

The XRD measurements allow us to identify the mineral phases that are present in the ceramic pastes; the composition of the samples is quantified with a full-pattern matching of the diffractograms. Three types of minerals are identified in all samples: i) major phases that are relevant for the elaboration process (i.e., they appear after annealing at high temperatures): diopside, gehlenite, kalsilite and cristobalite; ii) minor phases that also appear (or are altered) by the application of high temperatures: forsterite-fayalite, mullite and hematite; iii) phases that are present in the pastes but do not play any significant role in the elaboration process: illite, calcite, K-feldspars, plagioclase and quartz.

An inspection of the XRD data from 18th-century jars with a well-established manufacture location suggests that the presence and relative amount of the mineral phases in the pastes is linked to the provenance of the objects. To further assess this point, we have performed a principal component analysis (PCA) of the XRD data. The intensities of the main XRD peaks from the major mineral phases in the pastes have been taken as variables for the analysis. The PCA reveals that pharmacy jars crafted in different geographical locations tend to cluster in a score plot of the first and second principal components, PC₁ and PC₂. This confirms that relevant information about the origin of the objects is gained from the XRD measurements.

To illustrate the ability of powder diffraction and subsequent PCA to determine the provenance of pottery objects, we have applied the method to investigate a series of 18th-century pharmacy jars of unknown origin from an old pharmacy at Barbadillo del Mercado, in Burgos, Spain, owned by a private collector. Our XRD data and subsequent PCA reveal that all the samples investigated were crafted in Villafeliche, Zaragoza, an important center of pottery and gunpowder fabrication during the 17th, 18th and 19th centuries. Our results are in excellent agreement with those obtained independently by authentication experts, which confirms the usefulness of powder diffraction for the study and authentication of pottery art objects.

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Difficulties in identification of copper-based pigments in objects of art

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Material identification and the description of painting techniques by modern analytical and/or micro-analytical methods should be integrated into the artistic or art-historic evaluation of the fine art. Correct identification of pigments and all other components found in colour layers of objects of art is relevant for searching the origin, preparation pathways and for specification of their degradation including colour changes. The success of that identification depends on the nature of materials and the correct choice of analytical methods. There are many materials used in objects of art which indisputable identification is possible only on the basis of phase analysis. Copper salts, existing in a wide range of chemical and/or structural varieties, can be a good example. They were used for centuries as blue or green pigments [1].

In the presented study we will focus on two main groups of Cu pigments having close chemical composition: 1) copper carbonates (malachite, azurite), 2) copper acetates (neutral and basic verdigris).

When looking into literature, there are indications for the existence

of several phases with the different ratio between copper, acetate and hydroxyl within one molecule. On contrary, looking into the databases of crystal structures, only the structure of neutral copper acetate is well described. Basic copper acetate was described by Masciocchi *et al* [2] on the basis of structure solution from powder data. The authors stated the difficulties in preparing crystals of good quality and therefore the structure has not been solved completely. Some peculiarities in the location of acetate groups persisted.

On the basis of literature data and historical recipes for preparing various variants of verdigris we tried to prepare model compounds to put the light into this complicated system of copper acetates. In the majority of cases the results of our model syntheses showed that only complicated mixture of phases came up giving very complicated X-ray powder pattern that could not be attributed to a single phase. As the best result, we came back to the synthesis of the simplest copper acetate phases that are probably the only which could be prepared in the pure form. We re-examined the synthetic procedure of the basic copper acetate. We succeeded in obtaining crystals of good quality to solve the structure completely, describing the positions of all atoms correctly.

Analysing a large number of real samples by X-ray powder micro-diffraction (μ -XRD) we found that copper carbonates are much more stable and retain their crystal structure for centuries. On the contrary, copper acetates that are originally well crystalline undergo degradation to be amorphous. Their identification is then either very complicated, or almost impossible by means of μ -XRD. There are only very few cases of positive identification of verdigris in the real samples of objects of art because of its readily degradation leading mostly to amorphous products.

[1] S. Švarcová, D. Hradil, J. Hradilová, E. Kočí, P. Bezdička *Anal. Bioanal. Chem.* **2009**, 395, 2037-2050. [2] N. Masciocchi, E. Corradi, A. Sironi, G. Moretti, G. Minelli, P. Porta, *J. Solid State Chem.* **1997**, 131, 252-262.

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Determination of the metallurgical properties of six ferrous Japanese arrow tips through time of flight neutron diffraction

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The phase composition of six ferrous Japanese arrows of the Edo period (17th-19th century) has been determined through Time of Flight Neutron Diffraction (ToF-ND).

ToF-ND has been applied on all the samples by using the INES diffractometer at the ISIS pulsed neutron source in UK [1]. The measurements have been performed on the average gauge volume of all the samples in order to determine the quantitative distribution of the metal and non metal phases. The data have been processed by using the GSAS code in order to perform Rietveld refinement of all the diffractograms. The cementite to ferrite ratio has been used in order to quantify the carbon content. The comparative analysis of the phase distribution among the samples permitted to identify peculiar characteristics related to the type of arrow. The carbon content, the fayalite amount, the presence of wuestite and troilite have been exploited to gain knowledge about the quality of the material and smelting and smithing methods. The shape of the ferrite peak has also been studied in order to semiquantitatively determine the texture level, the strain level and the domain size of the grains of each of the