Probing the past with state of the art science

One of the breakthroughs in textile coloration achieved during the 19th century was the development of synthetic dyestuffs and in particular those with the colour purple. Prior to this time purple textiles were expensive and relegated to use by royalty or people of high status. Tyrian purple, in use since antiquity, is a natural dye derived from the mucous secretion of predatory sea snails. The early synthetic purple dyes include:

Perkin’s purple or mauve, discovered by Henry Perkin in 1856 is a mixture of four related aromatic compounds and was marketed for 10 years starting in 1859.
Fuchsin or magenta was independently discovered by Hofmann and Verguin in 1858 and was more widely used than mauve.
Crystal violet, one of a family of three methyl violet compounds synthesized by Charles Lauth in 1861, was marketed under the name “Violet de Paris”.
Hofmann's violet which shares the same base structure as methyl violet was discovered in 1863 and is redder.

The identification of specific dyestuffs on textiles, especially when only small amounts of sample are available, is challenging due to a number of complexities including contamination and decomposition. In this work we investigated the purple coloration of three 19th century English dresses and one Australian wedding gown using a combination of thin layer chromatography (TLC) and surface enhanced Raman spectroscopy (SERS).

Fig. 1. Dress 1 circa 1865, dress 2 circa 1898, dress 3 circa 1878 and wedding gown circa 1885.

The dyes were extracted from very small yarn samples and separated on a TLC plate. As the solvent carries the extract molecules up the plate, those with different structures interact differently with the stationary phase resulting in their separation into bands. The use of Raman spectroscopy
allows us to obtain chemical information from these differently coloured areas.

![Diagram of silver nano particles and Raman scattering](image)

Fig. 2. Molecules of the separated dye are transferred onto the silver nano particles resulting in an enhanced Raman scattering signal and dye identification.

Application of a silver colloid to the TLC bands results in the transfer of some dye molecules to the surfaces of the silver nano particles. The electromagnetic (EM) field incident on the silver nano-aggregates is greatly enhanced at the junction between nano particles resulting in a very large enhancement ($>10^4$) in the Raman scattering signal of the dye molecules adsorbed there. This enhancement enables very small quantities of the separated dye molecules to be identified.

The analysis of these dyes revealed important information for conservators and curators of fashion, raising interesting observations and questions. The c.1865 dress containing methyl violet just four years after its initial synthesis suggests that the new synthetic dyes were embraced quite rapidly by the textile dye trade and the fashion world of the day. Perkin’s mauve, an extremely historically significant dye, was produced for less than ten years starting in 1859. Its presence in the c. 1885 Australian made wedding gown is curious. Does the presence of Perkin’s mauve relate to trade delays between Europe and Australia? Or was this precious fabric woven decades earlier and kept for the special purpose of a wedding.

To arrive at a conclusion without further research is difficult, however the questions raised by the results of this study highlight that analysis of this type provides vital material evidence, and opportunities for enhanced provenance and preservation investigations by museum professionals.

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