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Technical Note

A definitive analytical spectroscopic study of Indian yellow, an ancient pigment used for dating purposes

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ABSTRACT

The Raman spectrum of tartrazine has been mistakenly reported as being that of Indian yellow in the literature, which has serious consequences for the identification of this pigment in art works regarding their authentication. Unlike tartrazine, Indian yellow (a natural mixture of the magnesium and calcium salts of euxanthic acid) exhibits in its Raman spectrum a strong fluorescent background when visible excitation is used, however, excitation in the near infrared (1064 nm) permitted the observation of the Raman bands from the raw pigment with the main features placed at 1346, 1368, 1425, 1441 and 1626 cm^{-1}. Indian yellow identification was assured by ^{1}H and ^{13}C Nuclear Magnetic Resonance characterization and the complete assignment of the proton and carbon resonances was accomplished using heteronuclear single quantum correlation (HSQC), heteronuclear multiple bond correlation (HMBC), nuclear overhauser effect spectroscopy (NOESY) and ^{1}H–^{1}H correlation spectroscopy (COSY). Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and X-ray fluorescence (XRF) analyzes were also conducted on a genuine sample of this historical pigment.

1. Introduction

A major factor in the deployment of analytical Raman and infrared spectroscopy for the characterization of pigments in works of art is the existence of a database in the literature which facilitates the comparison of spectral signals with those of standards for the recognition of the spectra recorded from single pigments and from components in admixture. The interpretation of these spectral data and their assignment to particular molecular species enables the presence or otherwise of a pigment to be determined in the specimens which itself can be used to identify materials which may be out-of-context chronologically in disputed artworks. There are several notable case studies in the literature which exemplify this forensic art role for vibrational spectroscopy, including the Vinland Map [1], a Syriac lectionary (also known as Angels with Black Faces) [2], the exposure to out-of-context pigments on a Chagall painting [3] and a papyrus supposedly originating from Ramses I [4].

Caution must always be exercised in the interpretation of spectroscopic data from ancient art works because of the natural degradation experienced by pigments and the use of contemporary alternatives for unrecorded restoration, but perhaps the most difficult area of assessment occurs where a pigment has been misnamed or where a disputed nomenclature exists. A case in point regarding the latter is “minium” which in Roman art was red lead (lead(II) lead(IV) tetroxide) but the same terminology in mediaeval palettes was used to describe mercury(II) sulfide, which although originally termed cinnabar itself became known as vermilion in Renaissance times [5]. The most difficult area, however, is where the standard spectra for a pigment in the literature do not actually relate to the original pigment at all but refer to a later replacement in artists’ palettes—a situation which has occurred on account of supply difficulties or non-availability of the original material. The

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resultant identification, therefore, of an original naturally sourced pigment from spectroscopic data interpretation is prejudiced by inappropriate characteristic spectral signatures belonging to a completely different synthetic pigment.

Indian yellow is usually described chemically as the magnesium salt of euxanthic acid, $C_{19}H_{16}O_{10}$, which has the official chemical name: (2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-Trihydroxy-6-(8-hydroxy-9-oxo-9H-xanthen-2-yloxy)-tetrahydro-pyran-2-carboxylic acid. Hence, we can infer from this formulation that Indian yellow is Mg $(C_{19}H_{15}O_{10})_2$, but there are reports that it also contains significant quantities of the analogous calcium salt, both salts occurring as the basic hydrates [6]. The origin of Indian yellow is apparently well documented in the literature and is said to be derived from the urine of cows fed on a diet of mango leaves [7] which was then evaporated and the resultant precipitate was formed into small balls by hand—the toxins in the leaves had a debilitating effect on the cows, hence the ban on its production and importation into the UK and afterwards worldwide from 1908 [8]. However, Finlay in her book [9] questions this origin and claims that the whole idea was generated from a single and perhaps disputable observation in an Indian village when Mukharji [10] studied the process in 1883/4 in Mirzapur, north-east Bihar, India. The nature of the process meant that the product was of indefinite composition and was further complicated by unrecorded attempts at purification by European color suppliers. It is reported that typically, different grades of the pigment could contain 34–65% of euxanthic acid associated with a few percent of Ca and Mg [7]. Indian yellow pigment was in use in India in the guise of *puree*,*peoli* and *gogili*, in the fifteenth century until it was subsumed four hundred years later by other synthetic alternatives, also called Indian yellow, comprising azo yellow dyestuffs, so creating a problem for modern analytical differentiation and characterisation as highlighted above. There is even a report of cobalt yellow (Aureolin) being marketed and used as Indian yellow [11]. One of the replacement pigments for Indian yellow in the 20th Century was tartrazine [12], $C_{16}H_9N_4Na_3O_9S_2$:trisodium-4E-5-oxo-1-(4-sulfonatophenyl)-4-((4-sulfonatophenyl)hydrazono)-3-pyrazolecarboxylate, for which the name Indian yellow was maintained, so creating a confusion for modern analysts.

Evidence of the adoption of Indian yellow into western art stems firstly from Dutch paintings in the 17th Century and later usage in English art in the 1780s [13] where it was believed to originate from the urine of animals fed on a diet of turmeric, giving its bright yellow color. Indian yellow was prized as a watercolor because of its transparency and light-fastness; the earliest mention of Indian yellow in Western literature is by Gartside [14] and Varley [15]. It was believed to be a superior yellow to gamboge and especially useful for making green colors and was listed as one of the most important pigments in landscape and figure painting [16].

It seems that the current literature data which define the characteristic Raman spectroscopic bands for Indian yellow pigment actually are based on the modern tartrazine substitute and these have also been adopted as definitive erroneously for the ancient pigment: there is therefore a need to characterize the genuine pigment to enable its proper verification and presence in works of art predating the early 20th Century, and this is the purpose of this spectroscopic and analytical study.

2. Experimental

Indian yellow was kindly provided from the specimen archive of L. Cornelissen & Son (London) and tartrazine was purchased from Sigma–Aldrich; both of these were analyzed as received.

The FT-Raman spectra were obtained using a Bruker RFS 100/S equipment, fitted with a liquid N_2 cooled Ge detector and with a Nd^{3+}/YAG laser; spectral resolution was 4 cm^{-1} and the laser power was ca. 50 mW at the sample. FTIR spectra were obtained with a LUMOS microscope (Bruker), operating with an ATR objective (Ge crystal) and fitted with a liquid N_2 cooled MCT detector; the spectral resolution was also 4 cm^{-1}.

X-ray fluorescence (XRF) data were obtained with a Bruker Tracer III (Rh source) operating at 40 kV and 17 or 30 μA. Micrographs and elemental analyses were obtained using both a field environmental scanning electron microscope (FESEM) Zeiss: Supra 40 coupled with an energy-dispersive X-ray spectrometer (SEM-EDS) INCA X Sight (Oxford Instruments) and with a Jeol JSM-7401 F Field Emission Gun Scanning Electron Microscope (FEG-SEM), using LEI (lower secondary electron image) detection configuration at 1.0 kV and with a 7.7–8.1 mm working distance; in this case, the EDS signals were measured using a Thermo Scientific Noran System Six fitted to a Pioneer detector coupled to the FEG-SEM equipment.

^{1}H NMR, ^{13}C NMR, HSQC, HMBC, NOESY and COSY spectra were recorded on a Bruker AM 500 spectrometer. Chemical shifts (δ) are given in ppm downfield from TMS (tetramethylsilane) as the internal standard. 2D NMR spectra were obtained using standard Bruker software. High resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed on a Bruker micrOTOF-Q II mass spectrometer in the negative ion mode.

Analytical HPLC with diode array detection (HPLC-DAD) was carried out on a Gilson 506C HPLC system using a Phenomenex Gemini 5 μm column (25 cm × 4.6 mm internal diameter). Gradient elution was performed using mixtures of MeOH and 1% (v/v) aqueous orthophosphoric acid as solvents. The gradient started with 36% MeOH during 5 min and was raised to 90% MeOH within 10 min, followed by 20 min at this condition. Solvents utilized in the HPLC were filtered through a 0.45 mm nylon filter prior to use. The sample of Indian yellow was dissolved in a mixture of ACN/MeOH/DMSO (1:1:1, v/v/v). Hydrolysis of the Indian yellow sample was performed following the procedure described previously [17]. The sample solutions were filtered through inorganic membrane filters of 0.2 mm prior to injection. The flow rate was 0.8 ml/min and the detection wavelength was 255 nm.

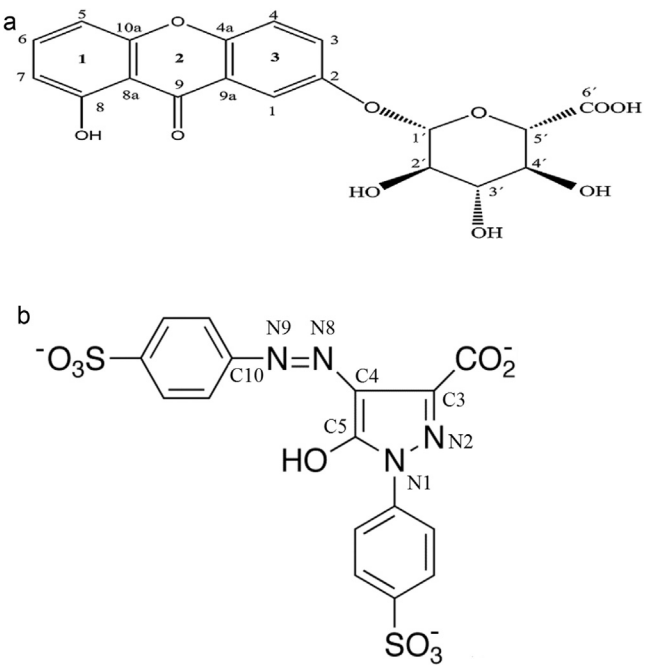

Fig. 1. Chemical structures: (a) euxanthic acid and (b) tartrazine. The atoms are labeled for the spectroscopic assignment (Raman and NMR).