Raman spectroscopic studies of the underglaze pigments of porcelain shards of archaeological origins

by

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Declaration

I, Lesotlho David Kock, the author of the current thesis entitled "Raman spectroscopic studies of the underglaze pigments of porcelain shards of archaeological origins", declare that the thesis contains only original work and that all the results included were generated by the author.

Signature:....

Date:....

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Summary

The technique of Raman spectroscopy was used in a study of shards of known (Ming and Meissen) and unknown (archaeological) origin. A tile shard from the Citadel of Algiers was included in this study as further confirmation of the consistency of the methods that are developed. The Citadel from which the tile shard was obtained was built in 1516 and represents a landmark from pre-colonial Algeria. The results were compared with those obtained from studies on intact museum pieces of known (Ming) origin. A consistent method of studying underglaze pigments on glazed ceramic artifacts by directing the laser beam through the predominantly silicate glaze was developed. The glaze depth profiling method developed proved to be very useful in the analysis and gives not only a detailed composition for the glaze/ceramic interfacial pigment, but also the order in which the various interfacial pigment layers were applied at the time of manufacture.

The information acquired leads to an understanding of the level of technological development of the manufacturers. The detailed study and characterisation of the pigments that were analysed in this way gives insight into trade relations among ancient societies of the Mediterranean and will also assist archaeologists in establishing cut-off dates for the archaeological sites from which the artifacts were recovered. All the shards, except one from Meissen (Germany), were provided by the National Cultural History Museum of South Africa and the intact Ming dynasty plates were provided by the J.A. van Tilburg Museum of the University of Pretoria. The tile shard sample from the Citadel of Algiers was donated for the study.

The results indicate that none of the archaeological shards could possibly be of Ming dynasty origin based on, firstly, the use of amorphous carbon to darken the cobalt blue (CoAl₂O₄) used as decoration on the shards, and secondly on the use of white (synthetic) anatase to whiten the ceramic surface before the application of the

pigment since this synthetic anatase is known to have been manufactured for the first time around 1920.

An ancient rediscovered ternary pigment (Pb₂SnSbO_{6.5}) previously found on Italian paintings of the 16th century, for example, "Lot and his daughters" by G.B. Langetti and "Entrance of Christ in Jerusalem" by Luca Giordano, was identified on the Citadel tile and successfully characterised. A Pb-O vibrational Raman band at 127 cm⁻¹ for this pigment was assigned for the first time. Additional pigments identified on the tile include Naples yellow (Pb₂Sb₂O₇), lead (II) stannate (Pb₂SnO₄), cobalt blue (CoAl₂O₄) and cassiterite (SnO₂). The bulk of the tile body is composed mainly of hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄) and quartz (α -SiO₂), with traces of calcite (CaCO₃) and amorphous carbon. The unique non-destructive depth profiling method that was developed in this study can now be applied to the study of underglaze pigments on intact porcelain artifacts in museums and private collections around the world for authentication purposes and for comparison with archaeological shard samples.

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