Supplementary information for *Raman Spectroscopy in Archaeology and Art History*

Colouring Agents for Glass, Glaze and Enamel: Tracing Innovation and Exchange Routes

PHILIPPE COLOMBAN*

Sorbonne Université, UPMC, MONARIS umr8133 CNRS, c49, 4 Place Jussieu, 75005 Paris, France. E-mail: philippe.colomban@upmc.fr

Abstract

After a brief historical survey of enamelling on stone, glass, metal and pottery, the main parameters needed to produce high quality enamels are covered and the different techniques to opacify or colour glassy silicates white, black, blue, yellow, red and green are presented. The potential of micro-Raman spectroscopy for identifying colouring agents is discussed. The non-destructive/non-invasive Raman technique, especially using mobile instruments and an ultra-high magnification (×200) microscope objective, facilitates the documentation of historical innovation and the exchange of knowledge from antiquity to the 19th century.

S.1 Enamelling Technology

Enamelling is one of the most sophisticated technologies developed to decorate artefacts with metal, stone, glass and ceramic substrates. Enamelled stone (quartzite), metal, glass and pottery were first produced by Mesopotamian and Egyptian potters (>1500/2000 BC),[1,2] Celtic and Greek blacksmiths (enamel on metal, >800 BC), and Roman glassmakers (~>100 BC).[3-6] An enamel consists of a glassy coating (from about 10 µm to a few mm thick) deposited on a much thicker substrate (1 to 20 mm, typically).[7] When deposited on a ceramic body it is referred to as a glaze, while a glass coating on a metal is more contemporarily referred to as porcelain enamel or more simply enamel.[7] The French word '*glaçure*' is used when the glaze is deposited on a porous substrate (such as *terra cotta*, faience). The glass can be coloured by dissolving transition metal and rare earth ions, or by dispersing small already coloured (crystalline) grains—the so-called pigment—in the glass.[7,8] The resolution of the human eye is close to 1–10 µm, so the grain size must therefore be micron or sub-micron to offer a homogeneous colouration. In rare cases (such as lustre pottery), colour arises from the diffraction of the light by the alternation of metal nanoparticle-rich and -free layers within the glaze, giving rise to the so-called lustre pottery.[5,6] Bonding the glass coating with the metal or ceramic substrate involves a controlled reaction with the oxide layer at the surface (the metal surface is always oxidised and the reaction takes place with the oxide film at the metal surface). Copper and iron alloys were the first to be utilised in this way because they can be developed easily whilst heating an adhesive interphase.

To achieve a nice gloss, the coating should melt in totality during the firing process, but the thickness should remain almost constant from the top to the bottom part of the artefact: thus, control of the wettability and viscosity is critical.[7] The distribution and homogeneity of the colour should also be controlled. For all the above-mentioned reasons, it is necessary that the precursor mixture consisted of a fine powder that could be deposited on the body. Grinding and firing being the most energy-consuming operations, enamelling techniques only developed concomitantly with the emergence of hydraulic energy during the Roman period and well into the Middle-ages. Consequently, ancient craftsmen used alternative ways to get fine powders. The subsequent combination of calcination of plants, shells, bones (to produce ashes), calcareous stones (to produce chalk) or flint pebbles (to produce pure silica), and water treatment led to very fine powders, sometimes with already the correct composition to be used in the enamel.[9] Control of the liquid glaze–substrate contact angle and the thermal expansion mismatch between the molten/solid glaze and its substrate is needed. A glaze with the same composition can be made matt or glossy, and well coated or "crawled" depending upon the grinding and firing times.[7,10-12]

The huge variety of glaze compositions utilised by craftsmen was imposed by the variety of substrates used and their different thermal expansions and firing temperatures. Glassy coatings can be fired with a green body, *e.g.* for porcelain (the firing temperature typically ranges between 1200 and 1450 °C, this is the *Grand Feu* technique and such a glaze is called '*couverte*') but the colour palette is rather limited.[7-12] Alternatively, a second (or third) firing cycle can be made at a temperature sufficiently low to avoid modifications of the already fired (enamelled) substrate (the so-called *Petit Feu*—or *minai* in Iran—technique). In that case, the firing temperature usually ranges between 1050 and 600°C and a larger palette of colours is available.[8,12] Decrease of the melting temperature is obtained by substituting part of the silicon with sodium, potassium, calcium and/or lead, and more rarely by the addition of boron or bismuth.

S.2 Raman Analysis of Enamels

As non-invasive technique Raman microscopy is a well-known method to identify crystalline phases.[13-16] The technique is also very useful for the identification of amorphous phases.[17-19] Indeed, because the intrinsic sub-nanometre probe in this technique is the chemical bond itself, the method is useful for the study of any covalently bonded matter whatever its degree of order (amorphous, nanophase or crystalline).[18,19] Refractory properties require strong bonds such as covalent bonds and hence refractory materials are good Raman scatterers. The Raman scattering produced is very useful for the study of coloured materials because resonance Raman scattering enhances the detection of the particular chromophore when the exciting laser wavelength approaches/corresponds to the energy of an electronic transition (which implies a strong absorption of the light and hence a localised heating, see later). Reviews on glass/glaze and pigment studies using this technique have already been published[20-27] and a focus of attention has been the study of amorphous silicates: how to identify the type of glass from the centre of gravity of the SiO_4 bending and stretching bands, and how to deduce the melting temperature of a glass from the ratio of the bending *vs.* stretching band areas.[17-19,22-28]

Another great advantage of Raman micro-spectroscopy is the availability of high sensitivity, good resolution, mobile Raman set-ups that facilitate the analysis of outstanding rare artefacts in museum exhibition rooms and archives as well as on archaeological/natural sites.[27-30]

The focus of this chapter will be on white, black, red, blue and green coloured glazes. There are many technical solutions to obtain these colours and the solution can be specific to the period (or place) of production and consequently offers a way to trace historical exchanges of knowledge. Characteristic peak wavenumbers are listed in Table S.1.

Table S.1 Characteristic Raman signatures of white, black, red, blue and green colouring agents of glass, glaze and enamel.

Colour	Phases	Characteristic wavenumber (cm^{-1})
White	Bubbles	60(N_2), 1555(O_2), 2350(CO_2)
	α quartz SiO_2	464
	Calcite $CaCO_3$	1085
	Cassiterite SnO_2	635,775
	Calcium antimonates	52,-670 ($CaSb_2O_6$) 480,632 ($Ca_2Sb_2O_7$)
	Wollastonite $CaSiO_3$	995 (α) 970 (β)
	Fluorite CaF_2	322
	Rutile TiO_2	445,610
	Zircon $ZrSiO_4$	353,1005
Black	Carbon C	~1350–1600
	Copper oxide	295,345 (CuO)
	Cobalt oxide	490,530 (CoO) 560,705 (Co_3O_4)
	Spinels	485,525,695 (Co_3O_4) 475,520,690 ($ZnCo_2O_4$) 540,670 (Fe_3O_4) 515,695 (Cr_2MnO_4) 845 $(Cr,Fe,Mn)_3O_4$
	Manganese oxides (Sienna earth)	580–650 (bixbyite α Mn_2O_3) 572–670 (pyrolusite β MnO_2) 575–650 (ramsdelite MnO_2)
	Fe–S chromophore	320–420
Red	Co°	< 100
	Au°	<100
	CdSe, $CdS_{1-x}Se_x$	200,300
	Hercynite $FeAlO_4$ (spinel)	Very similar to other spinels
	haematite $Fe_{2-x}Al_xO_3$	200,225, 405,605,1315
	Pink malayite Cr:$CaSnSiO_5$	750,950
Blue	Co^{2+}	No specific signature
	Lapis lazuli $Na_8[Al_6Si_6O_{24}]S_n$	548,1096 (green to red laser) 980 (host, UV laser)
	Ultramarine (synthetic)	548,1096 (green to red laser) 510 (host, UV laser)
	Egyptian blue $CaCuSi_4O_{10}$	
	Han violet $BaCuSi_2O_6$	500–580
	olivine Co_2SiO_4	820–830
Green	Cu^{2+}	No specific signature
	Cr^{3+}	No specific signature
	Yellow+blue	See below and above
Yellow	Naples yellow $Pb_2Sb_{2-x}M_xO_{7-d}$ Pyrochlore solid solution	130 to140;450(Sn) or 501(Sb)
	PbO	80,110
	Ag°	<30
	Rutile $(Ti,Ni,Nb)O_2$	445,605
	Cassiterite V:SnO_2	See above
	Uranyl $PbUO_4$	840

S.3 White Colour: Opacification

A homogeneous colourless glass free of small bubbles and cracks is optically clear in the visible range up to a thickness of tens of cm. Opalescence takes place if a second phase with dimensions close to that of the human eye's resolution (a few microns) is dispersed in the glass. The opacification degree increases with the amount of the second phase and the contrast between the optical indices of the two phases. Consequently, the simplest technique of opacification is the dispersion of micron sized bubbles in the matter (as in ice).[30,31] The mismatch between the optical index of the glass and that of the surrounding air is sufficient to give some opalescence. Bubbles form easily from the reaction between the molten glaze and its substrate or by addition of carbonates or sulphates. The presence of bubbles is easily detected in the Raman spectrum with the *ca.* 60 cm^{-1} and *ca.* 1555 cm^{-1} peaks of N_2 and O_2 ro-vibrational spectra, respectively. Sometimes, a CO_2 spectrum can be also observed at *ca.* 2350 cm^{-1}, indicating that firing has occurred under a strong reducing atmosphere. These spectra are intense because the multi-reflexions at the bubble–matrix interface artificially enhance the number of Raman active molecules. This opacification technique was used for instance in Vietnamese celadons (13–16th centuries)[31] and in the first hard-paste porcelains made in Europe (in Meissen, Saxony, at the very beginning of the 18th century).[30]

Another indirect technique to get a nice white colour was invented by Iznik potters: a layer (slip) of angular crushed quartz grains is deposited on the body of first Iznik and then Kütahya fritwares:[32,33] the grains scatter and reflect the light. *Petit Feu* enamels are then deposited and fired before being covered with a colourless, highly transparent, lead- and sodium-based glaze.[34] Red lead-rich enamel (for example, the so-called 'Armenian bowl' the precursor of red enamel, a mixture of natural hematite-quartz and lead oxide) is finally deposited and fired at lower temperature. The quartz grains reflect the light, thus giving an unequalled vivid and brilliant colour to the decoration. In depth Raman profiling easily distinguishes between the different layers.

Dispersion of a crystalline phase is the most common technique of opacification. The high optical index of tin oxide, cassiterite (with its characteristic 635–775 cm^{-1} spectral doublet), makes this phase the most used opacifier in ancient pottery.[35,36] The technique was first used during the Roman Empire in Europe to opacify glass[37-39] and then applied to glaze by Islamic potters.[38] Originally, Abbasid potters tried to imitate Tang 3-colour porcelain wares and experimented with the depositing of lead-based glaze on an earthenware body glazed with an alkaline glaze.[36] Indeed, cassiterite only precipitates at the glaze interface. Potters then added a layer of cassiterite onto the body, which reacted with the glaze.[35] Finally, to minimize the amount of tin used (a costly material then) they controlled the homogeneous precipitation of cassiterite in a lead glaze saturated with tin oxide (~5–6% wt). [36,39] Tin is commonly present in lead-based glazes due to the use of bronze residues. The white coated earthenware, so-called *terra cotta* (coarse grain, high porous and coloured body), faience or majolica (fine grain, less porous body: open porosity ~10 to 20%) first produced in Mesopotamia spread out alongside Islam's expansion in Persia and around the Mediterranean Sea (in Egypt, Maghreb, Sicilia, *al Andalous*, North of Spain, Italy and France).[5] With this white pottery, Islamic potters could compete at lower cost with the intrinsically white hard-paste Chinese porcelain made using iron-free/-purified kaolin and a reduced firing atmosphere.

Calcium antimonates ($CaSb_2O_6$, $Ca_2Sb_2O_7$, $Ca_3Sb_2O_8$) are old opacifiers (≳1500 BC, Egypt) continuously used up to modern times.[40] They comprised the main opacifier of Roman glass[37] and are easily detected with their strong *ca.* 520–670 ($CaSb_2O_6$) or 480–632 cm^{-1} ($Ca_2Sb_2O_7$) spectral doublets.[20,41,42]

Calcium phosphate ($Ca_3(PO_4)_2$) opacification, obtained by the addition of bone ashes, is easily detected by Raman scattering thanks to the narrow symmetric stretching mode peaking at ~960 cm^{-1}.[42,43] This opacification technique is observed in Islamic glass artefacts,[42] as well as in Medici porcelain,[43] in some glass objects of the Perrot workshop (16th century, Orléans),[42] in English bone china[44] and in French soft-paste porcelains.[45] The saturation of glaze with calcium led to the precipitation of wollastonite ($CaSiO_3$) and both calcium phosphate and silicate are often simultaneously present.[45] The Raman spectrum of this nesosilicate exhibits strong narrow peaks at *ca.* 995 and 970 cm^{-1} for the α and β phases, respectively.[45,46] This type of opacification was used in some celadon as calcium-rich ashes were used as glaze precursor[46] and in almost all glazes (and pastes) of soft-paste European porcelains.[45,47]

Lead arsenate is also a very good opacifier,[48-53] giving a nice milky white finish rather similar to that obtained with calcium phosphate precipitates in English bone china bodies.[44] Raman signatures of arsenates are intense because of the very covalent character of the bond and the high number of electrons involved in the chemical bond, which makes them very easily detectable. The stretching mode peaks occur around ~820 cm^{-1} for lead arsenate,[48-53] but small wavenumber shifts are observed as a function of the composition (Pb/Ca/K/Na substitution). Venetian *lattimo* glass objects, often opacified with lead arsenate, appeared at the end of the 16th century.[42] Due to the very high toxicity and volatility of arsenic, the kilns were located on a small island in the Venice Laguna.[54,55] Production remained limited (objects and beads),[56] and in Europe the use of arsenic white only developed in a large scale during the second half of the 19th century (especially for enamel on metal[48] and for glass objects such as beads, vases, *etc.*[50-56]). Arsenic also contributes to optimization of the blue shade of many European porcelains and enamels on metal as the very high arsenic content of cobalt ores extracted from Erzgebirge (Saxony) indicates.[57-60] During the Kangxi and Yongzheng reigns, attempts at producing 'opaque', realistic glazed decoration on porcelain at the Imperial Court workshop under the guidance of French Jesuits initiated the use of cobalt ores (imported from Europe),[51-53] and led to a homogeneous precipitation of lead arsenate in the blue glaze. Then, Chinese craftsmen developed the use of lead arsenate for white decoration (Qianlong and Yixing productions).[52]

Fluorite (CaF_2) is rarely used as an opacifier except in some enamels on metal.[7] It can be detected from its narrow, rather weak peak at 322 cm^{-1} as in white *cloisonné* Chinese enamels, for instance.[61] In rare cases, the dispersion of α quartz fine grains (464 cm^{-1}), of calcite (1085 cm^{-1}) or calcined white clay/kaolin can be used.

Glazed artefacts produced during the second half of the 20th century and afterwards[7] are opacified with rutile (TiO_2, very strong peaks at *ca.* 445 and 610 cm^{-1}),[62] zircon ($ZrSiO_4$, narrow peaks at 353 and 1005 cm^{-1}),[63] or more rarely, with monoclinic zirconia (spectral doublet at 190–210 cm^{-1}). [7] The latter phases and some others such as anatase (TiO_2) and garnet/sphene are also present as minor phases or traces in raw materials and remain undissolved in many ancient glazes as anatase.

S.4 Black Colour

A black colour is difficult to achieve, especially with a nice and homogeneous gloss. The first black decorations were obtained with manganese oxides either alone or mixed with iron oxide. Manganese oxides are extremely sensitive to the laser heating when undergoing

Raman spectroscopic study (because of the high number of valence states which offer a great possibility for intermediate phases) and a few μW per μm^2 are sufficient to transform them into other species resulting in the observation of a broad two-peak, spinel-like feature at ~540 and 670 cm^{-1}.[64,65] Many spinels are made of manganese, iron and/or cobalt or chromium and also offer the opportunity to colour glazes black. Chromite is also a powerful colorant. The identification of the spinel composition only from the Raman spectrum is difficult because the strongest peak is the stretching mode (in which only oxygen atoms move!). Consequently, the wavenumber shifts due to the contribution of the other atoms is very small, and differentiation between the different types of spinel is therefore very subtle.

An amber chromophore, comprising a Fe–S complex dissolved in a silicate amorphous network, also adds yellow to black glass (the colour depending upon the iron/sulphur content), and is characterized by strong bands at ~370 to 415 cm^{-1} as a function of the exciting laser line wavelength.[66] Carbon black is also used in this respect.[52] Lead oxide and sulphur also give black colours, but in most cases this occurs as the result of the degradation of the glaze surface and not the original pigment used.[35]

S.5 Red Colour

It is also difficult to obtain "nice" reds. The oldest technique, largely used by Roman glassmakers but invented by Celtic enamellers,[3,5] is based on the dispersion of copper (metal) nanoparticles in the glass. The red colour arises from the strong absorption of the light at *ca.* 550 nm by copper plasmons (an electron gas at the metal particle surface) and at higher energy by associated interband transitions.[5,67,68] Raman signatures of metal nanoparticles are not normally detectable because they are located at very low wavenumbers (2–50 cm^{-1}) and require very high resolution instruments.[36,68,69] Other ancient techniques leading to red colours were those used by Roman potters to prepare *sigillata*: the use of clay-rich slips that led to the formation of a thin (~10 μm) glazed varnish at the pottery surface with small hematite (Fe_2O_3 with a corundum structure, where the iron ions become more or less partially substituted with aluminium or titanium) or hercynite (an Fe_2AlO_4 spinel, where non-stoichiometry is also common) inclusions.[70] Except when the grains are very small, the colour obtained with iron oxide is not very good. To solve this problem, a natural dispersion of hematite grains in quartz is used: *e.g.* by Iznik potters (the so-called 'Armenian bowl') or the Grès de Thiviers by some French factories making majolica.[65] Meissen craftsmen first discovered that almost the same result could be obtained with a deep over-grinding of the hematite-rich precursor of glaze (called *Mars red*) and succeeded in achieving a very nice orange colour using this technique.[30] Hematite and hercynite are easily identified by Raman scattering[65,70] and it can be observed that band broadening and some relative intensity changes arise from the non-stoichiometry.[65] The strongest band of hematite in these Raman spectra is the *ca.* 1320 cm^{-1} resonance, two-phonon peak.

Red and violet can be also prepared with the dispersion of gold metal nanoparticles in the glass. Although the famous text of Agricola, *De Re metallica*, published in 1556, reports that ruby glass was coloured with gold, the analyses show that the technique seems to be first used by the Perot Workshop (or Perotti, Italian glassmakers invited to Orléans, France, in the 17th century)[6] and then largely used for *Camaïeu* decoration during the 18th century (also called *Cassius' purple* because of the publication in 1685 of Cassius' book describing also the recipe for its manufacture).[45,46]

During the 19th century, the search for new pigments led to the discovery of $CdS_{1-x}Se_x$ solid solutions with colours ranging from yellow (CdS) to red (CdSe) with the possibility to choose any intermediate colour by adjusting the composition.[71,72] Mastering the precipitation of the sulphide/selenide nanocrystals within a glass matrix requires a perfect control of the homogenisation–nucleation–growth thermal cycles and this could be only achieved in the beginning of the 20th century for the production of Art Nouveau (also called Tiffany (USA), Secession (Hungary), Liberty (Italy), *etc.*) stained glasses and artefacts (vases, beads, *etc.*).[73,74] Pottery enamelled with cadmium-based glazes was really developed in the 1960s but production stopped in the 1990s in many countries due to the interdiction of use of the hazardous cadmium derivatives. Under green laser excitation, the resonance Raman signature of these solid solutions is strong (but sometimes covered by a strong fluorescence) and allows the determination of the exact composition from the exact peak position (at *ca.* 200 and 300 cm^{-1}).[73,74]

S.6 Blue Colour

Natural inorganic blue pigments are rare (being only azurite, lazurite and sapphire) and for a long time it has been commonly admitted that only Co^{2+} ions and pigments hosting them could produce this coloured glass in blue. Cobalt ores are rare. Egypt for a short time (18th Dynasty)[75] experienced glazes coloured with cobalt in place of Egyptian Blue a calcium-copper silicate (cuprorivaite: $CaCuSi_4O_{10}$ with a characteristic spectral 430–465 cm^{-1} doublet,[20,76] a pigment dating from the 3rd millennium BC with a characteristic Raman signature. Of a similar composition, but with barium in the place of calcium, is the Han blue ($BaCuSi_4O_{10}$, 500 BC)[77,78] and its deeper coloured variety the Han violet ($BaCuSi_2O_6$, 200 BC; 500–580 cm^{-1} doublet, Figure S.1). Ptolemaic glassmakers and potters (*ca.* 1st century

AD) discovered that lapis lazuli grains can be used as a pigment to colour enamel[79-81] (the resonance Raman spectrum of this material is characterised spectrally with bands at 545 and 1090 cm^{-1}, *etc.* and associated combination and overtone bands)[82] and the technique continued to be used in the Roman Empire and then by Norman–Swabian and Islamic glassmakers,[82-85] and surprisingly by J. F. Böttger (Meissen, early 18th century, see ref. 30). Synthetic ultramarine also uses S_2^- and S_3^- ions as chromophores but the host structure is different: a zeolite (although the coloured phase of the lapis lazuli rock—lazurite—is a feldspar). The collection of the non-resonance Raman spectrum under UV excitation allows for the identification of the host framework.[57,84]

Saturation of a glass with cobalt leads to the precipitation of Co_2SiO_4 olivine (spectral doublet at ~825 cm^{-1}) and $CoAl_2O_4$ spinel (spectral strong band at ~700 cm^{-1}) in silica-rich and alumina-rich compositions,[8] *i.e.* in soft-paste and hard-paste porcelain glazes. Note that 0.1 % wt of cobalt is sufficient to colour the glaze and most of them contain less than 1% wt, which is far below the saturation limit. Thus, in many cases, olivine and spinel are not detected and the only effect of cobalt on the Raman spectrum is the decrease of the spectral baseline due to the absorption of radiation in the red region.

Cobalt-containing glass has been recycled since antiquity as demonstrated by the discovery of a Roman shipwreck containing broken pieces of blue glass.[86]

A variety of spinels associating cobalt and zinc, aluminium, chromium, *etc.* appeared during the 20th century. Now, the most used blue pigment is vanadium doped zircon ($ZrSiO_4$:V).[7]

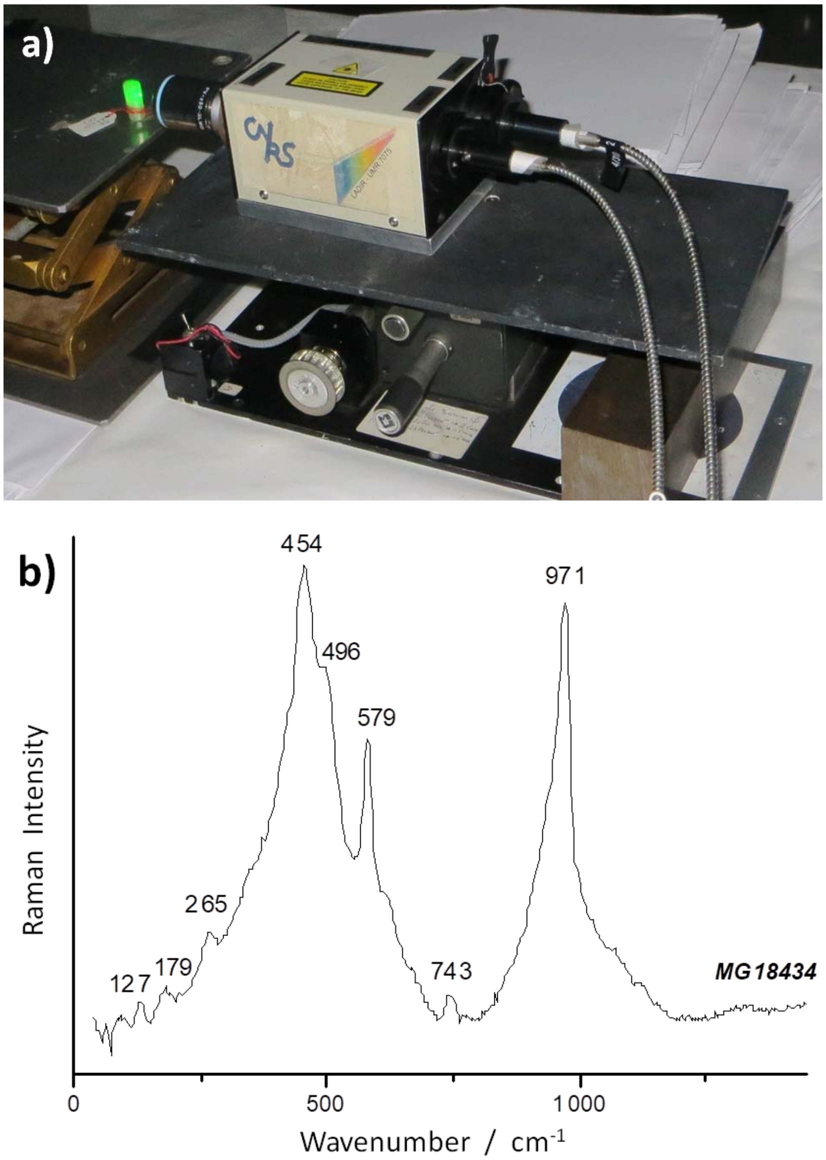

Figure S.1: On-site analysis of a violet prismatic ear stopper (Han Dynasty) at the Musée National des Arts Asiatique-Guimet (Paris) with a mobile Raman set-up (a) and a x50 long working distance microscope objective; corresponding Raman spectrum (b) after baseline subtraction: Han blue (*ca.* 500 and 580 cm^{-1} doublet) and wollastonite (971 cm^{-1}) are identified in a calcium-rich glass.

S.7 Green Colour

The simplest technique to obtain a green colour is through the addition of copper ion Cu^{2+} to a silicate glass: jade green is obtained in lead-based glaze[36] although a turquoise colour is obtained in alkali-based glass.[67] There are no specific Raman signatures associated with these because the ions responsible for the colour are dissolved in the glass network. However, characteristic UV-visible absorption identifies the site of the colouring ion.[7] Up to the discovery of Victoria Green pigments (19th century), a chromium-based garnet[7,8] with characteristic Cr–O stretching mode at *ca.* 850 cm^{-1},[8] green coloured enamels were obtained by dispersing a yellow pigment (in most cases the so-called 'Naples yellow', a pyrochlore lead-based solid solution) in a cobalt-containing glass.[8] However, Ottoman (Iznik production, 15th century)[32] and Meissen (end of the 18th century) potters prepared green chromium-containing glazes. Green spinels and nickel green olivine are also good green 19th century pigments.[7] Malachite was also reported as green pigment in some Chinese porcelains.[49]

S.8 Yellow Colour

Yellow pyrochlore pigments, Pb_2SnO_4 and $Pb_2Sb_2O_7$ ('Naples yellow' *stricto sensu*) are considered one of the oldest colorants, and their use dates back to antiquity (Mesopotamia and Egypt).[38] Their composition is more complex than it might appear, because of the very large range of pyrochlore solid solutions obtained by the substitution of Sn and Sb with Fe, Si, Zn, *etc.* and the multivalence of the element (2^+, 3^+, 4^+ and 5^+) and the associated oxygen non-stoichiometry.[48,51,61] Due to the heavy mass and the high polarisability of lead atoms, the strongest Raman peak is measured between 125 and 140 cm^{-1} as a function of the structure (unit-cell distortion), composition and stoichiometry, *i.e.* as a function of the raw materials and firing. Saturation of a lead-based glaze with lead will provoke the precipitation of yellow lead oxides with characteristic spectral peaks at ~80 and/or 110 cm^{-1}.[35]

Silver metal nanoparticules are also used to colour (stained) glass and (lustre) glaze in yellow. The technique is ascribed to the Abbasid glassmakers and potters[5] but was really developed during the Middle-ages with the Fatimids for pottery and medieval European Masters for stained glasses. As for Cu° and Ag° coloured glass, the Raman signature is subtle and should be searched at very low wavenumbers (Lamb's modes).[36,69]

Uranyl ion also gives a very nice colour and was widely used during the 19th and 20th century before the customers became frightened by the radioactivity associated with the use of uranium (at that time uranium devoted to chemistry was not purified from its most radioactive isotope). Uranyl ion exhibits a very characteristic band at ~840 cm^{-1}.[87] Now yellow rutile and praesodymium-doped glass are presently the most used colouring agents. [7]

S.9 Technology exchanges

The identification of colouring agents informs on the degree of technical advancement of ancient craftsmen. However, due to the huge sensitivity of human vision, the preparation of coloured synthetic matter was always an advanced technology and the dissemination of innovation may also provide information about knowledge exchange and trade routes. We will consider two different cases: namely, blue and white colourations (opacification).

The first evidence of lapis lazuli used as a colouring agent for glass comes from enamelled Ptolemaic glass objects (Begram Hoard, Afganistan) and pottery (Pompeii faience).[79-81] Because lapis lazuli is very difficult to identify from elemental composition measurements (SEM-EDS, XRF or LA-ICP) and because Egyptian enamelled objects have not been seriously studied by Raman microspectroscopy it is not possible to know if the use of lapis lazuli is much older. In 1998 some scholars noted that it was not possible to detect cobalt in some Islamic blue glass[88] but they ignored the work of Clark, Laganara *et al.*[79] which demonstrated one year before that some potteries excavated from Frederician castles in South Italy (Lucera, Capo di Monte, 14th century) were coloured in blue with lapis lazuli. Colomban pointed out that some very common Lajvardina artefacts (Iran, 13th century) were also coloured with lapis lazuli, but these also contained a rather large amount of cobalt (0.9 %at), which was alone insufficient to give an ultramarine hue.[82] Similar features were observed for enamelled glass pieces excavated from different 13th Frederician Melfi castles,[81,84,85] and on-site studies of enamelled Mameluk mosque lamps and a bottle (14th century) demonstrated the large use of lapis lazuli both for blue and green enamels[81,89] at that time. We can infer that the use of lapis lazuli was much larger than first theorized by historians, the evidence having been limited by the small number of Raman studies. Very surprisingly, lapis lazuli was detected in white hard-paste porcelain (*i.e.* made with kaolin and feldspar) made at Meissen by J. F. Böttger in the very early 18th century.[30] However, these first European porcelains were made with raw materials (kaolin, feldspar and sand) containing impurities and the fired body was grey, not white. The glaze does not contain specific opacifiers, only bubbles. Consequently, to whiten the tint of the porcelain, grains of lapis lazuli were dispersed at the body-glaze interface, similar to the use of blue dye in contemporary washing powder! The technique of whitening with blue dye, smalt powder for instance, was largely used in the Low-Countries for linen.

The first use of cobalt as a glass colouring agent dates back to the New Kingdom (16th century BC) but seems to stop shortly afterwards.[75] One can assume that other blue colouring agents might have supplanted it. Thus, the use of lapis lazuli as a pigment in glass originates in Egypt, then developed in Egyptian workshops during the Roman Empire and then continued into the Islamic caliphate(s). The Norman Court is said to have attracted the best of Levantine and European craftsmen, thus explaining the production of glass objects enamelled with lapis lazuli there. Around the same time, the Mongol Empire secured the access to lapis lazuli sources: Sar-e-Sang' mining in Pandjchir (Badakhshan) was the only significant source before the discovery and operation of another mine in Chile during 17th century.[57] This could explain the use of lapis lazuli for the production of common objects in Iran. The good relations between the Burdjites Mameluks and Iranian Safavides may explain the continued use of lapis lazuli in Mameluk glass masterpieces. [81] We may well wonder how this technique reached J. F. Böttger. It is known that the famous Saxon arcanist was first educated as a stonecutter and the idea of adding blue dye could also be related to the clothier's practice.

The second question for which Raman analysis contributes to the documentation of knowledge exchange is the opacification with lead arsenate. The achievement of an opaque and vivid coloured (thin) layer of glass deposited on a substrate is not easy: too much colouring agent will darken the colour, too weak a content of colouring agent led to a faint colour. An alternative is the mixing of colouring and opacifying agents at source. Luckily, the European cobalt ores mined in Schneeberg, Erzgebirge, *etc.* (Saxony), but also in many other places (Alpen, Sweden, *etc.*) are mainly made of skutterite $(Co,Ni)As_{3-x}$, smaltite $((Co,Fe,Ni)As_2)$ or cobaltite (CoAsS), all these ores being very rich in arsenic. These ores can be used directly and it is well established that blue glasses from the 17th century are very rich in arsenic and that the arsenic content decreases during the 18th century.[57-60] Ores can also be grilled and transformed first in sulphates and then by the action of water and sodium carbonate in almost pure cobalt carbonate.[59] Studies of Limoges enamels and of European soft-paste porcelains confirm that blue enamels generally contain lead arsenate(s), but some workshops were already preparing blue enamels free of arsenates.[51] The large amount of arsenic in cobalt ores leads to a nice blue because white lead arsenate (lead coming from the glaze) makes the blue colour lighter and more vivid. The use of European cobalt ores can also be identified through the rather large amount of nickel,[58] however nickel addition led to a greenish hue which might have led to a preference for ores with a lower nickel content.

In Europe, cobalt (as well as silver) ores are vein deposits in young granite. In Asia, cobalt mine geology is different: cobalt is found in sea nodules rich in manganese, cobalt, nickel and iron oxyhydroxides (and without arsenic) formed in the deep sea and transferred through tectonic actions into earth layers.[57,62,90] Fired in a reducing atmosphere (this is the case for porcelain to warrant the whiteness of the body), manganese and iron ions do not colour glass and only cobalt acts as a blue colouring agent. Both French and Chinese historical records[52] report that enamelling knowledge, as well as French and Italian craftsmen expert in glass production and enamelling, went to the Qing court under the guidance of the Jesuits and contributed to the production of enamelled artefacts at the Beijing Palace.[52] On-site Raman analyses of very rare *huafalang* items (also called *falangcai* ware) based on style and thought to have been fired at the Imperial Court Workshop under the end of the Kangxi reign (~1715–1722) identify lead arsenate in blue decoration, demonstrating the use of European cobalt ore, a proposal confirmed by elemental composition analysis of some *wucai* shards.[53,91] Rather similar bowls produced at the same period and workshop show different features, demonstrating a period of intense innovation. Lead can be partially substituted by potassium or calcium during the reaction between the cobalt ores and the glaze giving complex solid solution.[92] Chinese 18th century craftsmen developed the use of lead arsenate for white enamel on porcelain but also on stoneware (Yixing production) and on metal (cloisonné and painted enamels), while European craftsmen only significantly used arsenic as an opacifier for white beads and metal enamelling during the second part of the 19th century.[48] Note the much higher quality of the Raman spectra recorded with a ×200 microscope objective (Figure S.2): the reduction of the analysed volume allows the selection of a volume with a high concentration of pigment and freedom from background fluorescence emission

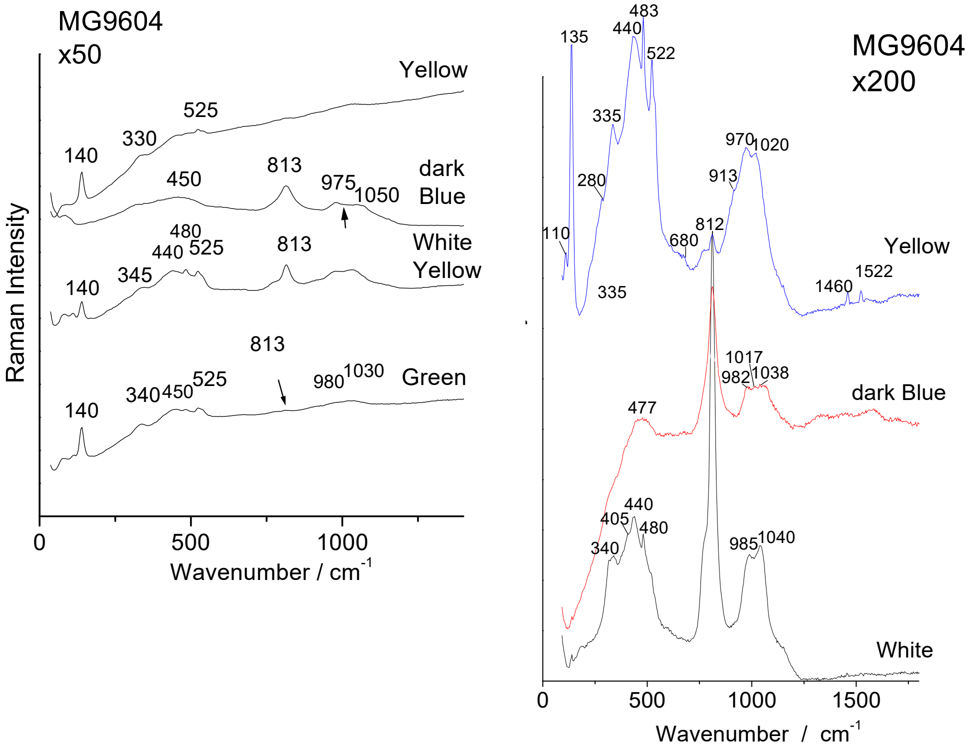

Figure S.2 On-site analysis of a Yixing teapot (18th century) at the Musée National des Arts Asiatique-Guimet (Paris) with a mobile Raman set-up; comparison between the 'as recorded' spectra recorded with a ×50 (Nikon) and a ×200 (Mitutoyo) long working distance microscope objective. Note the highest quality of the spectra recorded with the ×200 objective.

S.10 Conclusion

Raman microspectrometry is now a well-established technique for the identification of crystalline and amorphous phases in minerals and materials. The possibility of working outside of the laboratory with a mobile Raman set-up is a great advantage in the field of cultural heritage. Identification of crystalline phases with a Raman signature comprising narrow peaks (*i.e.* composed of covalent moieties like carbonates, sulphates, nitrates, oxalates, *etc.*) or under resonance conditions (lapis lazuli, CdS, CdSe, carbon, carotenes, *etc.*) is possible with (low cost) handheld or palm instruments with limited spectral and spatial resolution and operating over a limited spectral window.[93,94] However, the identification of many amorphous or disordered phases exhibiting a signature made of broad bands[16-19] requires the use of advanced mobile Raman set-ups (Figures S.1 and S.2) with a good spectral resolution and equipped with advanced optics (×50, ×100 and ×200 long working distance microscope objectives). The availability of different exciting wavelengths is sometimes necessary.

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