

# The identification of early synthetic organic dyestuffs using Raman spectroscopy

L.O.E.S. Vermeij<sup>ab</sup>, S. de Groot<sup>a</sup>, and M. R. van Bommel<sup>a</sup>

<sup>a</sup>Netherlands Institute for Cultural Heritage (ICN), P.O. Box 76709, 1070 KA Amsterdam, The Netherlands, +31203054740, [suzan.de.groot@icn.nl](mailto:suzan.de.groot@icn.nl)

<sup>b</sup>Inorganic Chemistry and Catalysis group, Debye Institute for NanoMaterials Science, Department of Chemistry, Utrecht University, The Netherlands.

## Introduction

ICN is in the possession of the 'Schweppe collection', a selection of 65 historically documented synthetic organic dyestuffs from the period 1856-1900 which include most dye classes.

Currently, the identification of synthetic dyestuffs is performed by High Performance Liquid Chromatography (HPLC) coupled to a Photo Diode Array detector (PDA). HPLC requires different systems for acidic and basic dyestuffs [1].

Raman spectra are measured for each of the 65 dyestuffs, both pure dyestuffs and dyestuffs on single wool fibres. These spectra are collected in a reference library and are used to develop a flow chart [2], based on characteristics of functional groups, to distinguish between the different dye classes and between acidic and basic dyestuffs as a pre selection for HPLC.

This poster presents the current state of this work in progress.

## Method

Spectra were measured with a PerkinElmer Raman Spectrograph 400F equipped with a CCD detector using a diode laser operating at 785 nm with a maximum power of 80 mW.

The pure dyestuff sample size was about 1 mm<sup>2</sup>. To prevent sample destruction low laser power, 5-10 mW, and therefore long accumulation times, 40-360 s, were necessary. Single wool fibre spectra were obtained with an Olympus microscope using a 50x objective and accumulation times of 360 s. The single wool fibres were irradiated with a power of 75 mW without destruction of the fibre.

## Results

Dyestuffs from dye classes aminoketone, azo, diphenylmethane, indigoid, nitro, thiazine, triarylmethane and xanthene gave 56 spectra with good quality and a few spectra that show fluorescence. Nevertheless, these fluorescent spectra are useful for the flow chart. The addition of a drop of water to some dyestuffs can reduce fluorescence [Fig. 1].

Spectra of dyestuffs from dye classes anthraquinone [3], azine, and quinoline show extreme fluorescence, from these spectra no information for the flow chart was gained.

The measured dyed single wool fibres gave 35 spectra with good quality, 10 poor spectra, and 20 spectra where only wool was visible [Fig.2].

The flow chart is composed to distinguish between the different dye classes and between acidic and basic dyestuffs [Fig. 3].

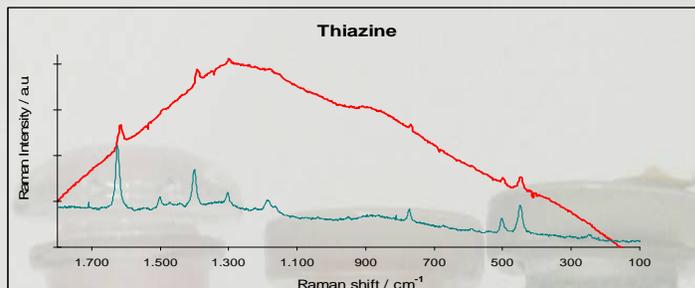


Fig. 1: Raman spectra of Thiazine measured with 785 nm laser. Blue line: Thiazine with an additional drop of water, power of 75 mW, accumulation time 360 s. Red line: pure Thiazine, power of 7 mW, accumulation time 360 s.

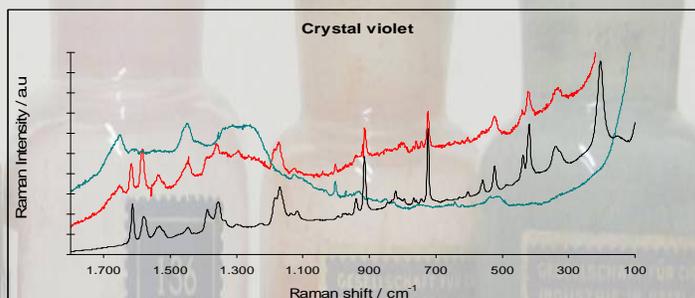


Fig. 2: Raman spectra of Crystal violet measured with 785 nm laser. Black line: Crystal violet, power of 5 mW, accumulation time 40 s. Blue line: Pure wool fibre, power of 75 mW, accumulation time 360 s. Red line: wool fibre dyed with Crystal violet, power of 75 mW, accumulation time 360 s.

## Discussion and Conclusion

Raman spectroscopy provides the possibility to develop a flow chart to distinguish between the different dye classes and between acidic and basic dyestuffs based on their Raman shift. However, some dye classes show only fluorescence and are therefore not inserted into the flow chart.

Addition of a drop of water reduces the contribution of fluorescence in several cases resulting in higher quality spectra.

To improve spectra of dyestuffs which are poor Raman scatterers and/or show extreme fluorescence the possibility of using Surface Enhanced Raman Scattering (SERS) will be explored.

## Acknowledgements

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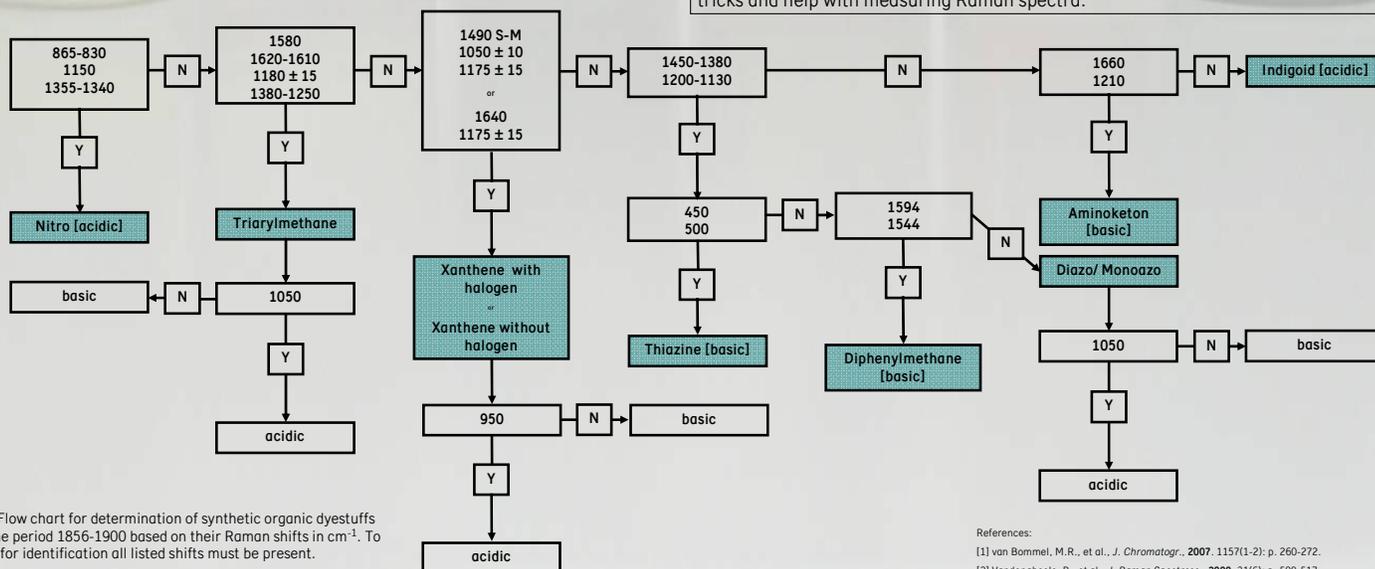


Fig. 3: Flow chart for determination of synthetic organic dyestuffs from the period 1856-1900 based on their Raman shifts in cm<sup>-1</sup>. To qualify for identification all listed shifts must be present.

## References:

- [1] van Bommel, M.R., et al., *J. Chromatogr.*, **2007**, 1157(1-2): p. 260-272.
- [2] Vandenberghe, P., et al., *J. Raman Spectrosc.*, **2000**, 31(6): p. 509-517.
- [3] Chen, K., et al., *J. Raman Spectrosc.*, **2006**, 37(4): p. 520-527.