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Identification and characterization of the Indian Yellow dyestuff and its degradation products in historical oil paint tube by liquid chromatography mass spectrometry†

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An analytical protocol for identification of dyes using reversed phase liquid chromatography-mass spectrometry with atmospheric pressure electrospray ionization (LC-ESI/MS) is presented. The developed method has been successfully applied in identification of euxanthic acid and euxanthon, the main components of the Indian Yellow dye in a historical oil paint tube produced by Richard Aïnès, a recognizable French company supplying art materials. The paint tube from which the sample has been taken belonged to a famous Polish painter from the 19th century – Jan Matejko. Various methods of extraction of the Indian Yellow dyestuff from the oil paint were systematically investigated. Efficiencies of the nine extraction procedures (based respectively on use of: HCl, HF, acetylacetone, and formic, tartaric, oxalic, trifluoroacetic and citric acids) were compared on the basis of euxanthic acid to euxanthon chromatographic peak areas ratio. It was found that use of HF, acetylacetone and the organic acids ensures a non-destructive recovery of intact acid-labile components, while the strong HCl mineral acid not only allowed extraction of the colorant from the binding medium, but also decomposes the glycosidic dye into the parent aglycon and causes a formation of methyl euxanthonate and numerous products which may hinder the proper identification of the dye. The Indian Yellow was fully characterized with the use of spectrochromatographic techniques for the first time. The fragmentation pathways of the identified colorant ions and their degradation products were proposed.

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Introduction

Analysis of natural dyes in historical objects is fundamental for the development of effective and appropriate conservation strategies; to determine origin of an artifact; as well as to obtain historical information necessary for the purposes of documenting an artwork and a work's authenticity. Identification of a particular dyestuff is usually based on the presence of its main components, while minor components are important for differentiating between dyes originating from closely related sources.¹ Numerous analytical techniques have been utilized to characterize dye based pigments, including vibrational spectroscopic techniques (IR and FTIR), X-ray fluorescence (XRF) or Raman and UV spectroscopy. For many years, examination of dyestuff components has been generally unfeasible due to the

unacceptably large size of sample necessary to solubilize the contained dyestuffs prior to spectroscopic or chromatographic analysis. Determination of dyes extracted from paint samples became possible when the analytical methods became more sophisticated, and the sample size might possibly be reduced, although the sample preparation procedure can still have crucial effects on the analytical results. Natural organic dyes in objects of the cultural heritage are commonly identified by means of the high performance liquid chromatography (HPLC) as it was reviewed in detail by Rosenberg² and recently by Pauk *et al.*³ Nowadays, HPLC with mass spectrometric detection offers solution to difficult problems encountered in the analysis of real samples of unknown composition, especially ones connected with the lack of proper analytical standards. While HPLC-MS has been used for the identification of natural organic dyes in the historical textile samples, this method has not been widely employed in case of samples extracted from oil paints.

Our study is aimed at identification of organic dyes in the yellow oil paint used by Jan Matejko (1838–1893), and extends the LC-MS analytical technique for identification of the coloring matters present in the art paint tube with partially preserved paper label with the name *Jaune de Indien*. Calcium and

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