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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.

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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).

Table 1
Summary of the alpha-PIXE system.

Parameter	Value
Primary beam	α particle of 5 MeV energy
Beam size	8 mm diameter obtained by using a collimator
SDD detector	20 mm^2 active area; 125 eV energy resolution at 5.9 keV
Measurement time	3600 s
Measurement geometry[a]	45°–90° incidence-detecting angles; 4 mm–6 mm incidence-detecting distances

[a] With respect to the sample surface.

The measurement head is fixed during the measurement while the sample under investigation is moved by using an XY motorized stage with a micrometric precision. The distance between the measurement head and the sample is adjusted by an additional motorized stage oriented along the Z axis. A magnifying microscope and two lasers allow to position the sample at the measurement distance.

A sample holder is installed in the scanning system for fixing the sample. This device is equipped with a manual goniometer to be used with samples of a non-flat geometry. However, the control of the goniometer is not automated and the measurement of this typology of samples is performed by using slices.

Dimensions and weight of the XRF scanner are minimal and optimized for its use *in situ* and for the investigation of medium and small size cultural objects. Table 2 summarizes the XRF scanner and the main settings used for the measurements.

The measurement parameters to be used during the scanning of the samples are defined by means of a custom-programmed software. It allows defining the dimension of the area to be investigated, the step size and the dwell time.

The scanning micro-XRF is used to obtain high spatial resolution elemental maps in a limited area of the investigated samples (local analysis). It is performed by positioning the sample in the focus of the polycapillary where the primary beam exhibits a minimum size (*i.e.*, about 45 μm at 45° incidence angle).

Due to the high divergence of the primary radiation, it is possible to operate measurement with a larger beam size by positioning the samples out of the focus of the polycapillary. The spot diameter is about 470 μm by moving the sample ± 3 mm from the focal distance. This setting is used in the scanning macro-XRF where samples of larger dimensions should be investigated (global analysis).

The elemental imaging is performed by analyzing the XRF spectra acquired step-by-step in the scanning process. This analytical procedure is performed offline, by using the fast XRF fitting option of the PyMca package [20].

In addition, a matrix factorization analysis (included as a tool of PyMca), is used for evidencing correlations among chemical elements

Table 2
Summary of the XRF scanner.

Parameter	Value
X-ray source	30 W Rh-anode tube
Focusing optic	Polycapillary with a focal distance of 1 cm
Beam size at the focus	26 μm diameter at the energy of the Rh K-lines
SDD detector	50 mm^2 active area; 133 eV energy resolution at 5.9 keV
Measurement geometry[a]	45°–45° incidence-detecting angles
Area of scansion	20 × 20 cm^2 (maximum value)
Step-size[b]	1–50 μm in the scanning micro-XRF; 50–500 μm in the scanning macro-XRF
X-ray source parameters	38 kV and 0.6 mA
Dwell time	150 ms (including overhead)
Measurement time	6.7 h for a 400 × 400 pixel image corresponding to 16 × 10^4 local XRF spectra measured in the sample surface

[a] With respect to the sample surface.
[b] Depending on applications and sample dimensions.

that can result hidden in the raw spectral data. Due to the non-negative nature of counts in the X-ray spectra, a Non Negative Matrix Analysis (NNMA) is used for the calculation. NNMA allows to obtain a set of new XRF spectra (and a set of new XRF images). Each new spectrum contains mainly the elements that are spatially correlated in the experimental XRF data.

3. Results and discussion

Enamel composition has changed during time. A different compositional pattern is expected by analyzing artworks dated back to different periods. Therefore, it is possible to distinguish among the different typologies of enamels and to approach question concerning the authenticity.

The alpha-PIXE analysis was used to obtain quantitative data of the glass matrix composing the enamels in Fig. 1. The PIXE investigation was limited to enamels in the sample surface presenting a dimension larger than the spot size of the alpha beam emitted by the ^{210}Po source installed on the spectrometer. Table 3 summarizes the quantitative results.

The concentration values obtained by PIXE are not consistent with the ones expected for artworks manufactured during the XI–XII century AD. The glass matrix is an alkali silica typology even if the quantity of lead oxide (PbO) exceeds 20%. The presence of Na as a fluxing agent was detected only in two of the measured samples. The concentration value of K is rather higher than the expected one. Moreover, manganese (Mn), antimony (Sb) or tin (Sn) are not present (within the detection limits of the system).

Since the PIXE analysis was performed only on a limited number of enamels decorating the artworks, a late restoration of the objects or their embellishing in a more recent time cannot be excluded *a priori*.

In order to obtain the elemental composition of the full objects, a macro-XRF scanning has been performed. The plaque in Fig. 1a was fully scanned. The cylindrical pot in Fig. 1b was investigated by rotating the sample and by scanning its surface in a mosaic of slices; the investigation of the bottle in Fig. 1c has been limited to the bottom area of the object, presenting a flat geometry.

Fig. 2 shows the elemental distribution of the enamels in the plaque. As in the case of the PIXE data, the elemental maps evidenced the presence of inconsistent elements with respect to the ones expected in historical enamels.

The presence of zinc (Zn) in the red and arsenic (As) in the yellow/white enamels is an indicator of a recent manufacturing. In particular the use of As was introduced in the enamel production as white opacifier during the XVIII century AD [21].

Cadmium (Cd), selenium (Se) and barium (Ba) are also present in the full spectrum even if they were detected with a low accuracy due to the overlap with different X-ray lines. The low detection limit could hide the chemical associations among these elements, limiting the possibility to identify the precursor raw materials used in the manufacturing.

In fact, the simultaneous presence of Cd, Se, Zn and Ba suggests the use of the modern cadmium lithopone ($ZnS \cdot CdS(Se) \cdot BaSO_4$) for the red enamels.

The identification of a Cd based red pigment is an interesting result since it allows to make a more precise dating of the sample under

Table 3
PIXE quantitative data obtained by measuring some enamels decorating artworks in Fig. 1.

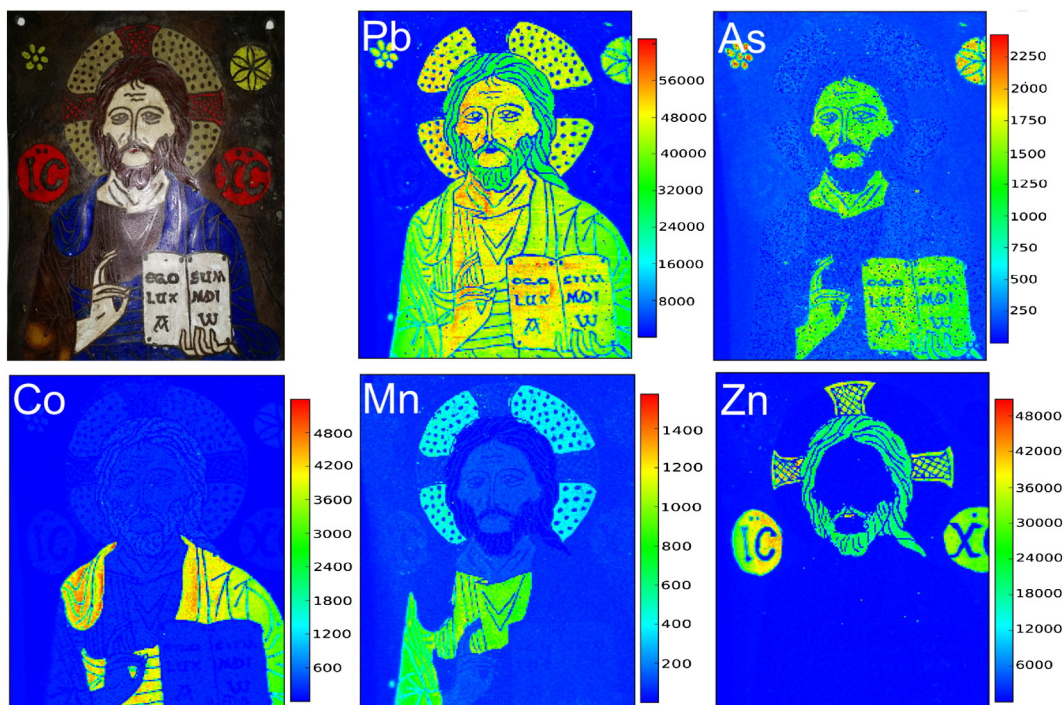| Enamel (sample)	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	Fe$_2$O$_3$	PbO
White (plaque)	6.6	1.9	1.1	36.8	3.7	2.0	–	38.4
Blue (plaque)	–	–	2.4	34.5	3.3	4.8	0.7	24.2
Brown (plaque)	–	–	2.4	32.2	4.5	1.4	2.3	27.4
Light blue (bottle)	–	–	4.3	49.0	7.9	1.0	–	18.8
White (pot)	9.0	1.8	–	34.1	2.0	1.4	–	29.8

Fig. 2. Elemental maps of enameled plaque obtained by the scanning macro-XRF.

investigation. The early evidence of the use of cadmium sulfide (CdS) as a yellow pigment dates back to the first half of the XIX century AD. A new family of pigments – in a form of ((Cd,Zn)S) and (Cd,(S,Se)) and with shades of color ranging from yellow to red – was then obtained by the substitution of Cd or sulfur (S) in the yellow CdS with Zn or Se, respectively. Due to the prohibitive costs of raw materials (metallic cadmium and cadmium oxides and carbonates), CdS and CdSe were not largely sold as artist pigments.

This limit was covered by the development of cadmium lithopone in 1921 [22,23].

A first form of cadmium lithopone was obtained by a co-precipitation with barium sulfide (BaS) added to cadmium sulfate (CdSO$_4$) solutions in the reaction: CdSO$_4$ + BaS → CdS↓ + BaSO$_4$↓.

As evident, the result is essentially a mixture; the properties of CdS as a pigment are maintained even in this new form.

This early production of cadmium lithopone contained around 5% barium sulfate (BaSO$_4$). Over time, this quantity was increased to around 62%. Also, the chemical process for the production of cadmium lithopone changed by including the use of zinc sulfide (ZnS) and cadmium sulfoselenide Cd(S,Se) with Ba compounds in order to obtain a red color.

The presence of cadmium lithopone in the red enamels was clarified by performing a NNMA analysis of the raw macro-XRF data.
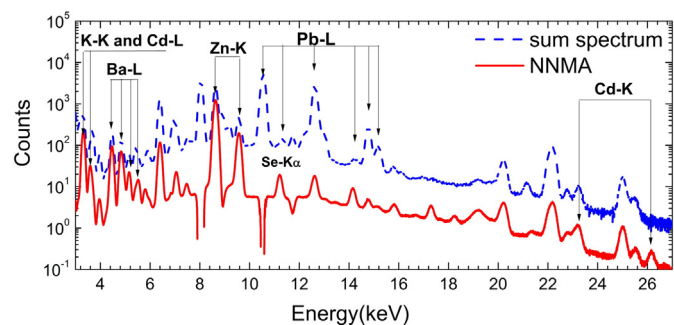
Fig. 3 shows the comparison of the full spectrum obtained during the scanning of the silvered plaque with one of the spectra obtained by applying the NNMA to the data.

NNMA spectrum allows a more efficient detection of Cd, Se, Ba and Zn. Cadmium shows both the contribution of K$_\alpha$ and K$_\beta$ lines at 23.16 keV and 26.06 keV respectively while in the raw data the presence of the Cd-lines was unclear. Cadmium is also detected by means of the L-lines in the low energy domain, even if the overlap with K should be considered.

The contribution of Pb to this NNMA spectrum is minimal; selenium is well visible through both its K-lines. Finally, the peak-to-background ratio of Zn and Ba is improved with respect to the one in the experimental spectrum.

Fig. 4 shows the image associated to the NNMA spectrum in Fig. 3. It is clear that elements (mainly Ba, Se, Cd and Zn) in the NNMA spectrum are the ones that contribute to the brilliant red of the silvered plaque. This confirms the use of cadmium lithopone as hypothesized.

The same analytical approach was used for the yellow enamels. They are characterized by a chromium (Cr) based component as expected for a glass production dated from the XIX century AD.

Fig. 3. Comparison between an experimental spectrum and one obtained by NNMA analysis allowing a better detection of Cd, Se, Zn and Ba.

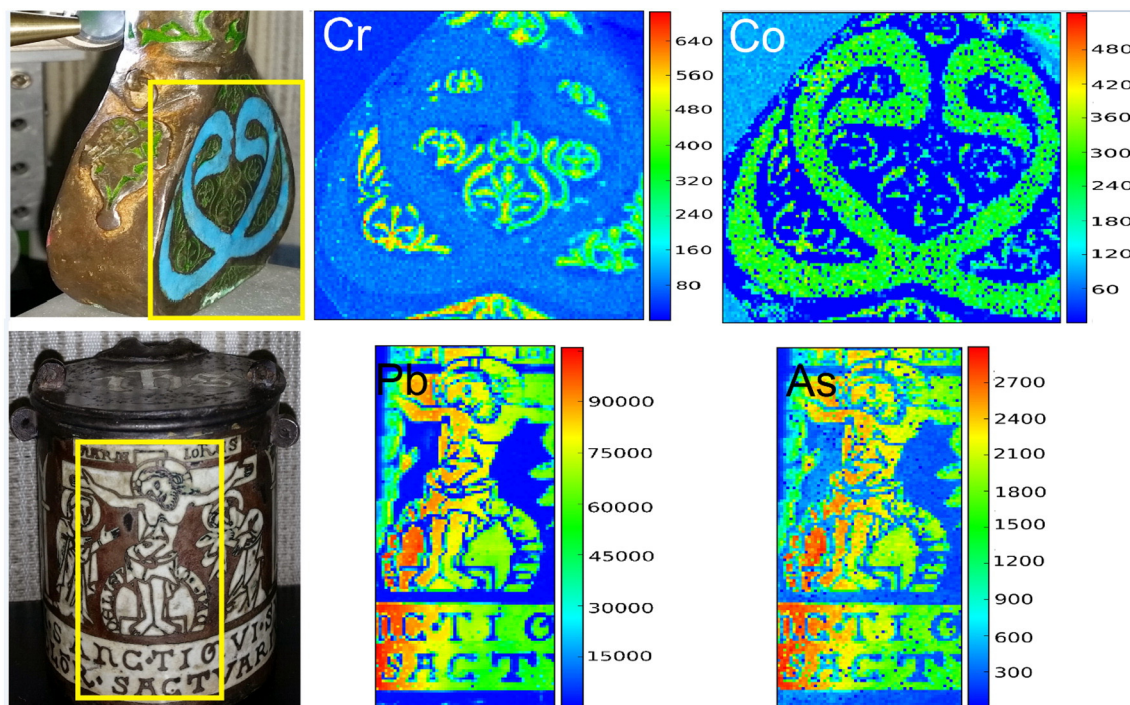Fig. 4. Elemental map associated to NNMA spectrum of Fig. 3.

Fig. 5. Elemental maps of enamels by the macro-XRF imaging for the bottle and the pot.

Fig. 5 shows the elemental distribution of the artworks in Figs. 1b and c, respectively.

The bluish enamel of the bottle is composed by cobalt (Co) and As (the latter is not shown in the figure); the green one by Cr. Both As and Cr are again not consistent with the historical artwork. The white enamel of the pot is characterized by Pb and As suggesting the use of lead arsenate as white opacifier in the glass manufacturing.

In order to exclude the presence of Cr as an inclusion of the green glass, its homogeneity was investigated by using a scanning micro-XRF. The scanning was limited to a small area of the green enamel. It consisted of 40 × 40 pixels, scanned with a step size of 10 μm.

Fig. 6 shows the result. Chromium appears uniformly distributed in the matrix. This is indicating its use as coloring agent in the enamel. A similar behavior is observed for Pb and K. In this case, some fluctuations in the concentration are observed as typical heterogeneities of the enamel composition. The spotted areas are inclusions or impurities of Ca and Fe in the glass matrix.

4. Conclusions

In this paper, alpha-PIXE and the scanning XRF imaging were used for the non-destructive investigation of three enameled artworks dated back to the XI–XII century AD. The objects were never investigated with scientific methods to confirm this attribution.

The alpha-PIXE was used for the quantitative analysis of the major elements in the glass matrix. Results evidenced a high Pb content. Additionally, the compositional data of Na, Ca and K were not consistent with the ones expected for medieval enamels.
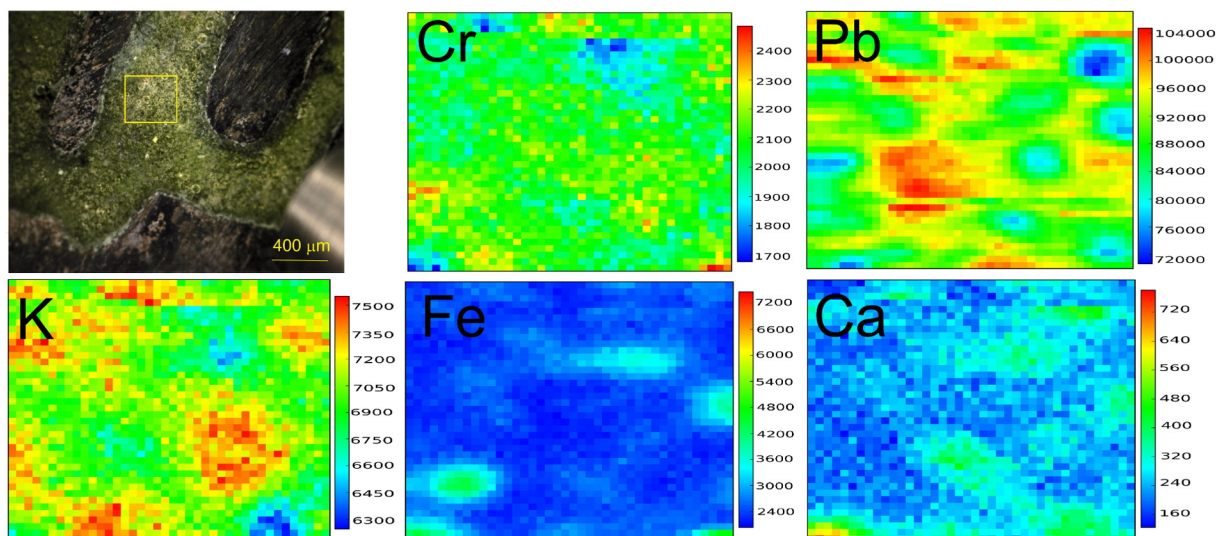

Fig. 6. Elemental maps of green enamel for the bottle by a micro-XRF imaging confirming Cr as coloring agent.

Scanning XRF imaging was used to map the elemental distribution in the samples.

A macro-XRF scanning was performed on the full objects (or on large parts of them). Red enamels evidenced the presence of Zn. The white and yellow samples were characterized by As. The presence of other elements like Se, Cd and Ba was not very clear in the raw spectral data since the possible overlap with X-ray lines of different elements. Chromium characterized the green enamels. This latter element was further investigated in order to exclude its presence as an impurity of the glass matrix. The scanning micro-XRF imaging on the green enamels evidenced the uniform distribution of Cr at the micro scale and confirmed its use as a colorant. These analytical results suggested a more recent manufacturing of the samples and a preliminary dating from the XVIII–XIX century AD.

The simultaneous presence of Zn, Cd, Se and Ba was used to gain more insight on the manufacturing period of the objects. Data were treated with a matrix factorization analysis. Due to the non-negative nature of the X-ray counts in the spectra, a Non Negative Matrix Approximation (NNMA) was used in the calculation.

The NNMA allowed to extrapolate from the raw data the presence of Se, Cd, and Ba and to evidence their association with Zn in the red enamels. This result gives a strong indication of the use of cadmium lithopone as red pigment, produced for the first time in 1921.

Since the similar compositional pattern was detected in the three objects, all of them were definitely classified as modern forgeries.

Acknowledgments

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