AD. Finally, different metal oxides (based on Fe, Mn, Cu, Co) were the main colorants of the glass matrix.

Enamel composition changed over time based on the raw materials available for their production. Consequently, the chemical analysis of the enameled artworks could serve as a tool for identifying their typology, provenance and for discriminating among genuine, embellished and fake objects [15,16].

Copies and forgeries of historical enamels were made mainly in the XIX century AD [16]. However, they were manufactured with a composition slightly different to the original one. Therefore, the analytical determination of this modern composition can provide information concerning dating and authentication of artworks.

The aim of this work was to investigate the composition of some historical enamels belonging to a private collection by combining alpha-PIXE (Particle Induced X-ray Emission) [17,18] and scanning XRF (X-ray Fluorescence) imaging.

The integration of the proposed analytical techniques is particularly suited for the analysis of enamels. The alpha-PIXE method presents a high ionization cross-section for elements with low atomic number that typically characterize the former, fluxes and stabilizers of ancient vitreous samples. In addition, the penetration depth of the charged particles is limited to 10–20 μm allowing the possibility to obtain quantitative data of the glass matrix without any influence from the substrate.

The use of the scanning XRF imaging in the analysis of enameled artworks is relatively new. Its application allows mapping the spatial distribution of medium and high atomic number elements that compose colorants and opacifiers. The images provided by the XRF scanning allow to detect the associations among chemical elements and to classify the raw materials used in the manufacturing process. In the case of enamels, this information is crucial for approaching questions of dating and authenticity.

2. Materials and methods

2.1. Samples

The artworks investigated in the present work consist of enamels on a silvered support. They are shown in Fig. 1. The samples belong to a private collection. They are dated back to the XI–XII century AD based on art historical considerations. However, they were never investigated with analytical methods and there is no information concerning the materials used for their production.

The three objects are religious items consisting of: a) a plaque (Fig. 1a) representing Christ with dimensions of 25 cm × 20 cm. The silvered substrate of the object is decorated with enamels of different colors and dimensions (down to the millimeter scale); b) a pot (Fig. 1b) with a cylindrical shape of 15 cm in height and 8 cm in diameter. The sample is decorated with white enamels representing the crucifixions and resurrection of Christ. This kind of objects was usually used for storing wafers during celebrations; c) a bottle for the sacred water or wine (Fig. 1c), decorated with Arabic decorative motif in green and blue enamels.

2.2. The alpha-PIXE portable system

The portable alpha-PIXE spectrometer is based on a low activity ^{210}Po radioactive source emitting alpha particles of 5 MeV energy. The source is coupled to a silicon drift detector (SDD) for the detection of X-ray fluorescence induced by the alpha beam on the samples [17,18]. The compact geometry of the system and the presence of a helium flux during measurements enable the detection of X-rays down to an energy of 1 keV.

Sampling or sample preparation are not required for the investigation.

Compositional data are obtained by using the GUPIX code [19]. Since the half-life of ^{210}Po is 138 days, the chemical sensitivity of the system (*i.e.*, the number of fluorescence counts per second per unit of mass of a given element) changes during the decay period. This effect is taken into consideration in the quantitative analysis by a preliminary calibration of the system with reference materials of known composition. Table 1 summarizes the alpha-PIXE system.

2.3. The mobile XRF scanner

The mobile XRF scanner consists of a measurement head equipped with a microfocus X-ray tube coupled to a strongly focusing polycapillary. A SDD detector is used for detecting the X-ray fluorescence induced on the samples by the primary X-ray radiation.

Fig. 1. Investigated enamels in a silvered support. The objects consist of a plaque (a); a pot (b); and a bottle (c).