Combined vibrational and chromatographic study of historical lakes and dyes

F. Gabrieli[1,4], D. Uldanck[2], I. Bonaduce[2], E. Buzzegoli[3], I. Degano[2], D. Kunzelman[3], C.Miliani[1], F.Modugno[2], F.Rosi[1]

(1) Istituto CNR di Scienze e Tecnologie Molecolari (CNR-ISTM), via Elce di Sotto 8, I-06123 Perugia, Italy.
(2) Università di Pisa, Dipartimento di Chimica e Chimica Industriale, via Moruzzi 3, Pisa (Italy)
(3) Opificio delle Pietre Dure di Firenze, Via degli Alfani 78 Florence (Italy)
(4) Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy.

Twenty different formulations of red lakes belonging to the Lefranc & Bourgeois Archive in Le Mans (France) and dating from 1890 to 1921 have been investigated using spectroscopic and chromatographic techniques. In this historical period many such variants or combinations were exploited to improve the quality of artists' pigments. Therefore advances in methods for characterisation and analytical models for data interpretation, are particularly important, especially for conservation purposes due to different degrees of stability of the various formulations. The study was conducted with the goal of combining information from Raman spectroscopy and High Performance Liquid Chromatography (HPLC) for the characterization of organic pigment formulations.

Raman as well as Surface Enhanced Raman spectroscopy (SERS) were applied for the study of the historical samples. Conventional Raman offered the opportunity to directly investigate the molecular composition of the unknown materials discriminating between the formulations based on mordent-based lake pigments and dyestuffs. When fluorescence complicated the conventional Raman measurements SERS experiments permitted the identification of the main colorants and also some minor components. In absence of luminescence problems, SERS and Raman provided complementary information about the material composition.

HPLC analyses, using both DAD and ESI-Q-ToF detectors allowed for the identification of several minor components and ultimately to distinguish among natural and synthetic formulations or to discriminate between different recipes for the extraction of dyes from the raw materials.

Advantages, shortcomings, as well as complementarities of the two methods will be discussed. The study was supplemented by an investigation based on multispectral imaging at various wavelengths (NIR, UV fluorescence, reflected UV, and corresponding false colour reconstructions) proposed as a non-invasive tool to guide educated and selective samplings.

Acknowledgments

This research was funded by MIUR (FIRB 2012, FUTURAHMA-Tecniche pittoriche, critica delle varianti e problemi conservativi. Tra Futurismo e ritorno al classico (1910-1922), RBFR12PHL4_002.