Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 154 (2016) 185–192

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The purple coloration of four late 19th century silk dresses: A spectroscopic investigation

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ARTICLE INFO

Article history:
Received 12 June 2015
Received in revised form 28 August 2015
Accepted 22 October 2015
Available online 24 October 2015

Keywords:
Surface enhanced Raman spectroscopy
Infrared spectroscopy
Thin layer chromatography
Late 19th century silk dresses
Synthetic purple dyes
Mordants

ABSTRACT

Prior to the 19th century the use of purple dyes for textile coloration was expensive and usually limited to royalty. The discovery of several synthetic purple dyes during the 19th century made the production of purple textiles more affordable and thus more readily available. The identification of the source of the purple coloration is of historical interest. Small yarn samples from four late 19th century silk dresses were analyzed using a combination of thin layer chromatography and surface enhanced Raman spectroscopy, Fourier transform infrared spectroscopy and energy dispersive x-ray spectroscopy. This combination of techniques enabled the analysis of the complex extraction products. While three of the dresses were found to be dyed using methyl violet, the fourth dress was found to be constructed from a warp yarn dyed with methyl violet in the presence of a tannic acid mordant, and a weft yarn dyed with mauve and a tin mordant.

1. Introduction

One of the breakthroughs in textile coloration achieved during the 19th century was the development of synthetic dyestuffs and in particular those with a purple color. Four such dresses, the subjects of this work, are shown in Fig. 1. Prior to this time purple textiles were expensive and relegated to use by royalty or people of high status. Tyrian purple, also known as royal or imperial purple is a natural dye derived from the mucous secretion of predatory sea snails belonging to the family Muricidae. The genus *Bolinus brandaris* L., commonly known as the spiny dye-murex, is found in the eastern Mediterranean. In use since antiquity, the first record of dyeing with Tyrian purple comes from Crete in the 16th century BC [1,2].

The first synthetic purple dyestuff, mauve, was discovered in 1856 by William Henry Perkin [2]. It was originally called Tyrian purple after the ancient natural dye but upon marketing in 1859 it became known as mauve, mauveine or aniline purple [3]. Mauve, the first aniline or basic dye was determined to actually be a mixture of four related aromatic compounds based on the phenazine ring system (dibenzo-*p*-diazine) differing in number and placement of methyl groups and designated as mauve A, B, B2 and C (Fig. 2, top).

In 1858 August Wilhelm von Hofmann and François-Emmanuel Verguin independently discovered the second basic purple dye, fuchsine (Fig. 2, bottom left structure) [4]. This dye, also known as magenta, was patented by Verguin and became more widely used than mauve, the production of which stopped after only 10 years.

Methyl violet is a family of three compounds that differ in the number of methyl groups attached to the amine functional group (see Fig. 2, bottom right 3 structures). The basic structure is closely related to that of fuchsine (Fig. 2, bottom left). Crystal violet, one of the components of methyl violet (methyl violet 10B) was first synthesized in 1861 by Charles Lauth [4]. From 1866 it was manufactured and marketed under the name “Violet de Paris”.

Hofmann's violet which was discovered in 1863, shares the same base structure as methyl violet [3]. It was found that as the number of methyl groups increases, the violet color shifts from more red to more blue. Hofmann's violet, which came on the market in 1866, is a mixture of lowest substitution products and thus is redder compared to methyl violet.

The final synthetic purple dye of this period was benzopurpurin, a direct dye produced by Carl Duisberg in 1885 [5]. This dye, which is bright and highly substantive, is known today as benzopurpurin 4B (C.I. Direct Red 2). The structure of this dye (Supp. Fig. 1) is based on a central bis-phenyl group connected symmetrically by azo linkages to two amino and sulfonate substituted naphtha groups. Due to its two sulfonate groups the dye can also be considered an acid dye and thus it can be applied to silk.

The identification of specific dyestuffs on textiles, especially when only small amounts of sample are available, is challenging due to a number of complexities. The analysis often requires isolation of the dye, which can be a mixture of components including contaminants and

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http://dx.doi.org/10.1016/j.saa.2015.10.024

Fig. 1. Dress 1 circa 1865, dress 2 circa 1898, dress 3 circa 1878 and dress 4 circa 1885 (clock-wise from left top). Details of these dresses are presented in the Experimental section.

decomposition products, from the substrate. The extract would then have to be purified so as to obtain the actual dyestuff. Analytical techniques recently applied to the study of Perkin's purple include high performance liquid chromatography, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectroscopy [6] and surface enhanced Raman spectroscopy (SERS) [7,8].

SERS has been demonstrated to be a valuable tool for the accurate identification of dyes and pigments in materials of historical interest

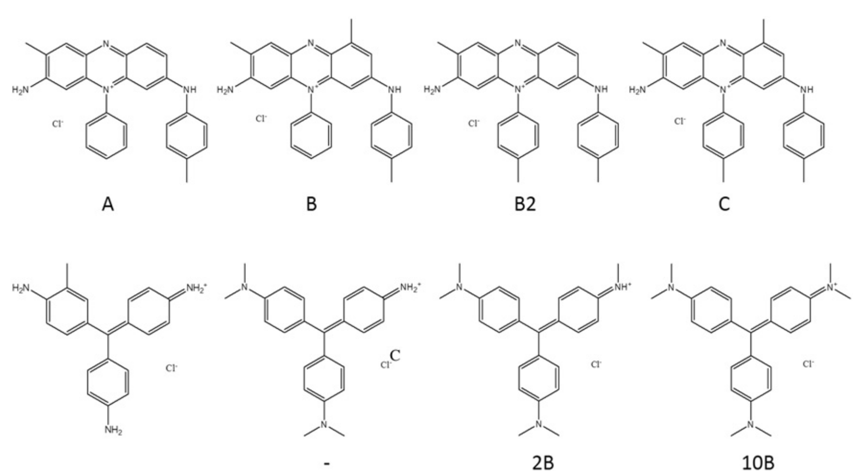

Fig. 2. Structures of mauve A, B, B2 and C (top), fuchsine (left bottom) and methyl violets (right bottom): -, 2B (6B) and 10B or crystal violet.