CHAPTER 13

Case Study: Glasses, Glazes and Ceramics – Recognition of Ancient Technology from the Raman Spectra

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13.1 Introduction

Certification of ancient artefacts by leading experts is generally made on the basis of the analysis of style and on personal feelings gained through the five senses (touch, sight, etc.). More objective proofs are, however, necessary. In this chapter we demonstrate the utility of Raman spectroscopy as a technique for characterising ceramics and glasses. Examples have been chosen from glasses from the Punic/Roman time (2nd century BC to AD), celadons and porcelains from Vietnam (the 13–16th centuries), soft- and hard-paste porcelains from Europe (18–20th centuries) and faïences or pottery from the Islamic world (Ifriqiya, Samarkand, Silk Road, 13th–17th centuries). We try to present here the salient features for identification purposes of spectra of bodies, glazes and pigments from the different products.

13.1.1 Ceramics, Glass Processing and Glazes

A ceramic is an artificial rock obtained by firing different raw materials together, which are to a greater or lesser extent transformed by the thermal treatment. Ceramics are composite in nature and their microstructure consists of sintered grains. For ancient ceramics, their dimensions range typically from 10–500 μm. Crystalline and glassy phases are present together; un-reacted, incompletely dissolved raw materials as well as some phases formed during the processing are crystalline. Although a (small) part of the material is molten during the firing process of the ceramic body and forms glassy phases on cooling, raw materials are
fully melted to produce a glass or a glaze. Rarely, small crystals (\(<0.1\,\mu m\) if optically clarity is to be maintained) precipitate in glassy phases. Enamel is the general name given to a glass coating on a substrate. The term glaze (‘couverte’ in French) is used if the substrate contains a large proportion of a glassy phase, for instance porcelain, stoneware and celadon. The term glaçure is used for enamels fired at low temperature on porous substrates such as faience and earthenware. Paints are pigment-rich enamels fired at low temperature and applied for decorative purposes to already deposited enamel. The thickness of a paint and of a glaze ranges between 10–50 and 100–2000\,\mu m, respectively (Figure 13.1).

Different kinds of products were made from the same starting materials by applying different technologies, or different products could be produced if the same technology was applied to different materials (or by different processing of the raw materials). However, different technologies applied to different starting materials could yield products with very similar outward appearances from the visual and sensory point of view, although completely different in their micro/nanostructure. Thus, the secrets of the processing remain hidden within the sample. The analysis of the micro- (for ceramics) and nanostructure (for glasses and enamels) offers a way of identifying and sometimes dating ancient artefacts. For ceramics, the identification of the crystalline phases (incompletely transformed raw materials or phases formed during the firing cycle) informs one about the composition and the processing temperature. Similarly, glass/glaze can be recognised from parameters extracted from the Raman spectra.

13.1.2 Nature of the Glass Network: Relationship Between Processing and Raman Spectra

Glasses are silicate networks in which the SiO4 tetrahedra are joined together by the oxygen atoms located at the vertices. These SiO4 tetrahedral connections are modified by the incorporation of aluminium, magnesium, iron etc. and alkali/alkaline earth metallic ions which change the properties (colour, viscosity, chemical resistance, etc.) of glasses. Raman spectra can reveal these modifications of the SiO4 tetrahedral vibrational units (and combinations) mostly through the intensity, line-width and spectral position of their bands.3,10 By comparing Raman spectra of glassy or crystalline pure silicates and aluminates, it appears clear that the Raman cross-section of Si–O bending and stretching modes is orders of magnitude stronger than that of their Al–O bond counterparts. This arises from the more covalent character of the Si–O bond. To a first approximation we can consider the SiO4 entities as the only vibrational unit because of the more covalent character of the Si–O bond; since the Raman scattering cross-section of the very ionic Al–O bond may be neglected.10

Glass (nano)structure is actually a consequence of two key factors: bulk composition and the temperature of melt equilibration. Glass and glaze can be differentiated at temperatures ranging from \(ca.\ 700\,^\circ\text{C}\) or less (for instance for pottery lustre) to 1,450\,^\circ\text{C} (high temperature fired porcelain glaze). Consequently, the composition variation of glass/glaze can be very large. Also, the techniques of preparation employed depend on the use of different kiln/furnace temperatures,
Figure 13.1  Schematic of the analysis of different parts of a ceramic: glaze, interphase and body. Shard excavated from Termez (Uzbekistan) and the spectra recorded from the surface into the body using a confocal Raman micro-spectrograph. 252/2-7 is the Registry number of the piece [See plate section].
which are required by the use of different ceramic compositions; an added difficulty is the temperature variation within the kiln, which was not fully controllable in ancient techniques. We have deduced a correlation between the processing and the raw materials, which is implicit in the preparation technique and should be reflected in the Raman spectra by correlating spectral differences with effects of temperature and composition.\textsuperscript{1,10}

13.2 Experimental

Raman spectroscopy, being an optical technique, can be performed through different optical devices: camera lenses, microscopes, etc. The size of the laser beam determines the surface analysed in a single examination. In a macro configuration 100 to 500 $\mu m^2$ are illuminated, typically. The laser spot is reduced to about 2 $\mu m^2$ for measurements with long focus, high magnification microscope objectives. Because the ceramic body is composite in nature, analysis at different locations is required. Because of the grain size and its distribution, macro-examination is required in order to obtain an overall spectrum containing the fingerprints of different phases. However, more revealing spectra are obtained by examining small grains through a microscope (giving higher irradiance, larger solid angle collection of the scattered light, etc.). An invaluable method is to map the sample surface by using an XY motorised stage, thereby selecting the most representative spectra from regions of different constituents and optimising the lateral spatial resolution to ca. 2 $\mu m$. Analysis of the object body can be performed on glazed or unglazed regions (rim, bottom or support spurs). Analysis through the glaze is also possible (Figure 13.1). The use of a confocal microscope enhances the depth resolution by maximising the proportion of Raman radiation that is detected from the laser focus position by screening Raman signals originating from above and below this position. Under a microscope, the glaze surface can be clearly seen and the area of spectral examination precisely located. For instance, Figure 13.1 shows a shard from Termez (Uzbekistan) analysed from the top surface using a long focal-length objective (total magnification 1000 $\times$); from sequential depth analysis we see the spectrum of the glaze, then that of an underglaze cassiterite ($SnO_2$)-rich layer and finally the different spectra from within the body (\textit{\alpha}-quartz and magnetite phases in this case).

The choice of the exciting radiation must be optimised. Blue or violet short wavelength excitation promotes strong Raman scattering and provides a large spectral range when used with multichannel spectrographs, whereas red light is preferred to analyse specifically the low wavenumber region, below 200 cm$^{-1}$. The exciting line power used is typically 0.5–5 mW on colourless samples. The power of illumination needs to be reduced for coloured glazes if the excitation energy corresponds to the chromophore electronic absorption (resonance Raman spectra) and hence induces local heating, which could modify the material through phase transition, oxidation of burning. Sometimes, fluorescence is observed, for instance for excavated samples. Although, this phenomenon is rather rare for dense samples such as glass, porcelains, etc. An example of fluorescence, shown in Figure 13.2,
features Vietnamese celadon. Fluorescence is generally eliminated after tens of minutes illumination using a blue laser ('bleaching'). The use of other exciting laser lines shifts the fluorescence phenomenon and allows better recording of the Raman spectrum. Baseline subtraction using appropriate software can also be a useful approach.

13.3 Classification From the Raman Spectra of Glassy Phases

A clear differentiation between the various glasses is possible, because the connectivity of the SiO₄ polymeric units can be investigated through the relative intensities of Si–O stretching and bending modes, whose peaks occur at ca. 1000 and 500 cm⁻¹, respectively (see Figure 13.2). In silica-rich glass, the Raman spectra show the strongest intensity at ca. 500 cm⁻¹ (see PDA Sèvres spectrum in Figure 13.2) because large amplitude motion of oxygen atoms is only possible perpendicular to the Si–O–Si bridge. On the other hand, the highest intensity band of Islamic glazes is the stretching mode envelope (800–1200 cm⁻¹), characteristic of structures made with ‘isolated’ and poorly connected tetrahedra (see Dougga spectrum in Figure 13.2). In this case, the largest amplitude oxygen atom motion is found in the Si–O stretching modes. This behaviour is observed in any glassy networks containing a large amount of elements such as alkali or alkali earth metals, lead or zinc ions, which disrupt many of the Si-O links.

Figure 13.3a compares the \( \frac{A_{500}}{A_{1000}} \) ratio (\( A_{500} \) area of the Raman 500 cm⁻¹ band; \( A_{1000} \) area of the Raman 1000 cm⁻¹ band) for many samples studied in our
Figure 13.3  Plots of the area ratio of Si-O bending ($A_{500}$) and stretching ($A_{1000}$) envelopes derived from Raman spectra: (a) Enamel/glass; Key: gC, Carthage glass; Timour, Samarkand Bibi Khanum mausoleum; IDG, Islamic Dougga potteries; ITZ, Islamic Termez and Sind ceramics; SVR, Sévres porcelains; IMRF, Islamic ceramics from Iran and Syria; VHL, Vietnamese Ha Lan celadon; VCL, Vietnamese Chu Đaú porcelains; StC, Saint-Cloud porcelains; NG, modern hard-paste porcelains). (b) Different glasses from Punic/Roman times. (c) Different product from Chantilly (solid circles), Saint-Cloud (triangle symbols) and Mennecy (square symbols) factories [See plate section].
laboratory. This allows one to identify principal pottery groups. An initial plateau 
\( A_{500/A1000} < 0.3 \), family \#1 \) corresponds to most Islamic lead-containing \( \text{glacçures} \) of pottery from Dougga or to Islamic faiences with lustre as well as two of the blue glasses from Carthage. The second family \( (0.3 < A_{500/A1000} < 0.8) \) consists of some \( 19^{th} \) century lead-based soft-paste porcelain enamels and some Carthage glasses (blue, green and colourless). The large second plateau defines family \#3 \( (0.8 < A_{500/A1000} < 1.1) \), to which most Carthage glasses and the \( 18^{th} \) century soft-paste porcelain enamels belong. Family \#4 \) corresponds to Vietnamese celadon Ca-based enamels and family \#5 \) to Vietnamese porcelain enamels. Family \#6 \) corresponds to hard-paste porcelain enamels.

It is clear that the \( A_{500/A1000} \) ratio is strongly correlated to the processing temperature (from \( \text{ca.} \ 1,400°C \) for \( A_{500/A1000} \approx 7 \), \( 1,000°C \) for \( A_{500/A1000} \approx 1 \) and \( \text{ca.} \ 600°C \) or less, for \( A_{500/A1000} \approx 0.3 \)). The \( A_{500/A1000} \) ratio is plotted in Figure 13.3b for selected Punic/Roman glasses. As expected because of their similar origin, the ratios are very close. Three groups can however, be, discerned: i) samples with ratios below 0.8, ii) samples with ratios ranging from \( \text{ca.} \ 0.8 \) to 1 and iii) samples with ratios >1. We can expect that each group corresponds to a similar processing temperature, e.g. \( \text{ca.} \ 1,000°C \) for \( A_{500/A1000} \approx 1 \).

We have applied this procedure to the glazes of three main soft-paste porcelains from factories in the Paris area from the \( 18^{th} \) century: viz. the Chantilly factory established in 1725 by the Duke of Bourbon and closed in \( \text{ca.} \ 1800 \), the Mennecy factory found in 1737 and closed in \( \text{ca.} \ 1773 \) and the Saint-Cloud factory established in 1675 and closed around 1766. Glazes were classified from the ratio of bending/stretching Raman intensity as mentioned above. It was clear that the glazes of Mennecy productions had been fired at low temperature and that different glazes, all fired at much higher temperatures had been used for the Saint-Cloud production. Two of the glazes studied are deposited on soft-paste porcelain bodies and belong to the group of hard-paste glazes \( (A_{500/A1000} > 1.5) \) consisting of blue under-glaze artefacts designed to imitate China production. From such investigation it is clear that the Raman technique is viable for classifying artefacts according to their method of production. Comparison with surviving ancient records and receipts will also contribute to improved correlation between the spectra and firing temperatures.

The different spectral components \( (Q^n \text{ for stretching}, \ Q^{n'} \text{ for bending}) \) of the band envelopes have been assigned in the literature\(^{3,5,10,11}\) to the vibrations of different tetrahedra constituting the glass network (Figure 13.2): tetrahedra with zero \( (Q^0, \text{monomer, i.e. isolated SiO4, ca.} \ 800–850 \text{cm}^{-1}) \), one \( (Q^{1}, \text{Si}_2\text{O}_7 \text{groups, ca.} \ 950 \text{cm}^{-1}) \), two \( (Q^{2}, \text{silicate chains, ca.} \ 1050–1100 \text{cm}^{-1}) \), three \( (Q^{3}, \text{sheet-like region, ca.} \ 1100 \text{cm}^{-1}) \) and four \( (Q^{4}, \text{SiO}_2 \text{and tectosilicates, ca.} \ 1150–1250 \text{cm}^{-1}) \) bridging oxygen atoms \( (\text{i.e. four, three, two, one or zero non-bridging oxygen atoms, respectively}) \) per silica tetrahedral structure group. Figure 13.4 shows a typical deconvolution of the Si–O stretching envelope, into \( Q^0, Q^{1}, Q^{2} \) and \( Q^{3–Q^{4}} \) stretching component peaks at \( \text{ca.} \ 800, 950–1000, 1040–1100 \) and \( 1150–1200 \text{cm}^{-1} \). Figure 13.4b compares the centre of gravity of these components determined for the different samples belonging to celadon excavated from two kilns in North Vietnam; data are scattered but the different groups of \( Q^n \) components are obvious.
Figure 13.4  Left, deconvolution of representative Raman spectra of the 13th century Ha Lan celadon after baseline subtraction. The different components are shown. In a modern copy (the lower spectrum) the narrow peaks of α-wollastonite precipitate dominate. Right, spectral positions and relative areas of the components extracted from the Raman spectra recorded (solid squares) normal to the glaze surface and (solid triangles) across the shard section of 13th century Ha Lan celadon (* symbols) and 15th century Chu-Dâu porcelain (open circles) [See plate section].
Similar decomposition can be performed for all glasses and glazes. The spectral component set is however not unequivocal and comparison makes sense only for parent materials belonging to the same or contiguous families.

13.4 Classification From the Raman Spectra of Crystalline Phases

A few databases are currently available. Pioneering work was undertaken by geologists\textsuperscript{12} and mineralogists.\textsuperscript{13,14} But more specific databases now exist.\textsuperscript{15–23}

13.4.1 Soft- and Hard-Paste Porcelains

Typical examples of spectra obtained from porcelain bodies are given in Figure 13.5. The easy discrimination between soft- and hard-paste ceramics results from the high peak intensity of $\beta$-wollastonite ($\text{CaSiO}_3$, main bands at ca. 970 and 635 cm$^{-1}$) and/or calcium phosphate ($\beta$-$\text{Ca}_3(\text{PO}_4)_2$, main bands at ca. 960 and 415 cm$^{-1}$) phases in soft-pastes; these phases are absent in hard-pastes. On the other hand, mullite or mullite-like glassy phase spectra (main bands at ca. 480, 960 and 1130 cm$^{-1}$) are observed in high-temperature fired hard-paste porcelains (prepared with kaolin and feldspars)\textsuperscript{5} – for instance, Meissen porcelains exhibit a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13_5.png}
\caption{Left, representative micro-Raman spectra (10× objective, $\lambda_{exc} = 457.94 \text{ nm}$) of the porcelain bodies from Sèvres PDN (19\textsuperscript{th} century), Meissen hard-paste (18\textsuperscript{th} century), Saint-Cloud and Chantilly soft-paste (18\textsuperscript{th} century). Main peaks are labelled: Q: quartz, F: Feldspar, M: mullite, W: $\beta$-wollastonite. Right, representative glaze spectra recorded with the 457.9 nm laser line using the macro-configuration on Chantilly, Saint-Cloud and Mennecy production (18\textsuperscript{th} century). Baselines were subtracted. The Registry numbers are shown to the right.}
\end{figure}
nearly pure mullite spectrum – but α-quartz bands (main bands at ca. 200 and 465 cm\(^{-1}\)) dominate the spectrum of hard pastes like those prepared at the Sèvres Factory.\(^5\,6\) The spectra of medium-temperature fired porcelains often reveal a band ca. 510 cm\(^{-1}\) originating from incompletely reacted feldspar grains. Ancient Asian porcelains generally show the strong doublet of rutile at ca. 445 and 610 cm\(^{-1}\) (\(\text{TiO}_2\) polymorph).\(^2\) The rutile proportion is only 0.5–1 wt\% but the Raman scattering cross-section of the Ti–O bond is large (Raman intensity increases very rapidly with bond polarisability, \(i.e.\) the more covalent the chemical bond and the higher the number of electrons involved in the bond motion, the stronger is the Raman peak) This secondary phase is eliminated when the refining techniques of raw materials (clay, kaolin and sand) attain the high quality required for the preparation of translucent, white porcelains.

Crystalline precipitates within the glaze or at the glaze/body interface are very useful for identifying porcelains. Figure 13.5 (right) shows representative spectra recorded from the glazes of three main factories in the Paris area in the 18\(^{th}\) century, namely, those of Chantilly, Mennecy and Saint-Cloud. Identification of the phases is obvious from comparisons of Raman scattering from within the body, on the glaze and at the glaze/body interface (Table 13.1).\(^7\)

### 13.4.2 Probing the Production Process: Trace Phases

\([AQ4]\) Raman spectra, which correspond to stable phases, can be used to confirm the source of raw materials and/or the processing route. Some phases are rare or appear in some samples only. For instance, in Vietnamese celadons from the 15\(^{th}\) century, anatase, a rare natural \(\text{TiO}_2\) polymorph, was found in the voids formed inside the glaze.\(^3\,4\) This polymorph usually transforms into rutile in the 800 to 1,100 °C temperature range, depending on the grain size and dwell duration.\(^24\) This phase indicates that a two-step process had been used: first, the body was shaped and fired at high temperature, then the glaze was coated with anatase-containing materials and fired at a lower temperature (differential thermal analysis, DTA, shows glaze melting at ca. 940 °C\(^2\,4\)).

Comparison of Raman spectra obtained from modern and ancient Vietnamese celadon is shown in Figure 15.4. The narrow peak spectrum of modern celadon corresponds to crystalline α-wollastonite, \(\text{CaSiO}_3\), in the glaze (main bands at

<table>
<thead>
<tr>
<th>Factory</th>
<th>Body phases</th>
<th>Precipitates within the glaze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chantilly</td>
<td>α-quartz, (\beta)-wollastonite, cristobalite</td>
<td>cassiterite, (\beta)-wollastonite</td>
</tr>
<tr>
<td>Mennecy</td>
<td>α-quartz, (\beta)-wollastonite, cristobalite</td>
<td>(\beta)-wollastonite</td>
</tr>
<tr>
<td>Saint-Cloud</td>
<td>α-quartz, (\beta)-wollastonite, Ca-phosphate</td>
<td>(\beta)-wollastonite, Ca-phosphate</td>
</tr>
</tbody>
</table>

Main phases are written in bold.
ca. 985 and 580 cm\(^{-1}\)). Examination of ancient celadons under a microscope shows that bubbles of several tens of micrometers in size are almost homogeneously distributed.\(^25\) Optically, these bubbles result in a deep translucence. A similar effect may be obtained with the precipitation of \(\alpha\)-wollastonite. Chromium traces in wollastonite give green colours, whereas in ancient celadon a greenish colour is obtained from iron doping.

### 13.5 Identification From the Raman Spectra of Pigments and Paints

Heterogeneity can be visually seen even on a sub-micrometre scale. The size of crystalline pigments dispersed in glassy host coatings must be close to 100 nm or less to obtain a high-gloss glaze; otherwise, the glaze will appear matt or satin. Thus, pigments are some of the oldest materials for which the nanocrystalline state is required and tailored. For a given colouring ion, the result depends on the glaze composition, the firing temperature, the atmosphere and the grinding (\textit{i.e.} a decrease in the particle size can shift the electronic gap and hence the colour). In other words, the final colour depends on the technology used: single-firing, bisque- or multi-firing. The use of coloured crystals is severely limited by the simultaneous requirement of intense colour and other properties such as homogeneity, high-gloss, low cost, safety, and stability versus leaching.

The different ways of colouring matrices produce different Raman features:\(^6,26\)

i) Certain transition metal ions (\(\text{Cu}^{2+}, \text{Co}^{2+} \text{or} \text{Co}^{3+}, \text{Mn}^{2+} \text{or} \text{Mn}^{3+}, \text{etc.}\)) become part of the glassy coating. In this case, the Raman scattering will not be very sensitive, since only the glassy matrix fingerprint will appear. This is the case for many blue and green glazes, the so-called ‘\textit{couleurs transparentes}’. The Raman spectrum of the glassy host-matrix can be characteristic, however, because specific compositions are needed to develop the right colour. In this case a deconvolution of the Si–O stretching band is essential for glaze identification.

ii) The second way is to induce the precipitation of ‘small’ (coloured) crystals. This technique is widely used to opacify the matrix (many oxides dissolve in glass at high temperatures but their solubility drastically decreases on cooling and hence precipitation occurs). Cassiterite (\(\text{SnO}_2\)) was used in the past, rutile (\(\text{TiO}_2\)), zircon (\(\text{ZrSiO}_4\)) or zirconia (\(\text{ZrO}_2\)) are being used presently. The small sizes of the crystals can induce a characteristic band-broadening in the Raman spectrum. Wavenumber shifts of bands can arise from the stress imposed by the body on the glaze and the crystals embedded in it.\(^27\) As the crystal grows, the precipitate can absorb other elements from the surrounding matrix (\textit{e.g.} \(\text{TiO}_2\) absorbs iron) and change the colour.

iii) The third way is to disperse an insoluble coloured crystal (a pigment) in the coating matrix. Well-known examples include cobalt aluminate blue, Victoria green (a chromium-doped garnet), Naples yellow (a lead-antimony oxide pyrochlore), pink (chromium-doped sphene) and zinc-iron-chromite.
brown. Representative spectra are shown in Figure 13.6. A specific grain-by-grain analysis by micro-Raman scattering is possible when the colour results from a two-pigment association. Unexpected natural pigments can be detected, e.g. lapis lazuli in 13th century ceramic from Lajvardina in Iran\textsuperscript{28} and in medieval Italian pottery\textsuperscript{29}

iv) A fourth method is the dispersion of metal nanoparticles as in gold,\textsuperscript{6} silver and copper lustreware.\textsuperscript{30,31} Only the Raman spectrum of the glaze can be detected, however, second phases with very high Raman scattering cross-section, and characteristic of the process (e.g. SnO\textsubscript{2} as a mineraliser in many gold Cassius purples) or of the raw materials can serve as a probe.

It should be noted that, because pigments are coloured, some resonance effects can occur, in which case Raman spectra depend on the wavelength of the exciting light and of the chromophore amount. We have clearly observed intensity variations for Cr\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2}, CoO, Sb\textsubscript{2}O\textsubscript{5}, CuO.\textsuperscript{6,8} See, for instance, the spectrum of pink glaze in Figure 13.6: the intensity of the 745 cm\textsuperscript{-1} peak related to the Sn–O stretching mode increases with chromium addition, and harmonic

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**Figure 13.6** Left, representative Raman spectra recorded on blue enamel of Saint-Cloud, Mennecy and Chantilly production; Raman spectrum of a pink pigment prepared at Sévres factory: see the Sn–O stretching resonant mode at ca. 745 cm\textsuperscript{-1}; below are presented the spectra recorded on the bowl in Figure 13.7, corresponding to the green paint, a yellow grain, the red festoon line and blue zone analysed under a microscope. Right, examples of Raman spectra recorded from yellow (including Naples yellow), white, pink, green, sepia, black and purple glazes (\(\lambda_{exc} = 457.94\) nm). Numbers are the Sévres factory references (See Reference [6] for details).
and combination vibration bands become visible at ca. $1235\text{ cm}^{-1} = 745\text{ cm}^{-1} + 490\text{ cm}^{-1}$; ca. $1490\text{ cm}^{-1} = 745\text{ cm}^{-1} \times 2$; ca. $2235\text{ cm}^{-1} = 745\text{ cm}^{-1} \times 3$; ca. $1690\text{ cm}^{-1} = 745\text{ cm}^{-1} + 945\text{ cm}^{-1}$, and ca. $2435\text{ cm}^{-1} = [(745 \times 2) + 945]\text{ cm}^{-1}$; the 490 cm$^{-1}$ band belongs to the sphene type (malayite, CaO.SnO$_2$.SiO$_2$) host framework. The spectrum of $\alpha$-Fe$_2$O$_3$, haematite, changes with exciting line wavelength, in particular the ‘magnon’ peak at ca. $1350\text{ cm}^{-1}$ arising from the coupling between magnetic and vibrational excitations.

The low wavenumber region is very important for the identification of phases comprising heavy atoms; for instance, Naples yellow gives rise to a strong peak at ca. $135–145\text{ cm}^{-1}$. On the other hand, the difference between spinel solid solutions is not easy to distinguish because in this very symmetric structure the main peak corresponds to the oxygen motion only and is not sensitive to the heavy metal.

Phase assignments have been made from Raman spectra recorded on palettes and on the corresponding pigments. Each pigment has been studied by X-ray diffraction and the powder patterns have been assigned using the JCPDS (Joint Committee on Powder Diffraction Standards) database. The bandwidth and the relative intensity depend on the crystallinity and doping.

### 13.6 Examples of Raman Analysis

Figure 13.7 shows a bowl assigned on the basis of visual examination to a European production of the 18th century. Corresponding spectra are given in Figure 13.6. The body spectrum, recorded on the unglazed foot rim, shows features typical of a hard-paste porcelain fired at relatively low temperature: a strong, narrow peak at ca. $460\text{ cm}^{-1}$ and a broader one at ca. $510\text{ cm}^{-1}$ are characteristic of un-dissolved quartz and feldspar, respectively. No peaks characteristic of soft-paste porcelain are observed. The glaze spectrum clearly indicates a hard-paste porcelain. Detailed microscope investigation of the green paint shows that the colour results from a
dispersion of yellow grains in a ‘blue’ enamel coating. The spectrum of yellow grains corresponds to Naples yellow, Pb₂Sb₂O₇ pyrochlore. The spectrum recorded on the blue daisy flower shows a strong 820 cm⁻¹ peak. Note the bandwidth and the wavenumbers of the blue pigment spectra are different from one production to another (see the spectra of blue Saint-Cloud, Chantilly and Mennecy porcelains, Figure 13.6), which can be used to recognise the production origin. The red-orange flower and rim lines and scrolls of the bowl exhibit very characteristic haematite bands. In contrast, the spectrum of the pigment used for the pink rose is very similar to that of the glaze, except there is a rather strong fluorescence background. This is consistent with assignment to a gold Cassius purple which confirms its production as 18th century european.

13.7 Conclusion
Macro- and micro-Raman spectroscopy are good tools for the non-destructive identification of old glasses and ceramics. Recent generation Raman optic probe heads fitted with a microscope objective allow for remote and on-site examination. Discrimination between soft- and hard-paste ceramics is feasible and has been demonstrated by considering the fingerprint of crystalline phases. Extracting some parameters from the Raman spectra of glass/glaze allows their classification as a function of composition and/or temperature processing. Spectra of amorphous matrices coloured by different coloured (nano-)crystalline phases allow the identification of the colouring pigment as well as recognition of artefacts prepared with the same technology. The Raman technique appears well suited for the analysis of white, green, yellow, blue, brown, black and red colours. It is efficient in spite of the small size, low crystallinity and low amount of the probed phases. Criteria for selecting the most applicable among various exciting lines to obtain (pre-)resonant Raman scattering are under investigation.

13.8 Acknowledgements
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13.9 References