The enamels of the first (soft-paste) European blue-and-white porcelains: Rouen, Saint-Cloud and Paris factories: Complementarity of Raman and X-ray fluorescence analyses with mobile instruments to identify the cobalt ore

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special issue dedicated to late Prof. D. LONG

The Enamels of the First (Soft-paste) European Blue-and-white Porcelains: Rouen, Saint-Cloud and Paris Factories: Complementarity of Raman and X-ray Fluorescence analyses with Mobile Instruments to identify the cobalt ore.

Short title: **The Enamels of the First (Soft-paste) European Blue-and-white Porcelains:**

Philippe Colomban[1], Michele Gironda[2], Howell G.M. Edwards[3], Viviane Mesqui[4]

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

[2]XGLab S.R.L – Bruker, 23 Via Conte Rosso, 20134 Milan, Italy

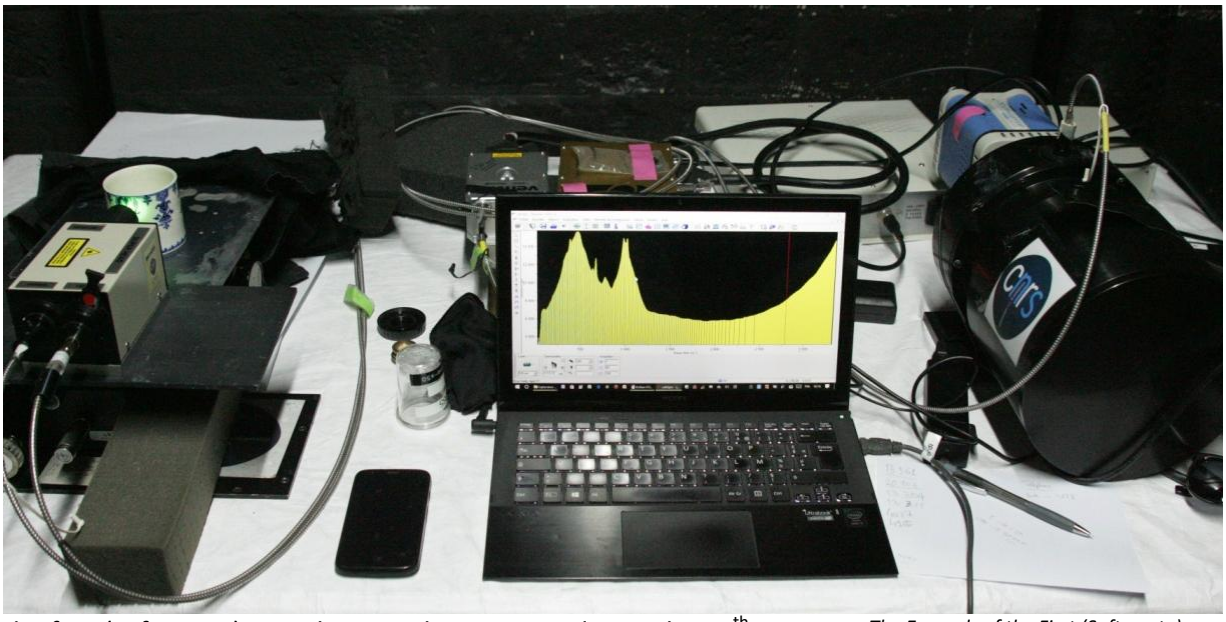
[3] School of Chemistry and Biosciences, Faculty of Life Sciences, University of Bradford, Bradford BD7 1DP, United Kingdom.

[4] Cité de la Céramique, Grande Rue, 92310 Sèvres, France

Abstract

The first porcelains made in Europe during the 17th century and the very beginning of the 18th century, i.e. before the discovery of kaolin in Saxony (Germany), are rare and technical analyses very limited. In contrast with Meissen Böttger porcelain based on kaolin, these porcelains are made with sand and '*chymie*', like Ottoman fritware. A selection of the blue-and-white artefacts belonging to the French national collection is analyzed on-site with mobile pXRF and Raman set-ups: two were assigned to the Poterat Factory at Rouen, three to the Saint-Cloud Factory and two to the Pavie Factory (Paris). Three types of enamels are identified, lead-rich (as expected) but also two different lead-alkaline-earth- alkali enamels, one artefact being covered both with lead-rich and lead-poor enamel. The polymerisation index deduced from the relative intensity of SiO_4 bending and stretching bands indicates different temperatures of firing. Tin is detected in most of the enamels by XRF but cassiterite opacification is only observed for the Pavie factory artefacts. Arsenic is detected in the blue areas due to the use of European cobalt ores. Comparison of trace and minor elements as well as the type of enamel used suggest that the pot assigned to the Rouen factory fits much better with a production from the Saint-Cloud factory. The two porcelains assigned to the Pavie factory exhibit similar XRF and Raman signatures that support the attribution based on visual criteria. Combination of the mobile non-invasive XRF and Raman instruments may allow the reliable classification of artefacts on-site. Raman scattering is very efficient to detect (on-site) As-based minor phases.

Keywords: Cultural Heritage; porcelain; blue-and-white; cobalt; glaze;



The first (soft-paste) porcelains made in Europe during the 17th century and the very beginning of the 18th century, i.e. before the discovery of kaolin in Saxony (Germany), are rare and technical analyses very limited. A selection of the artefacts belonging to the French national collection is analyzed on-site with mobile pXRF and Raman set-ups. Combination of the mobile techniques may allow the reliable classification of artefacts on-site by considering the type of glaze (lead-rich or lead-poor) and the elements associated to cobalt (As, Ni, Cu, Zn, Cd, Ga, Sr).

The Enamels of the First (Soft-paste) European Blue-and-white Porcelains: Rouen, Saint-Cloud and Paris Factories: Complementarity of Raman and X-ray Fluorescence analyses with Mobile Instruments to identify the cobalt ore.

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1. Introduction: Historical context

The enamels of the first soft-paste porcelains produced in France from the second half of the 17th century up to the very beginning of the 18th century, before the production in Meissen in 1708 of the first hard paste porcelain based on kaolin,[1-3] are not well characterized because these rare objects have only been incompletely analyzed or not analysed at all.[2-10] Indeed shards are even rarer than artefacts, as for Medici porcelains, a very specific hybrid porcelain produced at Florence from 1575 to 1587.[11,12] The specimen attribution of these porcelains is poorly supported and the technical and historical documentation on their first manufacture is rather limited, both considering academic and scholarly reports[7-10,12-23] and auction house information.[24,25] Because of their rarity, logistical restrictions make it impractical to examine these specimens in the laboratory, in particular with invasive techniques and out of their secure locations, and shards from the factory sites are also very rarely available. On-site non-invasive analysis with mobile Raman and X-ray fluorescence microspectrometers offers an alternative and non-invasive analytical procedure, which allows the identification of the types of pigment enamels and their crystalline phases present[26-34] as well as to collect information on the glassy matrix.[30,31] The refractivity of the materials allows the use of rather high illumination power, up to 10 mW that provides 'good' spectra, even with mobile Raman set-up. This makes it possible to differentiate the technologies used for the production of each specimen. Later examples of soft-paste porcelains and hard paste porcelains have received much more attention analytically and the availability of many shards has allowed a wide range of laboratory analytical techniques to be adopted for their studies.[3,4,33,34] These 18th Century factories also have associated texts and historical documentation from which manufacturing recipes are obtained.[2,6-8,10,14-23,33]

If we exclude the Medici porcelain above mentioned, the first production of European porcelain takes place in Rouen: Nicolas Poirel de Grandval, former bailiff of the Queen Regent of France, Anne of Austria, received from the French King in 1644 a fifty-year privilege authorizing him to produce all kinds of white faience crockery covered with enamel of all colours. Poirel de Grandval then cedes the exploitation of his privilege to Edmé Poterat. Rouen with the Masséot Abaquesne Factory was one of the major places of production of majolica in the Kingdom of France.[35] On October 1st, 1673, Louis XIV granted by letters patent a new privilege to Edmé Poterat in the name of his eldest son Louis. Recalling in the preamble that *Louis Poterat by travels in foreign countries & by continual applications, he has found the secret of making genuine china porcelain, this privilege authorizes him to establish (...) a manufacture of all kinds of chinaware, pots & vases similar to that of China, & purple earthenware, painted white & blue, & other colours to shape of which similar to Flemish productions (...) and have their own furnaces, mills & workshops built for the so-called porcelain & faience aforesaid*. This is twenty years before the Chicaneau children made soft porcelain in Saint-Cloud, thirty-five years before Ehrenfriede von Tschirnhaus and Johann Friedrich Böttger discovered kaolin rock and the secret of hard paste porcelain in Meissen and about forty years before the soft-paste porcelain production in Vincennes.[17] It is not known how Poterat managed to find the secret of porcelain. Did Louis Poterat and his brother Michel, who also owned the secret of porcelain, actually travel? Régine de Plinval de Guillebon quotes research on porcelain carried out in Padua between 1627 and 1638 (the V&A Museum seem to have two examples of these dated to 1627 and 1638 attributed by John Mallett but the glaze/enamel of these artefacts was not analysed) and in Fulham in England between 1671 and 1673 (shards have been studied by Tite et al.).[19-21,36] Chantal Soudée Lacombe put forward an hypothesis[22]: the possible links between the Poterat and Jean Chardin, a

young jeweller originally from Rouen, who left his town to sell jewellery at the Persian Châh in 1665 where he noted the manufacturing processes of 'translucent' ceramics of the Safavids: Safavid potters produced fritwares imitating china porcelains on the basis of a material rich in quartz sand and welded by a frit (a glass)[37-39], i.e. a stonepaste, in a rather similar way to that of Iznik Ottoman production (from the 15th century).[26] In 1694, Louis Poterat still produced porcelain but he declared to be the only one to possess the secrets and he feared that his workers will discover them, and it is for this reason that he did not dare to do make fine porcelain except only in very small quantities and working by himself, without the help of workers. This is probably the reason why only nine pieces of porcelain from Rouen are listed today. Albert Jacquemart, in his *Histoire de la Céramique* published in 1873,[39] had an alternative explanation: a potter, an earthenware maker, accustomed to operating an industry in which he was an expert, did not want to let go of the secret and embark on the chances of a dubious enterprise. You should thus rather see Louis Poterat working alone on his porcelain, once the workers have left the factory. Examination of the Rouen porcelains shows that Louis Poterat was experimenting and that it was more important for him to create distinct, special and precious objects rather than producing a copious quantity. This is evidenced by the diversity of the decorations on the nine objects assigned to his production and their sometimes distant kinship with the decorations applied to the faience of Rouen. The untimely death of Louis Poterat of typhus in 1696 probably put an end to the production of porcelain in Rouen at this time.

A factory which was contemporary with the factories at Rouen and St Cloud was the early English manufactory at Fulham, the precursor of later English factories at Pomona, Bow, Chelsea and Limehouse, founded by John Dwight in 1671, who experimented with refractory silicaceous and porcellaneous materials under the auspices of the Royal Society of London and with savants such as Robert Boyle, Robert Hooke and Isaac Newton.[40] It is quite clear that these early English and French porcelain manufactories had little evidence of interchange of knowledge transfer between them from their body compositions. Yet Ehrenfriede von Tschirnhaus, who with Johann Böttger, was engaged by Augustus, Elector of Saxony, in the early 1700s to manufacture the "white gold" (porcelain) which they did successfully in Meissen in 1708 and which went into production in 1710,[17] is recorded as meeting with Dwight in Fulham and having related discussions there. In the 1690s von Tschirnhaus visited an experimental porcelain manufacturing site in Paris and it is inconceivable that he did not also there meet with like-minded people at the Rouen and St Cloud manufactories before moving to Meissen. In fact, he reported back to Saxony on some purchases of porcelain he had made at St Cloud in 1701. He died in 1708 before Meissen went into full production in 1710 but he shares the accolade with Böttger of being the first to manufacture hard paste porcelain in Europe in competition with the imported Chinese wares.

From 1690 to 1766, the date of the final closure of the kilns, the Saint-Cloud factory produced a number of porcelain pieces, generally small in size, of a rare quality, shaped by moulding, inspired by Chinese models while creating its own vocabulary, available in shades of blue, white and colour as well as being decorated by gilding. In 1702, Philippe I, Duke of Orléans gave letters-patent to the family of Pierre Chicaneau, who were said to have been making porcelain as "perfect as the Chinese" since 1693. Information on the 18th century productions using sand, chalk (or gypsum) and frit, in particular at Vincennes is better documented[2,16,18-23] and preliminary Raman studies have been published.[3,4,41]

The Pavie faience factory was established in 1692 in rue de la Muette, Paris. Antoine Pavie, the son of the founder Nicolas Pavie, developed the factory after 1726. Nicolas Pavie established a subsidiary dedicated to porcelain production in 1703 in association with Pierre Pelissier, son of the spouse of Pierre Chicanneau, owner of the Saint-Cloud factory. Pelissier married Madeleine Vallet, the daughter of a master from the Saint-Cloud factory, and was previously in Rouen. Links between Rouen, Saint-Cloud and Pavie factory productions are hence numerous.[18-23,42,43]

This work focuses on the productions attributed to the manufactory of Poterat at Rouen (17th century), the first pieces produced in Saint-Cloud and at the Pavie workshop in Paris (beginning of the 18th century). Preliminary conclusions of the Raman analyses have already been published[4,41] and we will discuss them and complementary on-site measurements (Figure 1) here in comparison with the X-ray fluorescence results with a focus on the search for arsenic-based phases, characteristic of the use of European cobalt ores during the period from the middle of the 17th century to the 18th century.

2. Expérimental

Raman scattering: Information concerning the analyses carried out either in the laboratory in 2003[4] with excitation in the blue (458 and 488 nm, at that time moving the artefact to the laboratory was allowed) using a high resolution spectrometer (XY DILOR, ~ 1 cm^{-1}) and also on site[41] with green excitation (532 nm) and a medium resolution spectrometer (HE532 HORIBA Jobin-Yvon, ~ 4 cm^{-1}) are available in the articles cited. The first measurements were made using a x50 LWD Nikon objective (Figure 1b') and for confirmation complementary measurements were made with a x200 LWD Mitutoyo microscope objective (Figure 1b,c). Note that the excitation carried out with a blue laser is more efficient for the study of aluminosilicates: this can be ascribed to a pre-resonance enhancement of the Si-O bonds and the surface laser cleaning for incident laser powers greater than ~ 5 mW which serves to eliminate some of the fluorescence emission resulting from the corrosion of the vitreous phases at the superficial surface.

X-ray fluorescence: A portable instrument (ELIO, XGLab Bruker, Fig. 1a) equipped with a rhodium anode X-ray source (voltage <50 kV, current <0.2 mA, collimation diameter: 1 mm), and a Silicon Drift Detector (SDD) with an active area of 50 mm^2) with a resolution of <140 eV for the Mn Kα line, and a range from 1 keV to 40 keV was used. The measurements are made in a punctual mode at 40 KeV and 100 µA for 40 s, without adding a filter. The distance between the object and the detector is ~ 15mm and the distance between the object and the front of the instrument is ~ 10mm. The measurement position is adjudged to be satisfactory when the two red laser spots (Fig. 1a') coincide on the chosen measurement point; this focus is achieved with the XYZ micrometric displacements of the instrument support. These settings allow the minimal noise on the data. Unfortunately, the measurement of the low-Z elements with p-XRF constitutes some problems, as very light elements (Na, O, C, and B) cannot be measured at all, or the measurement is very limited for others (Mg, Al) and cannot be determined without the complete fitting of the data. The depth analyzed varies with energy and is of the order of ~ 4 µm for the Si K_α line at very low energy, 130 µm for Cu K_α and 220 µm for Au L_α at medium energies and 2.5 mm for Sn K_α at high energy.[44] The data is processed by the instrument's software which automatically identifies the different lines of the proposed elements and performs a complete fitting of the spectrum. The thickness of the material analysed must meet

the criterion of infinite thickness for the elements considered to allow a (semi) quantitative measurement to be made.

3. Objects and microstructure

The 7 objects analysed are listed in Table 1 and shown in Figures 2 to 4. Representative XRF spectra are shown in Figures 5 and 6. Raman spectra are compared with XRF evidence of arsenic in Figures 7 to 9. All porcelains have a blue-and-white décor imitating to some extent Chinese Ming productions. The décor of the MNC 18432 (Rouen, Figure 2) pot is a Chinese garden; the other decors are characteristic of French 17th century décor with lambrequins (Figure 3 and Figure 4). The marks present are shown in the figures. Due to the limited plasticity of the sand-clay/chalk mixture used the size of the artefact remains small (height about 10 cm or less).

The procedure of preparation of soft-paste porcelain in Vincennes after 1740 is well documented with the book of Hellot, studied in detail by d'Albis[7,8] and papers of Kingery and Smith[2] and Kingery[43]. Some information collected by Lister in 1698 was also reported[2,4,7,8]: the soft-paste was prepared by mixing quartz sand and clay or lime or marl and '*chymie*'; the addition/replacement of the carbonate materials by calcined alum ($KAl(SO_4)_2 \cdot 12H_2O$ gives a pure almost K-beta alumina[45]) or gypsum/alabaster (calcium sulphate: $CaSO_4$, H_2O), plant soda ash (Alicante soda: NaOH), sea salt (NaCl), and saltpetre (KNO_3). It is important to note that all the compounds are 'pure' chemicals and not minerals, as used for 'traditional' pottery. This is the reason that Alexandre Brongniart classified the French soft-paste as an 'artificial' porcelain.[6] The mixture is finely milled together and heated for 30 to 35 hours up to biscuit temperature (~950°C) and quenched. The resulting sinter (frit) is milled and mixed with additional limestone and a calcareous illitic clay from Argenteuil (8-10% alumina, close to Paris), and "*chymie*". The latter material is not well identified but believed to consist mainly of animal glue. The mixture is thrown or pressed into shape (moulded), trimmed or turned, and biscuit-fired before applying a lead silicate glaze. Whatever the good plasticity of illite clay, the final mixture easily cracks (see Fig. 4) and the largest dimension achieved is about 10 cm, at least for the first Saint-Cloud productions. As a result the phases than can be formed on heating are wollastonite ($CaSiO_3$), tridymite and cristobalite (SiO_2) and a vitreous phase.[2,3,9,33,34,43] As the firing temperature is increased up to about 1100°C, the concentration of the glassy phase increases – and hence the translucency- but, at the same time, the composition of the liquid phase shifts to be richer in calcium and the viscosity decreases. Artefacts soften and deform very easily (see Supplementary Materials in reference [41]) and the soft-paste composition remains difficult to form and fire. This is the reason why hard-paste porcelain replaced soft-paste porcelain, despite the more aesthetic quality of the whiteness of soft-paste porcelain that enhanced the coloured décor applied.

The cup with lid (Figure 2) marked with the coat of arms of Jacques Asselin de Villequier, (1669-1728), counselor to the parliament of Normandy in 1695,[46] is considered to be the oldest French porcelain in existence, and also European porcelain with the exception of Medici porcelains, with a hybrid paste that is intermediate between a hard paste and a soft-paste.[11]

4. Results

4.1. Elemental analysis of enamels

Glassy matrix: The elements identified by X-ray fluorescence are listed in Table 2. The enamel (or covering if baked with the paste) is qualified as 'white' but this colour may come from the whiteness of the paste and Raman scattering will make it possible to specify whether a crystalline phase has opacified and contributes to the resultant whiteness (see Table 1 and further). Figure 5 shows the three types of XRF spectra obtained. The bottom spectrum (MNC 18432 Rouen, white, from the lower part of the pot) with the two intense L_α lead (+ the eventual contribution of K_α line from arsenic that cannot be separated visually with this instrument) and L_β lines at ~ 11 and 13 KeV, respectively, is characteristic of a lead-rich enamel. The centre spectrum (MNC 4027 Saint-Cloud), with the intense K_α and Ca K_α lines at ~3 keV and the significant Si K_α peak at lower energy is characteristic of an alkaline earth enamel with minor lead addition. It should be remembered that since the measurement is carried out in air, low-energy X-ray photons (identifying light elements) are more strongly absorbed than more energetic photons, characteristic of the heavy elements: consequently, the relative intensity of peaks located at different energy does not reflect the relative elemental content. Sodium and lighter elements are not measurable with the mobile XRF instrument. The weaker intensity of the doublet of lead therefore corresponds to a low content of only a few %wt Pb for the MNC 4027 Saint-Cloud pot. A rather similar spectrum is obtained from the top part of the MNC 18432 pot. The relative intensity of the Pb L_α and L_β is different due to the contribution of the As L_α peak; the L_β As peak is observed just before the L_β Pb peak.

Two very different enamelling technologies were therefore used and the MNC 18432 and MNC 4027 objects appear to have an enamel similar or close to those of hard paste porcelains,[3,43,47] in which a small amount of lead has been added. This had already been noted during the preliminary Raman analyses of the MNC 4027 salt cup.[4,41] It is well established that the thickness probed with XRF on the enamelled surface depends on the energy[44]: the measurement of light elements (Si, K, Ca) is limited to the very surface of the enamel and it is important that the glass surface was not corroded (this is applicable to our case). Transition elements are measured over hundred(s) of microns, i. e. corresponding to the thickness of the enamel/glaze. The measurement of lead is made over a large thickness, up to the body surface and a minor addition in the body can thus contribute to the spectrum recorded by focusing the spot at the surface of the enamel. Due to the different depths probed the data extracted from XRF cannot be quantitative,[44] but the differences are too great to be explained by the perturbation from the contribution of the porcelain body.

All other objects have signatures of lead enamel similar to that of the bottom spectrum of Figure 5. Small differences can however be distinguished between them according to the different types of enamels identified by the Raman analysis (see Table 1 and further). We will consider the XRF patterns recorded in the low energy range (Figure 6), the most informative range. A first classification can now be made by considering the relative intensity of the K and Ca elements.

Considering the white areas, the first group is characterized by a stronger potassium peak (MNC 4006 and MNC 18432 (Figure 6top), Rouen; MNC 8800 Saint-Cloud (Figure 6centre)) and the second group with a similar peak-intensity for both the K and Ca elements (MNC4027 and MNC4165 Saint-Cloud artefacts; MNC13369 and MNC 13371 Pavie (Figure 6bottom)). Two different types of spectra are recorded for the MNC 18432 Rouen artefact, one free of lead with similar K and Ca peaks for the bottom part of the pot, the other lead-rich but with the K peak intensity now higher than that of the Ca.

Considering the blue areas, similar K-Ca doublets are observed as for the white areas except for the MNC 13371 Pavie décor where both the intensities of the K and Co are strongly increased. Previous studies on enamels coloured in blue (by addition of a cobalt source) pointed out that in fact smalt (*saffre* in French), a potassium silicate glass made by mixing with (thermally/chemically treated) cobalt ores, was used.[48-59]

Cobalt sources: Peaks characteristic of metals such as iron and cobalt, but also other transition metals associated with cobalt ores (Ni, Cu, Zn), are observed in the region between 6 and 8 keV (Figure 6).[4,49-52,] Residual iron is observed in all cases, a low iron content being sought in order to obtain white porcelain, and the relative intensity of Co and Fe can be considered to estimate the cobalt content. Note that a secondary peak characteristic of iron, about 1/6 the intensity of the main one, situated just before it in the spectrum, is superimposed with the most intense peak of cobalt. Cobalt is a very efficient colouring agent and 0.1 %wt is sufficient to obtain a nice blue colour and hence XRF failed to detect, at least visually, traces of cobalt sufficient to give a light blue colour.[57,60] The cobalt content is seen to be variable in the studied areas: the stronger peak (compared with that of the Fe) is observed for the MNC 4006 Rouen artefact according to the dark blue décor observed visually (Figure 2). Cobalt is also well detected in the 'white' area, the cobalt addition leading to a nicer 'white' appearance visually. Addition of blue colouring agent was also used by Böttger to whiten the first enamelled hard-paste porcelain, but in this case he used lapis lazuli.[1] In both cases, nickel is associated with cobalt and also traces of copper. The lower and heterogeneous cobalt content observed for the MNC 18432 artefact is consistent with the light blue décor.

High levels of cobalt are also observed for the Pavie factory artefacts (MNC 13369 and MNC 13371 (Figure 6bottom)); nickel is also associated here but the relationship with the cobalt content is less straightforward, as for the MNC 4165 and MNC 8800 Saint-Cloud artefacts (Figure 6centre). No copper was detected in the Pavie artefacts. Copper appears characteristic in the MNC 4006 Rouen artefact (Figure 6top) and likely contributes to the darkness of the blue decor.

Other characteristic impurities are detected by fitting with the instrument software (Table 2). Titanium is observed in all cases. Rutile and/or anatase titanium oxides are very common secondary phases of clays and sands. Cadmium is identified in the two artefacts assigned to the Rouen factory. This is consistent with the use of a common raw material. Cadmium is rare and found associated with copper and lead,[53] major elements of the enamel. Its non-detection in the white enamel of the MNC 18432 artefact demonstrates that cadmium is probably associated with copper used in the blue décor. Another rare element is detected, namely, gallium in the blue enamel of the MNC 18432 artefact. Gallium is commonly associated with aluminium and could be a characteristic of the alums used in the recipe. With this criteria there are similarities between the enamels of MNC 18432 (assigned to Rouen) and of MNC 4027 (Saint-Cloud). Strontium, an element associated with calcium is detected in the Saint-Cloud artefacts and also in the MNC 18432. This is a second argument in favour of the assignment of the MNC 18432 pot to a Saint-Cloud production.

For the cup attributed to the production of Louis Poterat (MNC 4006) the fluorescence spectrum indicates in addition to lead, silicon, and potassium, iron, cobalt and nickel, already discussed, the presence of arsenic, tin and traces of antimony; and it is clear that copper, plus titanium, and cadmium already mentioned are present. The measurement on the blue areas shows the presence of

zirconium traces; these are observed also on many other artefacts. Zircons are common impurities of many intrusive rocks and after corrosion are found in some sands.

Certain minor or trace elements observed for the points analyzed (a higher number of measurements is necessary to conclude whether these elements are good markers or not) for certain objects should be examined specifically, namely (Table 2):

- Tin is detected for MNC 4006 (white and blue), MNC 18432 (white and blue), MNC 13371 (white and blue) and MNC 13369 (white and blue), that is the Rouen (Poterat) and Paris (Pavie) attributions (see Supplementary Materials, Figure S1). We will see further that Raman analysis detects cassiterite (SnO_2) for MNC 13369 (Figure 9), and this is also possibly detected at trace levels in MNC 13371 (Figure S1) but no cassiterite was detected for MNC 4006. Cadmium trace is also detected for these objects. This reflects the use of identical or similar raw materials.
- Arsenic is detected in the blue zones of all the objects: this can observed visually by a very weak peak K_β between the doublet L_α and L_β of the lead, the line Pb L_α being superimposed on the line As K_α. This can be deduced from a visual inspection (Figures 7, 8 and 9) but here fitting by the instrument software is essential. Arsenic is thus identified in the white enamel of the objects MNC 4006 (Poterat, Rouen), MNC 18432 (Rouen?)(Figure 7) and MNC 4027 (St-Cloud, Figure 8). We will see that the Raman analysis sees the signature of the As-O bond in the blue areas of all objects except MNC 4165-2 and only in the white areas of MNC 13371 (Figure 9).
- Antimony is only detected in MNC 4006.
- Bismuth is detected for the blue areas of MNC 18432 (in some measurements) and MNC 13371. Bismuth is considered to be a marker of the use of cobalt ores from certain European mines.[54-58]

4.2. Raman analysis

Glaze: Two advantages of Raman analysis are useful in the analysis of pottery, namely the identification of crystalline phases, even in a minority, and that of amorphous phases, that is, the amorphous silicate network constituting the enamel. Due to the very covalent nature of the Si-O bond, the other Al-O and Na- / K- / Ca-O bonds being very ionic, to a first approximation the Raman spectrum of a silicate network consists of the bands of the stretching (between ~ 750 and 1200 cm^{-1}) and deformation (between 400 and 600 cm^{-1}) modes of the SiO_4 tetrahedra (Figure 7), the structural unit of the silicate network.[30,31] The remaining external (T') and librational (R') modes of the SiO_4 tetrahedron merge to form the broad component below 300 cm^{-1}, called the boson peak.

The highlights of the spectra (Figures 7 to 9) are summarized in Table 1. In all the objects, the wollastonite β ($CaSiO_3$) peaks characteristic of soft porcelains are observed as the intense doublet at 635 and 967 cm^{-1}).[3,4,34,40,41,61-63] It was not possible to obtain the spectral signatures of all the pastes due to some heavy fluorescence (the cleaning of these artefacts is not allowed), but the presence of β wollastonite recorded by focusing at the enamel/body interface gives a clear signature of the soft-paste porcelain composition for artefacts MNC 18432 (Rouen, Figure 7 top-left), MNC 4165 (Figure 8 top-left), MNC 8800 (Saint-Cloud, Figure 8 centre-left) and MNC 13371 (Pavie, not shown). A clear wollastonite signature is finally recorded for the MNC 4027 Saint-Cloud artefact after testing many

spots, the proof of a soft-paste body being important due to the very particular enamel that has been applied on this artefact.

Three types of enamels are observed:

- Lead-based enamels indicted by the strong Si-O stretching band at 980 cm^{-1} [61,64] (blue areas of objects MNC4006, MNC4165 and MNC13369), called a Pb-rich enamel (Tables 1 and 2, Figures 7-9)

- Alkali-lead enamels, less de-polymerized (called a K-rich (Pb) enamel, Tables 1 and 2), therefore having less flux, fired at a higher temperature and characterized by a component at ~ 1000 (Type 2) or ~ 1010 (Type 2bis) cm^{-1}; they are well observed, respectively, in objects MNC 8800 (blue), MNC 13371 (blue) and MNC 13369 (white) and in objects MNC 13371 and MNC 18432 (white).

- An enamel (MNC 4027) with two strong components at ~ 985 and 1070 cm^{-1} characteristic of an alkaline-rich glass, quite similar to that of Iznik fritwares[26] and later soft (and hard) porcelains. Comparison of XRF spectra also shows that this enamel has the lowest amount of lead.

Raman spectroscopy appears more efficient to differentiate qualitatively the different types of glassy silicates.

Presence of arsenic: Due to the high number of electrons involved in the As-O covalent bond, arsenic-based compounds are easily detected by Raman scattering. As we will discuss further the European raw material for the cobalt in the second half of the 17th century is rich in arsenic due to the minerals and the refining process.[55-57] Before this , due to a different technology (cobalt was a by-product) the cobalt source was free of arsenic. At least two different lead (calcium)-arsenates have been identified in the white and blue enamels and glazes[34,41,50,66-68] : a rather narrow peak at ~820-830 cm^{-1} with a marked shoulder at 775 cm^{-1} (e.g. MNC 18432 in Fig. 7, MNC 4027 in Fig.8, MNC 13371 and MNC 13369 in Fig. 9) characteristic of an apatite arsenate ($Na_{1-x-y}K_xCa_yPb_4(AsO_4)_3$)[69]; another component centred between 815 and 825 cm^{-1} can be also observed (MNC 4006, Fig. 7, MNC 13369, Fig. 8). It is not clear if this corresponds to other As-based compounds (feldspar? as identified by XRD in some majolicas[60,70,71], or partial substitution by fluorine ions due to the use of CaF_2 in the ore processing,[56] etc.) or if the broadening arises from a poor or nanocrystallinity of the apatite phase. More or less strong features are observed and the peak position shifts from 820 (MNC 4006, blue; MNC 13369 blue), 827 (MNC 8800 blue), 830 (MNC 13371 blue), 835 (MNC 18432 blue), to 837 (MNC 4027 blue). Obviously the As-O spectroscopic signature is observed in the blue coloured enamel and can be related to the arsenic associated with European cobalt.[55-59] Similar features are observed for blue enamels on French watches (gold substrate)[50], French porcelains[34,41] and enamelled glass artefacts,[67] as well on Chinese[41,52,65,66] and Japanese[49] artefacts made with European ingredients. Only MNC 4165 does not show an As-O signature. Note that arsenic was also not detected by XRF in this artefact. We therefore have a good agreement between the two analytical techniques. The understanding of the origin of the different Raman signatures requires a combination of the Raman microanalysis on sections with microdiffraction or SEM/TEM analysis, i.e. microdestructive studies on sherds.[33]

5. Discussion of technologies and attributions; Efficiency and limitation of on-site measurements

It is clear that with the exception of objects MNC 4027 and the décor area of MNC 18432 (the Chinese décor), the objects are covered with a lead-rich enamel (Table 1 and 2) in a similar continuation of the procedure used to produce majolica. The small differences noted for the blue areas are attributed to the incorporation of the compound providing the cobalt ions, a compound which is richer in potassium (probably smalt, the vector of cobalt in Europe is prepared by mixing potassium glass and arsenic-rich cobalt ore).[49,57-59] The arsenic supplied by the cobalt ore reacts with the flux. This particular character of the MNC 4027 enamel had already been noted in the earlier laboratory study in 2004.[4] The comparison of the spectra obtained for the 5 objects attributed to Saint-Cloud (MNC 868, MNC 4027, MNC 18434, MNC 5457, MNC 26659) and in particular the calculation of the polymerization index I_p,[30-32] which is determined by the ratio of the areas of the Si-O bands of deformation and stretching, had shown that the I_p of the enamels MNC 18432 and MNC 4027 (white-and-blue decoration) was ~ 2-3 while it was ~ 1-1.2 for the other objects (polychrome decoration) similar to those measured for Chantilly porcelain (in which the firing is carried out at a temperature less than 1100°C). According to Ms. Lahaussois[72] pieces with this type of blue decoration were produced in Saint-Cloud after the arrival of a master ceramist from a hard porcelain factory.[4] The I_p ratio measured for MNC 4027 is consistent with a firing at a temperature higher than 1200°C, lower than that required for the firing of a hard-paste body and glaze but higher than that of a standard soft-paste porcelain. It was not possible to record on-site spectra from the body but previous measurements made at the laboratory recorded the clear signature of wollastonite.[4] The flux content is certainly less than seen with the other artefacts.

It is obvious that the two objects attributed to Rouen were made with different technologies. The MNC 18432 pot appears close to the Saint-Cloud productions. The shape of MNC 18432 is similar to that of another artefact assigned to Poterat Factory[45] and with a décor more similar to the other artefacts assigned to Poterat. The later application of the Chinese décor on a pot made by Poterat is possible, but the rareness of this 17th century porcelain and the risk of degradation on firing make this hypothesis uncertain. The fact that arsenic was not detected, either by XRF or by Raman microspectroscopy is consistent with the fact that this artefact is the oldest. The change in the 'technology" of processing of cobalt ores takes place in the middle of the 17th century: prior to this the cobalt was a by-product of the production of silver that eliminated the presence of arsenic.[56,57] More studies of artefacts assigned to Poterat are needed to confirm this conclusion definitively.

6. Conclusions

A good agreement is observed between the X-ray fluorescence and Raman measurements. The Raman technique appears more efficient to detect arsenic-based phases than XRF: a visual inspection of the as-recorded spectrum is sufficient. Significant differences in the nature of the enamels used are highlighted with more than three types of enamels being identified. XRF and Raman analyses support the assignments based on marks and aesthetic criteria except for one artefact, previously assigned to Poterat Factory, Rouen that shows Chinese garden décor and XRF and the Raman signatures very close to that of the Saint-Cloud Factory. Alternatively, the Chinese décor was applied on an artefact made first without blue décor. The absence of arsenic in the cobalt used for the Poterat Factory artefact with the coat of arms of Asselin de Villequier is consistent with its very early production, close to the time at which the production of the cobalt ore was modified.

The access to the rare artefacts was restricted in time which limits the number of spots analysed. Another limitation of on-site analyses is the fact that measurements must be made from the top surface, that makes it difficult (or very costly in recording time) to study the stratigraphy. However, for the classification of the objects using the elemental information (major, minor and trace elements) collected by pXRF and/or by the set of crystalline phases identified by Raman microspectroscopy is often sufficient. Measurement of the polymerisation index of the enamel, a parameter related to the melting temperature of silicates is possible thanks to the high quality of spectra obtained with the x200 Mitutoyo microscope objective.

Figure captions

Fig. 1. pXRF (a) and remote Raman head (b,c) with their motorised and manual XYZ positioning stages; note the two laser spots in a'); when the two spots coincide, the focusing is good; b') focusing of the laser for Raman measurement.

Fig. 2. Soft-paste porcelains (MNC 4006 and MNC 18432) assigned to the Rouen Factory.

Fig. 3. Soft-paste porcelains assigned to the Factory of Saint-Cloud (MNC 4027, MNC 4165 and MNC 8800).

Fig. 4. Soft-paste porcelains (MNC 13369 and MNC13371) assigned to the Factory of Pavie, in Paris.

Fig. 5. Representative XRF patterns recorded on 'white' enamel for MNC 4027 (Saint-Cloud, white area) and MNC 18432 (Rouen, bottom white and blue décor part of the pot) artefacts.

Fig. 6. Representative XRF patterns recorded on 'white' and blue enamels in the low energy range for MNC 4006, MNC 4027, MNC 4165, MNC 8800, MNC 13369, MNC 18432, and MNC 13371, blue and white areas.

Fig.7. Representative Raman spectra of the MNC 4006 (Poterat factory, Rouen) and MNC 18432 (Rouen ?) artefacts and corresponding representative XRF patterns recorded on the 'white' and blue enamels in the medium energy range. The intensity of the MNC 18432 Pb peaks is 10 times less than for the other pieces studied.

Fig. 8. Representative Raman spectra of the MNC 4027, MNC 4165 and MNC 8800 Saint-Cloud artefacts.

Fig. 9. Representative Raman spectra of the MNC 13369 and MNC 13371 artefacts (Pavie factory).

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Table 1: List of objects (Characteristic bands of crystalline and amorphous phases identified by Raman micro-spectrometry are given, see further).

Object (Figure)	Provenance	Marks (Date)	Crystalline phases (Raman Peak wavenumber (cm^{-1}))			Ip	Glassy matrix(cm^{-1})		Remarks
			body	Enamel 'white'	Enamel 'blue'		Enamel 'white'	Enamel 'blue'	
MNC 4006 (2) Cup with lid	Rouen (L. Poterat)				405 : ? 458 : Q 820 : As			**450** **980** **(Pb-rich glass)**	Coat
MNC 18432 (1,2) Pot	Rouen ?			462 : Q 640 : W 837 : As 967 : W 1040 : W	462 : Q 835 : As		**480** **1010** **Type 2bis** **(lead-rich)**	**460** **1003** **(Pb-K-glass)**	Chinese decor and gadroons
MNC 4027 (3) Salt cup	St-Cloud	Soleil	640 : W 967 : W 1045 : W	640 : W 967 : W 1040 : W	400 : ? 458 : Q 837 : As			430 985 1070 (alkali-rich glass)	Lambrequins decor
MNC 4165-2 (3) Pot	St-Cloud				410 : W 635 : W 967 : W 1040 : W			**485** **980** **(Pb-rich glass)**	Lambrequins decor
MNC 8800 (3) Pot	St-Cloud	xS.C. T		635 : W 967 : W 1040 : W	390 : A 635 : W 665 :A 827 : As 875 967 : W 1006 : A			**455** **1000** **(Pb-alkali glass)**	Lambrequins decor
MNC 13371 (4) Salt cup		* AP		200 : Q 460 : Q 635 : W (+Sn ?) 690 : 835 : As 967 : W 1158 : Q	385 : 460 : Q 660 : A 812 : 830 : As 1000 : A (1300 : C) (1560 : C)		**450** **1010** **Type 2bis** **(lead-rich)**	**460** **1000** **(Pb-alkali glass)**	Lambrequins decor
MNC 13369 (4) Pot with lid	A. Pavie (Paris)	* .A.P.		462 : Q 635 : Sn + W 775 : Sn 967 : W	405 : 458 : Q 672 : 820 : As 1357 : C 1570 : C		**460** **1000** **Type 2** **(lead-rich)**	**450** **970** **(Pb-rich glass)**	Lambrequins decor

A : augite ; Q : quartz ; W : wollastonite ; As : lead arsenate ; c : carbon ; Sn : cassitérite ; [Colomban et al., 2004 ; Minceva-Sukarova et al.,

Table 2: Elements identified by X-ray fluorescence. Categorization into major, minor and traces is carried out by visual examination of the intensities of the different K and L transitions.

Object	Provenance (assignment)	Colour	Major	minor	minor/traces	Remarks
MNC 4006	Poterat	White1	Si,Pb,K	Fe,Mn,Sn,As	Ti,Ni,Cu, Cd,Sb	*Pb-rich Enamel*
		White2	Si,Pb,K	Fe,Sn	Ti,Ni,Cu	
		Blue1	Si,Pb,K	Fe,Sn,Co,As	Mn,Ti,Ni,Cd,Cu,Zr	
		Blue2	Si,Pb,K	Fe,Co,Sn	Ti,Cd,Ni,Cu	
MNC 18432	Rouen?	**White1**	**Si,K,Ca,**	Pb, Sn,Fe	Ti,Ga,Ni,Sr,Zr	**K-rich (Pb) Enamel**
		White2	**Si, K,Ca,**	Pb,Sn,Fe	Ti,Ni,Sr	
		Blue1	**Si, K,Ca,**	Pb,As,S,Fe,Co	Ti,Ni,Bi,Zn,Ga,Cd,Zr	
		Blue2	**Si, K,Ca,**	Pb,As,Sn,Fe,Co	Ga,Ni,Cd,Ga,Sr	
MNC 4027	Saint-Cloud	**White**	**Si,K,Ca**	Pb,As,S,Fe	Ti,Ni,Zn,Ga,Sr	***K-rich (Pb) Enamel***
		Blue	**Si,K,Ca**	Pb,As,Co,S,Fe	Ti,Ni,Zn,Sr	
		White1	**Si,Ca,K**	Pb,As,Fe	Ti,Sr,Ni,Ga	
		White2	**Si,Ca,K**	Pb,As,Fe,S	Ti,Ni,Sr,Zn,Ga,Rb	
MNC 4165	Saint-Cloud	White	Si,Pb,K,Ca	Fe,Ti	Ga,Ni,Sr,Zr	*Pb-rich Enamel*
		Blue	Si,Pb,K,Ca	Fe,Ti,Co	Ni,Ga,Zr	
MNC 8800	Saint-Cloud	White	Si,Pb,Ca	Fe,Ti	Ni,Ga,Sr	
		Blue	Si,Pb,K,Ca	As,Fe,Ti,Co	Ni,Sr,Zr	
MNC 13371	Pavie (Paris)	White	Si,Pb,K,Ca	Sn,Fe	Ti,Co,Zr	
		Blue1	Si,Pb ,K,Ca	As,Co,Fe,Sn	Bi,Ni,Ga	
		Blue2	Si,Pb,K,Ca	As,Co,Fe,Sn	Ni,Ti,Cd,Zr	
MNC 13369	Pavie (Paris)	White	Si,Pb,K	Sn,Fe	Ga,Cl,Ni,Cd,Zr	*Pb-rich Enamel*
		Blue	Si,Pb,K	Sn,As,Co,Fe	Ni,Ti,Zr,Br	

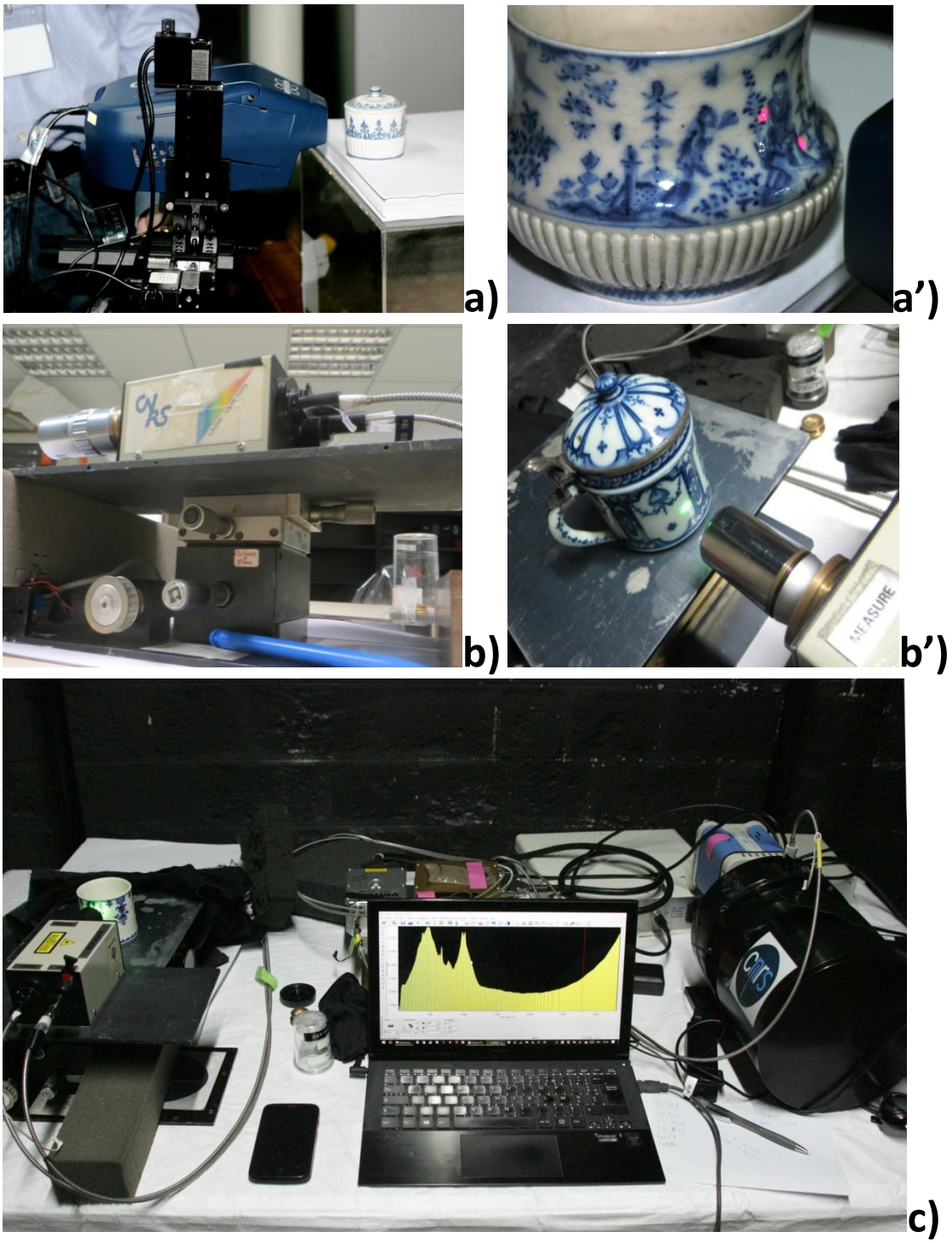

Fig. 1. pXRF (a) and remote Raman head (b,c) with their motorised and manual XYZ positioning stages; note the two laser spots in a'); when the two spots coincide, the focusing is good; b') focusing of the laser for Raman measurement.

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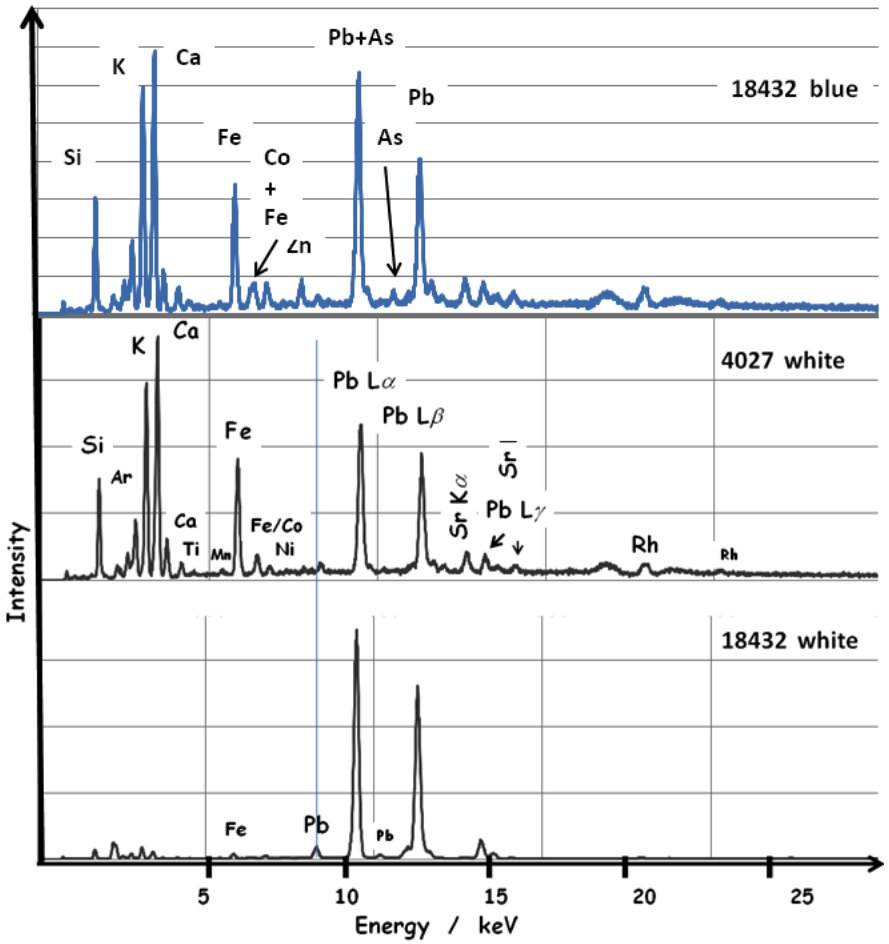
Fig. 4. Soft-paste porcelains (MNC 13369 and MNC 13371) assigned to the Factory of Pavie, in Paris.



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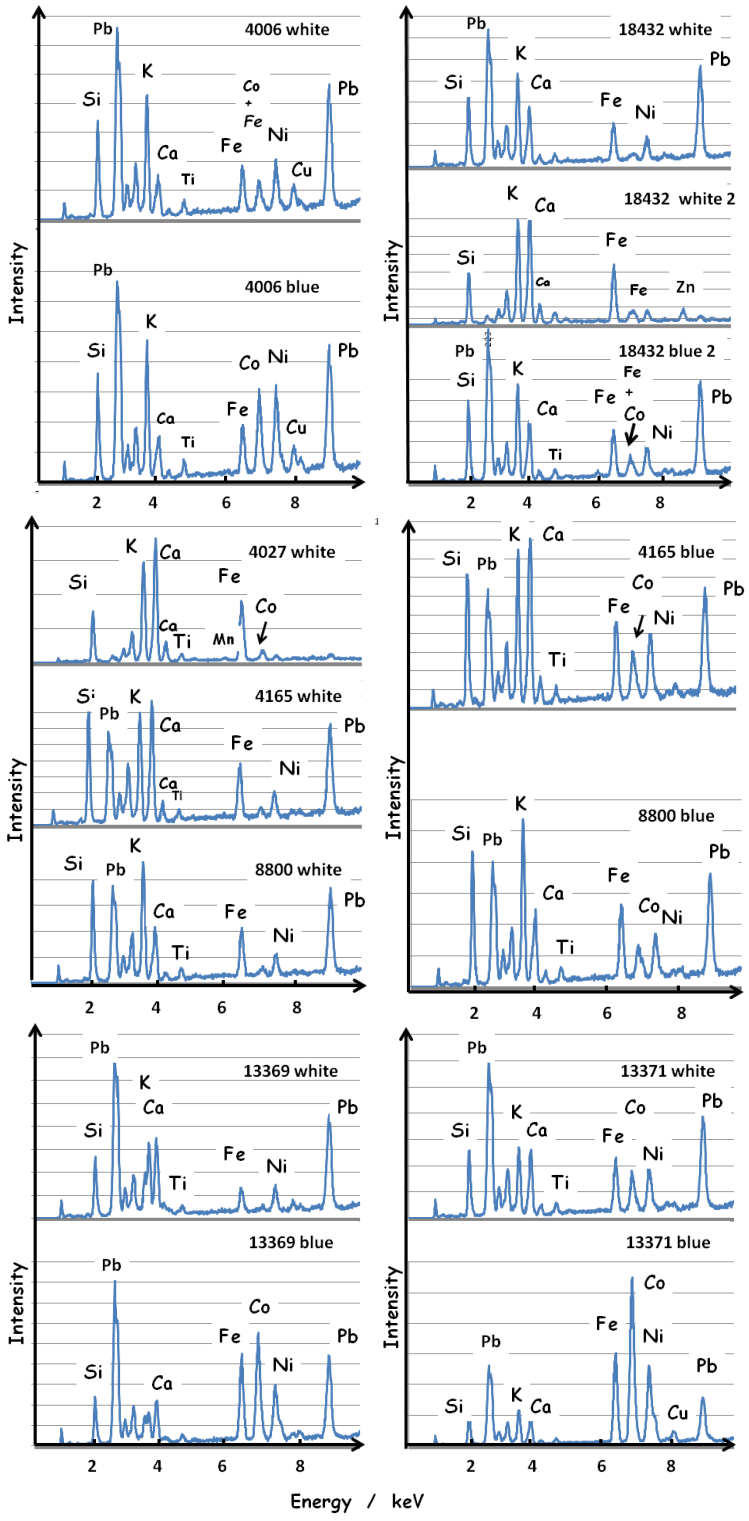

Fig. 6. Representative XRF patterns recorded on 'white' and blue enamels in the low energy range for MNC 4006, MNC 4027, MNC 4165, MNC 8800, MNC 13369, MNC 18432, and MNC 13371, blue and white areas.

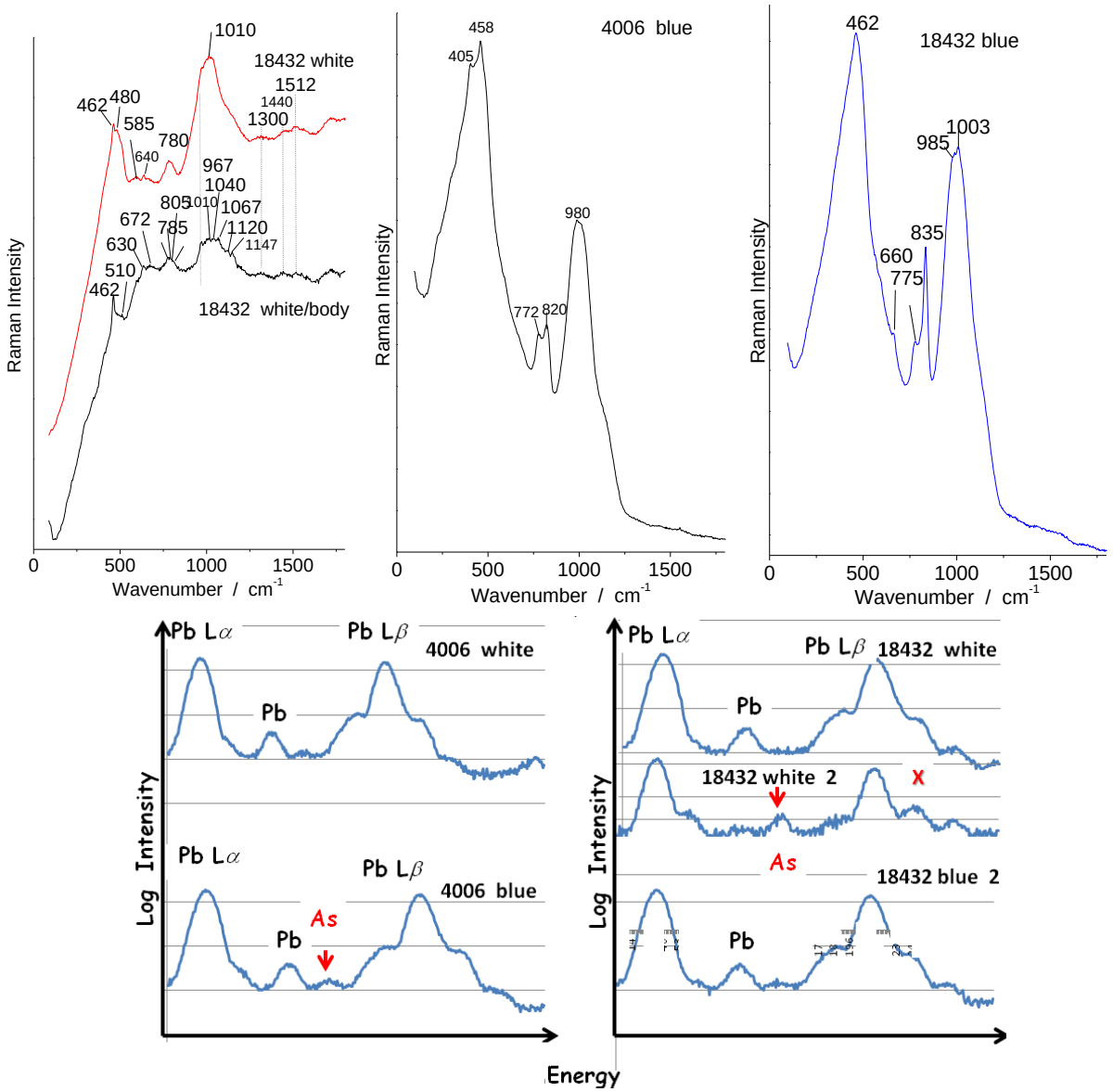

Fig.7. Representative Raman spectra of the MNC 4006 (Poterat factory, Rouen) and MNC 18432 (Rouen ?) artefacts and corresponding representative XRF patterns recorded on the 'white' and blue enamels in the medium energy range. The intensity of the MNC 18432 Pb peaks is 10 times less than for the other pieces studied.

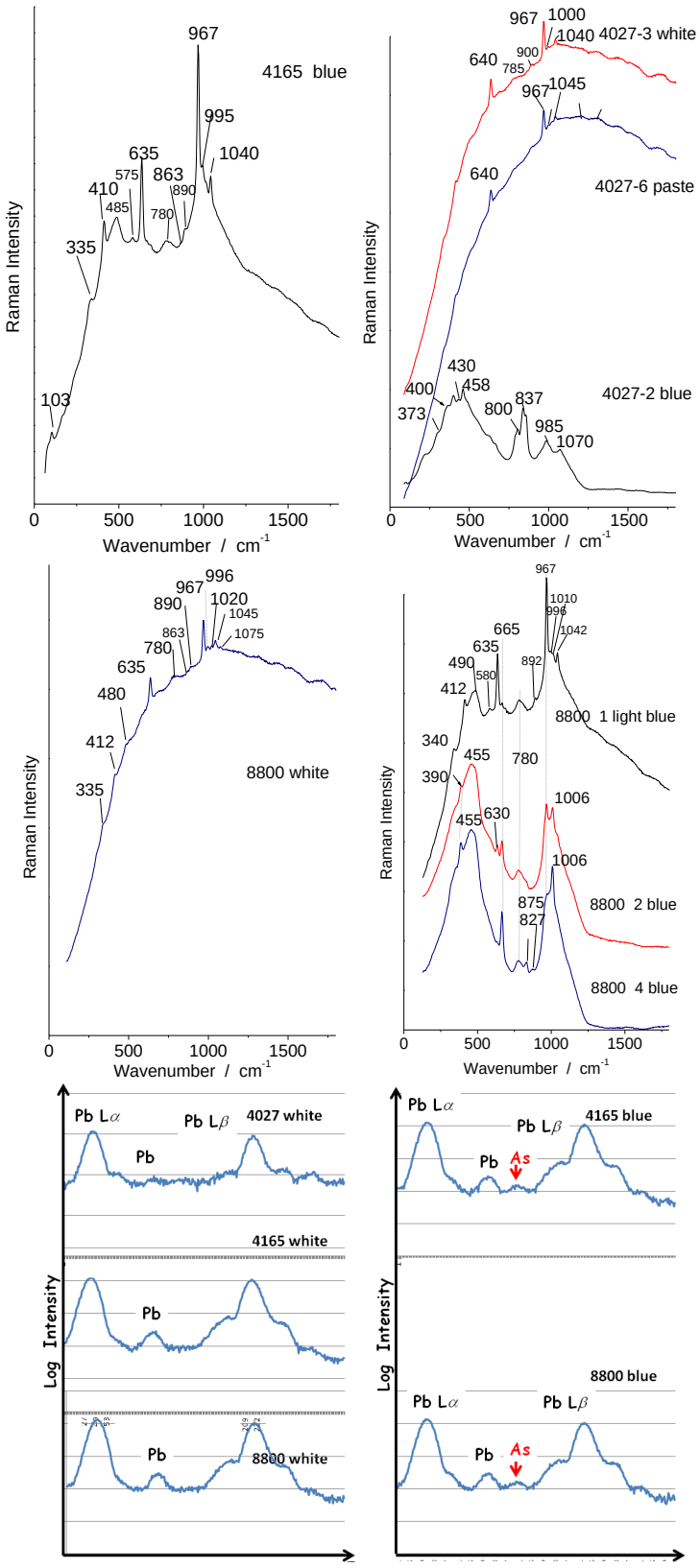

Fig. 8. Representative Raman spectra of the MNC 4027, MNC 4165 and MNC 8800 Saint-Cloud artefacts.

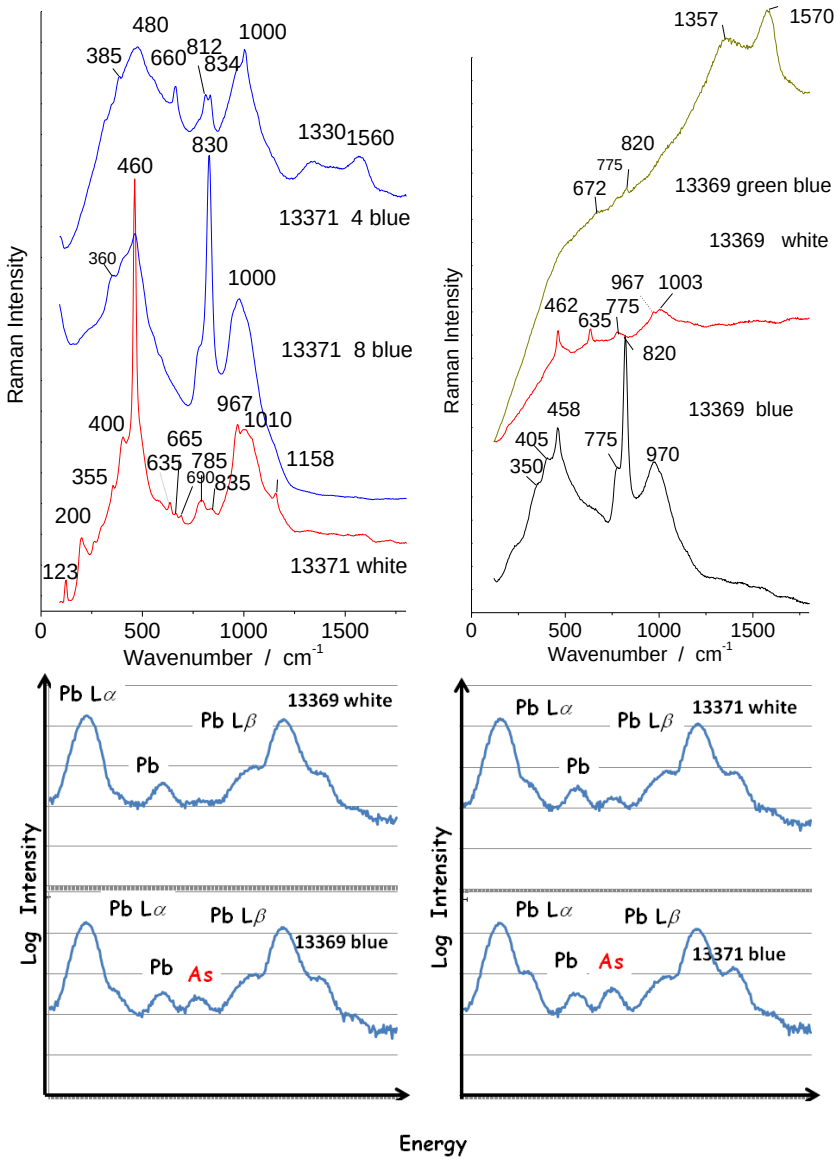

Fig. 9. Representative Raman spectra of the MNC 13369 and MNC 13371 artefacts (Pavie factory).

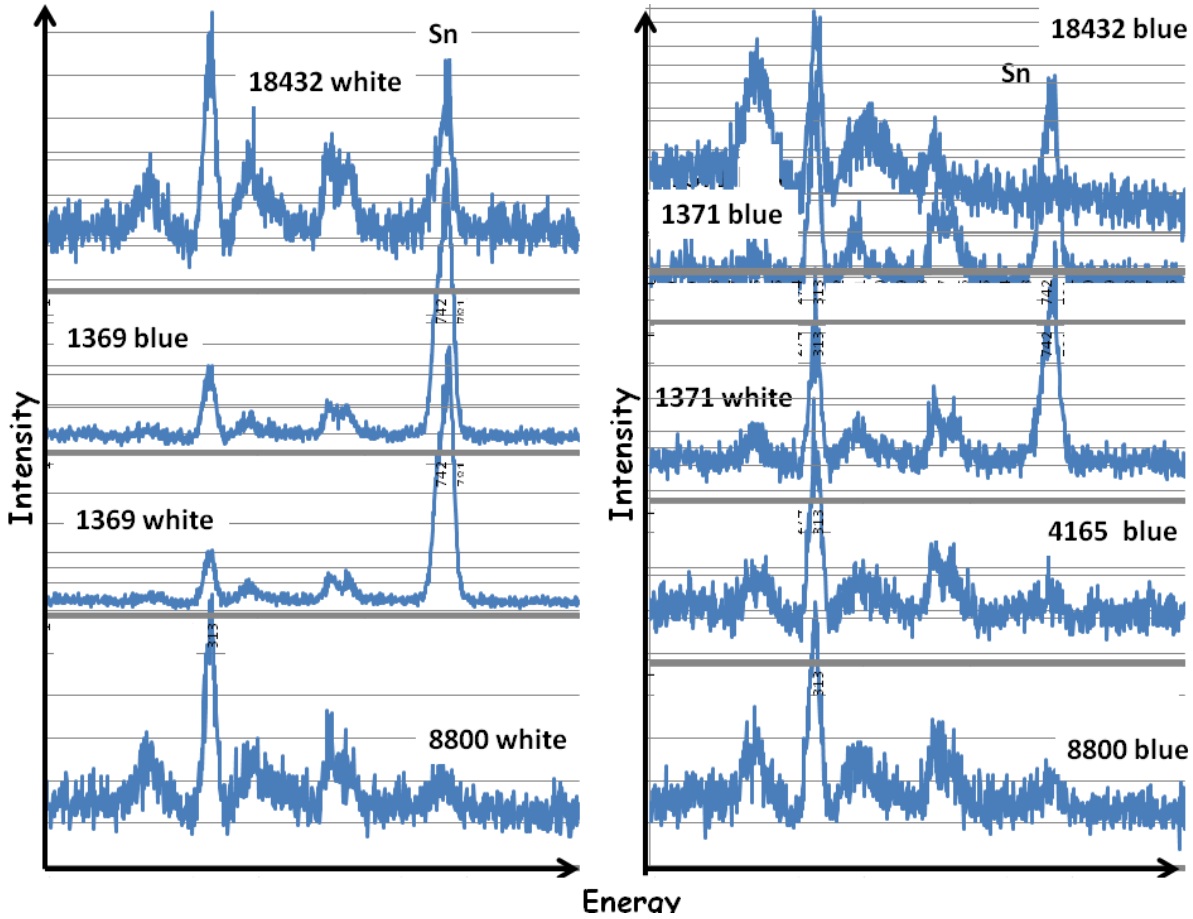

Figure S1. Representative XRF patterns recorded on 'white' and blue enamels in the high energy range for the comparison of Sn content (MNC 18432, MNC 1369, MNC 4165 and MNC 8800, blue and white areas).

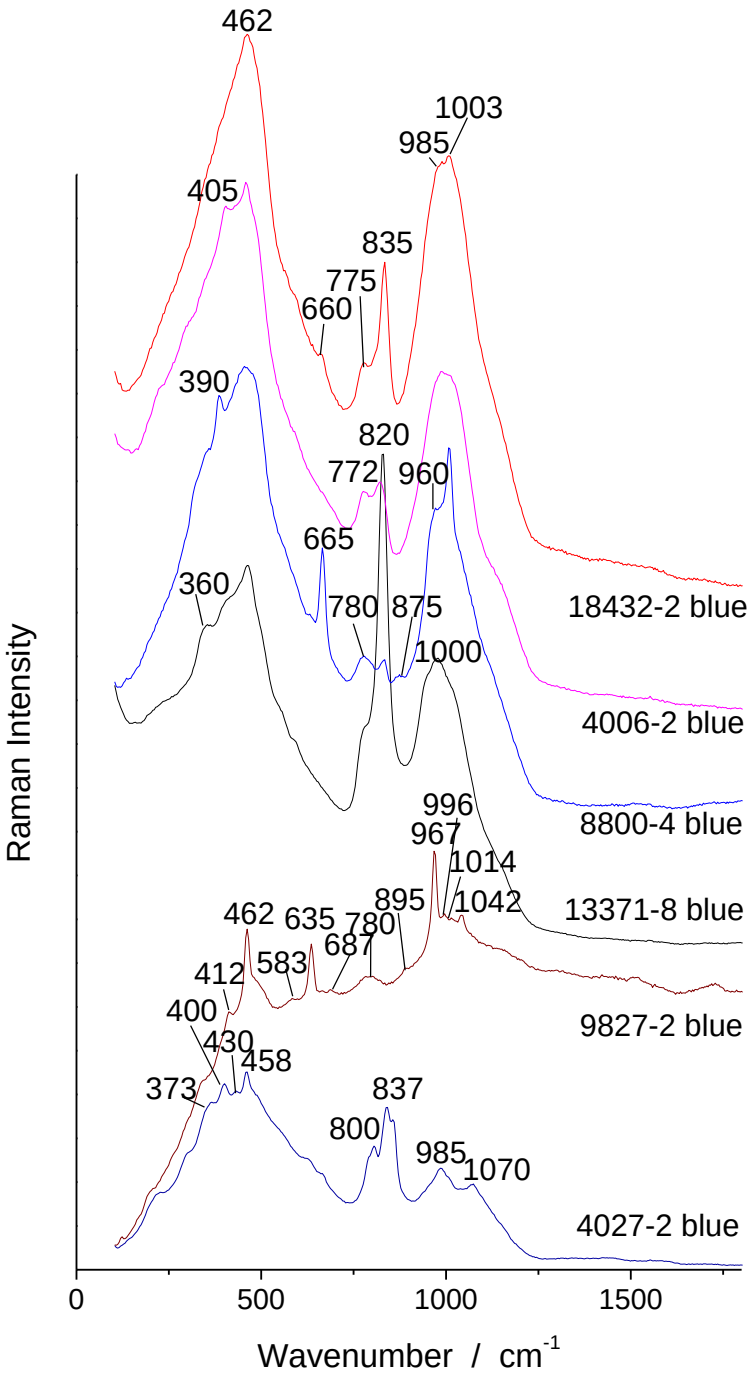

Figure S2. Comparison of the Raman spectra recorded on blue enamels .