Discussion and conclusions

One of the advantages on using this method is that it uses non-contact and non-destructive high precision photonic techniques, to collect important data on the quality and conservation status of the surface and the hidden layers of an artifact, which can be fragile to mechanical contacts of any kind.

A direct advantage of the digital model obtained in this way, is that it offers information very useful to the experts in the field of conservation-restoration of artworks, historians, insurers, curators. In short, the resulted model contains high precision data about the:

- Integrity, quality and the surface morphology of the object
- Conservation status and possible biological attacks, with the mapping of the signal intensity distribution on the investigated surface
- Differences between compositions of pigments with similar appearance that may belong to interventions following the original paintings
- Vital informations about the history of the investigated artwork restorations, by highlighting any touch-ups, existing or concealed detachments in substrates

In this way, the information is available with no need to move the concerned expert on the spot. So he can access and view the digital model from his bureau, home or another places, using a computer, and more importantly, the future studies on the object would be done without the need to handle physically the object.

References


LUSTRE RECIPES FROM A 16TH CENTURY SEVILLE WORKSHOP

A. Polvorinos\textsuperscript{1} and J. Castaing\textsuperscript{2}

\textsuperscript{1}Dept. Crystallography, Mineralogy and Agricultural Chemistry; Seville University; Avda. Reina Mercedes s/n 41071 Seville, Spain

\textsuperscript{2}C2RMF, CNRS UMR 171, Palais du Louvre, 14 quai François Mitterrand, 75001 Paris, France

Introduction

Lustre is a well known decoration of glaze ceramics that have a characteristic iridescent and metallic aspect. This is due to the presence in the glaze of a thin layer containing copper and/or silver nanoparticles (Kingery and Vandiver 1986; Perez-Arantegui et al. 2001).

Production of lustre requires an additional firing at low temperatures (550–600°C) after applying a pigment with Cu/Ag compounds (Molera et al. 2001a; Pérez-Arantegui et al. 2001; Chabanne et al. 2007, 2008) to form metallic copper and silver nano-precipitates near the surface of the ceramic glaze (Padovani et al. 2006; Roque et al. 2006).

The technology involved in the production of lustre decorated wares appeared progressively with the development of white opaque glazes in the Islamic world from the 8th to the 9th centuries (Mason and Tite 1997). The technology later spread through medieval times to Iran, Egypt, North Africa and Spain to reach ultimately Italy in the Renaissance.
During the past five to ten years, there have been considerable efforts in investigating the chemical and physical structures, the optical properties and the fabrication technologies of lustre decorated ceramics.

Detailed analytical studies of lustre ceramics aim at discovering the characteristic features of each production centre and how they influenced each other through time and space.

During the last five years three sets of uncovered Spanish lustre ceramics have been studied in our research group to characterize and analyze technological patterns of “loza dorada” manufacture. The studied groups of ceramics belong to the recovered set of Centro Arqueológico de Madinat Al-Zahara (Polvorinos et al. 2008, 2010a), a temporal sequence of Manises production between 14th and 18th centuries (Polvorinos et al. 2009, 2010c), and a set of 16th century production in Seville (Polvorinos et al. 2006, 2010b). Considered as very valuable objects we have used non-destructive techniques for their analyses, applying in addition to X-ray diffraction (XRD) and SEM, ion beam analysis (IBA) performed using an accelerator to make PIXE (particle induced X-ray emission) and RBS (Rutherford back-scattering spectrometry).

The processing to manufacture these ceramics is relatively complex with three steps. The body is made of fired clay (or of quartz-rich powder) with the aim of obtaining creamy or white earthenware. The glaze slip (generally a suspension with SiO₂-alkali-PbO-SnO₂ particles) is then applied and dried before firing in order to obtain a continuous white opaque glass layer thanks to the formation of SnO₂ tiny particles. These first two firings are usually performed in oxidizing atmospheres at relatively high temperatures (800–950°C). Then, the lustre decoration is formed by painting metal-containing compounds or lustre-paste, on the surface of the glaze that is submitted to a third firing. Suspensions of salts or oxides of copper and/or silver mixed with iron oxides or iron rich clays must wet the glaze surface so that at a given temperature, metallic ion diffusion in the glass is possible. With Cu and Ag ions present in the glaze, internal reduction must take place so that metals can form and precipitate as a thin layer of nanoparticles. Therefore, the last firing to obtain nano-structured lustre decoration requires short annealing time at moderate temperature (600–650°C) with a reducing atmosphere and a well controlled cooling. This reducing atmosphere was obtained introducing smoke-producing wood and/or plants, and iron oxides of the lustre-paste prevented Cu and Ag particles re-oxidation during the cooling phase. After firing the residual paste must be removed from the ceramic surface to reveal the lustre.

According to the places and to the centuries there have been many variations in the material formulations of lustre-paste (Caiger-Smith 1985), and also variations of colour nuances (gold-yellow, silvery or ruby-red), the metallic shine and iridescence.

The optical properties of the lustre decoration depend on many processing parameters that control the Cu and Ag concentrations, the sizes of the nanoparticles, the thickness of the layer (less than 1 µm) where they are included, or the development of multiple thin layers (Reillon et al. 2007). The formulae to make lustre can be considered as one of the
important know-how’s typical of each workshop. Except for the characteristics of the final product, little is known on the processing, in particular on the materials used for lustre fabrication. In this note we report on the chemical and mineralogical composition of the lustre-paste and on the residual-paste adherent to some of the sherds found in the 16th century Seville workshop (Polvorinos et al. 2006, 2010b).

Materials and methods

Inside two bowl fragments, referenced as pastes P1 and P2, a heterogeneous compact superficial layer of grey to black powdery material with green round crystals of malachite (Figure 1) overly a red layer.

The apparent heterogeneity of the P1 and P2 pastes has been characterized by sampling spots with different colours in each sherd for their X-ray diffraction powder analysis (Figure 2). Qualitative estimation of the different phases identified in each sample is indicated in Table 1.

Table 1. Abundance of mineral phases (Qtz: Quartz, Hemt: Hematite, Cupri: Cuprite, Mal: Malachite, Cinn: Cinnabar, and Illite), A: Major compound, M: Minor compound, IND: traces)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-red</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>P1-brown</td>
<td>A</td>
<td>-</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>P1-dark</td>
<td>M</td>
<td>A</td>
<td>IND</td>
<td>-</td>
<td>M</td>
<td>-</td>
</tr>
<tr>
<td>P2-red</td>
<td>A</td>
<td>A</td>
<td>-</td>
<td>IND</td>
<td>-</td>
<td>IND</td>
</tr>
<tr>
<td>P2-black</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>A</td>
<td>-</td>
</tr>
</tbody>
</table>

Cuprite is the main copper phase found in two P1 spots, and malachite, probably due to burial transformation in the P2-black spot (Figure 2b). Cinnabar was identified in the darker samples of P1 and P2 sherds. Although small diffraction lines could be assigned to silver sulphur phases it is not conclusive probably due to their low abundance.

The presence of calcite and diopside in some spectra suggests contamination from the burial conditions and diffraction of the sherd paste, respectively.

Mean compositions on a 0.5x0.5mm² surface (PIXE analysis) in five different spots of Seville workshop and three lustre-pastes recovered in Olleries Xiques (Paterna, Valence), analyzed by XRF and ICP/MS, are shown in Table 2. The dispersion of the concentration values of most elements is linked to the different aspect of the sampling spots. In every sampling spot Cu and Ag have been detected; the higher Hg content of P2-black spot is justified by the presence of XRD identified cinnabar (Figure 2). Seville lustre-pastes have a lower CaO (2.9-14.5%) but higher Al₂O₃ (11.8-26.8%) and Fe₂O₃ (12.7-26.8%) content than Paterna samples (CaO 10-27%, Al₂O₃ 6.7-11.8% and Fe₂O₃ 8.7-11%). This difference could be justified by the penetration of radiation in the ceramic body or by the recycling of recovered lustre-paste after lustre firing.

Average chemical compositions of Seville pastes and lustre formulations recovered in Olleries Xiques in Paterna (Molera et al. 2001b) of Table 2 suggest quite similar formulations; two kinds of formulae have been found in both workshops, one with low or non detected Hg (Lus-1 and Lus-2 from Paterna and Paste-1 from Seville), the other is the “active” formula with higher Hg contents (Lus-3 from Paterna and Paste-2 black from Seville).

In order to identify the small fractions of silver compounds, SEM-EDAX analysis has been carried out on the lustre-pastes.
The presence of particles rich in Ag-S, Ag-As-S and Ag-Hg-S that are consistent with raw “paint” materials used for lustre fabrication (Molera et al. 2001b) have been identified by SEM-EDAX punctual analysis (Figure 3).

Table 2. PIXE chemical composition (% oxide wt) of lustre-paste of Seville and XRF or ICP/MS of Paterna (Molera et al. 2001b) workshops.

<table>
<thead>
<tr>
<th></th>
<th>Seville</th>
<th></th>
<th>Paterna</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P1-red</td>
<td>P2-black</td>
<td>P2-brown</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.6</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.8</td>
<td>14.3</td>
<td>11.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>36.7</td>
<td>31.8</td>
<td>29.5</td>
</tr>
<tr>
<td>SΟ₃</td>
<td>1.9</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.1</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>CaO</td>
<td>2.9</td>
<td>5.8</td>
<td>14.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22.1</td>
<td>14.7</td>
<td>18.7</td>
</tr>
<tr>
<td>CuO</td>
<td>2.3</td>
<td>14.3</td>
<td>9.1</td>
</tr>
<tr>
<td>Ag₂O₅</td>
<td>0.4</td>
<td>2.2</td>
<td>0.5</td>
</tr>
<tr>
<td>HgO*</td>
<td>0.0</td>
<td>7.5</td>
<td>0.1</td>
</tr>
<tr>
<td>PbO</td>
<td>1.2</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Cu/Ag</td>
<td>6.8</td>
<td>6.6</td>
<td>18.6</td>
</tr>
</tbody>
</table>

*Hg concentrations in Paterna are calculated as HgS.

Several sherds were occasionally covered by areas of “paint” left after firing in a reducing atmosphere that remain after lustre production; they are named “cosela”. X-ray diffraction carried out on RFM10 remains (Polvorinos et al. 2010b) indicates firing in a reducing atmosphere as magnetite and/or maghemite and a vitreous phase have been identified (Figure 4).

The chemical composition of these “paint” remains is locally rich in Pb, Hg, Cu, Fe and Ag.

Conclusions
The use of Hg in the formulation of lustre-paste from Seville workshop has been evidenced. A mixture of cuprite and complex sulphur-arsenic–Ag compounds, and hematite are the main components of lustre-paste. This formulation and the Cu/Ag ratios are close to other well known compositions of medieval hispano-moresque lustre workshops.

Figure 3. A. Copper oxide crystal (light grey) and rounded quartz grain (dark grey) in Paste 1. B. Silver sulphide (SiO₂ 3%, SO₃ 17%, AgO 67%, Fe₂O₃ 4%, CuO 6%, PbO 3%) crystal (light grey) in Paste 1. C. Light grey crystal in Paste 1: Silver sulphide (SO₃ 32%, AgO 25%, Fe₂O₃ 3%, HgO 40%).
Figure 4. XRD of lustre-paste after third firing in reduction atmosphere with magnetite and/or maghemite.

References


COALITION
No. 20, July 2010


INVITATION TO CONTRIBUTE TO COALITION, A LEADING NEWSLETTER

COALITION is an open-access electronic newsletter that provides a forum for scholarly research in Conservation of the Cultural Heritage, and related public policy issues.

Scientists, conservators, restorers, who share an interest in cultural heritage studies, fostering an interdisciplinary communication between humanities, science and technology, are welcome.

In addition to research papers, the newsletter also publishes short communications, technical notes, description of activities in specialised centres, and book review articles.

The editors welcome contributions, as well as proposals for guest edited special issues.

As an official publication of the CSIC Thematic Network on Cultural Heritage, all full members receive COALITION as a member benefit. In addition, COALITION is distributed to circa 1,000 subscribers as pdf file, and later uploaded in the RTPHC web site. The distribution system ensures a wide dissemination of the papers.

For further information, to view a sample copy, and for submission details, please visit the Journal’s web page at www.rtphc.csic.es/boletin.htm.

All contributions should be submitted by e-mail to coalition@irnase.csic.es