



Original article

Non-invasive, non-destructive and portable identification of Indian yellow: Moving from highly purified standards to real watercolour, oil and historical samples

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ABSTRACT

The unambiguous identification of Indian yellow using spectroscopic techniques is challenging. Not long ago (2017), a reference spectrum of the pigment was produced using FT-Raman (an invasive and non-portable technique). Following this, the spectra of Indian yellow was also able to be acquired using confocal Raman microscopy (also non-portable) using VIS-NIR light sources. Finding a method to identify Indian yellow using portable instrumentation has many advantages when objects cannot be taken to a laboratory or is unfeasible to take microsamples. Here, results are described for the identification of the pigment Indian yellow in unpurified historical samples and real samples in different media (watercolour, oil and tempera). The following techniques were used: fluorescent imaging, portable Raman (1064 nm) and dispersive Visible - Near Infrared (VIS-NIR) as well as Fourier transform infrared (FTIR) diffuse reflectance. The advantages and problems associated with the use of such instrumentation were discussed. It is possible to identify Indian yellow using portable instrumentation (Raman at 1064 nm excitation and chemometric analysis using NIR diffuse reflectance).

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1. Introduction

It took until 2017 for the unambiguous spectral characterisation of the pigment Indian yellow [1]. There are several reasons for it to take such a long time. From very early, there has been a wide range of confusing terminology to name the pigment [2] and even before the production of Indian yellow stopped in the early 20th century, several adulterated/fraudulent products were in the market due the high cost of the original pigment. Therefore, it has been difficult to obtain an original and well documented sample to study. Likewise, as many substitutes of the pigment were sold as the original, the artists and consequently some heritage scientists have incorrectly claimed that original Indian yellow was used in works of art [2]. The confusion grew bigger when the Raman spectrum of an incorrect pigment was adopted as reference standard [1]. The pigment Indian yellow is characterised by its bright yellow photoluminescence (PL). Such PL makes it almost impossible to acquire a Raman signal in-situ using commercial VIS or even 785 nm NIR instruments [1,3]. The fact that many of Indian yellow substitutes did not present any PL issues when collecting a Raman signal may have contributed to the adoption of the erroneous Ra-

man spectrum for identification and incorporation into reference databases [1]. However, as pointed by the recent article about the unambiguous spectral characterisation of the pigment, the fact that it was easy to acquire a Raman signal for some Indian yellow substitutes should have raised suspicion rather than assurance [1].

Currently, the gold standard techniques to analyse Indian yellow are pyrolysis gas chromatography Py(GCMS), liquid chromatography with mass spectrometry and fluorescence/UV detection (HPLC and LC-MS) as well as Fourier transform Raman spectroscopy (FT-Raman), all destructive and non-portable techniques [4,5]. To our knowledge, there are only reports for the non-invasive identification of Indian yellow using confocal Raman microscopy with excitation in the VIS-NIR [3,4]. Such technique allows for the analysis to be non-destructive but it is still confined to a bench and is restricted to be used on small objects [6].

There have been huge advances in the development of portable Raman and Fourier transform infrared spectrometer (FTIR) instruments over the last 20 years [7]. In the case of Raman, solid state, miniaturised narrow band lasers and edge filters in combination with small dispersive spectrometers have allowed for instruments to fit in the palm of a hand [6,8,9]. Most common portable Raman instruments operate at 532 and 785 nm. However, there are few manufacturers that offer other excitation wavelengths, includ-

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ing 1064 nm. The reason for such a difference in availability at 1064 nm is the fact that a VIS Raman spectrometer detector, commonly a silicon charged-coupled device (CCD), has a spectral response that drops very sharply at 1050 nm (or 3215 cm^{-1} shift for a 785 nm excitation laser). This means that a different type of detector is needed for a longer excitation wavelength instrument, in the case of 1064 nm, commonly a cooled InGaAs is needed. Such detectors are less developed and are more expensive in comparison to CCD detectors [10]. In Raman spectroscopy there is always a trade-off between fluorescence reduction (lower at longer wavelengths) and Raman signal intensity (also lower at longer wavelengths) and so for that reason a Raman spectrometer at longer excitation wavelength of 1064 nm produces a weaker signal for the same applied laser power than a 785 or 532 nm instrument.

In spite their portability, handheld or portable Raman spectrometers suffer from poor resolution. This is because resolution is a function of the focal length and so it is constraint to its size. They also generally present higher fluorescence background problems compared to confocal Microscopes in which the contribution of out of focus light is suppressed by the use of a pinhole [6,11].

In the case of portable FTIR instruments for heritage applications, focus has concentrated in the sampling part of the technique, so as to allow for non-contact analysis. In this way, both specular and diffuse reflection sampling (DRIFTS), have been used and proven to be essential in the identification of organic pigments, binders, fillers, varnishes and polymers [12,13]. DRIFTS is focused on the diffuse contribution of a rough surface (such as the surface of a painting) that scatters in all directions. This is opposite to specular reflection in which the reflected light is measured at the same angle as the incidence light. One drawback of the DRIFTS technique is that the spectra generated are not always compatible or shows marked differences with existing and more studied databases based on transmittance or attenuated total reflection (ATR) measurements [14].

To our knowledge there are no reports on the use of portable non-invasive techniques to analyse the very important and somehow mysterious pigment Indian yellow.

1.1. Aim

To develop a methodology for the non-invasive and non-destructive identification of Indian yellow using portable Raman with 1064 nm excitation and portable dispersive near infrared (VIS-NIR) diffuse reflectance as well as FTIR with DRIFTS sampling. Several reference samples (watercolour, oil and tempera paint) were analysed and compared to newly developed spectral data in the literature [1,3].

2. Materials and methods

Several samples were chosen for investigation, all claiming Indian yellow pigment (except for the Jain manuscript) in their composition. The samples used for analysis are shown in Fig. 1.

2.1. Description of the samples analysed

Watercolour:

- Winsor and Newton (W&N) Indian yellow cakes, pre 1882 (does not bear Ltd on the brand). Ltd was introduced in 1882 [15]
- Crown Stationary Office, S&O Indian Yellow cake, unknown date
- Unknown (possible Reeves) Indian Yellow cake, unknown date
- W&N Indian yellow watercolour pan, unknown date
- W&N modern Indian yellow applied on commercial optical brightening agent-free cardboard (acquired in 2022, PO62, and PY139 pigment, benzimidazolone orange and isoindoline yellow respectively)



Fig. 1. Indian yellow samples used for analysis, oil paint tubes: A) Winsor and Newton (W&N) pre 1882 and A1) W&N post 1882, B) S&O watercolour cake, C) unknown watercolour cake, D) W&N watercolour cake, E) Modern W&N watercolour tube, F) W&N watercolour pan G) Jain watercolour manuscript, possible 17th century Indian, Historical colour charts, Das Deutsche Farbenbuch, H) Indischgelb watercolour and I) Indischgelb II imit tempera, J) Jackson's oil 019 (PY73 and PBr7, arylide Yellow GX and Brown Iron Oxide respectively), K) Michael Harding oil 203 (PY83,diarylde Yellow HR). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Oil paint tubes (tubes were opened in the past and their contents have dried out, traces of the dry pigment, found on the exterior of the tube, were used for all analysis):

- W&N pre 1882, Indian yellow tube (no Ltd on the brand)
- W&N post 1882, Indian yellow tube (Ltd can be seen on the brand)

Indian watercolour manuscript painting, possibly 17th century Jain devotional image of Ajita. Probably made in Jodhpur in Rajasthan, India in the late seventeenth century. The seated figure is the spiritual teacher Ajita (identified by his golden colour, and the elephant at his feet). The manuscript was placed on blue backing paper (source Somerset & Wood Fine Art Ltd, Wiltshire, UK).

Historical colour chart, Das Deutsche Farbenbuch (1923), H. Trillich, Das Deutsche Farbenbuch, Munich.

- Indischgelb (watercolour, unknown pigment code, Redeker and Hennis A. G. NurnBerg)
- Indischgelb imit II (tempera, unknown pigment code, possibly imitation (imit), Vereinigte Farben und Lackfabriken, Munich)

Modern colour charts:

- Michael Harding (MH) hand painted colour chart (linseed oil). Indian yellow 203 (PY83 pigment code, diarylide Yellow HR)
- Jackson's artist oil colours (refined linseed oil). Indian yellow hue 019 (PY73 and PBr7 pigment codes, arylide Yellow GX and Brown Iron Oxide respectively).

2.2. Imaging

Technical imaging was performed as described by Verry and Saunders [16]. Briefly, a Nikon D3200 camera was modified by removing the internal filter. A xenon flash lamp SB-80DX was used as illumination source. For UV induced luminescence in the visual (UIL) a bandpass filter (350–400 nm) was used as excitation and bandpass filter (400–700 nm) was placed in the camera. The shutter speed was 1/200 s, white balance setting was 5600 K and distance from the flashtube to the object was 50 cm. The aperture was set at f/4. A Cultural Heritage Science Open Source (CHSOS) TP-MSI calibration card was used to correct the technical images.

The narrow band images were taken using a multispectral Nuance FX camera (CRI Cambridge Instruments). The integration time

was 1532 ms and a spectral range of 420–720 nm in 10 nm steps. Only the 590 nm band was taken for analysis. The illumination source was a 365 nm LED lamp.

2.3. Spectroscopy

2.3.1. Raman analysis

A Bayspec Agility 1064 nm (Bayspec Ltd) was used for the portable analysis. The spectral range is 200–2400 cm^{-1} and 15–18 cm^{-1} resolution. The instrument uses a volume phase grating (VPG) for high-throughput, the laser was kept at 200 mW at the source after testing mock samples for damage. Sampling is performed via fibre optic Raman probe with 10 μm nominal spot diameter and 6.5 mm working distance. Integration time was 10 s with average of 10 spectra. Software used for collection was Spec 20/20.

Confocal Raman microscopy was performed using a Labram Aramis (Horiba Scientific) using a 633 nm HeNe and 785 nm laser (1% power), a 50X objective, 600 l/mm grating, 50 μm pinhole, 3 s integration time and average of 60 spectra accumulations. Instrument was calibrated using a silicon wafer and automatic software correction (Labspec 6). All reference spectra were taken from the Soprano, Marucci et al. and Sigma Aldrich Raman databases [17,18]. All Raman spectra show intensity in arbitrary units in the y-axis

2.3.2. FTIR

FTIR analysis was done using an Agilent 4300 portable handheld instrument (Agilent Technologies). The instrument has deuterated tryglycine sulphate (DGTS) detector and a ZnSe beam splitter, the range used was 650–4000 and 4 cm^{-1} resolution. Sampling was done using the DRIFTS accessory collecting the average of 200 background as well as sample spectra. A coarse gold reference cap was used for the background calibration for every sample. For ATR, an average of 32 background and sample spectra was collected. All FTIR spectra show absorbance units in the y-axis. Software used for collection was MicrolabPC.

The DRIFTS accessory reduces the collection of the specular reflectance element to about 4% depending on the refractive index of the material. For a more detailed description the readers are referred to Angelin et al. [12]

In order to allow direct comparison and for consistency, the x-axis in all spectra shows increasing wavenumbers from left to right.

2.3.3. VIS-NIR

VIS-NIR diffuse reflectance analysis was done using a Qualit-spec Trek (Analytical Spectral Devices Inc). The instrument range is 350–2500 nm, spectral resolution is 3 nm at 700 nm, 9.8 nm at 1400 nm and 8.1 nm at 2100 nm. Calibration was done using the provided spectralon white standard. The instrument uses an internal quartz tungsten halogen bulb and a fibre optic pointing to a quartz window (used for sampling at the other end). The angle from the window to the light source is 55° and the angle to the fibre optic is 78°, thus minimising specular reflection. The fibre optic cable has a field of view of 25°, giving a field of view of 0.82 cm on the window. Software used for collection is built-in the instrument.

2.3.4. X-ray fluorescence (XRF)

XRF analysis was performed using a portable Niton XL2 XRF (Thermo Scientific) with camera. A 20 s integration time was used for all samples in general metals mode. The analyser is fitted with a 50 kV X-ray tube (100 μA , 2 W maximum) and a silicon drift detector (SDD) with an active area of 5 mm^2 fitted with a polymer window (MOXTEK AP 3.3 film). The X-ray beam's focal-spot size is about 3 mm in diameter. Software used for collection is built-in the instrument.

2.4. Statistics

All spectra were processed/transformed using Omnic software 7.1 (Thermo Scientific). Baseline correction were applied to all spectra. DRIFTS spectra were smoothed by using Savitzky–Golay algorithm. VIS-NIR spectra were transformed using the first derivative. The multivariate analysis was done using Minitab 20, principal component analysis (PCA) was done using a correlation matrix. The cluster analysis was performed using complete and Euclidian distances.

3. Results

3.1. Imaging

One of the main attributes of Indian yellow is its bright yellow PL, therefore, UV induced luminescence (UIL) images of all the samples were taken. The images are shown in Fig. 2. Strong fluorescence of the cardboard on which samples were attached precluded the acquisition of UIL images of the modern colour charts for MH Indian yellow 203 and Jackson's Indian yellow hue 019.

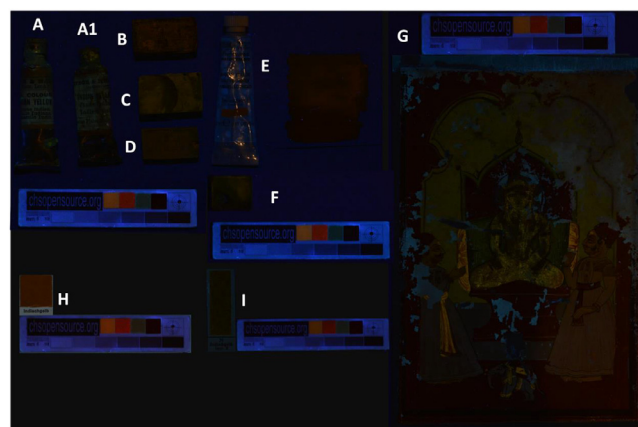


Fig. 2. UV induced luminescence images of Indian yellow samples, oil paint tubes A) W&N pre 1882 and A1) W&N post 1882, B) S&O watercolour cake, C) unknown watercolour cake, D) W&N watercolour cake, E) Modern W&N watercolour tube, F) W&N watercolour pan G) Jain watercolour manuscript, possible 17th century Indian, Historical colour charts, Das Deutsche Farbenbuch, H) Indischgelb watercolour and I) Indischgelb.

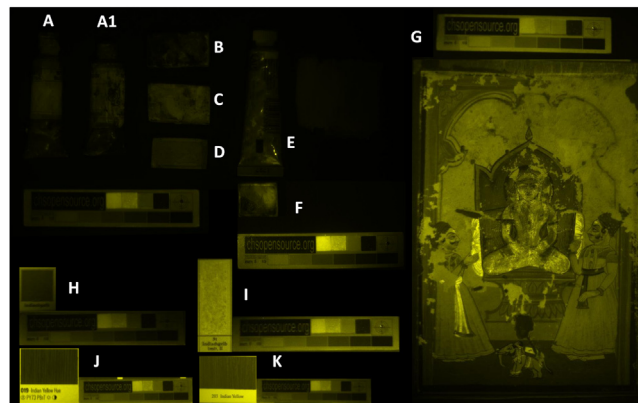


Fig. 3. UV induced luminescence images with emission at 590 nm of Indian yellow samples, Oil paint tubes A) pre 1882 and A1) post 1882, B) S&O watercolour cake, C) unknown watercolour cake, D) W&N watercolour cake, E) Modern W&N watercolour tube, F) W&N watercolour pan G) Jain watercolour manuscript, possible 17th century Indian, Historical colour charts, Das Deutsche Farbenbuch, H) Indischgelb watercolour and I) Indischgelb II imit tempera, J) Jackson's oil 019 (PY73 and PBr7, arylide Yellow GX and Brown Iron Oxide respectively), K) Michael Harding oil 203 (PY83, diarylide Yellow HR). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

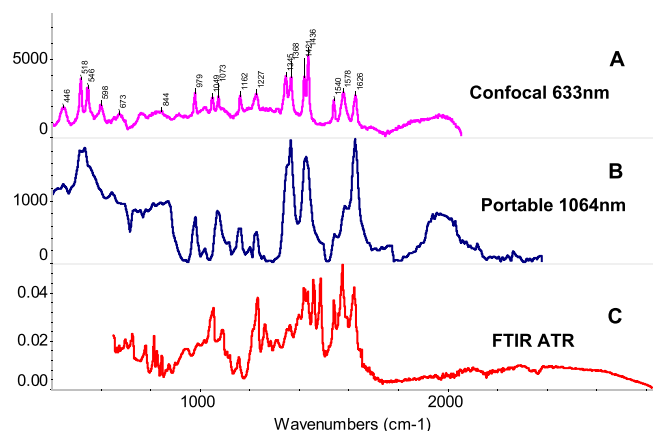


Fig. 4. Raman spectra of Indian yellow samples using a confocal microscope with 633 nm excitation (units of y-axis are arbitrary), A) W&N watercolour cake B) same sample W&N watercolour using 1064 nm portable instrument and C) same sample W&N watercolour analysed with FTIR ATR with the spectrum of gum Arabica subtracted (units of y-axis are absorbance). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It can be observed that both oil paint tubes (pre and post 1882, Fig. S1A and S1A1 respectively) present faint yellow luminescence on the dry spots outside the tubes. All 3 watercolour cakes and the pan (Fig. S1B-D and S1F) show some yellow luminescence with the unknown brand (possible Reeves) watercolour cake presenting a shorter (more yellow than red) emission profile.

The modern Indian yellow tube (Fig. S1E) also shows some luminescence. The historical colour chart (Fig. S1H), Indischgelb has a brighter luminescence than the imitation (Fig. S1I) Indischgelb II imit. The Jain watercolour manuscript painting (Fig. S1G) shows the most intense luminescence particularly to the sides of the God Ajita, on the body of Ajita itself as well as the decorations on the elephant. Interestingly, the green background that surrounds the shrine is also luminescent. In addition, the TP-MSI calibration chart contains shellac that also shows a yellow fluorescence similar to that of all possible Indian yellow pigments from the historical samples. It is clear from the UIL images that pigments other than Indian yellow can show a similar UIL profile.

In order to characterise in more detail such luminescence, multispectral images of the samples were taken and the maximum emission signal at 590 nm was isolated as reported by Fonjaudran et al. [19].

It can be observed that the UV induced luminescence with emission at 590 nm images (Fig. 3) show similar brightness than the images of UIL (Fig. S1). The fluorescence observed in the mod-

ern watercolour sample (Fig. S1E) is almost completely suppressed by narrowing the fluorescence band to 10 nm as observed in Fig. 3E. It is also more apparent that other elements than Indian yellow itself contribute to yellow fluorescence. This is very clear in the case of the historical samples Fig. 3H and I and the modern samples Fig. 3J and K, in which the substrates, cardboard and paper, show bright yellow fluorescence outside of the edges where the pigment was applied.

From such imaging results and as reported in the literature [19], the identification of Indian yellow on the basis of UV induced luminescence imaging alone is not accurate enough and it may and has led to suspicious attributions of original Indian yellow in works of art. This is because other pigments and elements on the art works show similar fluorescence profiles and it is therefore not recommended as sole means for identification of Indian yellow.

The next main task was to establish if the samples analysed in this study are consistent with the spectra of newly published and well characterised Indian yellow samples [1,3]. In such case, the samples could be considered as authentic Indian yellow. This will be shown in the following section.

3.2. Spectroscopy

3.2.1. Raman

Raman spectra of all samples were acquired using a confocal microscope with excitation at 633 nm and 785 nm. However, only good signal was obtained using the 633 nm laser, unlike the results reported by Smith [3].

The Raman and FTIR spectra of the W&N watercolour sample (pre 1882) were in very good agreement and are similar to the newly accepted and well documented Indian yellow standard (Fig. 4A and C respectively) [1].

The same W&N watercolour sample was compared with the spectra generated using the portable 1064 nm instrument. The comparison between the spectrum collected with the confocal set up and the portable set up can be seen in Fig. 4A and B respectively. It can be noticed the difference in resolution (4 cm^{-1} for the 633 nm and 18 cm^{-1} for the 1064 nm instrument). Also, the relative intensity of the bands at 1540, 1578 and 1626 cm^{-1} is different. However, the relative intensity of such bands is consistent with the Raman spectra collected using FT-Raman and therefore is a function of the laser excitation (1064 nm) [1]. Moreover, the position of the dominant bands in the range of 400 to 1700 cm^{-1} has good agreement with the reported in the literature [1,3].

On the basis of the reference spectra shown in Fig. 4, the following samples were considered to contain euxanthic acid and therefore authentic Indian yellow: S&O watercolour cake, unknown

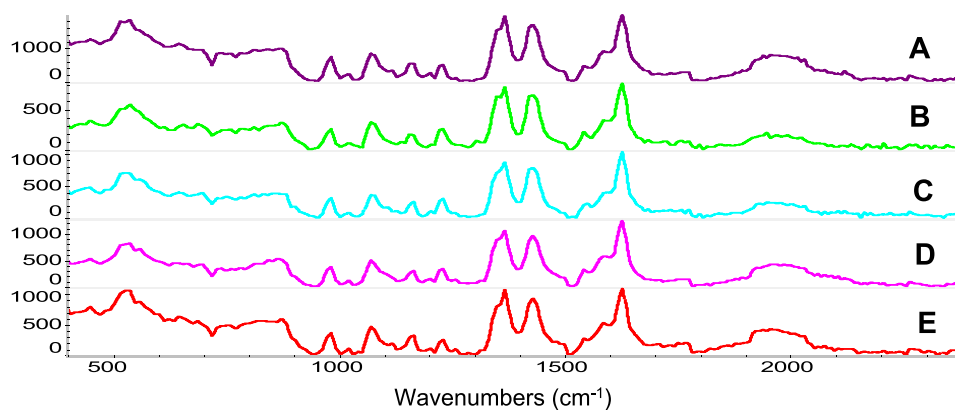


Fig. 5. Raman spectra of Indian yellow samples acquired using portable 1064 nm (units of y-axis are arbitrary) A) W&N watercolour, B) S&O watercolour, C) Unknown watercolour, D) W&N pan watercolour, E) W&N oil pre 1882. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

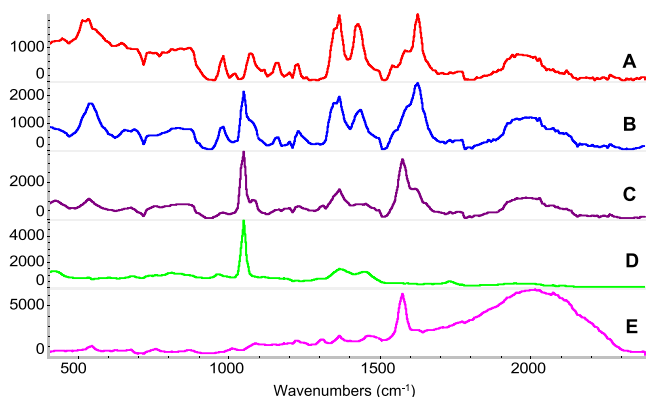


Fig. 6. Raman spectra of samples acquired using portable 1064 nm (units of y-axis are arbitrary). A) W&N watercolour B) Jain manuscript yellow area, C) Jain manuscript green area, D) lead white and E) Indigo. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

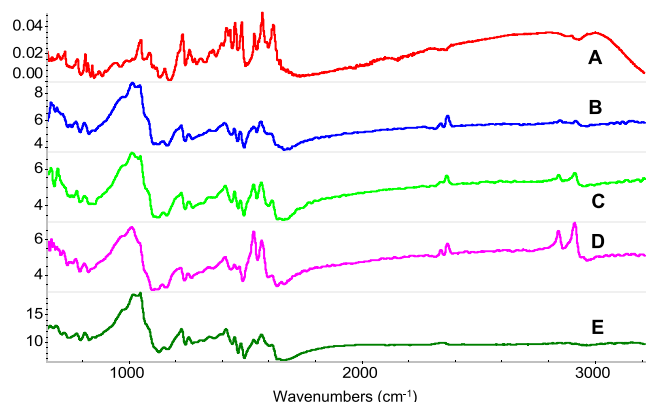


Fig. 7. Samples analysed using FTIR, A) W&N watercolour Arabica subtracted ATR (absorbance), rest transmittance B) W&N watercolour DRIFTS, C) S&O watercolour DRIFTS, D) Unknown watercolour DRIFTS, E) W&N watercolour pan.

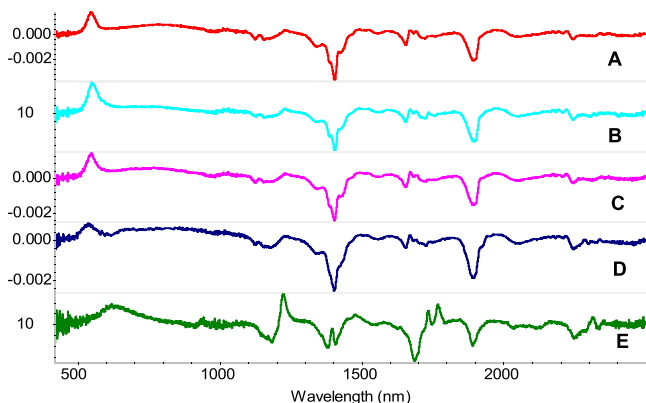


Fig. 8. Diffuse reflectance in the near infrared (VIS-NIR, 450–2500 nm) spectra of Indian yellow samples (units of y-axis are reflectance). A) W&N watercolour, B) S&O watercolour, C) Unknown watercolour, D) W&N pan watercolour, E) W&N oil pre 1882. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

watercolour cake, W&N watercolour cake, W&N watercolour pan, W&N oil, pre 1882, Fig. 5B–E respectively.

On the same basis the following samples were considered to not contain Indian yellow or were produced using substitutes of the pigment: W&N watercolour modern, W&N oil post 1882, historical charts Indischgelb watercolour, and Indischgelb II imit,

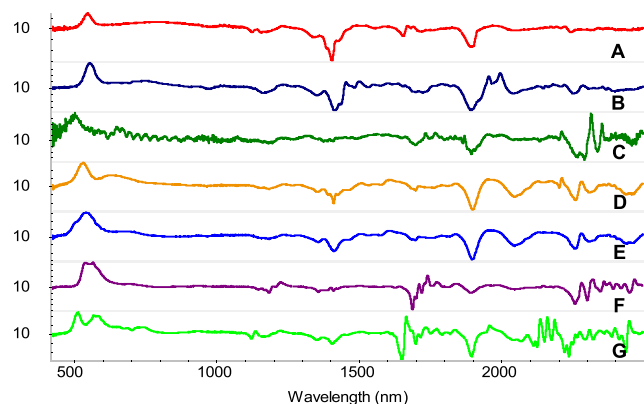


Fig. 9. Diffuse reflectance in the near infrared (VIS-NIR, 450–2500 nm) spectra of Indian yellow samples (units of y-axis are reflectance). A) W&N watercolour, B) W&N watercolour modern, C) W&N oil post 1882, D) Historical chart Indischgelb watercolour, E) Historical chart Indischgelb II imit, F) Modern chart Michael Harding 203, G) Modern chart Jackson 019. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tempera, modern charts MH 203 and Jackson 019, Figs. S2B to S2G respectively.

Recently, Sessa et al. set the task to characterise synthetic and natural organic pigments on Das Deutsche Farbenbuch historical charts similar to the ones used in the present manuscript [20]. They used a normal Raman Microscope (non-confocal) and Surface enhanced Raman Spectroscopy (SERS) as well as metal underlayer attenuated total reflection (ATR) Fourier transform infrared spectroscopy to characterise their samples. It was surprising that there is no mention of the pigment Indian yellow given that the focus of their investigation was on organic pigments. The pigment exists in two charts, one applied as watercolour and the other on tempera. The fact that the authors did not report any successful or failed attempts to acquire Raman spectra on the watercolour sample highlights the fact that Indian yellow is difficult to characterise even with advanced methodologies (SERS) that use micro sampling. The identification of the Indian yellow substitutes used in the present investigation is described in detail in the supplement material (Table S1). Briefly, the following pigments were found: PY1, PY83, PY73 as well as mixtures of PY139 with PO62 and gamboge with vermillion.

The Jain manuscript was subject to analysis using the portable Raman instrument. Results for such analysis are shown in Fig. 6. It can be seen that the spectra of the yellow area matches the spectra of Indian yellow (Fig. 6A and 6B). There are, however, some marked differences. There is an extra peak at 1049 cm^{-1} and the resolution of the peaks at 1540 , 1578 and 1626 cm^{-1} has dropped. The two differences can be explained by the presence of lead white, either mixed with Indian yellow or applied as a ground layer. The spectra of lead white, acquired using the same portable Raman instrument, is shown in Fig. 6D. The main peaks at 1049 cm^{-1} and a broad peak at 1560 cm^{-1} are visible. Those two peaks explain the difference between the spectra of Indian yellow and the yellow area in the Jain manuscript. The presence of lead was confirmed with the XRF spectra of the yellow area (Supplement material, Fig. S9).

The green area of the Jain manuscript, also believed to contain Indian yellow (given its luminescence) was analysed. In this case many differences were found when compared with the reference spectra (Fig. 6A and C). There is a report of an Indian manuscript containing Indian yellow (in a yellow part) and Indian yellow mixed with the blue pigment Indigo in a green part of the manuscript [5]. It is also known that pigments such as lead white and Indigo have been used in Mughal miniature paintings [21,22].

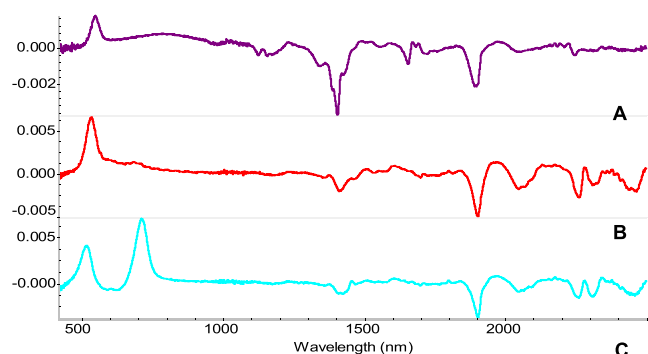


Fig. 10. Diffuse reflectance in the near infrared (VIS-NIR, 450–2500 nm) spectra of Indian yellow samples (units of y-axis are reflectance). A) W&N watercolour B) Jain manuscript yellow area, C) Jain manuscript green area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The spectra reported in the present manuscript for the colour green, contains, in addition to the aforementioned 1049 cm^{-1} peak of lead white (Fig. 6D), a band at 1585 cm^{-1} . This band is the most prominent peak of the pigment Indigo [18]. The spectra of the pigment Indigo can be seen in Fig. 6E acquired using the same portable instrument. On the basis of such observations, it was not possible to identify Indian yellow as component on the green part of the Jain manuscript using the portable Raman instrument alone. It is to note that a similar spectrum was obtained using the confocal Microscope and it was not possible to identify the green pigment either.

3.2.2. FTIR DRIFTS

The interpretation of FTIR spectra acquired using DRIFTS is not always comparable in the same way ATR and transmission experiments are, as pointed in the introduction. When DRIFTS is performed, the spectra can show “derivative” like spectra or the pres-

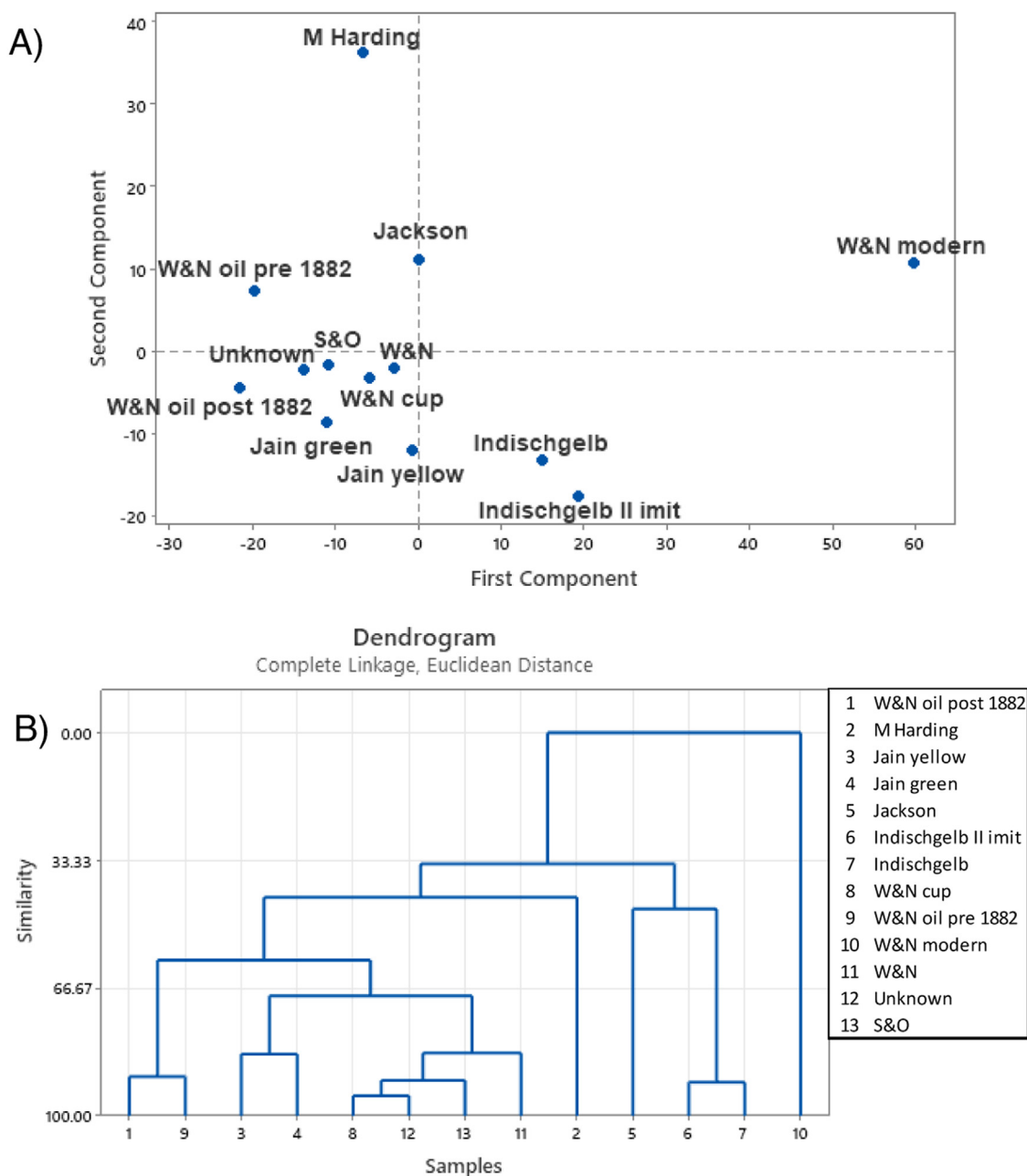


Fig. 11. VIS-NIR Multivariate analysis in the 1000–2000 nm region A) principal component analysis and B) cluster analysis.

ence of “inversed” bands [23]. For that reason, the DRIFTS spectra is presented as transmittance ($\%T = (S/B) \cdot 100$, S = sample signal and B = background) and compared to absorbance ATR (Omnisc user guide v7.1, Thermo Scientific). This comparison is only possible because the spectra show only “inverse” band behaviour. Such comparisons can be seen in Fig. 7. Since all the spectra in Fig. 7 are watercolours, the contribution of gum Arabic can be observed as a broad peak at 1050 cm^{-1} (except for the reference ATR spectra in which the contribution of gum arabica was software-subtracted, Fig. 7A). All the DRIFTS spectra (Fig. 7B–E) are similar but not identical to the one acquired with ATR (Fig. 7A).

As expected, the samples that did not match Indian yellow using the portable Raman instrument did not show similar features when the portable FTIR DRIFTS was used. This comparison is shown in Fig. S10. In addition, the spectra of the W&N oil pre 1882 sample (Fig. S10C) did not match the reference spectra. This oil sample was previously matched using the portable Raman instrument (Fig. 5E). The contribution of oil binder to the FTIR signal precludes the identification of Indian yellow in our results.

The identification of Indian yellow using portable FTIR DRIFTS was unsuccessful on the Jain manuscript in both the yellow and green areas. This can be seen in Fig. S11. The contribution of other pigments and unknown binders affects the infrared signal in a more pronounced way that it does when Raman spectroscopy at 1064 nm is used to identify the organic pigment Indian yellow. The PCA analysis and the cluster analysis in the region of $1000\text{--}2000\text{ cm}^{-1}$ is shown in the supplement material (Fig. S12). No clustering or similarities were observed on the FTIR spectra.

3.2.3. VIS-NIR diffuse reflectance

The spectra of samples (confirmed to contain Indian yellow) analysed using VIS-NIR ($350\text{--}2500\text{ nm}$) diffuse reflectance are shown in Fig. 8. The spectra show similar bands for the watercolour samples. In contrast, the oil sample has a very different profile, the spectra is dominated by the CH bands at 1208 , 1727 and 2301 nm . It is for that reason that the identification of Indian yellow in oil media samples using VIS-NIR is challenging. It was also confirmed that the samples containing Indian yellow substitutes show a different VIS-NIR spectra. This can be seen in Fig. 9. When the Jain manuscript was analysed using VIS-NIR, both the yellow and green areas showed prominent differences compared to the spectra of the watercolour samples (Fig. 10).

The multivariate analysis of the samples using diffuse reflectance VIS-NIR shows that only five components were necessary to classify 95% of the spectral features in the data, this is shown in Fig. 11. All the samples identified to contain original Indian yellow were correctly classified using the first two components and are clearly clustered with a similar Euclidean distance. This includes the oil samples and the Jain manuscript both in the yellow and green area. It was therefore possible to identify Indian yellow using multivariate analysis using diffuse reflectance in the NIR ($1000\text{--}2000\text{ nm}$).

4. Conclusions

In the present investigation, traditional fluorescent imaging techniques were used to visualise the pigment Indian yellow. Given our results, such imaging techniques are proven to be unsuitable to distinguish the pigment from other similar pigments and substrates. This is because other elements such as shellac, cardboard and some paper presented similar fluorescent profiles. The sole use of fluorescent imaging techniques for the identification of Indian yellow is therefore discouraged.

It was possible to identify Indian yellow using portable Raman using excitation of 1064 nm in watercolour samples of different

origins and one oil sample. The identification of Indian yellow with certainty when mixed with more than one component (lead white and Indigo in the green part of the Jain manuscript) using Raman was challenging and not successful. It required complementary techniques (e.g. portable XRF) to interpret the result obtained. Furthermore, it was possible to find unique principal components to correctly classify and cluster all samples known to contain Indian yellow using diffuse reflectance in the NIR ($1000\text{--}2000\text{ nm}$). The use of portable FTIR DRIFTS was unsuccessful to give an indication of Indian yellow. The watercolour samples could be compared, however for samples where another binder was used, the FTIR spectra was dominated by absorption coming from the binders (oil and protein) and the presence of other pigments.

It was therefore possible to get an indication of the pigments used and thus insights into the historical provenance of one work of art. It is known that pigments such as lead white and Indigo have been used in Mughal miniature paintings. The results presented here give more evidence of the use of Indian yellow and its combination with other pigments in such heritage objects.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.culher.2023.06.022](https://doi.org/10.1016/j.culher.2023.06.022).

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