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Technical Note

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

Dalva L.A. de Faria[a,b,*], Howell G.M. Edwards[c], Valeria Careaga[d], Nicholas Walt[e], Marta S. Maier[d]

[a] Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748, Butantã, 05508-000 São Paulo, SP, Brazil
[b] Interinstitutional Graduate Program in Museology (PPGMus-USP), University of São Paulo, Av. Prof. Almeida Prado, 1466, São Paulo, SP CEP 05508-070, Brazil
[c] Department of Chemical and Forensic Sciences, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK
[d] UMYMFOR and Departamento de Química Orgánica, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, 1428 Buenos Aires, Argentina
[e] L. Cornelissen & Son Ltd., 105 Great Russell Street, London WC1B 3RY, UK

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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

* Corresponding author at: Laboratório de Espectroscopia Molecular, Depto. de Química Fundamental—Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, Butantã, 05508-000 São Paulo, SP, Brazil.
E-mail addresses: dlafaria@iq.usp.br, dalvalux@gmail.com (D.L.A. de Faria), h.g.m.edwards@bradford.ac.uk (H.G.M. Edwards), pcareaga@qo.fcen.uba.ar (V. Careaga), nw@cornelissen.com (N. Walt), maier@qo.fcen.uba.ar (M.S. Maier).

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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.

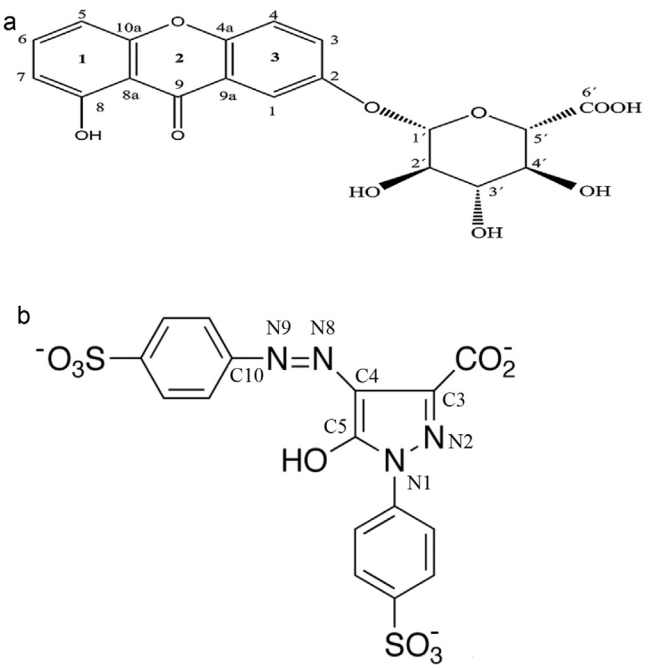

Fig. 1. Chemical structures: (a) euxanthic acid and (b) tartrazine. The atoms are labeled for the spectroscopic assignment (Raman and NMR).

Table 1
NMR data of euxanthic acid (Fig. 1a).[a,b]

Position	δ_H (J in Hz)	δ_c	HMBC	COSY	NOESY
1	7.72 (1H, d, J = 3 Hz)	109.8 CH	C-3, C-4a		
2		153.6C			
3	7.62 (1H, dd, J = 9.2 Hz, 3 Hz)	126.6 CH	C-4a, C-1		H-1′
4	7.68 (1H, d, J = 9.2 Hz)	119.8C	C-2, C-9a, C-4a		
4a		151.4C			
5	7.08 (1H, bd, J = 8,3 Hz)	107.4 CH	C-10a, C-8a	H-6, H-7	H-6
6	7.74 (1H, t, J = 8,3 Hz)	137.5 CH	C-8, C-10a	H-5, H-7	H-5, H-7
7	6.83 (1H, bd, J = 8,3 Hz)	110.1 CH	C-8, C-5	H-6, H-5	H-6
8		161.1C			
8a		108.5C			
9		181.5C			
9a		120.3C			
10a		156.1C			
1′	5.18 (1H, d (7,44)	101.5 CH	C-7	H-2′	H-3, H-3′, H-5′
2′	3.33 (1H, m)	73.1 CH	C1′, C5′	H-1′	
3′	3.35 (1H, m)	75.7 CH	C4′		H-1′, H-5′
4′	3.42 (1H, m)	71.2 CH	C3′, C6′	H-5′	
5′	3.97 (1H, m)	75.6 CH	C4′, C1′, C3′, C6′	H-4′	H-1′, H-3′
6′		170.4C			

[a] Recorded at 500 (^{1}H) and 125 MHz (^{13}C) in deuterated dimethylsulfoxide (DMSO-d_6) with a drop of non deuterated trifluoroacetic acid (TFA).
[b] The assignments were based on ^{1}H, ^{1}HCOSY, HMBC, HSQC, TOCSY, and NOESY experiments. Signal multiplicities were abbreviated by d (doublet), dd (doublet of doublets), bd (broad doublet), and m (multiplet).

3. Results and discussion

Euxanthic acid ($C_{19}H_{16}O_{10}$, Fig. 1a) is a naturally occuring glucuronide of euxanthone (a derivative of dibenzo-γ-pyrone), and its synthetic analog was prepared for the first time in 1905, by the reaction of diacetylbromoglucuronolactone with the potassium salt of euxanthone [18]. As mentioned before, Indian yellow is composed by Mg and Ca salts of euxanthic acid, therefore, the first step in the present investigation was to make sure that the pigment under investigation was the genuine historical pigment.

SEM-EDX data were obtained from the pigment powder dispersed on a copper tape, using a low accelerating voltage (10.0 kV) because the sample was not metal or carbon coated (higher voltages caused charge accumulation on the sample).

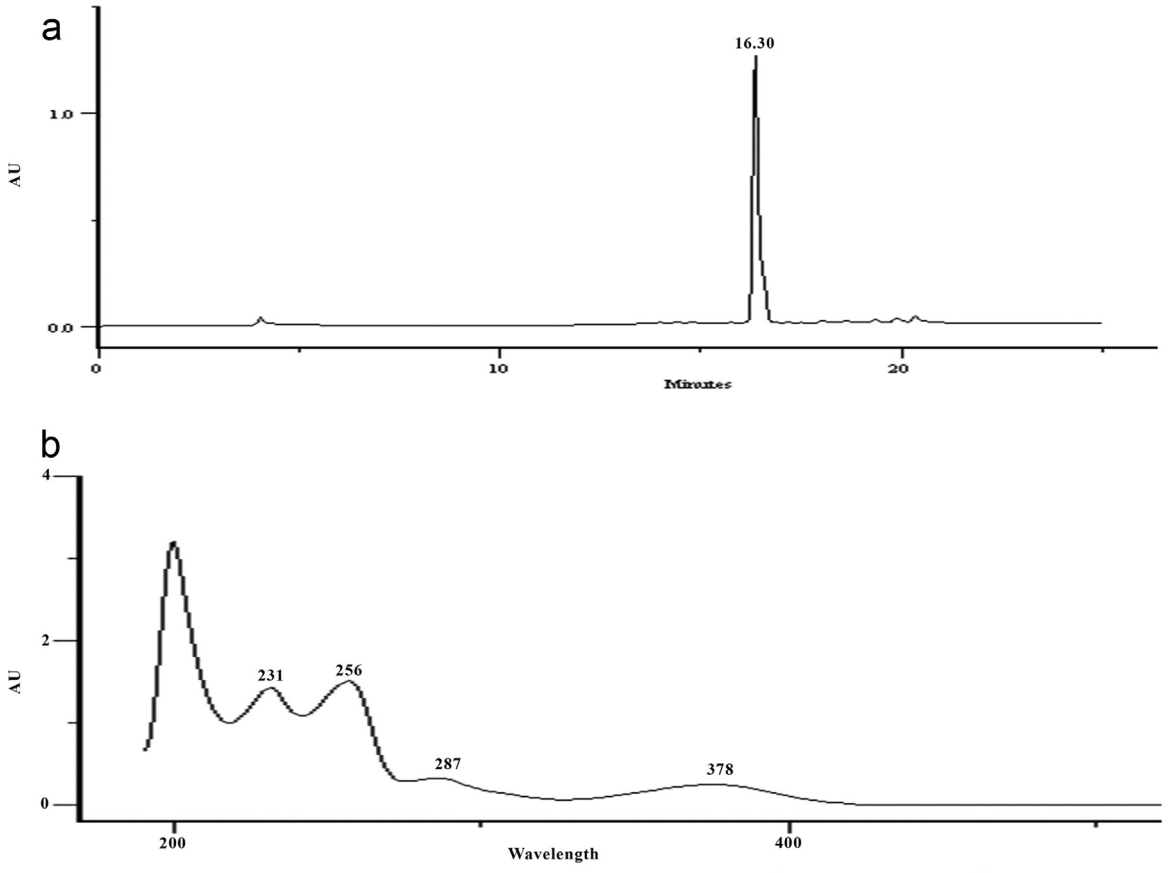

Fig. 2. (a) HPLC chromatogram of the ACN/MeOH/DMSO extract of the Indian yellow sample. (b) UV spectrum of the peak at 16.30 min.

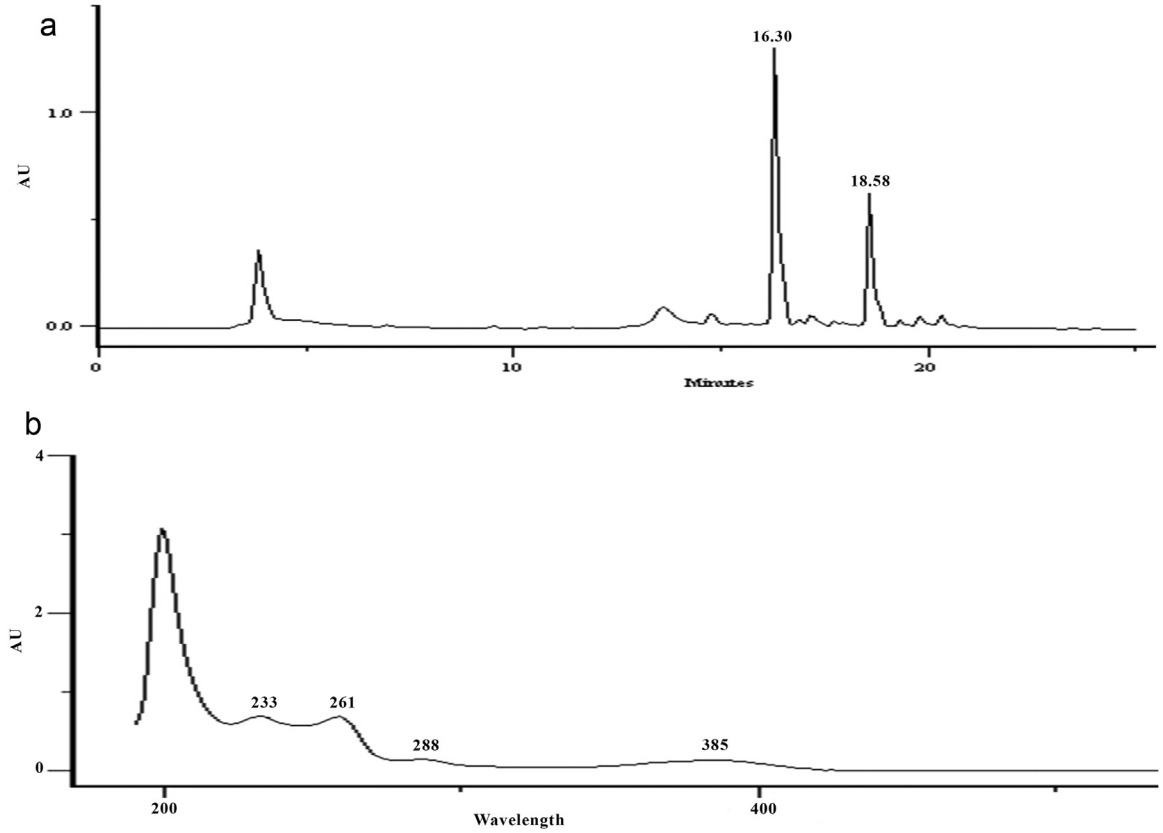

Fig. 3. (a) HPLC chromatogram of the MeOH/3 mol L^{-1} HCl extract of the Indian yellow sample. (b) UV spectrum of the peak at 18.58 min. The UV spectrum of the peak at 16.30 min is the same as that shown in Fig. 1.

Morphologically, the pigment is a mixture of plate-, needle- and undefined-shaped microcrystals (Fig. S1, Supplementary material). Chemically, EDX spectra obtained from different spots and using two different instruments provided the same elemental composition: C, O, Mg, K, Ca and minor amounts of Si, S, P, Cl, Fe and Al. The chemical composition changes slightly from spot to spot, indicating sample heterogeneity. XRF spectra clearly confirm the presence of K and Ca in the sample (Fig. S2, Supplementary material). These findings are in agreement with a previous analysis available in the literature [12].

The Indian yellow sample was also investigated, as received, by HR-EI-MS in the negative ion mode and showed a $(M-H)^-$ ion at m/z 403.0670 (calculated for $C_{19}H_{16}O_{10}$ $(M-H)^-$: 403.0671) and a product ion at m/z 227.0352 (calculated for $C_{13}H_8O_{14}$ (euxanthone–H)$^-$: 227.0350) by loss of the glucuronic acid moiety of euxanthic acid (Fig. 1a). The assignment of ^1H and ^{13}C NMR spectroscopic data of euxathic acid (Table 1) was based on HSQC, HMBC, NOESY and ^1H–^1H COSY spectra. To the best of the authors' knowledge, it is the first time that euxanthic acid has been fully characterized by ^1H and ^{13}C NMR spectroscopy.

Solubilization of the sample in a mixture of acetonitrile/methanol/dimethylsulfoxide (ACN/MeOH/DMSO) 1:1:1 (v/v/v) and further analysis of the solution by HPLC-DAD revealed the presence of one chromatographic peak at the retention time of 16.30 min with absorbance bands at 231, 256, 287 and 378 nm in the UV spectrum (Fig. 2), in accordance with reported data [19]. Hydrolysis of the sample in MeOH/3 mol L^{-1} HCl following a procedure previously described for the analysis of dyes and lakes [17] and analysis by HPLC-DAD of the acidic methanolic extract showed two chromatographic peaks at 16.30 (euxanthic acid) and 18.58 min (Fig. 3). The UV spectrum (Fig. 3b) of the peak at 18.58 min showed bands at 233, 261, 288, and 385 nm and was assigned to the aglycone euxanthone on comparison with reported data [19]. The acid treatment of the sample partially hydrolyzes the glycosidic bond giving a mixture of euxanthic acid and its aglycone.

From all of these analytical data it is beyond any doubt that the pigment specimen investigated here is what was known as Indian yellow in ancient times. The historical records for such pigment are very scarce and its physico-chemical characterization has been rather sparse. This is particularly true in the case of vibrational

Table 2
Tartrazine: band positions, relative intensities and assignment (extracted from Ref. [24]).

Band position and relative intensity	Assignment
1598 (vs)	ν(ph-1, ph-2 quadrant); ip C—H def. (ph-1, ph-2); δ(OH); $\nu_{as}(COO^-)$
1502 (s)	ν(ph-2); ν(C4=C5)
1470 (m)	ν(C—H) (ph-1, ph-2); ν(N8=N9—C10)
1357 (s)	ν(—C4—N8=N9—C10—); $\nu_s(COO^-)$
1216 (m)	τ(C—H); δ(N2=C3—C4); ν(C4=C5)
1177 (m)	δ(ph-2); ν(C4—N8); ν(C10—N9)
1129 (s)	op C—H def. (ph-1, ph-2)

Abbreviations: vs = very strong; s = strong; m = medium; ip = in plane; op = out of plane; ν = stretching; ν_s = symmetric stretching; ν_{as} = antisymmetric stretching; δ = bending; τ = twisting.

spectroscopy, especially Raman spectroscopy, and from an extensive search in the literature the Raman spectrum which is now adopted as the characteristic standard for Indian yellow corresponds, in fact, to tartrazine ($C_{16}H_9N_4Na_3O_9S_2$, Fig. 1b), a synthetic monoazo dye first prepared in 1884 by Ziegler and Locher [20] by the condensation of phenyl hydrazine-4-sulfonic acid and dioxosuccinic acid using pyrazolone as coupling agent.

Tartrazine is currently used as a food colorant (E102, F&D Yellow 5, C.I. 19140 and acid yellow 23) and it has been investigated as a potential neoplastic [21] and allergenic agent [22]; currently, most of the studies published in the literature are linked to the health implications arising from its use [23].

The Raman spectrum of tartrazine has been discussed in detail by Peica et al. [24] who used DFT calculations to support the band assignment. The main bands of the solid dye and their respective assignments are given in Table 2; the bands with the most significant contribution from the azo group (—N=N—) are seen at 1470 cm^{-1} and 1357 cm^{-1}.

Comparison of the spectrum reported by Peica et al. [24] for tartrazine and the spectra ascribed by several authors to Indian yellow pigment [25–27] reveal that they are indistinguishable; therefore, as far as the authors are aware all the Raman spectra reported in the literature as belonging to Indian yellow hitherto are in fact those of tartrazine. This was already suspected by Sodo et al. [28] when analyzing mark pen inks by Raman spectroscopy, however, the authors were unable to provide a Raman spectrum of a genuine Indian yellow specimen to support their conclusions.

The vibrational spectra of Indian yellow are shown in Fig. 4 and the main bands are listed in Table 3, together with band assignments that were supported by DFT calculations for the euxanthate ion; in Fig. 5 the spectra after baseline correction are detailed in the 600–1800 cm^{-1} spectral window. The Raman spectrum of Indian yellow (baseline corrected) and tartrazine are compared in Fig. 6 and it is clear that the main features observed in the tartrazine spectrum are not observed in that of the Indian yellow. Excitation in the NIR (1064 nm) was the only condition that afforded a vibrational Raman spectrum because a high luminescence background dominated the spectrum when excitation in the visible (457.9 nm, 488 nm, 514.5 nm, 532 nm, 632.8 nm and 785 nm) was used. This is possibly the main reason why the Raman spectrum of Indian yellow has never been reported hitherto and it is very likely that in the near future, when dispersive Raman microspectrometers using 1064 nm excitation become more widely used, this pigment will be more often detected in artworks from the revised standard characteristic bands cited in this work (the current FT-Raman microscopes require high laser power at the sample what can damage sensitive specimens like the pigment here investigated, whereas dispersive instruments are more efficient permitting the use of much lower laser powers).

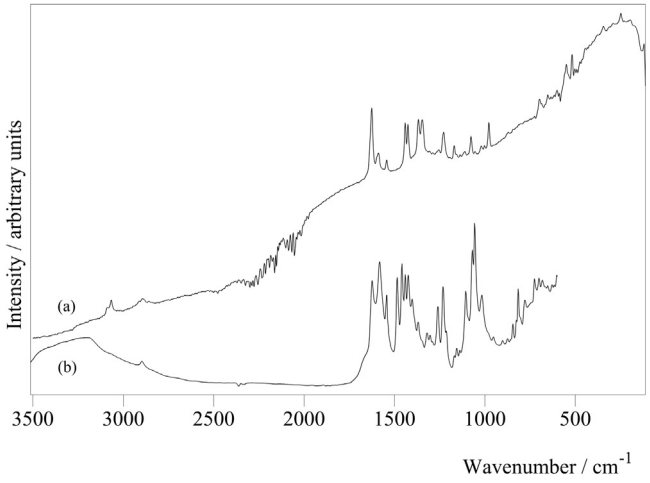

Fig. 4. (a) FT-Raman and (b) μFTIR-ATR spectra obtained from a genuine Indian yellow sample. Even with excitation in the NIR a significant luminescent background is observed in the FT-Raman spectrum.

Curiously, one of the most cited characteristics of genuine Indian yellow as a pigment is its luminescence, therefore it is intriguing why the ease of obtaining its Raman spectrum in paints was never called to the attention of the academic community; clearly, we can now explain the situation based in the fact that the "Indian yellow" was actually tartrazine.

The Indian yellow Raman spectrum is dominated by strong bands at 1346, 1368, 1425, 1441 and 1626 cm^{-1}, ascribed to euxanthic acid ring vibrations, whereas the strongest features observed in the μFTIR-ATR (1054, 1068, 1230, 1423, 1439, 1458, 1484, 1582, 1624 cm^{-1}) have a clear involvement of the —OH, carbonyl and carboxylate vibrations.

Table 3
FT-Raman and μFTIR-ATR spectra of Indian yellow: band positions of the main features with the respective relative intensities and tentative assignment based in DFT calculations for euxanthate ion.

FT-Raman	FTIR	Assignment[a]
	815 (m)	τ(O—H)(C-4′) + $\delta(COO^-)$
978 (m)	979 (vw)	$\delta(C—C)_{eux} + \delta(C—H)_{eux} + \delta(C—C)_{gluc} + \delta(C—H)_{gluc} + \delta$(O—H)(C-2′)
1020 (vw)	1016 (m)	$\delta(C—C)_{eux}(1) + \delta(C—H)_{eux}(1) + \delta$(O—H)(C-8) + ν(C—O—C)(2)
1054 (vw)	1054 (vs)	$\nu_{as}(C—O—C)_{gluc}$
	1068 (s)	$\delta(C—C)_{gluc} + \delta(O—C_{gluc}) + \delta$(O—H)(C-2′) + δ(O—H)(C-3′)
1111 (vw)	1105 (m)	$\nu(C—C)_{eux} + \delta(C—H)_{eux} + \nu_{as}(C_{eux}—O—C_{gluc}) + \delta$(O—H)(C-8) + ν(C—OH)(C-2′) + ν(C—OH)(C-4′) + δ(O—H)(C-8)
1229 (m)	1230 (s)	$\nu(C—C)_{eux}(3) + \delta\ (C—C)_{eux}(3) + \delta$(C—O—C)(2) + $\nu(C_{eux}—O_{gluc}) + \delta$(O—H)(C-8)
1254 (vw)	1258 (m)	$\delta(C—H)_{eux} + \nu(C—C)_{eux} + \nu(C_{eux}—O_{gluc}) + \nu$(C—OH)(C-8) + $\nu_s(C—O—C)(2) + \delta(C—H)_{gluc}$
1346 (s)	1345 (vw)	$\delta(C—H)_{eux} + \delta$(O—H)(C-3′) + $\nu(C—C)_{eux}$
1368 (s)	1368 (vw)	$\delta(C—H)_{eux} + \delta$(O—H)(C-3′) + $\nu(C—C)_{eux}$
1425 (s)	1423 (s)	$\nu(C—C)_{eux} + \delta(C—H)_{eux}$
1441 (s)	1439 (s)	$\nu(C—C)_{eux} + \delta(C—H)_{eux}$
	1458 (vs)	$\delta(C—H)_{eux} + \delta(C—C)_{eux} + \delta$(O—H)(C-8) + ν_{as}(C—O—C)(2)
	1484 (s)	$\delta(C—H)_{eux}(3) + \delta(C—C)_{eux}(3) + \nu(C_{eux}—O_{gluc})$
1543 (w)	1542 (m)	$\nu(C—C)_{eux} + \delta(C—H)_{eux} + \nu_s$(C—O—C)(2)
1589 (w)	1582 (vs)	δ(O—H)(C-4′) + $\nu_{as}(COO^-)$
1626 (vs)	1624 (s)	$\nu(C—C)_{eux} + \delta(C—H)_{eux} + \delta$(O—H)(C-8)
1635 (sh)		$\nu_{as}(COO^-) + \nu$(C=O) + δ(O—H)(C-4′)
1655 (vw)		ν(C=O) + $\nu_{as}(COO^-) + \delta$(O—H)(C-4′)

[a] *Abbreviations:* eux = euxanthic ring; gluc = glucuronic ring; the numbers refer to the —OH groups as represented in Fig. 1; relative intensities were abbreviated by w (weak), vw (very weak), m (medium), s (strong) and vs (very strong).

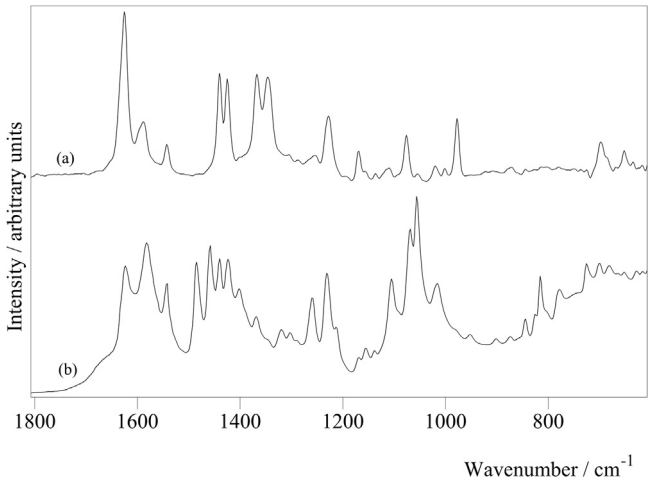

Fig. 5. (a) Baseline corrected FT-Raman and (b) μFTIR-ATR spectra obtained from a genuine Indian yellow sample.

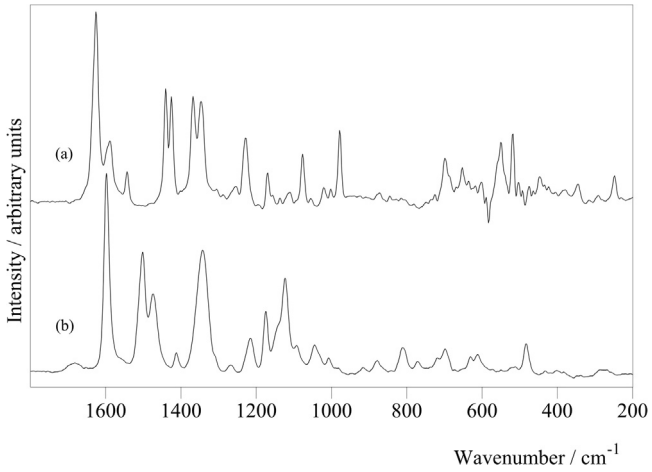

Fig. 6. FT-Raman spectra of (a) Indian yellow and (b) tartrazine; the luminescent background was removed from the Indian yellow spectrum to facilitate the comparison.

Specifically in the case of infrared absorption spectroscopy, as far as the authors are aware there are two reports in the literature: Baer et al. [12] obtained the Indian yellow IR spectrum from KBr pellet whereas Vetter and Schreiner [29] used the reflectance mode. In the first case the reported spectrum does not fully agree with the one here reported probably because the sample preparation method (cold fusion in the inorganic KBr matrix) is affecting the pigment structure. The authors described a complex spectrum with bands assigned to ether, phenol and alcohol (1000–1200 cm^{-1}) groups and, in the 1200–1650 cm^{-1} region, absorption bands ascribed to carbonyl, carboxylate and C=C stretching vibrations; a broad hydroxyl absorption was observed in the 3000–3500 cm^{-1} spectral window. The spectrum reported by Vetter and Schreiner [29] apparently matches the FTIR-ATR spectrum reported in the present work, but it is not possible to compare band positions because they were not provided by the authors.

4. Conclusions

The high luminescence showed by Indian yellow does not allow its Raman spectrum to be obtained using excitation in the visible or near infrared at 785 nm, however, in the FT-Raman spectrum (with excitation at 1064 nm) the pigment characteristic bands are clearly observed on an emission background.

A search in the literature confirms that all the spectra reported hitherto as belonging to Indian yellow pigment correspond, in fact, to tartrazine. This is a very important discovery from the forensic science point of view, due to the growing use of pigment identification to help in the authentication of art works: tartrazine is a synthetic dye which was first produced toward the end of the 19th Century, whereas genuine Indian yellow pigment is reported to have been in use since the 15th Century [7].

The genuine sample of Indian yellow was also characterized by SEM-EDX, XRF and ^{1}H and ^{13}C NMR; a full assignment of the ^{1}H and ^{13}C spectra is presented here for the first time in the literature, as far as we are aware.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.forsciint.2016.11.037.

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