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In situ non-invasive investigation on the painting techniques of early Meissen Stoneware

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ABSTRACT

In situ, non-invasive investigations by means of portable X-ray fluorescence and fibre optic reflectance mid-infrared (mid-FTIR) spectroscopy of painted Böttger Stoneware objects have been carried out through the MOLAB transnational access to the Porcelain Collection of the Staatliche Kunstsammlungen in Dresden. It has been possible to gather information regarding the composition of the black glaze by applying a principal component analysis to the elemental analysis to distinguish between the variations of lead, iron and manganese compositions of each glaze. It has been furthermore feasible to combine molecular spectroscopy for characterization of the constituent painting materials, namely lead white as cerusite and hydrocerusite, the use of cinnabar, azurite and Prussian blue leading to a better knowledge of the state of conservation and utility of certain pigments that may give rise to chronology of the decorative artwork. The identification of oxalates namely whedellite and moolooite are assigned as degradation products relative to the decorative areas.

1. Introduction

International historical patrimony consists in art objects of two main categories, incorporating monuments, sculptures, buildings in fixed locations and paintings, ceramics, gems or manuscripts in the case of movable patrimony. Technical investigations of the constituent materials of these artefacts may be examined through conventional micro-sampling with further laboratory studies or by in situ non-invasive analytical measurements. The latter approach have become a particular advantageous option in recent years especially when sampling is not permitted or the mobility of the object from its location to an analytical laboratory may be forbidden or impossible. Thus these in situ non-invasive analyses concede an infinite number of measurements that may lead to a broader representation of the entire artwork that can provide preliminary results moderating the necessity of sampling.

Due to miniaturization of electronic components and advances in fibre-optic technology, it has been feasible nowadays to improve performances of existing prototypes or to assemble portable instrumentation, having characteristics comparable to those of standard laboratory equipment. This led to the foundation of the European Transnational Access MOLAB, where a mobile laboratory composed of a unique collection of portable equipment is available to art-historians, conservators, or conservation scientists for in situ non-invasive measurements on works of art. Utilizing these instruments, it has been recently possible to carry out non-invasive measurements directly on several artworks, avoiding any sampling or even any contact with the object [1,2].

The inorganic composition of the Böttger Stoneware ceramic body has been investigated in previous studies [3,4] while no further information exists concerning the technology and chemical composition of the black glazes and the decorative artwork. It may be noted that the contents of major, minor and trace elements in ancient ceramic body and glaze are relied on its raw material and manufacturing technology [5]. Each can be used to research the provenance and the manufacturing technology of ancient porcelain [6].

Thanks to the portable and non-invasive equipments available through the MOLAB transnational access it has been possible, without any sampling, to obtain detailed information on the painting techniques and on the conservation state of the unfired decorations of black Böttger Stonewares belonging to the Porcelain Collection of the Staatliche Kunstsammlungen of Dresden.

2. Experimental

A representative selection of vases, teapots and other objects (Fig. 1) totalling 22 black glazed and subsequently painted Böttger

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Fig. 1. Böttger Stoneware objects under study.

Stoneware objects were examined collecting 176 XRF and 129 mid-FTIR spectra. The objects were examined in the repository of the Porcelain Collection, Staatliche Kunstsammlungen, Dresden.

2.1. X-ray fluorescence (XRF)

XRF spectra were recorded using portable equipment equipped with a miniaturized X-ray generator EIS P/N 9910, with a tungsten filament, and a silicon drift detector with a resolution <150 eV at 5.9 keV. For all measurements a tube voltage of 38 kV and a tube current of 0.05 mA were employed. The portable instrument permits the detection of elements with an atomic number higher than silicon ($Z > 13$), the sampled area is defined by the beam dimension which has a 4 mm diameter. All resulting data have been elaborated with the PyMCA 4.2.1 program [7]. The resulting areas have been reduced to counts per second (cps) by division by the acquisition time. Furthermore any instrumental fluctuations causing variations in experimental data are controlled by the standardization with zirconium in each spectra.

XRF spectra collected on black glazes have been subjected to principal component analysis (PCA) calculated by Golpe [8]. The matrix dataset is composed of the counts per second (cps) expressed as percentage of each element (as variable) found in the spectra (as objects). No other pretreatment has been applied.

2.2. Reflectance mid-infrared (mid-FTIR)

Spectra were recorded using a portable JASCO VIR 9500 spectrophotometer equipped with a Remspec mid-infrared fibre optic sampling probe. The bench is made up of a Midac Illuminator IR radiation source, a Michelson interferometer and a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The fibre optic probe is a bifurcated cable containing 19 chalcogenide glass fibre that allows the collection of spectra in the range 4000–900 cm^{-1} at a resolution of 4 cm^{-1}. The width of the investigated area is determined by the probe diameter, which is about 4 mm. The total reflectivity, R, due to the combined diffuse and specular components, is measured using the spectrum from an aluminium mirror plate for background correction. The spectrum intensity was defined as the pseudo absorbance A' where $A' = \log(1/R)$.

2.3. Optical microscopy

A Leica MS5 has been used equipped with a DC300camera.

3. Results and discussion

3.1. The black glaze: multivariate statistical analysis of experimental data

The black Böttger Stoneware glazes are all characterized by the presence of lead, iron, manganese, copper, nickel and cadmium by XRF. Some further elements are present in minor quantities such as cobalt, titanium, tin, calcium and potassium. Literature suggests that black coloured glazes are predominantly produced by introducing ceramic pigments synthesized at high temperatures (up to 1300 °C) [9]. Black pigments are usually produced firing batches consisting of oxides of iron, cobalt, manganese, nickel and copper mixed in certain ratios [10]. It is also suggested [11] that cobalt salt that is soluble in water can be used to effectively control the intensity and stability of black colour in the pigment-bearing glaze layer. The colour of glaze coating in this case substantially depends not only on the chemical–mineralogical composition of pigments and the temperature–time conditions of firing glazed products, but also on the acid–base properties of the silicate melt [10].

The elemental constituents as given by XRF of the different groups do not vary significantly enough to be able to allocate each of the pieces to its distinct group motivating a PCA multivariate method of analysis through GOLPE. This PCA has been used incorporating all the elements in order to understand the variations

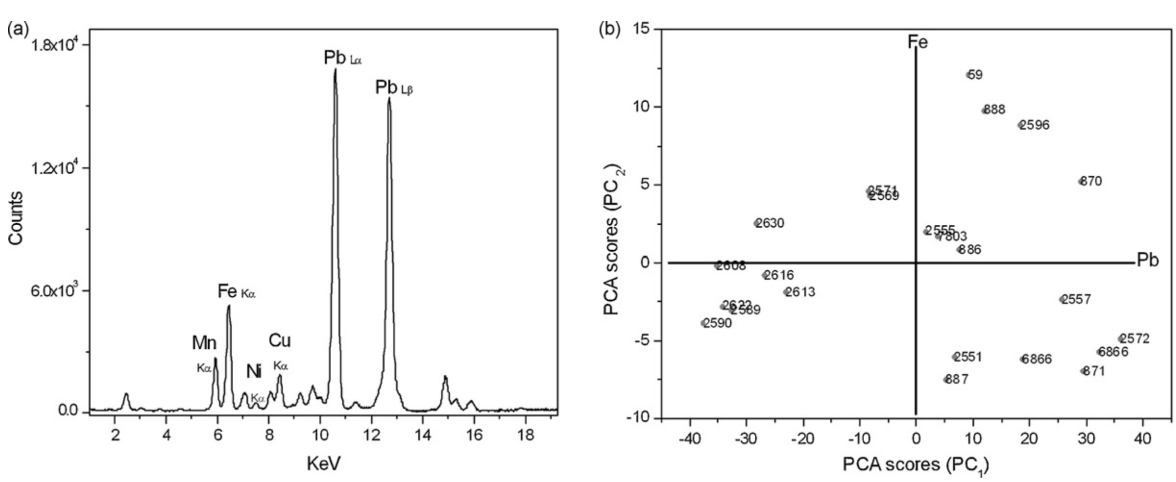

Fig. 2. (a) XRF spectra of glaze and (b) score plot of PC1 against PC2 for all glazes.