Non-invasive on-site Raman study of blue-decorated early soft-paste porcelain: The use of arsenic-rich (European) cobalt ores – Comparison with huafalang Chinese porcelains

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Non-Invasive on-site Raman study of blue-decorated early soft-paste porcelain: the use of Arsenic-rich (European) cobalt ores – Comparison with *huafalang* Chinese porcelains

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Abstract

Both European and Asian historical records report that Jesuits were at the origin of enamelling technology transfers from France (and Italy) to Asia during the 17th century. A mobile Raman set-up equipped with a high magnification (x200) microscope objective with long working distance is used to identify the use of European (arsenic-rich) cobalt in 17th and 18th century porcelains: twenty soft-paste porcelains from Rouen (L. Poterat' Factory), Saint-Cloud, Paris (Pavie', Hébert', Chicanneau', and Bellevaux' factories), Lille, Mennecy, and Vincennes factories, of which almost all were produced before 1750, belonging to the Cité de la Céramique Collection (formerly Musée national de Céramique, Sèvres), have been analysed in order to get a more representative view of the type of cobalt ore used. A large proportion of blue decors exhibit signs of lead arsenate, even for productions after ~1750, which proves the wilful interest given to arsenic phases in magnifying blue hues. Different lead arsenate signatures are observed, one assigned to the product of reaction of As-rich cobalt ore with lead-based glaze and another characteristic of added arsenic. At least two groups of glaze are identified: a lead-rich one and a mixed lead-alkali glaze. Porcelains made during the second half of the 18th century exhibit the very strong As-O modes characteristic of the voluntary addition of a lead-arsenate forming compound. Comparisons are made with Qing Chinese productions exhibiting similar Raman signatures and expected to have benefited from transfers of technologies .

Keywords

B: Impurities; B: Spectroscopies; C: colour; D: Glass; arsenic; porcelain

Graphical Abstract
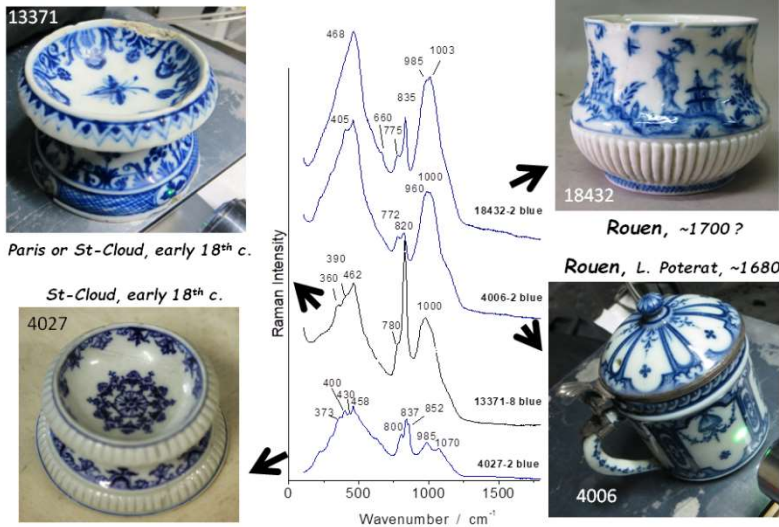
1. Introduction

Porcelains made from kaolin, feldspar, and sand are a Chinese innovation, a notable example of the many advancements in ceramic technology that occurred in China many centuries before reaching Europe [1]. However, some European technologies did inspire some Asian productions: for instance, the *cloisonné* enamel technique [2] is assumed to have spread from the Byzantine Empire to China by means of the Silk Road Trade. Important Jesuit Missions were established at the end of 16th century in Japan and during the 17th century in China, and, according to both Chinese and European historical records, facilitated access to experts in glass and enamelling technologies, as well as the importation of enamelled artefacts and glaze precursors to the Qing Court [3-6]. At that time, the decor of Asian porcelains didn't produce 'realistic' (overglaze) paintings, as opposed to the well delimited coloured areas made of opaque enamels which allowed for 'realistic' pictures as in European easel paintings. Indeed, Chinese pottery is decorated with pale enamels that looks like watercolours [7-9]. Blue decors of Asian porcelains are directly painted on the porous green body and then covered with a glaze precursor layer and subsequently fired at the high temperature required to form porcelains (~1300-1450°C) [1,9-11]. Consequently, the porcelain glaze melts at the (top) firing temperature of the body and its composition contains a significant level of alumina and a rather limited amount of flux (K_2O, Na_2O and CaO) [12-16]. In Europe, this technique is called '*Grand Feu*' firing [14-18]. The colour palette of '*Grand Feu*' porcelain is limited [17,18] and coloured enamels must be added on the already fired artefact and heated again using the '*Moufle*' or the '*Petit Feu*' techniques. Lead-based enamels are fired at *Moufle* (~1050°C) or '*Petit Feu*' (800 to 600°C) temperatures [15-20]. The '*Petit Feu*' technique was first used on soft-paste porcelains (i.e. porcelain made without kaolin, see further down) because the limited thermal stability of the paste and is linked to the glazing techniques developed for fritwares and faience/majolica [16,19]. '*Petit Feu*' technique allows for the preparation of realistic paintings visually similar to oil paintings as obtained by Limoges enamels (on metal) [20-22]. These complex painted decors were made using lead-rich mixtures deposed on already fired and glazed objects. The origin of the '*Petit Feu*' technique can be traced to Ottoman (Iznik) and Persian (*minai ware*) potters that develop complex decors obtained by successive firings of lead-based glazes [23-25] on fritware bodies: the body it-self was made by soldering a sand-rich mixture with lead-based

"cement" [15,19,23,24]. Soft-paste porcelains belong to the same type of pottery as fritware: due to the absence of kaolin, a mixture of sand, chalk/marl, and glue is shaped and fired. Hard-paste porcelain made with kaolin and feldspar accept a rather large shift in firing temperatures (up to ~100°C)[26], thanks to the prior formation of a network of acicular mullite crystals in the body during the firing. The mullite network retains the molten part of the body by capillarity [9,12,13,27,28], which while cooling, gives it its amorphous phase and hence translucence : on the contrary soft-paste porcelains requires a well-defined temperature; a small downward-shift of the firing temperature leads to porous bodies while a small upward-shift leads to a complete deformation or even a flattening of the object (Fig. S1, Supplementary Materials). The decor should be put on the already fired (non-porous) body in decreasing temperature increments of around 100/200°C if it requires the superposition of many colours [17,20].

Archaeometric studies of early produced soft-paste porcelains are rather limited. In the 1980s Kingery et al. [9,28] conducted optical and Scanning Electron Microscopy and fluorescence analyses on polished Saint-Cloud, Chantilly and Sèvres shards and measured the elemental composition of the body and of some glazes of soft- and hard-paste porcelains. Preliminary Raman study was conducted by Colomban and Treppoz [26]. The first comprehensive Raman microscopy study published in French in 2004 by Colomban et al. presented a selection of 17 artefacts of Saint-Cloud, Chantilly, Mennecy, Vincennes and Sèvres Factories; all item belonging to the Sèvres Musée National de Céramique (MNC) Collection [29]. The study performed at the laboratory with a fixed high-resolution spectrometer was focused on the identification of the crystalline phases in the body and in the glaze (opacifiers and pigments). Recently Sceaux Factory soft-paste artefacts (18 porcelains and a few faiences) were analysed on site by Raman microspectroscopy using the mobile set-up used in this work [30]. Reference European porcelain bodies and glazes have also been analysed in the same way [17,31-33]. Elemental and raw material compositions of soft-paste porcelain produced at Sèvres National Factory, the continuation of the Royal factory founded at Vincennes by Louis XV, King of France, were also published by d'Albis [15,18] and much earlier by Brongniart [16]. Bodies and glaze compositions were also given by Deck [19], Munier [34], Bertran [20] and de Plinval de Guillebon [35,36]. Recently,

Maggetti and d'Albis analysed in detail the microstructure of a 1781 soft-paste plate from Sèvres Royal Factory using SEM-EDS [37].

We present here an on-site Raman study at the Cité de la Céramique with a mobile Raman set-up of 20 soft-paste porcelain objects with blue décor. The artefacts were selected among the oldest ones in the collection (Table 1 and Supplementary Materials), in particular three pots attributed to the Rouen Factory: one assigned to Louis Poterat (circa 1680) and considered as the oldest European porcelain to be preserved [36-38], if we except very rare Medici porcelain objects made, one century before at Florence, with a very specific paste, intermediate between soft and hard paste ones [9,16,32]. Among a series of early European porcelains, we select three artefacts from the Saint-Cloud Factory (two of them made ca. 1700 or before) and 6 items from the famous early 18th century Paris Factories (Edouard Hébert, Dominique & Pierre Chicaneau, Antoine Pavie and Bellevaux) [35,36,38]. Soft-paste porcelains from Lille, Mennecy, Vincennes and Sèvres and some early hard-paste porcelains from Strasbourg (Hannong Factory) and Meissen (Saxony) complete the corpus. Comparison will be made with data collected on two very representative Chinese potteries: a *huafalang* Imperial bowl (Kangxi reign, ca. 1715-1722) and a Yixing tea pot stoneware (2nd half of the 18th century) selected from previous studies of 17th-18th centuries Chinese porcelains and stonewares [7].

French soft paste production was described by Hellot (reported in ref. [14]) and Brongniart [16] as a mixing of a frit and a very plastic illite calcareous clay from Argenteuil. The frit is made of soda ash, sea salt, potassium nitrate, silica and lime or gypsum, milled together and then fired (firing temperature, ~1100°C). The resulting matter is crushed, milled and mixed with the Argenteuil clay (8-10% wt) and then shaped, trimmed or turned, and bisque fired before the application of a lead-based glaze. More details can be found in d'Albis et al. papers [15,18,37]. The characteristic crystalline phase of soft-paste porcelain is wollastonite ($CaSiO_3$), but cristobalite (SiO_2), and trydimite (SiO_2) crystals form in smaller amount from the (partial) dissolution of quartz grains [14,15,26,29].

Erzgebirge mining (Saxony) was the principal source of cobalt ores in Europe at that times and consisted in a mixture of skutterite ($CoAs_3$), smaltite (($Co,Ni,Fe)As_2$), safflorite ($CoAs_2$), cobaltite (CoAsS) and arsenate erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$) [39,40]. Ores are more or less grilled that eliminates some arsenic and even incorporated in molten glass to form smalt

[40]. A source from the Pyrenees mountains is also reported by Magetti and d'Albis for artefacts made at the end of the 18th century [37]. The mixing of these arsenic-rich ores with a lead-rich glaze led to the precipitation of lead arsenate, e.g. as follow:

$$CoAs_3 + [Pb_3O_4 + nSiO_2]_{liq.} => 3\ PbAsO_4 + [Co^{2+}\ nSiO_2]_{glass}$$
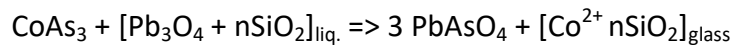
Indeed, the glaze may contain some other fluxing ions (Ca^{2+}, Na^+ and K^+) that could give more complex phases and compositions [41]. Because of the high toxicity of (soluble or volatile) arsenic derivatives, the number of studies on these compounds, especially from a vibrational point of view, is very limited, while studies of natural compounds are less scarce [42,43]. It is well known that the Raman intensity first depends on the bond polarisability, i.e. from the number of electrons involved in the bond. Due to its position in the Periodic Table (Z = 33), the As-O bond polarisability is large and its symmetric stretching mode strong [44]. Consequently, lead arsenates are easily detected by Raman scattering, with an intense feature at ca. 820 cm^{-1} [7,8,41-44]. We will thus focus our attention on this wavenumber range in order to get a representative view of the presence of lead-based arsenate in association with the blue decors of ancient porcelains.

2. Experimental

2.1. Technique

The mobile Raman set-up associates a HE532 Horiba Jobin-Yvon spectrometer, fibre optics connected to a remote Superhead(R) equipped with a high-magnification LWD (~13 mm) microscope objective and a 532 nm Ventus Quantum laser. For a recorded spectrum of higher quality, a x200 Mitutoyo microscope is preferred (laser spot waist < 0.4 μm, close to the diffraction limit [8]) regardless of the larger time required to adjust the focus [45,46]. The exceptional quality of this optic limits the extension of the focus volume along the Z direction to about 2 μm, regardless of the enlargement of the laser spot within the matter due to the optical index of the glaze. The thickness of the coloured film and the size of pigment's grains/crystals can be very small (a few μm), and it is necessary that the laser spot intercepts at the best the coloured matter. Due to the high sensitivity of the HE532 spectrometer, the recording time, including 3 to 100 accumulations to avoid cosmic ray spikes, ranges between 1 and 60 sec. The illumination power at the sample's position is

selected between ~20 mW (body and colourless glaze analysis) and 1 to 10 mW (more or less coloured areas).

2.2. Artefacts

Figs 1 and 2 show most of the studied artefacts. All items are listed in Table 1 and photographs of all artefacts, including their Factory' mark, dimension and origin (and the collected spectra) are given as Supplementary Materials. Assignments reported in Table 1 are those indicated in the MNC records. They will be further discussed. Complementary historical information, including mark assignments, can be found in refs [36,38].

3. Historical context

As said in the introduction, the studied corpus consists of a very representative set of early French porcelains with a blue décor. Exceptionally rare, they were first produced in the Rouen Factory by Louis Poterat, a faience producer that obtained in 1673 the first Royal Privilege from King Louis XIV of France in order to make porcelain. It's a very limited production which stopped in 1696 and thus only consisted of a very few number of items. The second group belongs to the Saint-Cloud Factory production, a factory founded by Pierre 1st Chicaneau, and which started to produce porcelain in 1693 under the patronage of Monsieur, the King' brother (Fig. 1). The latter factory was visited by E. Von Tchirnhaus [35] before he started making hard-paste porcelain in Dresden and Meissen [26]. The production stopped in 1766. Note that some of the selected artefacts come from a Paris subsidiary of the Saint-Cloud Factory (la Ville l'Evêque) managed by Pierre 2nd Chicaneau and Marie Moreau. Pierre Pélissier, in relation with the Saint-Cloud Factory, helped Antoine Pavie to produce soft-paste porcelains in Paris after 1703: three artefacts are assigned to this production. A Chicaneau's daughter married a member of the Hébert family and some porcelain produced by the Hébert Factory were also selected. Other artefacts were produced at Lille (Factory founded in 1711), Mennecy (founded in 1737) and Vincennes (founded circa 1738-1740, Fig. 2). The famous Chemist René Antoine Ferchault de Réaumur, with the help of Letters sent by Père d'Entrecolles describing the production of hard-paste porcelain at Jingdezhen (China)[47], worked with two masters of the Pavie' Factory (F. Barbin and P. Pélissé) and tried to make scientifically translucent 'porcelain' [35]. Artefacts with a specific JB mark are assigned to Jean-Baptiste Bellevaux's Factory (see Supplementary Materials). J.-B. Bellevaux also first worked at the Saint-Cloud Factory [35,36]. The selected

artefacts are thus important pieces of the history of porcelain. Note that because of the very poor plasticity of green porcelain pastes, the size of these first items is small. The better plasticity of hard-paste green body makes possible the preparation of bigger artefacts. Assignment of the origin of some artefacts remains disputed and thus a better knowledge of the technology used to produce these objects is welcome.

Treatment of cobalt ores by roasting incompletely eliminates arsenic, and consequently blue enamels from the 17th century still contain a significant level of arsenic [39,40]. Complementary treatments with sulphuric or hydrochloric acid increased the purity of cobalt. The decrease of the content of residual arsenic in blue glass during the 17th century is well established for Trade glass beads [48,49] and for Limoges enamels [21,22,50]. Recent on-site Raman analysis of Chinese porcelain masterpieces [7] and combined elemental and Raman analysis of similar shards [8,44] have demonstrated that many blue and green glazes of 18th century Chinese porcelains exhibit specific Raman signatures at ca. 830 cm^{-1} and a relatively high level of arsenic is detected in association to cobalt [8,44,51]. On the other hand, this signature was not observed on blue-decorated porcelains from the Ming Dynasty thanks to the use of arsenic-free Asian cobalt ores (rich in manganese and iron) [52-59].

4. Results

4.1. Raman signature of crystalline phases

Figs 3 and 4 show characteristic spectra recorded with the focused laser spot intercepting blue or blue-green areas, at the best as possible. Spectra recorded on the body, on white glaze, and on other coloured areas are given in Supplementary Materials. We will first consider the narrow peaks characteristic of crystalline phases dispersed within the glaze.

The peak observed at ~462 cm^{-1} in many spectra is the strongest one of α quartz signature (SiO$_4$ bending mode). However, incompletely dissolved grains of quartz are commonly detected by Raman scattering [10,17,26,29,30] in porcelain bodies and glazes. A more or less strong peak is observed at 815 cm^{-1} (Table 1) for a first series of blue (or green) regions (artefacts # 6638, 8102, 13371, 24780, 25330, 26296 and 26502). This peak is attributed to lead arsenate. In the past, some papers have attributed similar Raman features at this wavenumber to olivine CoSiO$_4$, a phase exhibiting a doublet at ~815-820 cm^{-1} [60]. However, the higher polarizability of the As-O bond will make the As-O stretching mode covers the Co-

O one, even if the number of As-O bonds is inferior to that of Co-O ones. The location of the peak shifts at 820 cm^{-1} in artefacts number 4006, 6638, 8800, 24780, 13371 and at ca. 830 (as in glass beads [49]) or 835 cm^{-1} for the last group of artefacts (4027, 13369, 13371, 17063, 18432 and 18433). When the intensity of the peak is small, the superimposition of Co-O and As-O components could explain the shift, but not when strong band intensity is observed: like in artefacts #4027, 8800, 13369 and 17063 (Fig. 4). A 870 cm^{-1} peak is observed in blue-green 17063 décor and is assigned to a chromate (this point will be discussed further down). The 815 cm^{-1} more or less strong peak is mainly observed in the Vincennes (or Sèvres) Factory production (1748 to 1764), while a 820 cm^{-1} peak is observed both in some mid-18th century Vincennes/Sèvres porcelains and in some early artefacts assigned to Poterat (4006), Saint-Cloud (8800) and Chicaneau-Moreau (13371) Factories. The last group dated to the end of the 17th century to the beginning of the 18th century (Rouen 18432; Saint-Cloud 4027; Chicaneau-Moreau 13371; Pavie 13369 & 18433; and Lille 17063) exhibits peaks at 830 or 835 cm^{-1}. The 13371 artefact, assigned to the Chicaneau-Moreau Paris workshop, exhibits the three types of signatures.

The above-mentioned peaks were not observed in some pots: those assigned to the Saint-Cloud Factory (4135), Hébert Factory (9827), in a bowl from the Pavie workshop (13385), in pots from Lille (13361), in an unassigned artefact (13354), a Mennecy (13281) one and in a coffee cup from the Hébert Factory (13345). No arsenate signatures were observed for blue decorated hard-paste porcelains (2274, Meissen; 13675 and 13399, Hannong-Strasbourg/Frankenthal) according the use of lead-free glaze, but an 815-823 cm^{-1} doublet was recorded for a multi-coloured hard paste from Strasbourg (13674) because the use of lead-based overglaze.

As a preliminary conclusion, three different signatures potentially attributed to arsenate-rich phases are thus observed. One group corresponds mainly to Saint-Cloud and its associated artefacts and to some Rouen productions. The second group corresponds to later productions. We will discuss the relationship with the glaze signature in the next paragraph.

Narrow doublets at 635 and 967 cm^{-1} characteristics of (beta) pseudo-wollastonite, a phase typical of soft-paste glaze [29,30], are observed in all glazes except in those of hard paste porcelains and of the Poterat MNC4006 pot. Pseudo wollastonite requires a temperature of 1050-1100°c or more to form in calcium-rich glass [61]. The Raman signature of

clinopyroxene phases with rather similar compositions ($(Mg,Fe,Ca)SiO_3$) (665-1007 cm^{-1} doublet [62]) is observed in some glazes (18432, 8800, 13371, 17063, 13361 and 13281). Note that these artefacts belong to the older group. This could indicate the use of a magnesium-rich raw material.

4.2. *Raman signature of amorphous phases*

The amorphous network of silicates is made of partially connected tetrahedron in which Na^+, K^+, Ca^{2+}, Pb^{2+} flux ions and Al^{3+} ions are distributed in the sites delimited by the SiO_4 network. The Raman signature of an amorphous silicate consists in two broad band at ca. 450-500 and 950-1050 cm^{-1} arising from the bending and stretching modes of SiO_4 tetrahedrons [60-64]. Because the stretching mode of an isolated regular (Td symmetry) tetrahedron has A_1 symmetry (e.g. a single peak) and because the Raman intensity of asymmetric stretching modes is order of magnitude lower than the totally symmetric mode, the different components of the ca 950-1050 cm^{-1} band can be associated to the different A_1 peaks characteristics of each types of tetrahedron (isolated, connected by 1, 2, 3 or 4 oxygen atoms) forming the silicate network [63-67]: the Raman spectrum is thus the fingerprint of the silicate network. The symmetric and asymmetric bending modes having E and F character respectively, the number of components is more important, 10 and 15 respectively, and it is not possible to individualise them! But it has been demonstrated experimentally [63,68], and theoretically [69Vanessa], that the area ratio of the bending band with respect to that of the stretching band, both for crystalline and amorphous silicates, is a measure of the polymerisation degree of the SiO_4 network and hence is directly linked to the melting temperature. Much information can thus be extracted from the Raman spectrum.

The position and shape of the SiO_4 stretching band gives information on the glaze type [63,64]. Three types of glaze signatures can be recognized: i) a first one with a SiO_4 stretching band peaking at ~980-1005 cm^{-1}, characteristic of lead-rich composition [23,64]; ii) a second one characterized by a band with two sub-maxima at about 980 and 1030-1040 cm^{-1}, and characteristic of a mixed lead-alkali glaze [64] as used for Iznik and Kutahya glazed fritware [24,70] for instance, and iii) the alkali glaze fired at high temperature with hard-paste porcelain body peaking at ~1060-1070 cm^{-1} [17,26,64]. A mixed lead-alkali glaze is observed for artefacts assigned to the second half of the 18th century and these glazes are free of

clinopyroxene. Note that yellow and green glazes belong to the LR group because the formation/conservation of Naples yellow pyrochlore requires a lead-rich glassy matrix [71].

5. Discussion

As proposed in previous Raman studies [26,29,30], wollastonite peaks are characteristic of soft-paste bodies and glazes and very efficient to discriminate between soft- and hard-paste porcelains, even with a mobile Raman set-up which performances remain inferior to that of an advanced laboratory instrument. The very characteristic huge fluorescence of Sanson's Factory production should be noted. Measurements on other artefacts from the same Factory already pointed out a huge fluorescence [72]. The observation of additional diopside (clinopyroxene) peaks appears characteristic of some early made soft-paste porcelains. As previously observed for Saint-Cloud's soft-pastes [9,29], at least two compositions of glaze have been used. And except for artefacts #4027 (Saint-Cloud, ~1700, sun mark, see Supplementary Materials) and 13281 (Mennecy, >1731), the lead-rich composition corresponds well to the beginning of the production. The mixed AL glaze corresponds to artefacts produced during the second part of the 18th century (Table 1, artefacts 6638 and after). This puts in questions the dating of these two 4027 and 13281 objects. The estimation of the processing temperature of the glazes from their SiO_4 bending-to-stretching area ratio, i.e. the Polymerization Index as defined in refs [63] and [68] led to ca. 1000-1100°C (Ip ~1-2) and 700-800°C (Ip ~0.3-0.8) is consistent with previous measurements [29] in accordance with a *Moufle* and *Petit Feu* firing, respectively.

The observation of a very strong As-O stretching mode in artefacts attributed to the second half of the 18th century is in accordance with the microstructure reported by Magetti and d'Albis for a 1781 Sèvres plate: lead arsenate forms large globules (1-5 μm diameters). The good focusing the laser spot (~0.5x0.5x2 μm^3) on a globule explain the huge intensity of the As-O mode. In 1781 Sèvres plate Maggetti and d'Albis identify the highest concentration of cobalt in the glassy phase in between the globules, which is consistent with the use of two precursors: one arsenate rich and the second cobalt-containing smalt/ore. The much lower intensity of As-O stretching mode measured in older artefacts confirms the use of different precursors. The shift of the As-O mode position indicates some variations in composition and/or structure. Potassium is detected by Magetti and d'Albis in the arsenate globules.

Potassium was also identified in 16th Spanish majolica [73]. However in these majolica shards, the arsenate does not form globules and is associated with the cobalt. Calcium-lead $((Ca,Pb)_3(AsO_2)_2)$ and more complex phases $(NaKPb_8(AsO_4)_6)$ have been identified and attributed to the use of arsenic-rich zaffre [74-76].

As visible on Fig. 1, the vivid blue colours of first produced soft-paste porcelains require a relatively high concentration of cobalt (> 0.5-1 wt%, locally). The depositing (painting) of cobalt ore powder directly on the body, fired or not, appears more reasonable that the use of zaffre (cobalt already dissolved a glass matrix). Examination of polished sections is needed to further the discussion. Identification of chromate in 17063 (Lille) blue-green spots indicates the use of a chromium-rich pigment denoting the use of raw heterogeneous cobalt ores.

Comparisons with spectra recorded on blue and green enamels of Qing porcelains and stonewares objects (Fig. 5 and refs [7,8]) show very similar signatures belonging to the AL group (mixed alkaline-lead glaze). As for soft-paste porcelains, the intensity of the arsenate phase is rather small in older artefacts and maximal for those produced in the second part of the 18th century. This is consistent with the initial formation of lead arsenate by reaction with the arsenic coming from the cobalt source in older artefacts. For the second group of artefacts, a deliberate addition of arsenate in order to optimize the colour is probable and explains the stronger intensity of the As-O stretching mode.

The observation of different types of glaze for the artefacts attributed to the Rouen production questions the attribution to a single workshop or demonstrates an intense period of innovation with the search for different technologies. The same question can be raised for the 4027 salt container with the Saint-Cloud 'sun' mark.

6. Conclusion

On-site Raman analysis appears very efficient to recognize soft-paste porcelain and to detect lead arsenate in the glaze. The use of high magnification objectives allows for the study of coloured areas very precisely and the recording of high quality spectra. The main advantage of the technique is the study of series of precious artefacts with good pedigrees in a perfectly non-invasive way. The variety of As-O vibrational signatures and the possibility to

have superimposition with that of olivine Co_2SiO_4 hinders a precise identification. Furthermore, due to the high toxicity of arsenic, the availability of vibrational data on well characterized arsenic-based phases remains very limited. Combined Raman, SEM-EDX and (micro)diffraction on polished sections of porcelain shards exhibiting similar Raman signatures is needed to go deeper in the identification of the arsenate phases and establishing a link with characteristic microstructures related to the ancient procedures used by the potters. We see in this work the advantages and the limits of non-invasive study of ceramic objects.

Acknowledgments

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Fig. 1: Selection of blue-and-white soft-paste porcelains from the Collection of the Musée national de la Céramique (Cité de la Céramique, Sèvres & Limoges): a) mustard or ointment pot assigned to Louis Poterat workshop (Rouen, circa 1680, MNC4006); b) ointment pot from Rouen Factory (end of 17th century, MNC18432); c) ointment pot, Rouen or Paris Factory (end of the 17th-beginning of 18th century, MNC13369); d) ointment pot from Saint-Cloud Factory (1695-1700, MNC4165); e) salt container from Saint-Cloud Factory (1691-1702, MNC4027); f) ointment pot from Saint-Cloud Factory (1715-1720, MNC8800); g) ointment pot assigned to Edouard Hébert Factory, Paris (circa 1710, MNC9827); h) salt container assigned to Dominique ou Pierre Chicaneau or Marie Moreau Saint-Cloud or Paris Factory (beginning of 18th century, MNC13371); i) cup, Antoine Pavie Factory (1710-1720, MNC18433); j) ointment pot, Lille Factory (early 18th century, MNC17063): k) ointment pot from Mennecy-Villiers Factory (after 1734; MNC13281); f) coffee cup from Edouard Hébert Factory, Paris (middle 18th century, MNC13345).

Fig. 2: Selection of artefacts with multi-colour decor from the Musée national de Céramique: a) Soft-paste porcelain pallet cup from Vincennes Royal Factory made by Pierre-Antoine-Henry Taunay (1748, MNC6639); soft-paste porcelain coffee cup from Vincennes Royal Factory (mark A: 1753, MNC25330); c) hard-paste porcelain salt container from Strasbourg Factory (midlle of 18th century, MNC13674); d) soft-paste porcelain ice cream cup from Vincennes Royal Factory (1764, MNC24780); e) soft-paste porcelain tea pot from Vincennes Royal Factory (middle of 18th century, MNC26296).
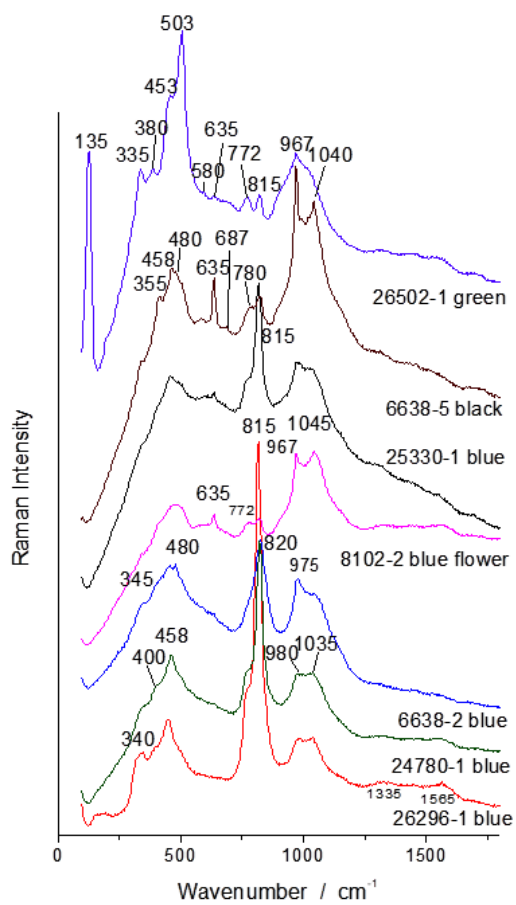
Fig. 3: Raman spectra collected on blue, green and black areas. See Table 1 and Supplementary Materials for information about the artefacts.
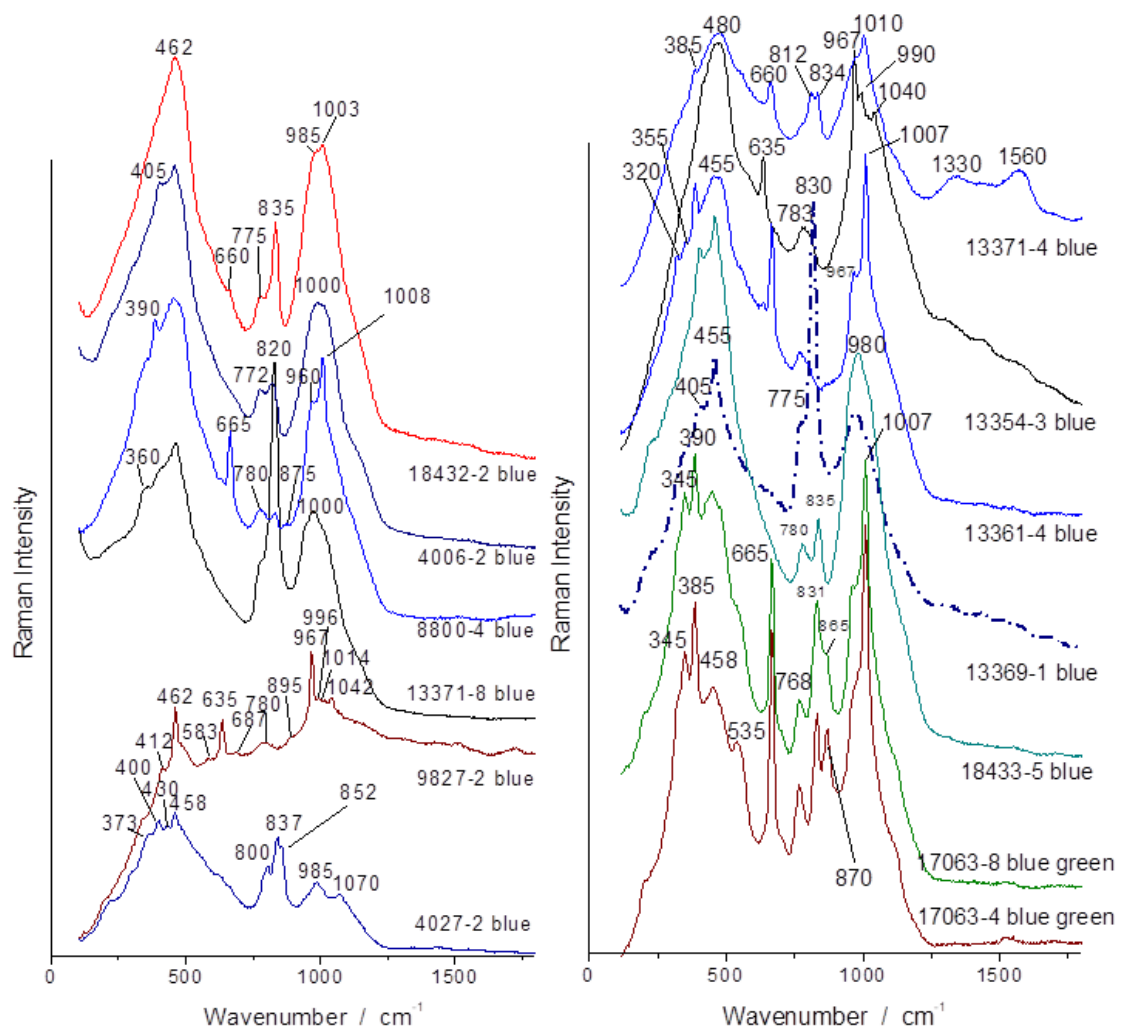
Fig. 4: Raman spectra collected on blue and blue- green areas. See table 1 and Supplementary Materials for details.
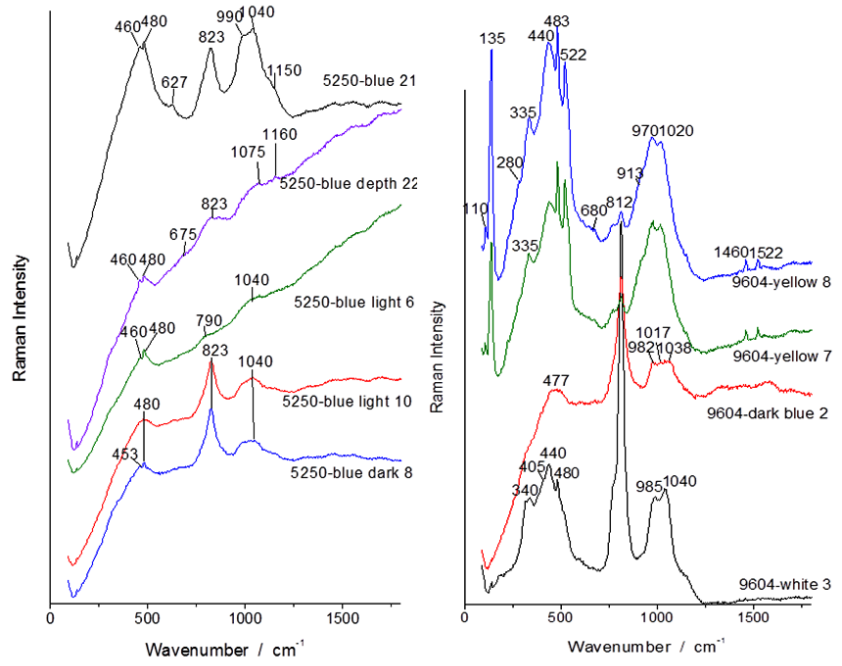
Fig. 5: Qing porcelain (MG5250, huafalang bowl, Kangxi yu zhi mark, ca. 1715-1722, imperial workshop) and stoneware (MG9604, Yixing Factory, 2nd half of 18th century) and representative Raman spectra recored on colored areas (see ref [] for details).