

RAMAN INVESTIGATION OF A PINK PIGMENT ON A SHARD FROM THE SÃO JOÃO BAPTISTA SHIPWRECK

Danita de Waal*

Department of Chemistry, University of Pretoria, 0002 Pretoria, South Africa;
E-mail: danita.dewaal@up.ac.za

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Abstract: This contribution reports on the identification of a pink pigment from its resonance Raman spectrum obtained by excitation with 514.5 nm. The pink originates from a ceramic shard found among blue and white porcelain shards from the 1622 shipwreck around the South African coast.

Introduction

Various ceramic samples have been investigated using Raman microscopy. Some of these included shards that originated from 16th and 17th century Portuguese shipwrecks around the South African coast. In these late Ming period blue and white Chinese porcelain shards, the blue pigment used by the Chinese was identified for the first time by means of Raman spectroscopy as the spinel phase of cobalt aluminate. Three shards from the São João Baptista shipwreck (1622, Cannon Rocks, Eastern Cape, South Africa) did not show the typical characteristics of the Ming period Chinese porcelain, which made out the majority of the ceramic cargo on this Portuguese ship. One of these shards contained a pink pigment in addition to the blue, in contrast with all other shards that only displayed blue as a colour on the white porcelain. The origin of the pink colour needed to be investigated in order to obtain more information on the origin of the particular shard.

Experimental

Raman spectra were recorded using the 50x objective of an Olympus microscope on a Dilor XY multichannel Raman spectrometer with 514.5 nm excitation from an Argon ion laser (Coherent). The laser power was 200 mW at the source, and about 10 percent of that at the sample under the microscope. Standard Labspec software was used for recordings. Collection time was 200s, with 3 accumulations for the pink pigment. Spectra were baseline corrected and filtered as needed with the same software in order to remove background fluorescence and excessive noise.

Results and Discussion

The resonance Raman spectrum obtained of the pink pigment shown in Figure 1 could be compared favourably to a series of pink ceramic pigments with the composition $\text{CaO} \cdot \text{SnO}_2 \cdot \text{SiO}_2$ or CaSnSiO_5 reported recently by Faurel *et al.*[1]. The pink colour can be obtained in this particular matrix known as malayaite or tin sphene after doping with a low concentration of chromium. Malayaite was reported as a new mineral in varlamoffite from Malaya by Alexander *et al.*[2]. The synthesis of the pigment is described in recent literature by the authors Lopez-Navarette *et al.*, 2002 and 2003 [3, 4] and Harisanov *et al.*[5]. The optical absorption spectrum that explains the origin of the resonance Raman effect obtained here was reported for a synthetic Cr-doped malayaite sample by Lopez-Navarette *et al.*[4].

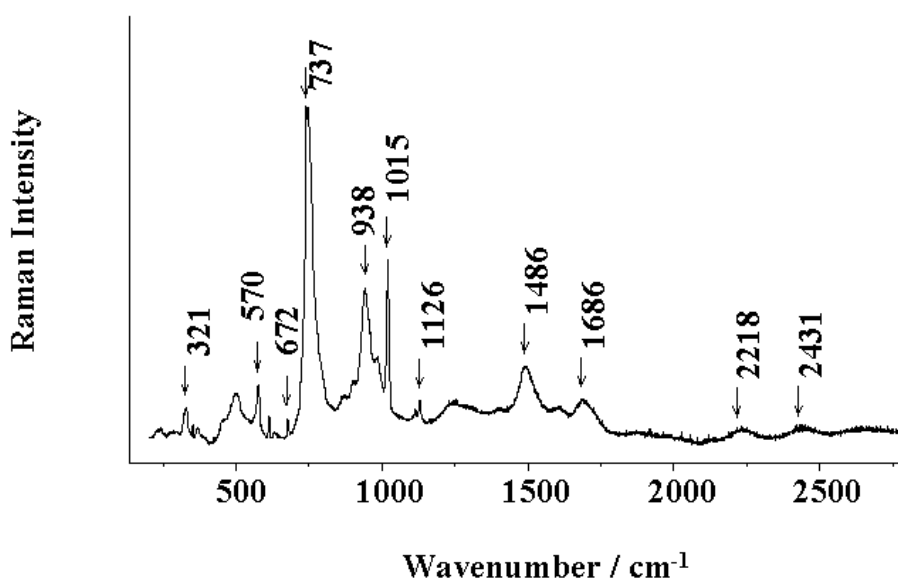


Figure 1. The resonance Raman spectrum (excitation 514.5nm) of the pink pigment on the shard found amongst shards from the shipwreck of the São João Baptista that sunk in 1622 at Cannon Rocks in the Eastern Cape, South Africa.

The additional sharp bands in the spectrum are different from those reported by Faurel *et al.*[1], and these will be interpreted in terms of the matrix for this particular sample. The composition of the ceramic body is also to be considered.

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