# Observations with a Portable X-ray Diffraction System of a Pb-Sn-Sb-O Yellow Pigment in Ceramics from the 15th–16th Centuries

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## INTRODUCTION.

A number of orange-yellow compounds manufactured with lead, tin and/or antimony have been used as pigments throughout the history of painting (Hradil et al., 2007) and of ceramics. Until now, the classification of the historic lead-based yellow pigments has been as follows: lead oxides, the two lead-tin yellows (types I and II), and lead antimonate yellow. In 1998, Roy and Berrie identified a "non-standardized" yellow pigment, a lead-tin-antimony triple oxide, very close in composition and structure (type pyrochlore) to lead-tin yellow type II and to lead antimonate yellow (Naples yellow). Lead-tin oxides and lead-antimony oxides have been employed intermittently since antiquity as opacifiers and yellow colourings, coinciding with specific periods and centres of glass, enamel and pottery production. One notable example is found in Italy, where antimony, widely used in Roman times, was re-introduced during the 16th century into glassmaking (Sandalinas et al., 2006). Sandalinas and Ruiz-Moreno (2004) give some historical information about the production and use of yellow pigments included the first recipes for yellows from lead and antimony used in the main centres of glazed ceramics in the current regions of Tuscany, Umbria and March. The Della Robbia workshop was very active during the 15th–16th centuries in Florence, producing ceramic wares covered with glazes having remarkable colours such as blue, white, green or yellow. They certainly used antimony pigments for yellows and for mixed greens (Pope-Henessy, 1980; Roy and Berrie, 1998). The identification of lead-tin-yellow oxide cannot be based only on the elemental analysis as it is currently done with portable X-ray fluorescence (XRF). In some examples of yellow glazes containing Pb, Sn and Sb, it was concluded that $SnO_2$ was used as ground on the ceramics and Naples yellow ($Pb_2Sb_2O_7$) was applied on the coloured layers. For the direct and unequivocal identification of the actual composition of pyrochlore-like Pb-yellows and differentiation from other pigments, X-ray diffraction (XRD) is necessary in view of the possible Pb-Sn-Sb-O phases.

## MATERIALS AND METHODS.

The portable XRF/XRD system, developed in the C2RMF has been employed (Gianoncelli et al., 2008). It combines XRF and XRD techniques, allowing simultaneous elemental analysis and phase identification of crystalline materials. A low power (30 W) air cooled Cu anode X-ray source is used, equipped with a polycapillary semi-lens to provide a parallel X-ray beam (diameter about 4 mm), and a 15 µm Ni filter to strongly attenuate the Cu $K_\beta$ line and avoid the presence of secondary diffraction peaks. The XRD 2-dimensional detector is an imaging plate (dimensions 15x30 cm), that it is irradiated by the diffracted beams (30 min) and read out in a scanner (fig. 1); then the image is analysed by using the free share software FIT2D, giving rise to the typical powder XRD diagram (fig. 2).

The XRF detector is a Silicon Drift Detector (150 eV FWHM at 5.9 keV and T=-10°C working temperature) located in the axis normal to the analyzed sample surface. XRF data were quantitatively analysed with the PyMCA software developed at the ESRF synchrotron by Solé et al. (2007), and based on the Fundamental Parameter Method. Artworks from the della Robbia workshop were analysed. We present here results concerning a work from the Bargello Museum in Florence and a fragment found in a reinforcement structure of a work from the Louvre Museum. Our study is centred about yellow and green colours.

## RESULTS AND DISCUSSION.

### X-ray diffraction.

The discrimination between Pb yellow pigments based on the elemental composition of the coloured glazes being impossible, it is necessary to identify the crystalline compounds present in the amorphous layer on the ceramic bodies. Before starting with the analysis, we measured a standard alumina specimen (fine grain polycrystalline corundum), in order to calibrate all the parameters for the XRD measurements.



fig. 1 XRD pattern collected on the Imaging Plate corresponding to yellow sample (yellow type I) from the Bargello work.

We use imaging plates to collect data, figure 1 corresponding to the image of one type of yellow studied on the work from the Bargello Museum. The presence of continuous rings is clear due to diffraction by a distribution of small grains in the first 5-10 µm of the glaze that corresponds to the penetration of Cu-$K_\alpha$ radiation. The first ring shows some preferred orientation of the crystals (dark portion on the first ring). From these images, after treatment with Fit2D software, peaks of crystalline phases are obtained in a standard XRD diagram at different 2θ angles.

The determination of the crystalline phases in green colour is shown in figure 2. It fits with $Pb_2SnSbO_{6.5}$ (PDF n° 39-0928) and cassiterite (PDF n° 21-1250), minerals that have also been found in the two yellows of the Bargello work and in the green of the ceramic fragment.

The presence of cassiterite with the yellow pigment is constant in all these ceramic glazes. In a Virgin and Child from Faenza (15th century), we found only $Pb_2SnSbO_{6.5}$ with no cassiterite. The presence of the lead-tin-antimony yellow oxide is readily evidenced using the new XRD portable equipment.

### X-ray fluorescence.

XRF is always performed during the XRD data collection thus preventing from detecting copper in the specimens since Cu lines (energy ~8 keV) from the source are always present in the XRF spectra. In order to solve the ambiguity concerning the possible presence of Cu, a 750 μm Al filter was placed at the exit of the tube that absorbs X-rays below 9 keV. The presence of copper is clear in green glazes. The two different types of yellow can be ascribed to different amounts of tin and iron in the Bargello work.

|  | Yellow type I | Yellow type II | Green |
|---|---|---|---|
| $SiO_2$ | 30.01 | 31.91 | 39.20 |
| $K_2O$ | 0.40 | 1.13 | 1.35 |
| $CaO$ | 0.62 | 1.11 | 0.90 |
| $TiO_2$ | 0.03 | 0.04 | 0.03 |
| $MnO$ | 0.01 | 0.01 | 0.03 |
| $Fe_2O_3$ | 0.33 | 5.19 | 0.17 |
| $CoO$ | 0.03 | 0.06 | 0.02 |
| $NiO$ | 0.19 | 0.14 | 0.05 |
| $CuO$ | 0.01 | 1.78 | 0.01 |
| $ZnO$ | 0.04 | 0.03 | 0.02 |
| $SnO_2 L$ | 1.71 | 7.84 | 1.86 |
| $Sb_2O_5 L$ | 3.16 | 1.26 | 2.36 |
| $PbO L$ | 63.44 | 49.51 | 54.00 |

Table 1. XRF quantitative analyses giving concentrations (weight percent) of three colours from the Bargello work.

For quantitative analysis, the data were analysed with PyMCA software as in a previous study on della Robbia works from the Seville Cathedral (Gianoncelli et al., 2006). The portable XRF system is limited in accuracy for concentration determinations for various reasons: the measurements are performed in air (absorption of X-rays emitted by elements below potassium in the periodic table); the homogeneity of the sample is assumed for data reduction and it cannot be established. Standard samples of known composition have been used with the Fundamental Parameter Method to verify the accuracy of the whole system and to evaluate the parameters which are otherwise difficult to measure.

Table 1 gives the chemical composition of three points of the studied Bargello work, two yellows and one green. Preliminary results of this quantitative analysis show a reasonable agreement with the results obtained for previous
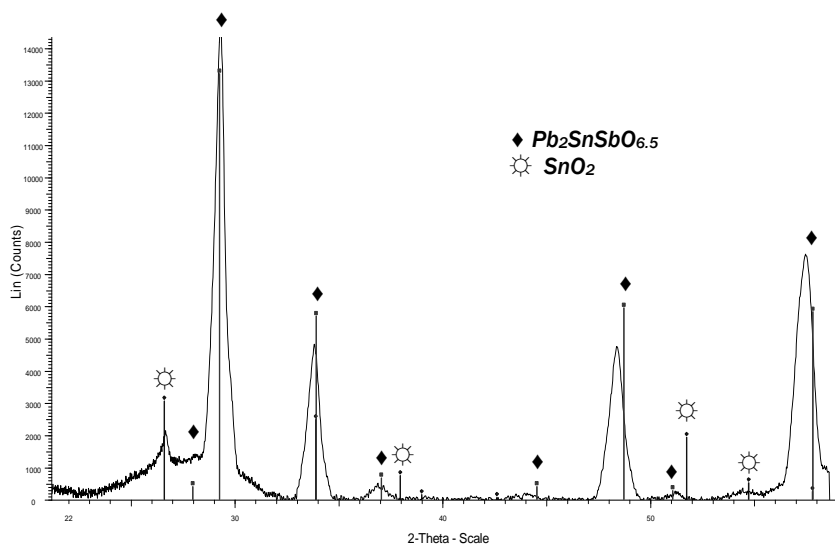


fig.2. XRD diagram corresponding to green colour of the Bargello artwork.

della Robbia artworks with other techniques such as PIXE or SEM-EDX (Gianoncelli et al., 2006). The geometrical parameters have been adjusted to give the same concentration for Pb L (> 10.5 keV) and Pb M lines (2.34 keV). The concentrations are normalized to 100 %. XRF with a Cu anode source strongly excites Fe, Mn even in low concentrations, and Si is hardly detected because of the absorption in about 2 cm of air of the 1.74 keV X-rays (95% absorption).

### CONCLUSIONS.

The portable X-ray diffraction equipment allowed us to identify the lead-tin-antimony triple oxide yellow pigment in ceramics from the 15th – 16th century. In contrast to other ancient ceramics, XRD diagrams are observed in della Robbia works showing that crystals are present in the first 5-10 μm layer of the glaze. These crystals are likely uniformly distributed within its thickness. Results of X-ray fluorescence give compositions of the glazes (amorphous phase) compatible with the productions from the Renaissance in Florence. The XRF measurement system needs improvement to achieve better quantitative analysis; even with these improvements, it is unlikely that such XRF analysis can reach the sensitivity and the accuracy of PIXE (Gianoncelli et al., 2006).

### ACKNOWLEDGEMENT.

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