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Study of modern Chinese cloisonné by means of small-spot energy dispersive X-ray fluorescence spectrometry and Raman spectroscopy

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ABSTRACT

In this work, we studied the features of a modern Chinese cloisonné vase by means of small-spot energy dispersive X-ray fluorescence (EDXRF) and micro-Raman spectroscopy. Quantitative elemental results of enamel have been obtained after calibration of EDXRF instrumentation with certified reference materials. Up to eleven different coloured enamels have been recognized and analysed (black, pink, red, white, yellow and three shades of both blue and green). Enamel paste is mainly formed by the main identified elemental colouring agents - chromium, manganese, iron, cobalt, copper, antimony and cadmium– in a lead alkali silicate matrix.

The body of the vase is made by copper with minor amounts of zinc and tin. Analysis of metallic decorations at the surface of the vase reveal the presence of metal coatings applied for the embellishment of the artwork. Thickness of layered metal structures have been obtained by XRF fundamental parameters assisted with data from pure metal spectra, thus revealing the gilded coatings consist of a thick layer made by silver-doped nickel.

1. Introduction

Cloisonné or *qiasi falang* is one of the most famous Chinese traditional handicraft artworks since the Song dynasty. It refers to a surface decoration technique of metal vessels consisting of coloured-glass paste placed within enclosures made of metal wires that are bent and shaped into intricate patterns by hands and tweezers. Known as *cloisons* (French term for "partitions"), the cell enclosures are generally soldered onto the metal body of copper, bronze or even sometimes on precious metals such as silver or gold. The glassy enamel is coloured with metallic oxides inserted into the enclosures. Objects are also gilded, often on the edges, in the interior, and on the base. The vessel is usually fired at a relatively low temperature, about 700–800 °C [1].

In most Chinese cloisonné objects, blue is usually the predominant colour, so this technique was also known as Jingtai blue ware, after Jingtai Emperor. Initially heavy bronze or brass bodies were used, and the wires were soldered, but later much lighter copper vessels were used, and the wires were glued on before firing. Additionally, the enamel composition and pigment chemistry changed with time.

Chinese cloisonné enamelling technique arrived from Byzantium through the vast Mongol Empire and was promoted by the Song dynasty before its defeat against Yuan rulers of Mongol origin in 1279. The technique was adopted, and it was used to produce larger vessels such as bowls and vases, during Yuan dynasty, when Chinese craftsmen called this kind of enamel *dashi yao* or 'Muslim ware'. There were seven popular enamel colours during the Yuan period (up to 1368): turquoise, dark blue, ruby red, white, purple, and dark green. The most sophisticated and highly-valued cloisonné Chinese pieces are from the Ming Dynasty, especially the reigns of the Xuande Emperor and Jingtai Emperor (1450–1457). Their forms and decorations closely follow the previous ones from Yuan dynasty. Turquoise, dark blue, sometimes white, and exceptionally purple is the common background colour in Xuande enamels. The most relevant motifs feature seven main colours: dark blue, red, purple, dark green, light green and yellow which was not common in Yuan period [1,2]. The most important development during this period was the standardization of cloisonné production, which was controlled by the official imperial workshop. Ending the 17th century, the so-called 'balanced wires with thick glaze' technique was introduced. This advanced technique became the prevailing trend for the rest of the Qing dynasty. During the Yongzheng reign, the imperial workshop developed a total of 21 enamel colour pastes to be used in both cloisonné and painted enamel. The combination of these colours originated a

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greater variety of dyes.

The Chinese objects based on *cloisonné* technique were intended, primarily, for the furnishing of temples and palaces, due to their flamboyant splendour. This sophisticated technique has been maintained up to now, and modern *cloisonné* objects reproducing the old patterns and shapes can be found.

Analytical studies of Chinese cloisonné objects from different periods have been contributing to the understanding of their technology of production along the dynasties. Considering the value of these objects, an effort has been made to provide non-destructive and non-invasive methodologies. These include mostly, optical microscopy, Energy dispersive X-ray fluorescence (EDXRF) and micro-Raman spectroscopies implemented on-site with portable equipment. The application of these techniques, provide large information on the colouring agents and opacifiers used in the enamels, as well as their glass types. Burcu and co-workers characterised twenty-two Chinese cloisonné objects from 15 to 19th century belonging to the Musée des Arts Décoratifs (Paris) [2]. Glassy matrix, pigments and opacifiers were assessed at the museum using a Raman spectrometer coupled with a fibre optic Raman probe dedicated to the 532 nm laser. Yan Su and co-workers studied the enamel materials in a cloisonné ware sample taken from a screen from the Qianlong reign of Qing Dynasty (1736–1795 CE) [3]. They used Raman spectroscopy to access the molecular vibration information on enamel materials and Laser Ablation Inductively Coupled Plasma Mass Spectrometry, as an elemental information technique, with higher sensibility than XRF although micro-destructive, to provide supplementary information. For instance, it enabled the identification of lighter elements like Boron, which seem to be a common element used in Chinese cloisonné ware as borax [4]. Colomban and co-workers have been looking for European influences in Chinese cloisonné objects from 17 to 18th century using portable XRF and Raman spectrometers [5,6]. Main results point for the use of the lead pyrochlore pigment, from European Naples yellow recipes, in yellow and green colours, as well as cassiterite as opacifier. The presence of lead arsenate apatite detected in some of the blue enamelled decors was related to the use of arsenic-rich European cobalt ores.

Regarding the analytical studies devoted to Chinese cloisonné objects, few attention has been paid to the characterisation of metal substrates, metal wires or gilding. In this study, small-spot EDXRF and micro-Raman spectroscopies were used for the characterisation of the metal substrate, metal coatings, metal wire, and enamel glassy paste of a modern cloisonné vase, replicating the old style. The analyses were carried out directly on the vase, with no need for sample removal. The proposed methodology is an added value for studying intact cloisonné vases with inestimable value and provided, for the first time, knowledge on the technological characterisation of a modern cloisonné vase.

2. Experimental

2.1. Specimen description

A *cloisonné* vase from a private collection was delivered for the study. The vase has been manufactured during 2014 by Beijing Haanyihuang Cloisonné Wares Ltd., (NongGuangLi Chaoyang District Beijing, China) following the procedures of the classical Chinese production. By visual inspection, it is possible to recognize up to eleven different enamel colorations: black, pink, red, white, yellow and three shades of both blue and green (Fig. S1 (Appendix A)). The base to maintain the vase standing up is made by some flat ring of metallic nature, the vase mouth is also of golden metallic shine and the *cloison* compartments are limited by twisted metallic wire (see Fig. 1).

2.2. Instrumentation and analytical conditions

2.2.1. EDXRF setup

EDXRF analyses were performed by using a commercial benchtop small-spot (four different collimators of 0.1, 0.3, 1 and 3 mm in diameter) EDXRF spectrometer (XDV-SD model, Helmut Fischer GmbH, Germany). It consists of a microfocus tungsten anode X-ray tube, operating at fixed voltages of 10, 30 or 50 kV using a current in the range of 0.1 to 1 mA (max power of 50 W) and a SD semiconductor detector (Peltier cooling at −50 °C; with 170 eV FWHM at Mn Kα line). The spectrometer is equipped with five primary filters (nickel 10 μm, molybdenum 70 μm, aluminium 500 μm, aluminium 1000 μm, and titanium 300 μm), which can be used to reduce the spectral background and eliminate undesirable tungsten tube signals. Once the sample was placed inside the spectrometer chamber, taking into consideration the main objective of the study, the analyses were carried out operating the X-ray generator with two different analytical conditions: a) voltage of 50 kV, current of 1 mA, collimator of 0.1 mm in diameter and aluminium filter of 1000 μm in thickness, mainly focused on the analysis of heavy elements, and b) voltage of 10 kV, current of 1 mA, collimator of 0.1 mm in diameter without any primary filter to determine light elements. All the analyses were performed at open-air conditions.

Fig. 1. Photograph of Cloisonné vase and studied features. a) Coloured enamels, b) Vase alloy and gilding coating, c) twisted wires limiting *cloisons*, d) basal supporting metal ring.

Analyses of enamelled parts in both analytical conditions were carried out using an effective acquisition time of 500 s. Five replicates, at different points, were obtained for each different colour to obtain reliable results. The analyses of metallic parts were done with an acquisition time of 300 s and five replicates were recorded.

To undertake the EDXRF analysis we used pure standard metals (Goodfellow GmbH, Germany) for the initial energy/channel calibration and to build the sensitivity curve library of the instrumentation. The obtained parameters were directly applied for the analysis of the metallic parts of the vase. For the enamel analyses, we also measured 9 certified reference materials of multi-elemental glasses (BCR-126a from IRMM-EU; SQN-1, SQN-2, SQN-3 and STG-2 from Breitlander, Germany; SRM-612 from NIST, USA; SGT-4, SGT-7 and SGT-8 from SCT, UK) having highly different composition to adjust the evaluation model used for the quantification routine.

2.2.2. Raman setup

Raman spectra of the colouring materials were measured using a Horiba-Jobin Yvon XploRA confocal spectrometer, equipped with 3 laser diodes sources operating at wavelength values of 532 nm, 638 nm and 785 nm. Although attempts were made with the three lasers, better results were rendered by the 532 nm laser. Measurements were performed directly on the *cloisonné* surface using an elbow adapter to attach the microscope objectives (Fig. S2 (Appendix A)). An entrance slit of 100 μm was used, and the scattered light collected by the microscope objective was dispersed onto the air-cooled CCD array of an Andor iDus detector by 1800 lines/mm grating. Depending on the shape of the surface, 10× or 100× magnification objectives were used, with a pinhole of 300 μm to optimize the spatial resolution and signal intensity. By making use of a series of neutral density filters, the maximum incident power on the sample was up to 5 mW. Different windows of acquisition were selected to obtain a wavenumber range of 130–2500 cm^{-1}. Energy calibration was performed for each laser with a silicon wafer (520 cm^{-1}).

2.3. *Spectral evaluation and calibration*

2.3.1. *EDXRF*

Spectral data from EDXRF analysis has been evaluated using the WinFTM™ software (commercial software from Helmut Fischer GmbH, Germany). The software was designed for the simultaneous analysis of layer thickness and composition with application to single layers or multi-layered materials. The fundamentals of this software are detailed in the work of Roessiger and Nensel [7]. This software program utilizes for the evaluation of the measured spectrum the Fundamental Parameters (FP) approach [8], with the support of pure elements spectral data, in a first approach. The WINFTM™ can be additionally improved by the support of spectral data from CRM's of the same nature of the materials being analysed.

Different modules of the software package can be used to adapt the evaluation to the nature of the problem to be solved such as bulk mass analysis, elemental surface heterogeneity analysis, layer thickness and composition of coatings or multi-layered samples.

The light matrix composed by elements such as B, C, O, Na, Mg, Al, or Si, existing in glassy samples has a significant influence on the results of the heavier elements determination and must, therefore, be known by the user and defined in the analytical model to obtain correct results. However, in common material analysis usually, the matrix of the samples is not known by the user and is not measured with the usual portable or benchtop EDXRF instrumentation operating at ambient atmosphere as it is done in our experimental work. To determine the elemental composition of the cloisonné enamels we used a new function for measuring heavy elements in a light unknown matrix implemented in the software, the Automatrix function [9]. In this approach, the mean atomic number of the scattering matrix is determined from the scattering background. The elements with visible fluorescence lines are defined and analysed and the light element matrix is considered by evaluating the scattering background through theoretical modelling or by polynomial adjustment by supporting points along the spectrum. The capability of this feature and the reliability of the results are increased by the addition of spectra from CRM's to the evaluation model.

The analysis of the metallic parts, and taking in account that all the parts are coated by electroplating, was carried out using the models for layered materials with the support of pure metals as calibrators of the model.

2.3.2. *Raman spectroscopy*

To obtain an accurate identification of the enamel pigments, a polynomial baseline correction was carried out on the measured Raman spectra to remove the background contribution due to fluorescence. The identification of pigments was made with good accuracy by using literature on enamels identification by Raman spectroscopy [2,10–12] and the same spectral databases (e-Visart, RRUFF), used in previous work [13,14].

3. Results and discussion

3.1. *EDXRF results of metallic parts*

Analytical results of metallic parts of *cloisonné* are shown in Table 1. The alloy used for the manufacturing is nearly pure copper (95.9 to 98.4%) with the presence of zinc, tin, and lead. Differences in the minor components for the three metallic parts, vase body alloy (Fig. 1b), twisted wire (Fig. 1c) and basal ring were found. Zinc content is nearly three times higher in the ring than in the vase body and both lead and tin contents are two times higher in the vase body alloy than in the basal ring.

These entire copper-based parts exhibit a nearly pure nickel coating with thickness ranging from 24.1 ± 0.4 to 30 ± 1 μm. The minor constituents of the coatings reveal some differences between the gilding of vase, with traces of silver and lead and those from wire and basal ring with silver and tin. Likewise, the basal ring has a bilayer coating, with an intermediate thin layer with a major presence of lead and tin.

3.2. *Cloisonné enamels*

Table 2 summarizes the compositional traits obtained by EDXRF for the eleven different coloured enamels in the cloisonné vase. Considering these results, all the enamels are based on lead-containing glass with content around 23% of lead.

Regarding Raman analysis, the obtained spectra for blue, green, yellow, and pink enamels present the typical signatures of characteristic glassy silicates with Si—O bending and stretching bands at ~500 and ≈ 1000 cm^{-1}, respectively. The intense band at ~1050 is indicative of a lead alkali glaze (Fig. 2) [2,15]. Raman signatures of the red, black, and white coloured glazes were not achieved.

The yellow enamel has a higher content of lead, around 35%. This increase of lead in yellow enamel agrees with the analysis of old cloisonné from the Qing Dynasty made by Su et al. [3] and Miao et al. [16].

In our modern *cloisonné* vase, calcium content is higher in white, blue, and green enamels as it often occurs in old objects. One of the differential features is the ubiquitous presence of zinc, not usually reported in old cloisonné materials and that in the form of zinc oxide, alike lead oxide, can act as a flux, aiding the melting of the glaze.

The Raman peak at ≈320 cm^{-1} in the blue enamels, could be assigned to fluorite (CaF_2), an opacifying agent which is a common opacifier in Chinese enamels [17].

The different contents of the other seven main elements (chromium, manganese, iron, cobalt, copper, cadmium, and antimony) can be suggested as responsible for different enamel colours. Besides, when the

Table 1
EDXRF analysis of metallic parts of Cloisonné vase. Mean elemental concentration and standard deviations (n = 5) of alloys and coating layers.

	Vase body alloy			Twisted wire alloy			Basal ring alloy		
Cu(%)	97.2	±	0.8	98.4	±	0.4	95.9	±	0.5
Zn(%)	0.9	±	0.1	0.14	±	0.08	3.1	±	0.3
Sn(%)	1.0	±	0.1	0.8	±	0.1	0.5	±	0.3
Pb(%)	1.1	±	0.3	0.7	±	0.3	0.6	±	0.1
	Coating layer			Coating layer			Upper layer		
Thickness (μm)	26.5	±	0.8	30	±	3	24.1	±	0.4
Ni(%)	99.6	±	0.1	97.8	±	0.5	99.5	±	0.1
Ag(%)	0.32	±	0.03	0.42	±	0.06	0.37	±	0.02
Pb(%)	0.12	±	0.04						
Sn(%)				0.8	±	0.3	0.16	±	0.04
							Intermediate layer		
Thickness (μm)							3.6	±	0.3
Ni(%)							76	±	1
Pb(%)							11.9	±	0.7
Sn(%)							12.2	±	0.8

Table 2
Mean elemental concentration and standard deviation (values in wt%) obtained from EDXRF analysis of different cloisonné enamel colours (n = 5).

	White	Yellow	Red	Pink	Black	Dark blue	Medium blue	Light blue	Dark green	Medium green	Light green
SiO_2	43 ± 2	43 ± 2	42 ± 1	40 ± 2	40 ± 2	41 ± 1	39 ± 1	39 ± 2	39 ± 1	40 ± 1	33 ± 1
K_2O	1.8 ± 0.1		2.2 ± 0.3	1.7 ± 0.2	1.5 ± 0.1	0.86 ± 0.06	1.45 ± 0.06	1.3 ± 0.1	1.57 ± 0.05	1.6 ± 0.2	0.5 ± 0.2
CaO	5.0 ± 0.3	1.2 ± 0.1	0.10 ± 0.01	1.2 ± 0.2	1.3 ± 0.1	2.3 ± 0.3	1.19 ± 0.08	1.9 ± 0.3	3.1 ± 0.3	3.2 ± 0.3	1.7 ± 0.5
MnO					3.7 ± 0.2						
Fe_2O_3					3.1 ± 0.3		0.17 ± 0.01				
PbO	25 ± 2	38 ± 2	25 ± 1	25.7 ± 0.3	22 ± 1	25.6 ± 0.3	25.9 ± 0.9	26 ± 1	25.3 ± 0.8	26.0 ± 0.7	27 ± 1
Cr_2O_3									0.83 ± 0.06	0.85 ± 0.09	0.28 ± 0.04
CoO					0.6 ± 0.1	1.14 ± 0.05	0.31 ± 0.03				
NiO		0.25 ± 0.03	0.23 ± 0.01		0.20 ± 0.05						
CuO	0.26 ± 0.07	0.39 ± 0.08	0.38 ± 0.05	0.19 ± 0.08	1.79 ± 0.08	0.51 ± 0.09	4.0 ± 0.2	3.00 ± 0.09	4.58 ± 0.02	4.5 ± 0.2	0.3 ± 0.1
ZnO	0.47 ± 0.05	5.1 ± 0.3	8.5 ± 0.3	1.00 ± 0.06	1.2 ± 0.08	0.65 ± 0.04	0.9 ± 0.1	0.8 ± 0.1	0.68 ± 0.03	0.9 ± 0.1	0.68 ± 0.03
SeO_2			0.18 ± 0.02								
Rb_2O	0.62 ± 0.08										
ZrO_2					0.35 ± 0.04						
CdO			6.5 ± 0.2								
SnO_2					0.23 ± 0.03	0.23 ± 0.03	0.17 ± 0.02	0.46 ± 0.03	0.36 ± 0.06	0.33 ± 0.04	
Sb_2O_3	10 ± 1	3.2 ± 0.1		0.3 ± 0.1							
BaO				2.3 ± 0.2	0.45 ± 0.07	0.50 ± 0.04		0.44 ± 0.03			

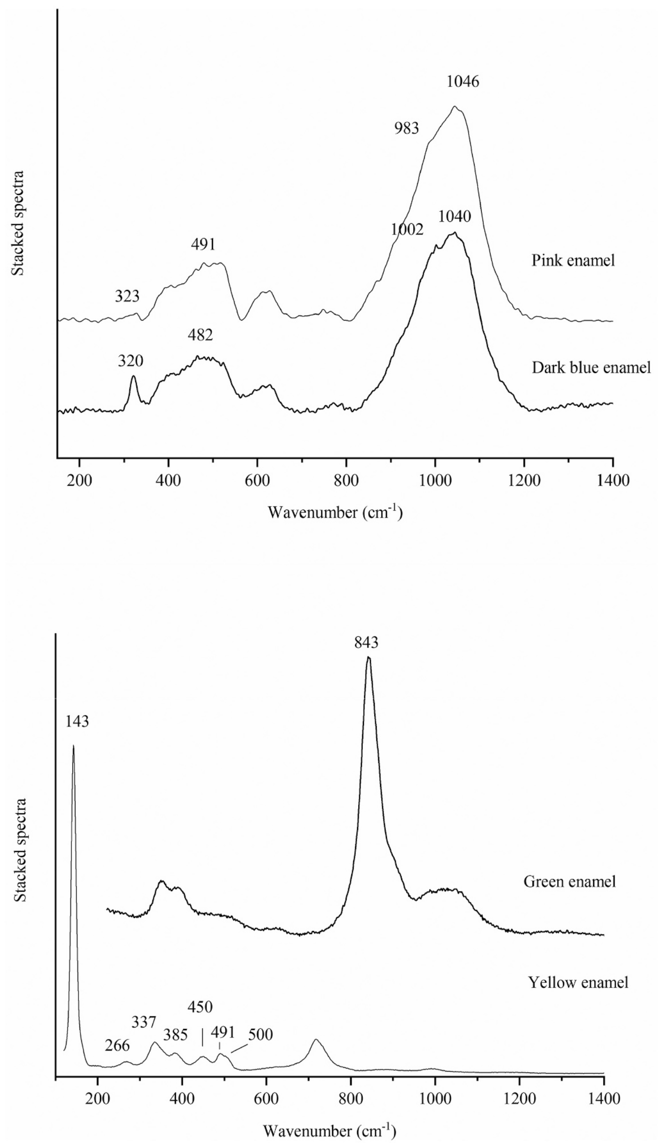

Fig. 2. Raman spectra of Cloisonné enamels.

colour arises from the dissolution of certain transition metal ions (e.g., Cu^{2+}, Co^{2+}, Co^{3+}, Mn^{2+} and Mn^{3+}) in the glass matrix, the coloured phase cannot be detected by Raman spectroscopy.

3.2.1. *White*

The white colour of a translucid lead-bearing silicate glass is commonly obtained by dispersing an opacifier phase within the glassy matrix having a higher refractive index than the glass. Around twenty different white pigments and opacifiers have been commonly used in the enamelling process [12]. In the present studied modern cloisonné, we found noticeable contents of antimony and calcium (Fig. S3a (Appendix), but no phase containing such elements could be identified in the obtained Raman spectra. The high fluorescence may have hampered the observation of the characteristic Raman bands.

3.2.2. *Black*

The preparation of pastes for black enamel formulations is difficult, mainly in oxidizing firing atmospheres. Few ancient black pigments have been reported up to now, being manganese oxides probably the most used from antiquity found in archaeological cave paintings. The common way to produce black colourations is the mixture of different transition metals oxides to develop spinel-type crystal structures [12]. In the present study, this colour was obtained by the combined presence of manganese, iron, cobalt, copper, zinc, and barium with a minor amount of tin and zirconium (Fig. S3a (Appendix)), being the most complex enamel from a compositional point of view.

3.2.3. *Yellow*

Intense yellow was one of the most favoured colours of the Chinese Emperors, frequently used in porcelain and less frequent in old cloisonné enamels where blue tonalities are prevailing. The ancient yellow colour was obtained by the unique addition of iron and later replaced by a more complex composition to produce highly stable and opaque enamel [18].

In the present study, we could identify a huge increase of lead content and the join presence of noticeable amounts of zinc and antimony (Fig. S3b (Appendix)), indicating that yellow enamel was probably obtained by the induced precipitation of lead oxide (PbO) and the addition of antimony, and zinc to promote lead antimonate yellow pyrochlore-type structure. These processes are well-known, and these phases have been reported for glazes in ancient ceramics [19]. The corresponding Raman bands have been identified in the yellow areas (Fig. 2).

3.2.4. *Red*

Red glass colourations in Chinese artworks are usually obtained by the dispersal of copper, copper oxides or iron oxides inside the glaze, but other possibilities such as the use of minium (lead oxide), realgar (arsenic sulphide) or vermilion (mercury sulphide) have been reported from antiquity.

The chemical composition of the analysed red glaze exhibits high content of both cadmium and zinc and minor amounts of selenium and copper (Fig. S3b). Cadmium was introduced as a pigmenting agent in glazed ceramic in modern times around the late 19th to early 20th century [12]. Cadmium red (CdS(Se)) is also a well-known pigment in the modern ceramic industry. Our EDXRF results reveal the presence of both cadmium and minor selenium in the red enamel suggesting the use of the later in the formulation of glaze. However, the pigment bands were not assigned using Raman spectroscopy.

3.2.5. *Pink*

In old *cloisonné* objects, pink coloured areas are laid on the surface of white enamel zones, without specific compartment for pink enamel, and the pink colour is obtained by mixing a red hematite-rich pigment with tin oxide [20]. According to the elemental analysis reported by Su et al. [3] pink colour in *cloisonné* ware from the Qing dynasty, is related with a small amount of dispersed noble gold and lead arsenate within the glassy matrix. Most of the pink colourations in modern enamelled ceramics are based on chromium-doped calcium-tin silicate with monoclinic sphene structure [21]. None of these different possibilities is compatible with the obtained elemental analysis in the present study (Fig. S3b (Appendix)). EDXRF analysis of pink enamel reveals the presence of barium and zinc with minor antimony and copper in its composition, a composition which is not usually reported for enamels or glassy materials. Barium in the form of barium oxide, alike lead oxide and zinc oxide, can act as a flux.

Raman spectra of pink areas did not render conclusive results, as well. As can be seen in Fig. 2 the only features obtained in the spectrum are related with the Si-based glassy matrix.

3.2.6. *Blue*

Three different tonalities of blue glazed areas have been observed: dark blue, medium blue and light blue near turquoise. The intensity of the blue colour is directly related to the presence of different amounts of cobalt and copper in the glazes as it can be observed in the spectra (Fig. S3c). Cobalt decreases from dark to medium blue colourations and it was not detected in the light blue enamel. On the opposite, the content of copper is higher in the less intense blue glazes. Zinc and tin are always found in blue coloured areas, and barium can be also identified in both light and dark blue. The use of cobalt and copper raw materials to obtain blue colours is widespread in glasses and enamels from antiquity, playing cobalt ions speciation the dominant chromophore role for the intensity of blue zones in Chinese glazes [22].

Raman spectra obtained for blue enamels, show no more than the stretching and bending massifs of the Si—O bond of the glassy matrix (Fig. 2). This could be due to the dissolution of cobalt ions in the matrix of both dark and medium blue glazes leaving no Raman signature [11].

3.2.7. *Green*

In classical Chinese cloisonné from Imperial periods, green glazed enamels are obtained by the mixture of blue and yellow pigments, usually containing iron as the promoter of yellowish coloration within a copper-blue glassy matrix [2,3,9]. The analysis of intense green tonalities of the studied modern cloisonné revealed (Fig. S3d) the presence of copper as major colouring element and the joint presence, in minor amounts, of zinc, tin and chromium. We only found this last element in the green colorations, clearly suggesting its major role on the colour, typically as Viridian ($Cr_2O_3{\cdot}2H_2O$), or Chrome green, the name given to the pigment made by co-precipitating Prussian blue [$Fe_4(Fe[CN]_6)_3$] and chromium yellow ($PbCrO_4$) [23]. Raman analysis of green samples pointed out the presence of lead chromate (Fig. 2) with a strong band at 843 cm^{-1} attributed to the v1 symmetric stretching mode of the CrO_4^{2-} in chromium yellow [24,25]. However, there is no significant signal from iron in the EDXRF spectra of the green regions, and the characteristic bands of Prussian blue (538, 2102 and 2154 cm^{-1}) are also missing from the Raman spectra. In this case, the blue pigment is most likely a copper-based one but the characteristic bands from the glassy-matrix are so intense that they mask any signal.

4. Conclusions

In this work, we analysed the materials used in a modern *cloisonné* vase and we were able to differentiate it from the original ancient pieces. Metallic parts (body, base support, and twisted wires) have been analysed thus revealing the presence of metal coatings to embellish the object. Coatings have been investigated to determine simultaneously layer thickness and composition through adequate software routines. Although with the turn of the 18th century, arsenic based opacifiers became more common in Chinese cloisonné enamels, as a result of European technology transfer, this modern vase still seems to present the traditionally used fluorite as opacifier [17]. Moreover, and as would be expected, artists made use of modern materials (based on cadmium, zirconium, or zinc compounds) and took advantage of the chemical novelties that were rising over time.

These results were mainly obtained with basis on EDXRF analysis, as the Raman spectra of enamels rendered information mainly on the glassy matrix. This information, had nevertheless, complemented the results obtained by EDXRF enabling the identification of a lead alkali glassy matrix. Moreover, with exception for the yellow and the green colours, regardless of the laser used, it was not possible to obtain the Raman bands to ascertain the molecular groups involved in most of the colour production.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sab.2022.106594.

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