



**SOCIETÀ CHIMICA ITALIANA**  
Divisione di Chimica dell'Ambiente e dei Beni Culturali

**Combined vibrational and chromatographic study of historical lakes and dyes**

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### **1. Introduction**

The study of atelier materials and of historical commercial formulation of paint materials has recently gain new interest in the field of conservation science applied to modern and contemporary art. Assessing the composition of the original materials purchased by artists can guide not only their identification in actual works of art, but also their restoration and preventive conservation. Moreover, when dealing with artists' materials the development of non invasive and non destructive analytical techniques is of paramount importance, being the collection of actual samples often impossible. Thus, the need has risen for reliable databases of materials studied by non invasive techniques and validated by micro-destructive state-of-the-art protocols.

### **2. Aims of the study and results**

More than thirty historical red lakes and colorants (dating from 1890 to 1921), provided by the Lefranc&Bourgeois Archive in Le Mans (France), have been investigated through a combined analytical approach mainly based on vibrational spectroscopy and chromatographic techniques. The focus of the research was to develop and apply a methodological approach based on the combination of the two techniques of election for the identification of such complex and interesting organic materials, namely: High Performance Liquid Chromatography (using DAD and ESI-Q-ToF detectors) and Raman spectroscopy. Raman as well as Surface Enhanced Raman spectroscopy (SERS) were applied for the study of the pigment samples. Conventional Raman offered the opportunity to investigate the molecular composition of the unknown materials, discriminating among the samples based on mordent-based lake pigments and dyestuffs. When fluorescence complicated the conventional Raman measurements, SERS experiments permitted the identification. In absence of luminescence problems, SERS and Raman provided complementary information about the material composition.

HPLC-DAD and HPLC-ESI-Q-ToF analyses allowed us to identify minor components in lakes and dyes composition, to discriminate between different recipes for the extraction of colours from the raw materials, and ultimately to distinguish among natural and synthetic formulations.

### **3. Conclusions**

The integration of vibrational and chromatographic data highlighted either agreements, apparent discrepancies, as well as complementary results that will be discussed. The analytical approach was supplemented by preliminary investigation based on multispectral imaging of the samples at various wavelengths (NIR, UV Fluorescence, Reflected UV, and corresponding False Colour reconstructions) proposed as non-invasive tools either for the material characterization and as a guideline for selective sampling. The survey was completed also with Fourier Transform Infrared (FTIR) and X-ray Fluorescence (XRF) analyses to assess the presence of inorganic salts used in the pigment production.



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In studying the transition period corresponding to industrial revolution, when many such variants or combinations were hypothetically possible in paint formulation, 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 materials.