



Non-invasive on-site Raman study of polychrome and white enamelled glass artefacts in imitation of porcelain assigned to Bernard Perrot and his followers

Philippe Colomban, Burcu Kirmizi

► To cite this version:

Philippe Colomban, Burcu Kirmizi. Non-invasive on-site Raman study of polychrome and white enamelled glass artefacts in imitation of porcelain assigned to Bernard Perrot and his followers. *Journal of Raman Spectroscopy*, In press, 10.1002/jrs.5745 . hal-02344503

HAL Id: hal-02344503

<https://hal.sorbonne-universite.fr/hal-02344503>

Submitted on 4 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Non-invasive on-site Raman study of white and polychrome enamelled glass artefacts in imitation of porcelain assigned to Bernard Perrot and his followers

Philippe Colomban¹, Burcu Kırmızı^{1,2}

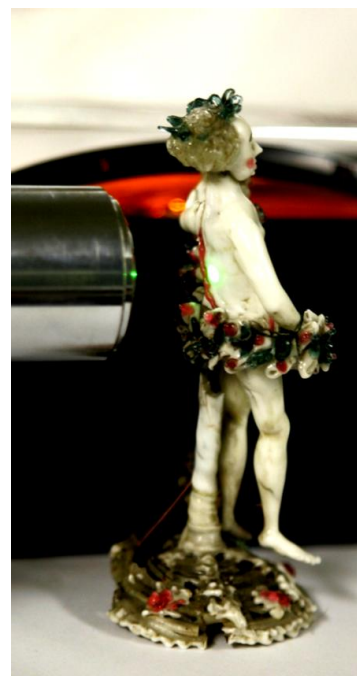
¹ Sorbonne Université, CNRS, MONARIS UMR8233, 4 Place Jussieu, 75005 Paris, France

² Yıldız Technical University Faculty of Architecture, Department of Conservation and Restoration of Cultural Property, Beşiktaş 34349 İstanbul, Turkey

philippe.colomban@sorbonne-universite.fr

Abstract

Bernard Perrot had produced sophisticated glass objects from ~1666 to 1709 in Orléans, particularly white enamelled artefacts and ruby glass. We present here the first non-invasive Raman study of sixteen white glass artefacts which are assigned to B. Perrot or his followers. These glasses are enamelled except one of them and belong to the museum collections of Orléans and Sèvres. The prominent characteristic of these artefacts is their white bodies which were produced in imitation of porcelain. The small thickness of enamel applied to these glasses imposes the use of a high magnification (x200) long working distance microscope objective for Raman analysis. Pigments and opacifiers were identified and the production technology was discussed. White opacification was obtained by three compounds: calcium phosphate (bone opacification) for blown utensils, calcium antimonate for figurines and cassiterite for thin enamels. The characteristic arsenic-rich European cobalt was identified in the blue enamels with the characteristic Raman signature of arsenic apatite as observed for 17th and 18th soft-paste porcelains and Limoges enamels. The easy Raman detection of arsenic-rich phases also allows on-site identification of ruby glass made according to Perrot's technique (precipitation of Au⁰ colloids by arsenic). The amount and crystallinity of calcium phosphate being variable appears to be a potential tool to discriminate between different production periods or workshops.



Keywords: Glass; enamels; pigments; 17th century; porcelain

1. INTRODUCTION

Enamelling is the craft of fine adornment in the form of mainly coloured glassy material executed on metal, glass or ceramic substrates. In history, one of the earliest use of enamel occurred on glass objects dating back to the 15th century B.C. in Egypt. Enamelling was probably invented in the search of permanent decoration by the craftsmen after the techniques of glassmaking and glazing had once been accomplished.^[1] Enamelled glass continued to be produced during the Roman and Byzantine periods.^[2] Then, Islamic glassmakers perfected the craft of glass enamelling during the 13th and 14th centuries in Egypt and Syria.^[3] From the 15th century onwards, Italy became a major glass production centre with the impetus of the Renaissance where the technique of glass enamelling reached a high level.^[4] The production of enamelled glass was particularly established in Venice and Altare and then spread to other parts of Europe as well.^[2,5]

Bernard Perrot (Bernardo Perroto, 1640, Altare-1709, Orléans), is the most famous “French” glassmaker who had been active during the reign of Louis XIV from ~1666 until his death.^[6] He was the first to be able to produce glass plates and mirrors by cooling on metal table (before St-Gobain Compagnie des glaces). Yet, he did not have the royal permission to produce and sell them. He is famous for the production of figurines, moulded glasses, polychrome jasper table plates, ruby glasses and enamelled white glasses imitating porcelain, also called as *lattimo*.^[7-11] *Lattimo* is the opaque white glass which had been particularly produced from the 15th century onwards in Venice in quest of highly prized Chinese porcelain.^[9,12] However, the artefacts produced by Perrot do not have specific marks and their assignments have remained to be under debate up to now. Perrot worked first at Nevers, a place where figurines had been produced before he arrived at Orléans and founded a factory there.^[6] The presence of some elements in his products was first determined by Barrelet and co-workers.^[7,8] Then, three artefacts assigned to Perrot or his followers were analysed by Raman spectroscopy at Musée de la Céramique, Sèvres in 2009.^[9] These preliminary works pointed out the use of calcium antimonate ($\text{Ca}_2\text{Sb}_2\text{O}_7$) and calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$] as white opacifiers as well as the use of colloidal gold (i.e. Au° nanoparticles) to colour glass in ruby. Then, detailed elemental compositions of thirty nine artefacts were measured by Biron et al.^[13,14] for the exhibition at Musée des Beaux-Arts d’Orléans in 2010: twenty five of these artefacts using Proton Induced X-ray Emission (PIXE) as a non-invasive technique at AGLAE Ion beam (C2RMF, Paris) and the others using micro-destructive Laser Ablation-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) (IRAMAT, Orléans). Four samples were also measured by both techniques. The half of these objects is white while the others are optically clear or coloured. Only one enamelled artefact – a small bottle with 1715 date written - was studied in detail.

Figure 1 summarizes the results regarding white and white enamelled artefacts measured by Biron et al.^[13,14]. They noted that the elemental compositions measured were very scattered: the silica content ranges typically between 50 and 70 %wt for the glass body and between 30 and 45 %wt for enamels with 30 to 50 %wt of PbO being added in the latter. As noted previously,^[7-9] the flux used is a mixture of K₂O and CaO and when the enamels contain SnO₂, the white bodies are opacified with Sb₂O₃. Regarding flux, Na₂O content ranges from 0.2 to 6.9 %wt with K₂O from 1.9 to 21.8 %wt and CaO from 0.1 to 13.7 %wt; P₂O₅ content also ranges between 0 (for transparent and some opaque glasses) and 6.27 %wt. As₂O₃ was detected in the ruby glasses (0.6 to 2.15 %wt) as well as in the blue glasses (0.15 to 1.38 %wt) with also some traces in many white glasses (this outcome and the detection of cobalt may indicate a deliberate addition of cobalt ores to whiten the colour, as made with lapis lazuli by J. F. Böttger for porcelain glaze).^[15] SnO₂ was measured in lead-based enamels (1.15 to 14.6 %wt) and Sb₂O₃ content ranges between 1.7 and 8.7 %wt in white artefacts (and yellow enamel). Chlorine (0.1 to 1 %wt) was measured in all samples that may indicate the use of salt but the major fluxing agents are wood/plant ashes. In fact, K, Ca and Na contents of ashes are extremely variable due to the part of the plant used and the conditions of growth.^[16]

The large scattering of chemical data may have different reasons. First of all, the dating and assignment of artefacts to Bernard Perrot or his followers is not certain (the factory and its subsidiaries had continued to be active up to ca. 1754).^[6] The inventiveness of B. Perrot was also well attested by historical records (Royal privilege demands, communications at the Royal Academy of Sciences, etc.), making it reasonable to think that different technologies had been experimented in his workshop.

It should be noted that the measurements with ion beam facilities are expensive which limit the number of artefacts studied and the laser ablation technique is risky for enamelled glass objects because of the huge thermal choc at the laser focus. As a non-invasive method, the use of on-site Raman spectroscopy without any contact has proved its efficiency in the study of enamelled artefacts.^[9, 17-20] In this study, sixteen enamelled artefacts assigned to Bernard Perrot or his followers from the collections of Musée des Beaux-Arts d'Orléans and Cité de la Céramique in Sèvres were studied by on-site Raman analyses to understand about the material characteristics and the production technology of the glass bodies and enamels of the artefacts. Some of these artefacts or very similar ones were represented at the former exhibitions in Musée des Beaux-Arts d'Orléans (2010)^[21] and Taiwan National Palace Museum (2011).^[22] This study is also expected to shed light on the characteristics of enamelling technology employed during the 17th century in France and is part of the international project about the enamelling technologies in France and China during the period mentioned for the identification of artefacts made at the Kangxi Court workshop under the

guidance/advice of Jesuits with European technology^[23], inspired by the taste of Louis XIV, the Sun King Court.

2. EXPERIMENTAL

2.1 Artefacts

The artefacts analysed are listed in Table 1 and shown in Figures 2 and 3. They belong to the collections of Musée des Beaux-Arts d'Orléans and Cité de la Céramique in Sèvres. Ten small figurines (~8-10 cm height, one of them white and the others polychrome), a beaker (~10 cm), a small pot (~6 cm), a bottle (~8 cm), a Baluster vase and a vase with a ball (~25 cm) which are all enamelled on a white body were analysed (see Table 1 for more details).

2.2 Raman microspectroscopy

Raman analyses were carried out at the museum collections of Orléans and Sèvres with a mobile HORIBA Scientific Jobin-Yvon Raman set-up. For each colour, at least 3 Raman spectra were recorded in order to check the representativeness of the collected data. This set-up includes a remote SuperHead® connected to HE532 spectrometer (920 lines/mm; resolution $\sim 4\text{ cm}^{-1}$) and 532 nm Ventus Quantum 300 mW laser by optic fibres. The SuperHead® was put on a heavy and very stable stage with XYZ micrometric displacements for the precise recording of the spectra. The Horiba Scientific CCD is cooled at 200 K. A reliable spectrum starts over 80 cm^{-1} but a flat background is only achieved over 500 cm^{-1} .

The height position of the artefact during the analysis was adjusted with the support of reams of copy paper. Two types of microscope objectives including x200 Mitutoyo (~13 mm long working distance) and x50 Nikon (~17 mm long working distance) were used. The power of illumination was roughly controlled at the SuperHead with a variable shutter. The focus quality was controlled by eye examination at very low laser power in the dark. A black textile was put on the Superhead® and artefact to prevent the contribution from the ambient light and protect the scientist's eyes from the laser scattering. Then, the laser power was increased to about 1 mW (black area) and 10 mW (colourless area) at the sample. The focus was first adjusted with the 3D micrometre stage up to have the maximum level of count on the laptop screen which corresponds to a focus at the sample surface; usually carbon signal is observed very rapidly due to the elimination of the dust at the surface of the artefact together with some decrease of the background level. Modification of the focus allows recording of good spectrum from the very surface to the substrate. The very small laser spot (about $0.5 \times 0.5 \times 2\text{ }\mu\text{m}^3$) obtained with x200 objective requires a very precise focus which is a

lengthy process but guarantees the analysis of the single enamelled layer without any contribution of the substrate, eliminating the fluorescence. Thus, it provides a spectrum with less background than those obtained with less expensive common objectives. In fact, the background shape allows controlling the colour of the studied spot: flat for a blue area, decreasing for a red area and increasing for yellow or green areas. Obviously, the signal level is low for a black area. Most of the spectra were recorded with x200 objective for the precise analysis of the enamels while some of them were recorded with x50 objective for comparison. The very high quality of spectra obtained with x200 objective is quite obvious (Fig. 4 top left compares spectra recorded with x200 (a & b) and x50 (c & d) objectives). Recording times range between a few seconds and a few minutes as a function of the number of accumulations required (3 to 100).

3. RESULTS

Representative spectra are shown in Figures 4 and 5. All spectra are shown as recorded except some obtained from the artefacts from Musée des Beaux-Arts d'Orléans recorded with X50 objective in which a baseline has been subtracted. However, the edge filter rejecting the Rayleigh scattering starts absorbing light progressively below $\sim 500\text{ cm}^{-1}$ up to the $\sim 80\text{ cm}^{-1}$ cut-off. The background shape makes the baseline subtraction difficult in the $200\text{-}600\text{ cm}^{-1}$ range and thus strongly affects the study of the Si-O bending modes.^[24-26] The background only vanishes for very strong spectra as those obtained on the yellow pigment.

We will present the results considering the opacifiers, the different coloured enamels and the glassy silicate matrix of the artefacts as respectively.

3.1 Opacifiers (White)

In order to obtain the whiteness required for porcelain imitations, opacifiers are added in glass bodies. Two types of opacifiers were identified in the white glass bodies of the artefacts studied: calcium antimonate ($\text{Ca}_2\text{Sb}_2\text{O}_7$) with characteristic doublet at ca. 480 and 633 cm^{-1} and calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$] with characteristic PO_4^{3-} stretching mode at ca. 960 cm^{-1} .^[9,27] The opacifier type seems to be related to the artefact type such as the modelled figurines being opacified with calcium antimonate (Figure 4-top left) and the blown utensils being opacified with calcium phosphate (please refer to the characteristic pontils on back photos given in Fig. S1, Supplementary Materials). The different intensities of the Raman band display that the crystallinity and/or amount of calcium phosphate are variable. For instance, strong intensity is observed in MNC 11226 (18th century pot)

(Fig. 4-bottom left) as well as in vase MNC 2014.14.1 (except the ball) (Fig. 5-bottom left). Production technologies used are thus different for the figurines and utensils.

Cassiterite (SnO_2) as another type of opacifier was detected in most of the enamels of the utensils with its characteristic $\sim 632\text{--}775\text{ cm}^{-1}$ doublet^[9] as shown in Figure 5: the blue, yellow and red enamels of beaker 999.4.1; the blue, yellow, green and red enamels of bottle MNC 2016.14.2; the light blue, yellow, green and red enamels of pot MNC 25017; the blue, pink, yellow, green and black enamels of Baluster vase MNC 2011.0125 and in the blue and yellow enamels of vase MNC 2014.141. It was also found in only one figurine (MNC 11234-4), in the black area of the face (eyes, eyebrows and hair) of the virgin (Figure 4-bottom right). Thus, cassiterite was used in the enamels of the artefacts opacified with calcium phosphate.

3.2 Enamels

3.2.1 Red and related colours

Different phases were identified in these enamels. Results are shown in Table 1 for each artefact. Orange and some of the red enamels were coloured with iron oxide, likely haematite ($\alpha\text{-Fe}_2\text{O}_3$) with its characteristic spectrum shown in Figure 5 (strong resonance magnon peak at $\sim 1310\text{ cm}^{-1}$ and bands at 222, 245, 295, 405, 495 and 605 cm^{-1}).^[28] However, a phase transition into haematite from a mixture of different types of iron oxides may have occurred by local heating due to the huge sensitivity of iron oxides to green laser irradiation. Ruby or carmine coloured enamels led to a spectrum displaying a rather strong peak at ca. 820 cm^{-1} : for instance, in the flower wreath of the shoulder strap of Bacchus (Figure 4- middle left, d, Figure 2b left). A similar feature was observed for the red garniture and cheek carnation of lady (MNC 11234-7, Figure 2b right) and virgin figurines (MNC 11234-4, Figure 2c right). This peak is characteristic of the As-O stretching mode arising from the arsenic ions used to obtain the precipitation of colloidal gold.^[10] The narrow 820 cm^{-1} peak is also an indicator of the apatite phase - $\text{Na}_{x-y-z}\text{K}_y\text{Ca}_{z/2}\text{Pb}_4(\text{AsO}_4)_3$ that forms by cooling from the reaction of cobalt ores containing arsenic (CoAs_2 , CoAs_3 , CoAsS , etc.) from European mines with lead-based glaze (see further).^[29] However, parent phases are possible and distinguishing the different phases from their sole Raman signature requires further studies.

3.2.2 Blue

There can only be two thermally stable blue chromophores present in glassy silicates: i) Co^{2+} ion dissolved in the silicate network or hosted in a pigment as a crystalline phase stable in the (molten) glass, namely a phase hosting cobalt ion and ii) a phase hosting S_3^- chromophore, lazurite (a feldspar like mineral present in lapis lazuli rock)^[29,30] or ultramarine (a synthetic zeolite).^[31] Co^{2+} dissolved in

the glassy silicate does not show a specific Raman signature while pigments have very characteristic Raman signatures .^[24-27, 32-42] In particular, the use of European arsenic-(very)rich cobalt ores lead to the precipitation of arsenic apatite characterized with a strong $\sim 820\text{ cm}^{-1}$ band in the case of lead-containing glazes coloured with As-rich cobalt source. This band is observed in the blue enamels analysed, except those of MNC 11234-4 and MNC 2014.141 (Figure 5). The presence of arsenic apatite was also reported for many kinds of enamels on metal as well as on porcelain.^[32-39] For other blue enamels as noted in the Raman study of 17th century-early 18th century soft-paste porcelains and Limoges enamels,^[36,37,39] peak wavenumbers shift among 815 cm^{-1} (lady figurine MNC 11234-7), $\sim 821\text{ cm}^{-1}$ (Baluster vase MNC 2011.0125), $\sim 823\text{ cm}^{-1}$ (beaker 999.4.1, bottle MNC 2016.14.2) and $\sim 825\text{ cm}^{-1}$ (pot MNC 11226, pot MNC 25017, ball MNC 2014.141). The bandwidth of the peak varies, as being very narrow in beaker 999.4.1 and bottle MNC 2016.14.2 and very broad in pot MNC 11226. The intensities are also variable, as very strong in figurine MNC 11234-7 and very weak in Baluster vase MNC 2011.0125. In the latter artefact, the signature of S_3^- chromophore (fundamental mode at 545 cm^{-1} and its first overtone at 1093 cm^{-1} , Figure 5-middle right) was observed in the restored area along with the signature of the epoxy-based glue (narrow peaks at 1035 , 1450 and 1600 cm^{-1}).^[40] Under green laser excitation, it is not possible to distinguish between (natural) lazurite or synthetic ultramarine since they are both pigments hosting the same chromophore.^[30, 32-33]

Although the 825 cm^{-1} band characteristic of arsenic apatite was detected in the ball, it was not identified on the vase (MNC 2014.141) (Figure 5-bottom left and right). This fact and the particular calcium phosphate signature (narrow and strong 960 cm^{-1} peak) indicate that the vase and the ball had been produced with different techniques, probably at different periods. Furthermore, the spectra recorded for figurine MNC 11234-4 (virgin) show a very broad peak extending up to 865 cm^{-1} , that could indicate the use of a different type of cobalt ore with chromium (Figure 4-bottom right).^[29,39] Similar spectra were measured in the green enamel of figurine MNC 11234-10 in combination with *Naples yellow* type pigment (Figure 4-top right, see further). Cassiterite was also found to be added to some blue enamels to adjust the hues (ball MNC 2014.141, bottle MNC 2016.14.2, pot MNC 25017, beaker 999.4.1, Baluster vase 2011.0125).

3.2.3 Yellow

All the yellow enamels display the characteristic Raman signature of Pb-Sb pyrochlores (Figure 4-bottom left, Figure 5). These compounds, more commonly defined as *Naples Yellow* type pigments had been used to obtain yellow colour in ceramic glazes and glasses throughout history since the prehistoric times. This type of pigment is a traditional colorant of Byzantine pottery and then of Islamic faience and Mediterranean majolica.^[36, 37, 39-41] The pyrochlore structure in the form of $\text{Pb}_2[\text{Sb}/\text{Sn}/\text{Fe}/\text{Zn}/\text{Si}]_2\text{O}_{7-8}$ solid solution is very variable and the exact composition of the pigment

affects the peak wavenumbers as well as the relative Raman intensity of its components.^[36,41,42] Due to its lead content (a heavy element with many electrons engaged in the chemical bond), the Raman spectrum of this pigment is very strong displaying a very characteristic narrow peak at $\sim 135\text{-}140\text{ cm}^{-1}$, with significant additional peaks at $335\text{ and }505\text{ cm}^{-1}$, characteristic of high Sb content.^[36, 41] A very nice spectrum can be obtained with x200 objective when the spot is focused on a pigment grain (Figure 5). In that case, a spectrum free of background is recorded.

3.2.4 Green

Green (jade) or turquoise-coloured glass is usually obtained by dissolving Cu^{2+} ions in lead-based or alkaline glassy silicate matrix. In this case, only the characteristic Raman signature of glass is detected.^[24,25] Raman spectra of most of the green enamels analysed display only the signature of glass (Figures 4 and 5). In order to achieve some specific hues of green, the colour is obtained by dispersing a yellow pigment in a blue glassy matrix rather than the 'classical' technique of dissolving Cu^{2+} ions.^[39] This time, the Raman spectrum both displays the signatures of the pigment and the glassy matrix. A few of the green enamels analysed (figurine MNC 11234-10 and bottle MNC 2016.142) show this type of Raman spectrum with the signatures of glass and *Naples yellow* type pigment (Figure 4-top right, Figure 5-middle left). It should be noted that Cr^{3+} ions may also contribute to green colouration. The type of glass will be discussed further.

3.2.5 Black

The black enamel of pot MNC 11226 shows the characteristic Raman signature of manganese-rich oxide, a broad peak at $\sim 650\text{ cm}^{-1}$.^[28] It is difficult to identify the exact composition of the phase because the high power of illumination required by on-site measurements may induce a phase transition to some extent. Traces of carbon were also detected ($1335\text{-}1570\text{ cm}^{-1}$ doublet).

Unexpectedly, black spots/lines show the addition of cassiterite to black chromophore for some of the figurines (Figure 4-bottom left and right) as well as Baluster vase (MNC 2011.0125, Figure 5-middle right). In the former case, the black chromophore is the amber one (Fe-S complex) with characteristic peaks at $\sim 300\text{-}430\text{-}560\text{ cm}^{-1}$.^[43]

3.3 Glassy matrix of the body and enamels

The composition type of the glassy silicate can be deduced from its Raman spectrum, namely the wavenumbers of the Si-O bending and stretching modes.^[24-26] Unfortunately, recording the spectrum with a mobile Raman set-up makes the exact wavenumber of the Si-O bending mode less reliable which is very dependent on the background subtraction procedure (bending modes are observed at

the point where the filter absorption changes from increasing to flat behaviour). Thus, we will consider only the Si-O stretching modes for the interpretation of the glass signature. Three different Raman spectra are observed (Figure 6: a-b; c, f, g; and d-e spectra), each type corresponding to a different group of chemical composition:

- Spectra a & b: peak maximum at $\sim 1090\text{-}1100\text{ cm}^{-1}$, measured on the white bodies, corresponds to highly polymerised silicate network, i.e. with high silica content. From the relationship established between the Raman spectrum and elemental composition,^[26,33] we can conclude that the glass type belongs to soda-lime group.
- Spectra c, f, g: stretching band with many components in between ~ 950 and 1100 cm^{-1} corresponds to mixed alkali-lead or mixed arsenic-lead glass such as some of the blue and red enamels.
- Spectra d & e: peak maximum at low wavenumber $\sim 950\text{-}975\text{ cm}^{-1}$, measured on the black, and green enamels, corresponds to heavy depolymerised glass such as lead-rich glaze.^[9,26]

Comparison with data extracted from Biron et al.^[14] reported in Figure 1 very well supports the above classification. Three groups of compositions are observed in the artefacts: i) silica rich glass with $\text{SiO}_2 > 65\text{ \%wt}$ and $\text{PbO} < 5\text{ \%wt}$ (for instance a-b spectra), ii) lead-rich enamels with $\text{PbO} > 30\text{ \%wt}$ and $\text{SiO}_2 < 60\text{ \%wt}$ (d-e spectra) and iii) mixed intermediate glass compositions (c,f,g).

4. DISCUSSION

As noted by Biron et al.^[14], elemental analyses of glass objects assigned to Bernard Perrot or his followers (Perrot was dead in 1709 but Orléans and St-Jean factories had continued production after up to 1754)^[6] show a large variety of compositions, both for glass bodies and enamels. As far as the ruby coloured enamel is concerned, the detection of As-O stretching mode in the Raman spectrum can be considered as the signature of Perrot glass, according to the unique association of arsenic and gold in red glasses reported by Geyssant.^[10] We can thus conclude that several figurines displaying this particular signature (Figures 2a and 2b left; 2a, 2b and 2c right) belong to the workshop of Bernard Perrot. Due to the high number of electrons involved in As-based compounds, their detection by Raman analysis is easier than that of SnO_2 traces,^[39] also resulting from the precipitation of colloidal gold. The latter technique using tin oxide is actually more common than the one using arsenic and was reported for Kunckel glass^[10] and Cassius purple glaze.^[39] The potential of on-site Raman analysis for the identification of Perrot recipe in ruby glass is thus an important outcome of the present study..

Opacification with calcium phosphate, likely by the addition of calcined bones as reported by the ancient literature, appears to be the main technique to produce opaque blown glass artefacts. The

technique was used by the Islamic glassmakers^[9,44] and it was also used to opacify the glaze of Medici porcelains at Florence which are the first porcelains to be produced in Europe (1575-1587). However, ancient reports indicate that the secret of the opacification was given by a Levantine master.^[45,46] Opacification of the figurines appears to have been made with calcium antimonite for the thick glass bodies along with cassiterite for thin enamels. The use of cassiterite was probably due to its high efficiency as opacifier in lead-based glass, as required by the thinness of enamels. The composition of thick glass bodies contains higher silica (> ~60 %wt) and lower lead oxide contents than those of thin enamels. This is certainly due to the viscosity required to model figurines, the last decor being made at lower temperature in order to preserve the shape of the already formed sculpture.

Technical differences between the artefacts assigned to Bernard Perrot workshop (Tables 1 and S1) and those from his followers (e.g. the 18th century pot MNC 11226) seem to be concerned with the glass body more than the enamels. Most of the utensils analysed display a more or less defined signature of calcium phosphate as an opacifier with the more intense peaks reflecting higher crystallisation in the productions after Perrot. Therefore, the signature of calcium phosphate with higher crystallinity is a characteristic of the artefacts which are assigned to the followers of Bernard Perrot. For this reason, a doubt is present about the association of the two parts of artefact MNC 2014.141, namely the vase and the ball. The Raman signature of calcium phosphate found in the ball body shows lower crystallinity than that of the vase. Furthermore, no arsenic apatite signature was detected for the blue enamel of the vase, suggesting the use of a different type of cobalt ore rather than the common one with European origin (Figure 5-bottom left). Thus, assignment of the vase to a replica made at the end of the 18th or 19th century is likely to be suggested.

Conclusion

The present study confirms that on-site Raman analysis is an efficient non-invasive technique for the characterization of the 17th century enamelled glass artefacts, thanks to the use of a high magnification microscope objective to avoid the contribution of the substrate. In particular, the fluorescence caused by the glass body masks the signature of the thin enamels applied, being the case for the artefacts analysed where the thickness of the enamels is much smaller than that of pottery glaze. Islamic artefacts such as Mamluk enamelled glass are also examples of thick enamels where the enamel layer can be hundreds of microns thick.^[33] As a non-invasive method, on-site Raman analysis competes very well with ion beam techniques which are not mobile and much more expensive. The high spatial resolution of Raman microspectroscopy is also a great advantage when compared to portable XRF which is commonly used for the non-invasive characterization of this glass artefacts.^[47] The information related to the composition type of glass and enamels which can also be

inferred from the Raman spectra contributes to the understanding of the production technology of the artefacts. Application of this method to figurines which are expected to have been produced in different workshops (Orléans, Nevers, Venice, etc.) may offer new information on these poorly studied artefacts. Furthermore, on-site Raman analysis, capable of identifying crystalline and amorphous phases, is also able to identify the small amount of the arsenate phase which was formed as a result of Perrot's recipe for the preparation of ruby glass. Finally, it can be suggested that the artefacts of Perrot's workshop were opacified with $\text{Ca}_2\text{Sb}_2\text{O}_7$ whereas the artefacts assigned to the followers such as the beaker 999.4.1 utilized the bone calcination route ($\text{Ca}_3(\text{PO}_4)_2$ opacifier).

ACKNOWLEDGMENTS

Mrs D. Plancher, keeper of Hotel Cabu' Collections in Orléans and V. Mesqui, curator of the porcelain collection and L. Tilliard, Head of Conservation Departement at Cité de la Céramique, Sèvres are kindly acknowledged for the permission to study the artefacts and many discussions.

ORCID

Philippe Colomban <https://orcid.org/0000-0001-6099-5423>

Burcu Kirmızı <https://orcid.org/0000-0003-2864-0221>

REFERENCES

- [1] C.H. Roehrig, Hatshepsut: From Queen to Pharaoh, in (Eds: C.H.Roehrig, R.Dreyfus, C.A. Keller), The Metropolitan Museum of Art, New York **2005**, 67-69.
- [2] W. Gudenrath, *J. Glass Stud.* **2006**, *48*, 23-70.
- [3] S. Carboni, D. Whitehouse, *Glass of the Sultans*, The Metropolitan Museum of Art, New York **2001**.
- [4] D.B. Harden, K.S. Painter, R.H. Pinder-Wilson, H. Tait, *Masterpieces of Glass*, The Trustees of the British Museum, London **1968**.
- [5] C. Hess (ed.), *The Arts of Fire-Islamic Influences on Glass and Ceramics of the Italian Renaissance*, The J. Paul Getty Museum, Los Angeles, **2004**.
- [6] C. de Valence, in *Bernard Perrot, 1640-1709, Secrets et chefs-d'œuvre des verreries royales d'Orléans*, Catalogue, Musée des Beaux-Arts d'Orléans – SOMOGY Editions d'Arts, Paris, **2013**, 14 & 35-42.
- [7] J. Barrelet, *Connaissance des Arts* **1958**, *78*(Août), 48-53.
- [8] J. Barrelet, *Cahiers de la céramique, du verre et des arts du feu*, **1965**, *36*, 294-310.
- [9] P. Ricciardi, Ph. Colomban, A. Tournié, V. Milande, *J. Raman Spectrosc.* **2009**, *40*[6], 604-617.
- [10] J. Geyssant, in *Bernard Perrot, 1640-1709, Secrets et chefs-d'œuvre des verreries royales d'Orléans*, Catalogue, Musée des Beaux-Arts d'Orléans – SOMOGY Editions d'Arts, Paris, **2013**, 51-54.
- [11] E. Baumgartner, J. Geyssant, in *Bernard Perrot, 1640-1709, Secrets et chefs-d'œuvre des verreries royales d'Orléans*, Catalogue, Musée des Beaux-Arts d'Orléans – SOMOGY Editions d'Arts, Paris, **2013**, 55-66.
- [12] J.-A. Page, *Beyond Venice-Glass in Venetian Style 1500-1750*, The Corning Museum of Glass, New York, **2004**.
- [13] I. Biron, B. Gratuze, S. Pistre, in *Bernard Perrot, 1640-1709, Secrets et chefs-d'œuvre des verreries royales d'Orléans*, Catalogue, Musée des Beaux-Arts d'Orléans – SOMOGY Editions d'Arts, Paris, **2013**, 87-94.
- [14] I. Biron, B. Gratuze, S. Pistre, P. Lehuède, *Bull. Ass. Fr. Archéologie Verre*, **2011**, 19-26.
- [15] Ph. Colomban, V. Milande, *J. Raman Spectrosc.* **2006**, *37*[5], 606-613.
- [16] Ph. Colomban, A. Tournié, D. de Montmollin, L. Krainhofer, Vegetable ash as raw material in the production of glasses and enamels, for example the contemporary vegetable ashes from Burgundy, France, <https://hal.archives-ouvertes.fr/hal-00542830> (accessed May 2019).
- [17] Ph. Colomban, *J. Raman Spectrosc.* **2012**, *43*[11], 1529-1535.
- [18] Ph. Colomban, *J. Raman Spectrosc.* **2018**, *49*[6], 921-634.

- [19] J.M. Madariaga, *Anal. Methods* **2015**, 7[12], 4848-4876.
- [20] P. Vandenabeele, H.G.M. Edwards, J. Jehlička, *Chem. Soc. Rev.* **2014**, 43[8], 2628-2649.
- [21] J. Geyssant, C. Gorget, F. Tétart-Vittu, in *Bernard Perrot, 1640-1709, Secrets et chefs-d'œuvre des verreries royales d'Orléans*, Catalogue, Musée des Beaux-Arts d'Orléans – SOMOGY Editions d'Arts, Paris, **2013**, 107-184.
- [22] National Palace Museum, Emperor Kangxi and the Sun King Louis XIV, Taipei, Taiwan, 2011.
- [23] Ph. Colomban, Y. Zhang, B. Zhao, *Ceram. Int.* **2017**, 43[15], 12079-12088.
- [24] Ph. Colomban, *J. Non-Crystalline Solids* **2003**, 323[1-3], 180-187.
- [25] Ph. Colomban, L.C. Prinsloo, in *Spectroscopic Properties of Inorganic and Organometallic Chemistry vol 40*, (Eds: J. Yarwood, R. Douthwaite and S. Duckett), RSC Publishing, Cambridge, **2009**, 128-150.
- [26] Ph. Colomban, A. Tournié, L. Bellot-Gurlet, *J. Raman Spectrosc.* **2006**, 37[8], 841-852.
- [27] P. Ricciardi, Ph. Colomban, A. Tournié, M. Macchiarola, N. Ayed, *J. Archaeolog. Sci.* **2009**, 36[11], 2551-2559.
- [28] F. Froment, A. Tournié, Ph. Colomban Ph., *J. Raman Spectrosc.* **2008**, 39[5], 560-568.
- [29] Ph. Colomban, *Eur. J. Miner.* **2013**, 25[5], 863-879.
- [30] Ph. Colomban, *J. Raman Spectrosc.* **2003**, 34[6], 420-423.
- [31] O. El Jaroudi, E. Picquenard, A. Demortier, J.P. Lelieur, J. Corset, *Inorg. Chem.* **1999**, 38[10], 2394-2401.
- [32] M.C. Caggiani, P. Acquafredda, Ph. Colomban, A. Mangone, *J. Raman Spectrosc.* **2014**, 45[11-12], 1251-1259.
- [33] M.C. Caggiani, Ph. Colomban, C. Valotteau, A. Mangone, P. Cambon, *Anal. Meth.* **2013**, 5[17], 4345-4354.
- [34] Ph. Colomban, F. Ambrosi, A.-T. Ngo, T.-A. Lu, X.-L. Feng, S. Chen, C.-L. Choi, *Ceram. Int.* **2017**, 43[16], 14244-14256.
- [35] J. Van Pevenage, D. Lauwers, D. Herremans, E. Verhaeven, B. Vekemans, W. De Clercq, L. Vincze, L. Moens, P. Vandenabeele, *Anal. Meth.* **2014**, 6[2], 387-394.
- [36] Ph. Colomban, L. Arberet, B. Kirmızı, *Ceram. Int.* **2017**, 43[13], 10158-10165.
- [37] Ph. Colomban, T.-A. Lu, V. Milande, *Ceram. Int.* **2018**, 44[8], 9018-9026.
- [38] Ph. Colomban, M. Maggetti, A. d'Albis, *J. Eur. Ceram. Soc.* **2018**, 38[15], 5228-5233.
- [39] Ph. Colomban, G. Sagon, X. Faurel, *J. Raman Spectrosc.* **2001**, 32[5], 351-360.
- [40] M. Asquier, Ph. Colomban, V. Milande, *J. Raman Spectrosc.* **2009**, 40[11], 1641-1644.

- [41] F. Rosi, V. Manuali, C. Miliani, B.G. Brunetti, A. Sgamellotti, T. Grygar, D. Hradil, *J. Raman Spectrosc.* **2009**, *40*[1], 107-111.
- [42] B. Kırmızı, E. H. Göktürk, Ph. Colomban, *Archaeometry* **2015**, *57*[3], 476-496.
- [43] L.C. Prinsloo, Ph. Colomban, *J. Raman Spectrosc.* **2008**, *39*[1], 79-90.
- [44] J. Barrelet, *Cahiers de la céramique, du verre et des arts du feu*, **1965**, *36*, 54-70.
- [45] Ph. Colomban, V. Milande, H. Lucas, *J. Raman Spectrosc.* **2004**, *35*[1], 68-72.
- [46] Ph. Colomban, in *MRS 2004 Fall Meetings Proc., 29th November-3 December 2004, Symposium OO, vol 852*, (Eds: P. Vandiver, J. Mass, A. Murray), Boston, **2004**, 153-160.
- [47] G. Şimşek, Ph Colomban, F. Casadio, L. Bellot-Gurlet, K. Faber, G. Zelleke, V. Milande, L. Tilliard, *J. Am. Ceram. Soc.* **2015**, *98*[10], 3006–3013.

Table 1: Information on the glass artefacts studied regarding their type, assignment, collection and inventory number

Type	Remarks	Collection	Inventory number	Refs	Body opacifier	Pigment identified
Figurine (page)	Blue coat and hat (Fig. 2a#1)	Musée des Beaux-Arts d'Orléans	A.12004			Ca ₂ Sb ₂ O ₇
Figurine (flower merchant)	Blue dress (Fig. 2a#2)		A.12026		Ca ₂ Sb ₂ O ₇	Ca ₂ Sb ₂ O ₇
Figurine (flower merchant)	Red dress (Fig. 2a#3)		A.12025		Ca ₂ Sb ₂ O ₇	Ca ₂ Sb ₂ O ₇
Figurine (man)	Turquoise coat (Fig. 2a#4)		A.11998			Ca ₂ Sb ₂ O ₇
Figurine (Bacchus ?)	(Fig. 2b)		A.12015		Ca ₂ Sb ₂ O ₇	As-apatite Ca ₂ Sb ₂ O ₇
Figurine (priest with crucifix)	(Fig. 2c)		A.11920		Ca ₂ Sb ₂ O ₇	Ca ₂ Sb ₂ O ₇
Group of 2 personages and a sphinx	(Fig. 2d)		A.12086		Ca ₂ Sb ₂ O ₇	No, monochrome
Beaker	With the inscription: ARCAN.DUPL (<i>Arcanum Duplicatum</i>) corresponding to alchemic <i>panacea duplicata</i> (K ₂ SO ₄) a purgative (Fig. 2)		999.4.1	# 178 in ref. 21	Ca ₃ (PO ₄) ₂	SnO ₂ As-apatite Naples Yellow α -Fe ₂ O ₃
pot	With the inscription: Vive le Roi, 1715 and bird and palms decor (Fig. 3a)	Sèvres Cité de la Céramique	MNC 25017	# 160 in ref. 21	Ca ₃ (PO ₄) ₂	α -Fe ₂ O ₃ SnO ₂ As-apatite Naples Yellow
Figurine (young man)	Broken arms showing the optically clear core (Fig. 2a)		MNC 11234-10		Ca ₂ Sb ₂ O ₇	Naples Yellow As-based compound
Figurine (lady)	White dress (Fig. 2b)		MNC 11234-7		Ca ₂ Sb ₂ O ₇ Ca ₂	As-apatite
Figurine (Virgin?)	White dress and blue scarf (Fig. 2c)		MNC 11234-4		Ca ₂ Sb ₂ O ₇	SnO ₂ As-apatite
Bottle	Palm decor (Fig. 3b)		MNC 2016.14.2	Similar to # 136 in ref. 21	Ca ₃ (PO ₄) ₂	α -Fe ₂ O ₃ SnO ₂ As-apatite Naples Yellow CaSiO ₃ ?
Baluster vase	With Lion and palms decor (Fig. 3c)		MNC 2011.0125	Similar in ref. 21		Ca ₃ (PO ₄) ₂ α -Fe ₂ O ₃ Naples Yellow
Vase with glass ball	With lion and palms decor (Fig. 3d)		MNC 2014.14.1		Ca ₃ (PO ₄) ₂	α -Fe ₂ O ₃ SnO ₂ As-apatite Naples Yellow
Glass ball	Palm decor (Fig. 3d)				Ca ₃ (PO ₄) ₂	SnO ₂ As-apatite Naples Yellow α -Fe ₂ O ₃
Pot with cover	Flower decor (Fig. 3a)		MNC 11226		Ca ₃ (PO ₄) ₂	α -Fe ₂ O ₃ As-apatite Naples Yellow Spinel

FIGURE CAPTIONS

Fig. 1: Oxide compositions of (enamelled) white glass artefacts assigned to Bernard Perrot (data extracted from ref. ^[14]); data labelled W correspond to white body (B and I to Q to artefacts); data labelled E correspond to enamels.

Fig. 2: Artefacts assigned to Bernard Perrot or his followers (see Table 1). Little characters from Musée des Beaux-Arts d'Orléans (a-d, left side: A-12004, A-12026, A-12025, A.11998, A.12015, A.11920, A.12086) and Cité de la Céramique Collections (a-c, right side: MNC 11234-10, MNC 11234-7, MNC 11234-4); the beaker (999.4.1) belonging to the collection in Orléans' is assigned to the followers, beginning of the 18th century; inscription ARCAN.DUPL; see Table 1 for details.

Fig. 3: Artefacts assigned to Bernard Perrot or his followers: a) (bottom) pot (25017), b) bottle (MNC 2016.14.2), c) Baluster vase (MNC 2011.0125) and d) vase with glass ball (MNC 2014.14.1). Top a) pot with cover is assigned to an 18th century production (11226).

Fig. 4: Representative Raman spectra collected on figurines MNC 11234-10, 11234-7, 11234-4 and A.11998 (a, top left), 12086 (b, idem), 12026 (centre, left, light blue), 11998(idem, green), 12004 (idem, dark blue and red), 12025 (idem, light blue). Comparison is made with the 18th century MNC 11226 pot. Spectra shown top- and centre-left, were recorded with a 50x Nikon objective; a baseline has been subtracted for the spectra at the top and centre left.

Fig. 5: Representative Raman spectra collected on the artefacts MNC 2016.14.2 bottle, 25017 pot, MNC 2011.0125 Baluster vase, MNC 2014.141 (vase and ball) and Orléans 999.4.1 beaker (for the latter artefact, a baseline has been subtracted).

Fig. 6: Representative Raman spectra of glassy phases: a) green (figurine MNC 11234-10), b) white body (pot MNC 11226), c) blue (lady figurine MNC 11234-7), d) black (virgin figurine MNC 11234-4), e) green (Baluster vase, MNC 2011.0125), f) blue (ball MNC 2014.14.1), g) blue (pot MNC 25017).

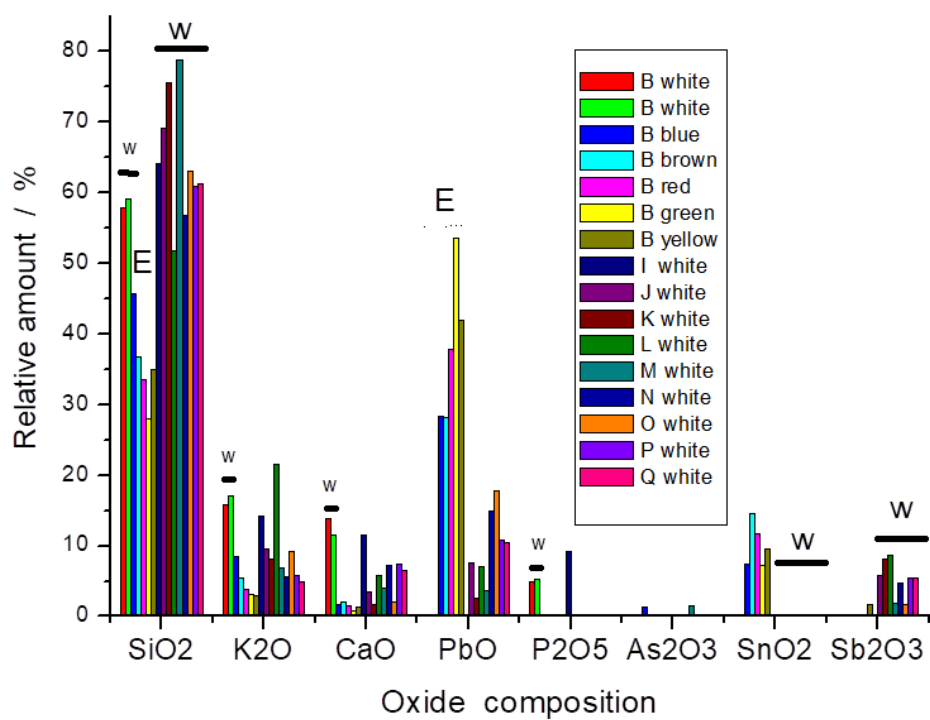


Fig. 1: Oxide compositions of (enamelled) white glass objects assigned to B. Perrot (data extracted from ref. [8]). Data labelled w correspond to white body (B and I to Q objects); data labelled E correspond to enamels.



Fig. 2: Artefacts assigned to B. Perrot or followers (see Table 1); little characters from Musée des Beaux-Arts d'Orléans (a-d, left side) and Cité de la Céramique Collections (a-c, right side); the beaker belonging to Orléans' collection is assigned to followers, beginning 18th century; inscription ARCAN.DUPL; see Table 1 for details.



Fig. 3: Artefacts assigned to B. Perrot or followers: a) (bottom) pot, b) bottle, c) Balluster vase and d) vase with glass ball. Top a) pot with cover is assigned to an 18th century production.

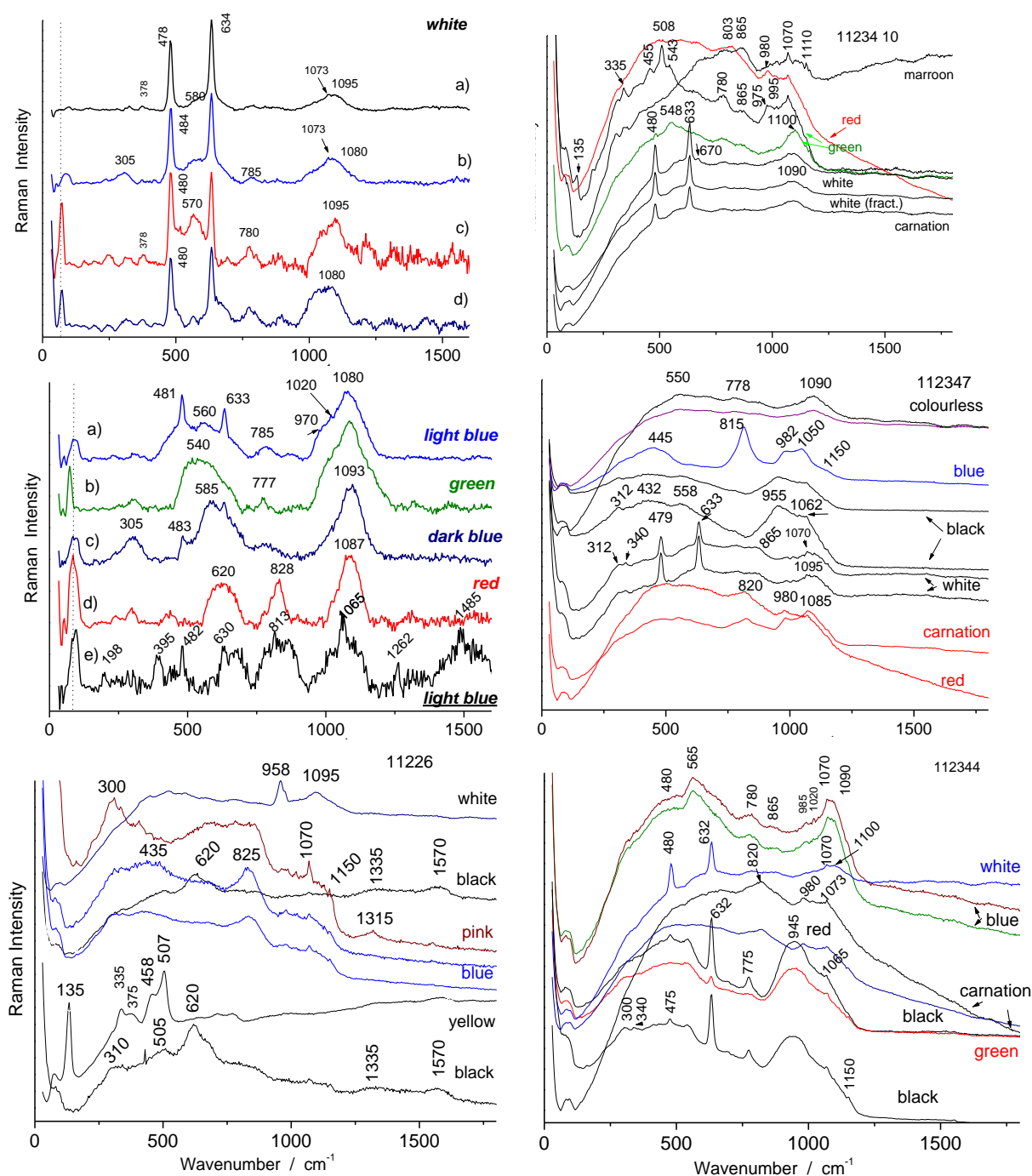


Fig. 4: Representative Raman spectra collected on figurines MNC 11234-10, 11234-7, 11234-4 and A.11998 (a, top left), 12086 (b, idem), 12026 (centre, left, light blue, 11998, idem, green), 12004 (idem, dark blue and red, 12025 (idem, light blue); comparison is made with 18th century MNC11226 pot. Spectra noted c & d, top and red and light blue, centre left, have been recorded with a 50x Nikon objective; a baseline has been subtracted for top and centre left spectra.

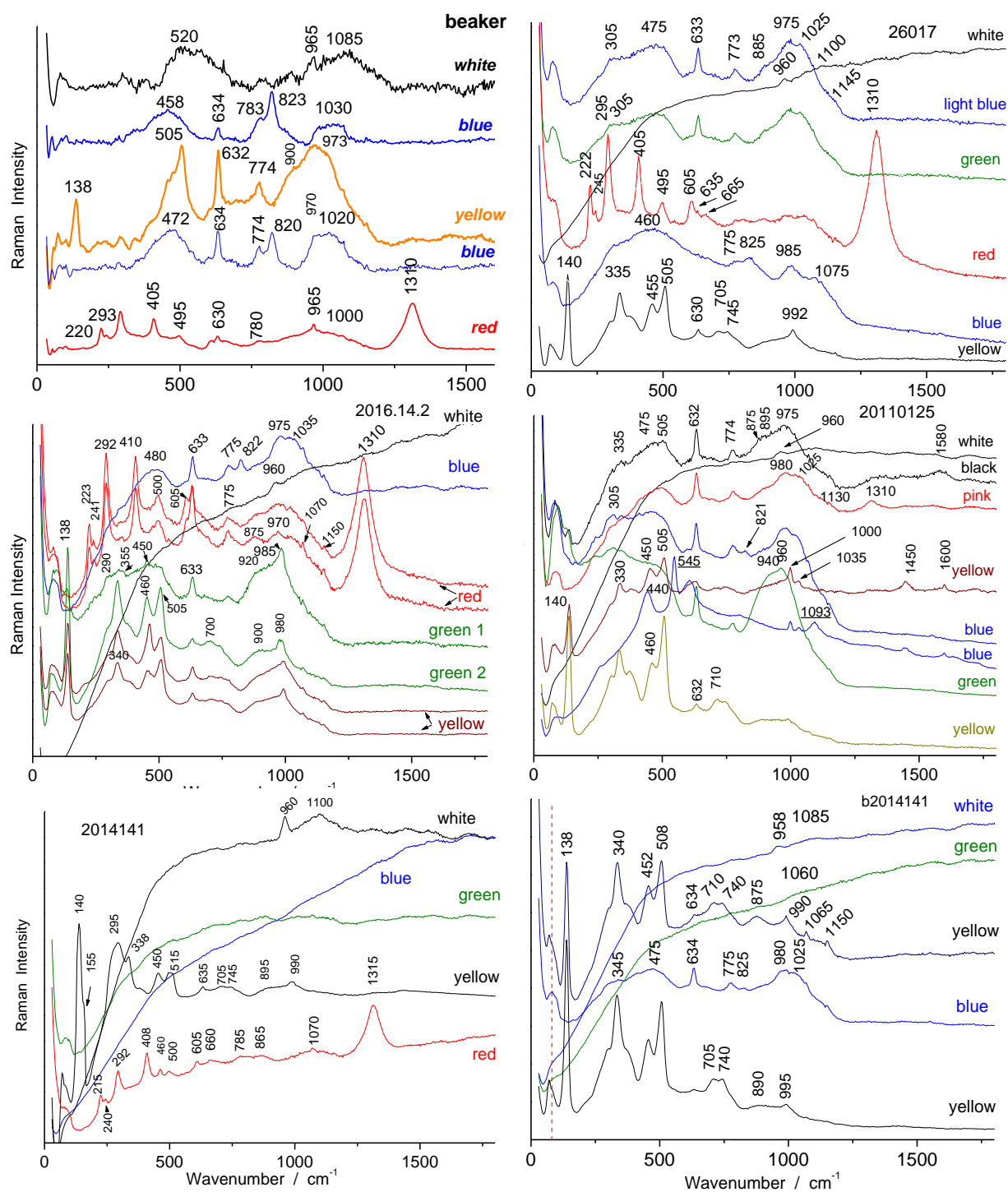


Fig. 5: Representative Raman spectra collected on artefacts MNC2016.14.2 bottle, 25017 pot, 2011.0125 Balluster vase, 2014141 (vase and ball) and Orléans 999.4.1 beaker (for the later artefact, a baseline has been subtracted).

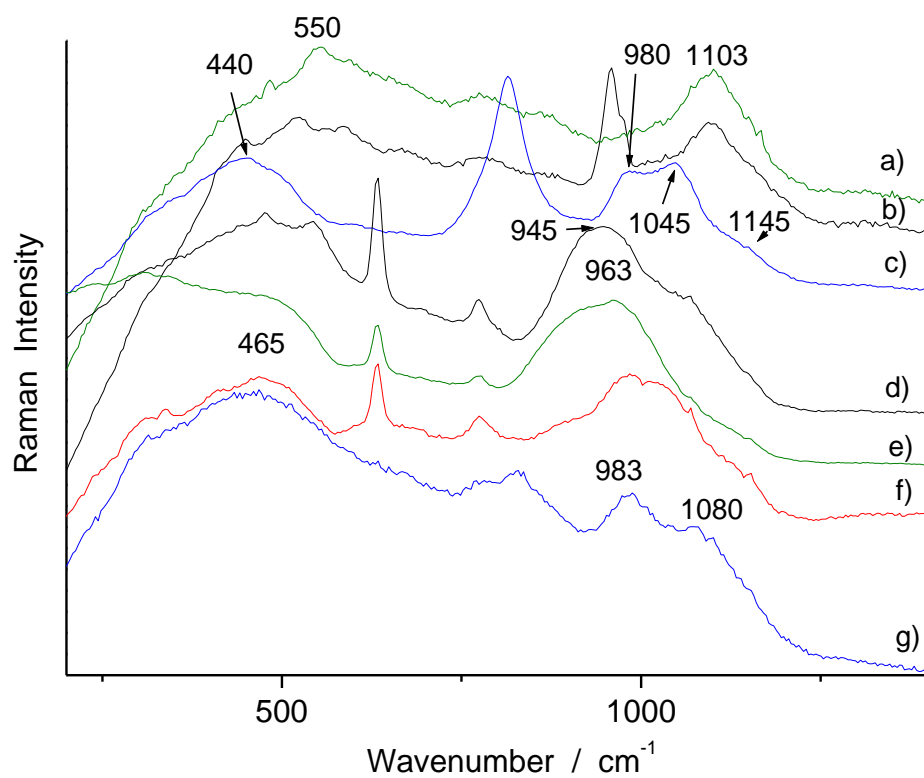


Fig. 5: Representative Raman spectra of glassy phases: a) green (MNC 11234-10 figurine), b) white body (pot, MNC 11226), c) blue (MNC 112347 lady figurine), d) black (MNC 112344 virgin figurine), e) green (Baluster vase, MNC 20110125), f) blue (ball, MNC 2014141), g) blue (pot, MNC25017).

Supplementary Information



Fig. S1: bottom view of artefacts MNC: 2016.14.2, 2016.15.2.5 (2016.14.1), 11270, 25017, 16046 and 11226.