



## Rapid Communication

## Cow urine, Indian yellow, and art forgeries: An update



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## ABSTRACT

In a recent technical note in this *Journal*, de Faria et al., 2017 [1] reported the Raman spectrum of authentic Indian yellow artists' pigment, correcting a decades old reference spectrum that has led to the misidentification of this pigment in artworks that actually contained tartrazine yellow. The present communication provides additional information and corrects important experimental details mentioned by de Faria et al. that should lead to further identifications of the authentic pigment in artworks. Despite their claim that the analysis of this naturally fluorescent colorant is only possible with Fourier transform (FT) instruments, the ready characterization of two authentic samples of historic Indian yellow pigment is demonstrated here using commonly available visible and near-infrared excitation sources on a dispersive Raman microspectrometer. To highlight the importance of the proper identification of dyes and colorants, the authentication and art historical implications of previous literature reports that have misidentified Indian yellow on historic documents are more thoroughly discussed here from a forensic science point of view. The numerous modern pigments that are sold as imitation Indian yellow are addressed and analyzed, allowing the ready noninvasive detection of anachronistic colorants in attempted forgeries. Finally, this unusual pigment is positively identified for the first time using non-invasive dispersive Raman microspectroscopy on a historic object of uncertain date, a highly decorative manuscript from the Indian subcontinent.

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## 1. Introduction

In a recent issue of this *Journal* [1], de Faria et al. reported for the first time the actual Raman spectrum of Indian yellow pigment, correcting an inaccurate reference spectrum that has been available in the literature for decades [2]. Indian yellow is a storied pigment common to the artist's palette in Persia and India since the 15th century and imported into Europe from the 18th century until its discontinuation around 1908 [3]. The translucent yellow color is comprised of hydrated magnesium and/or calcium salts of euxanthic acid,  $\text{Mg,Ca}[\text{C}_{19}\text{H}_{15}\text{O}_{10}]_2 \cdot n\text{H}_2\text{O}$ , purportedly harvested from the urine of cows or camels fed an exclusive diet of mango leaves. Despite relatively recent arguments questioning this source for the pigment [4], a thorough literature review by Ploeger and Shugar [5] that covered technical manuals on pigments as well as medical publications dealing with metabolism has lent credence to the animal origins of this fascinating colorant.

De Faria et al. showed that the earlier reference spectrum was actually that of tartrazine yellow (PY100, C.I. 19140) [1], a late 19th century monoazo dye that served as an early imitation for Indian

yellow [3]. The implications of this mistake for the dating of artwork based on date-marker pigments (i.e. pigments introduced at a known date following their discovery) and the detection of forgeries were implicit in their publication; however, the ramifications of their discovery were not fully explored. For instance, two research groups have used the earlier, erroneous Raman spectral reference data to identify Indian yellow in a series of illuminated manuscripts held by important national collections. Clark and Gibbs [6] discovered Indian yellow used in a set of three rare 16th century copies of the manuscript *The Wonders of Creation and Oddities of Existence* by the Arab scholar Qazwini held by the British Library. The illustrations are in Arabic, Persian, and Indian styles, apparently produced by different artists, but all bearing strikingly similar palettes. Each of the volumes is described differently in terms of their previous restoration: the first is in poor condition and appeared untouched by conservation, the second seemed only lightly conserved, and the third had obviously been conserved in a heavy-handed way. The identification of Indian yellow on each of these volumes, now shown to be a tartrazine-based modern imitation instead, has potential implications for their authenticity, technical art history, and the record of modern alterations to the artwork. Although the authenticity of these manuscripts has not been previously challenged by historians, it is

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obvious that at least the illuminations have been augmented to improve the appearance of the artworks, possibly to enhance their sale, sometime after the discovery of tartrazine in 1884 [7]. The extent of reworking and whether an original yellow colorant was used – possibly even authentic Indian yellow – cannot be known without a re-examination of the manuscripts. The impact on the technical art history of the pieces is also affected. The presence of Indian yellow used liberally throughout the illuminations was argued as supporting evidence for codicologists' views that the manuscripts originated in India. This support based on these experimental data must now be withdrawn.

Subsequently, Ravindran et al. tentatively identified Indian yellow in a 17th century Mogul painting from the Madras Museum in Chennai based on the same incorrect literature reference spectrum [8]. In that research, the spectral quality is far inferior to the data generated from the Arabic manuscripts. However, based on weak spectral features centered at 1345, 1460, and 1584  $\text{cm}^{-1}$ , the authors assigned the yellowy-orange paint to Indian yellow, which is now known to be more likely tartrazine. The possible presence of this late 19th century pigment combined with the reported presence of studio red (PR3: C.I. 12120), first available in 1904 [7], now suggests either modern restoration or a possible forgery.

The power of Raman spectroscopy to identify nondestructively the molecular composition and crystalline form of pigments and dyes directly on objects makes it a powerful technique in forensic science and technical art history investigations. However, these identifications rely on high quality reference data from genuine examples of artists' materials. De Faria et al. have corrected the earlier erroneous data on this important pigment by presenting the FT-Raman spectrum of a single authentic and well-characterized specimen of Indian yellow. They concluded that the few identifications of this colorant on artworks to date have been a result of the previously inaccurate reference data and the fact that the authentic pigment is too luminescent to be analyzed by the type of dispersive Raman spectrometers that are common to museum and forensic laboratories. Unfortunately, this last statement too is inaccurate and can potentially discourage scientists from exploring objects for the presence of Indian yellow when their laboratories are not equipped with FT-Raman instrumentation. The conservation science laboratory at the Indianapolis Museum of Art (IMA) has previously acquired high quality Raman data from two authentic samples of Indian yellow using visible and NIR diode laser excitation sources with a dispersive Raman microspectrometer. Additionally, in the preparation for an exhibition on the history of colorants, the author has identified for the first time genuine Indian yellow on a museum artwork, a historic manuscript with an uncertain date of creation. These new data are presented and discussed here.

## 2. Materials and methods

### 2.1. Samples

Two examples of authentic Indian yellow pigment were acquired from the well-known Forbes Collection (#3.14.3) and from the private collection of Dr. David Hill. The bulk of the former sample resides at Harvard University while that of the latter sample is now held by the Economic Botany Collection of the Royal Botanic Kew Gardens. The Forbes sample exists as a small cake of agglomerated pigment particles while the Hill sample presents finely divided needle-like crystals of Indian yellow. The latter appears to be a purer specimen than the former. Imitation Indian yellow samples were obtained from the paintings conservation studio at the IMA. A Kremer Pigments (#23350) Imitation Indian Yellow in casein medium, an acrylic paint swatch of Indian Yellow

Hue from Golden Artist Colors (#1455), and a dry pigment powder of unknown origin labeled simply 'Indian Yellow' were analyzed using dispersive Raman spectroscopy.

### 2.2. Raman microspectroscopy

Raman spectra were acquired using a Bruker Senterra dispersive microspectrometer on a Z-axis gantry. The spectrometer utilizes 3 selectable excitation lasers (532, 633, and 785 nm), an Andor Peltier-cooled CCD detector, and a 50  $\mu\text{m}$  confocal pinhole. Laser power at the sample was always below 4 mW. The spectra are the result of 3 or 5 s integrations with 40–50 coadditions. A 50X ultra-long working distance objective was used to focus on pigment particles or on the surface of paints. The analysis spot size diameter was on the order of 1  $\mu\text{m}$ , and the spectral resolution was in the range of 9–18  $\text{cm}^{-1}$  or 3–5  $\text{cm}^{-1}$ . OPUS software allowed for automated cosmic spike removal, peak shape correction, and spectral calibration. An Automatic Fluorescence Rejection (AFR) routine can be used with the diode laser at 785 nm to remove fluorescence interference.

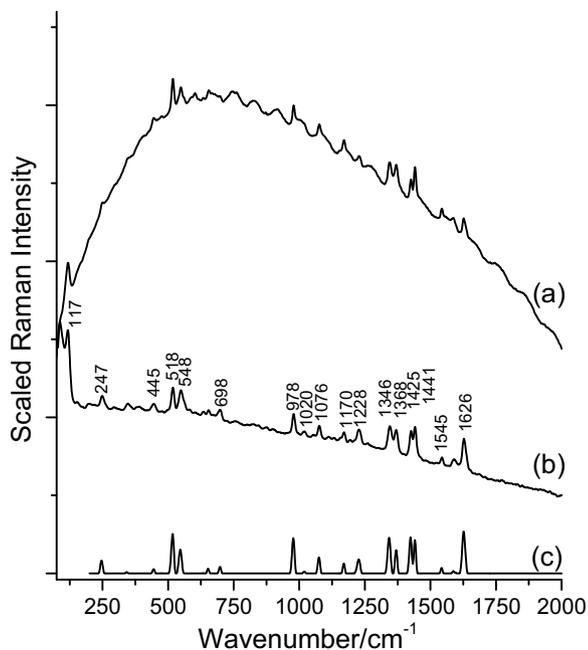
### 2.3. Photographic images

Visible and ultraviolet-induced visible fluorescence images were captured using a Nikon D700 camera under diffuse irradiation conditions with either a daylight fluorescent lamp (4000K, OSRAM Dulux L 2G11) or a long wavelength blacklight (Norelco F40/BLB). For fluorescence imaging a Kodak Wratten 2E and Peca 918 filter set was used to limit the spectral sensitivity of the camera sensor. A visible light AIC Photodocumentation color target (Robin Myers Imaging) and a UV fluorescence color standard (UV Innovations) were used to adjust the images for color accuracy before being cropped out of the final images.

## 3. Results and discussion

Bell, Clark, and Gibbs' Raman spectral database has been instrumental in bringing conventional Raman spectroscopy into the mainstream of cultural heritage chemistry in the last two decades [2]. This dispersive Raman spectral library has been cited extensively in the cultural heritage literature, and the accompanying website of Raman data is a much used resource in the field [9]. Fig. 1 shows Raman spectra of an authentic sample of Indian yellow from the Hill collection, confirming the conclusion of de Faria et al. that Bell et al.'s reference spectrum of Indian yellow is not correct. Importantly, the spectrum presented in Fig. 1(a) was collected using a 633 nm visible excitation laser, contradicting the assertion by de Faria et al. that visible lasers are incapable of analyzing the pigment due to overwhelming fluorescence. Fig. 1(b) shows an analysis of the same sample using a 785 nm diode excitation source, also conditions suggested to be unworkable by the earlier authors. As indicated on the figure, all the spectral features observed by de Faria et al. using FT-Raman spectroscopy are also observed using conventional dispersive techniques, as well as additional characteristic bands at lower wavenumbers. Furthermore, the fluorescence intensity observed here using 785 nm excitation is noticeably less than that observed in their FT-Raman spectrum prior to baseline correction. An attempt to analyze this pigment sample with a 532 nm excitation source did fail due to detector saturation from the native luminescence of the pigment. Baer et al. note that the pigment's peak fluorescence excitation wavelength is 435 nm with maximum emission centered at 535 nm [3], so this is not surprising.

Although some fluorescence is observed for the analysis of the Hill collection sample of Indian yellow, clearly red and near-infrared lasers are effective in measuring the Raman spectrum



**Fig. 1.** Raman spectra of an authentic Indian yellow pigment sample from the collection of Dr. David Hill obtained using (a) 633 nm, (b) 785 nm, and (c) 785 nm with AFR excitation sources.

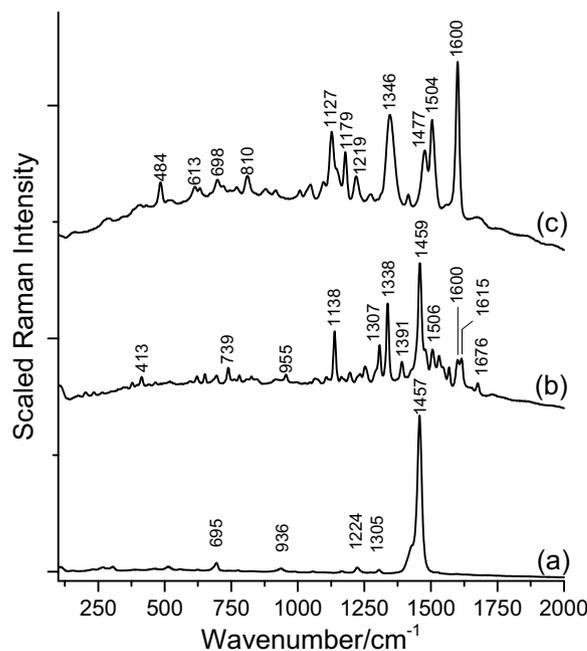
using dispersive instrumentation commonly found in museum and forensic laboratories, and at laser excitation powers suitable for the examination of precious objects. Bruker's patented AFR accessory for Raman spectroscopy further clarifies the spectrum, as seen in Fig. 1(c). AFR uses applied heat to 'mode hop' the NIR diode excitation laser to a slightly different wavelength, which causes a corresponding shift in the Raman spectral features but an imperceptible change in the fluorescence background [10]. Shifted excitation Raman difference spectroscopy (SERDS) of two spectra collected at slightly different NIR excitation wavelengths leads to a near elimination of the fluorescence background. All of the major bands from the Indian yellow pigment are clearly extracted from the background signal by AFR. Practically, however, AFR requires more than twice the experimental time, which can be prohibitively long when working with paper or canvas based artworks or evidence that tend to shift out of focus due to constant expansion and contraction.

Clearly the analysis of Indian yellow pigment is within the grasp of museum or forensic scientists whose labs are outfitted with common dispersive Raman spectrometers. De Faria et al.'s inability to achieve a suitable signal-to-noise ratio spectrum using dispersive Raman techniques is perhaps due to impurities in their sample, although this can only be speculation. It is noted that the elemental analysis of their L. Cornelissen & Son sample showed the presence of Si, S, P, Cl, Fe and Al [1], which are not inherent in the chemical composition of the pigment, and could indicate impurities that potentially increase the fluorescence background. The Hill collection sample of Indian yellow analyzed here produced far better results with less background fluorescence than the Forbes collection Indian yellow that was also studied, although the Forbes collection sample was successfully identified as an authentic Indian yellow based on data generated at both 633 nm and 785 nm excitation. Interestingly, under microscopic examination, the Hill collection sample exists as a collection of interwoven acicular crystals whereas the Forbes collection sample appears as a cake of agglomerated particles of irregular shape. Both of these types are

described by Baer et al. [3]. This perhaps indicates a more highly purified sample in the former and a less pure sample in the latter.

De Faria et al. identified the earlier reference spectrum of Indian yellow as that of tartrazine yellow, a synthetic azo dye first available in 1884 [7]. As noted previously, tartrazine has been used as an early imitation of Indian yellow [3], however today it appears that few art materials manufacturers rely on that dye to simulate the translucent warm yellow color of the original pigment. Three samples of modern-day mimics of Indian yellow were found in the stores of the IMA paintings conservation studio and were analyzed by Raman spectroscopy with 633 nm excitation. None of these imitations exhibited the strong yellow luminescence of true Indian yellow when viewed under a blacklight. Fig. 2(a) shows the Raman spectrum derived from Kremer Pigments' imitation Indian yellow prepared 1:2 in a casein binding medium. This yellow-brown paint relies on the modern organometallic complex nickel azo yellow (PG10, C.I. 12775), which was discovered in 1941 [7]. Interestingly, this same Kremer product was incorrectly listed as "Sample 50 Indian Yellow" in another Raman spectral pigment database appearing in the literature and made available online as the ColoRaman Project [11]. Golden Artist Colors (GAC) also produces an Indian yellow hue in acrylic emulsion binder, which is made by mixing a slightly different nickel azo yellow (PY150, C.I. 12764) with quinacridone burnt orange (PR206, C.I. 73903) and Hansa yellow medium (PY73, C.I. 11738). As a result, its Raman spectrum shown in Fig. 2(b) is rich in spectral features for all three colorants. Quinacridone pigments first appeared after 1935 [12], and PY73 was first synthesized in 1957 [7]. A plain jar of yellow pigment simply labeled 'Indian Yellow' and thought to originate from the 1970s was also analyzed. The resulting Raman spectrum shown in Fig. 2(c) is clearly that of tartrazine yellow.

Even within a single art material vendor's product line the pigments used to simulate Indian yellow can change depending on the paint medium being sold. For instance, Windsor and Newton Indian Yellow Hue in oil paint contains a mixture of isoindoline yellow (PY139, C.I. 56298) and synthetic iron oxide (PR101, C.I. 77491), whereas the corresponding watercolor paint blends



**Fig. 2.** Raman spectra collected using 633 nm excitation on (a) Kremer imitation Indian yellow in casein, (b) GAC Indian Yellow Hue in acrylic, and (c) a dry powder labeled "Indian Yellow" of unknown origin.

PY139 with a benzimidazolone orange (PO62, C.I. 11775). Changes have also occurred temporally in a single product; Kremer Pigments' Imitation Indian Yellow (#23350) used PG10 in 2005, PY150 in 2007, PY10 (Hansa Yellow R, C.I. 12710) in 2009, and again back to PY150 in 2017 according to their product catalogues. Clearly the imitations of Indian yellow are diverse and therefore offer ample opportunity for refined dating of artworks or other objects that attempt to mimic the appearance of traditional Indian yellow using modern pigments.

In preparation for an IMA exhibition on the intertwined history of chemistry and the expansion of the artists' palette, a highly decorated Hindu manuscript was analyzed to determine the colorants used in its illuminations. The show, *Chemistry of Color*, is part of a series of science-based exhibitions called *CSI: Conservation Science Indianapolis*, which uses the mystery, discovery, clues and evidence that are a significant feature of conservation science research to teach visitors chemical concepts related to the study and preservation of artworks. The illuminated manuscript shown in Fig. 3 was purchased by the museum in 1969 and contains decorated text and illuminations throughout. A modern board cover to the text block was embossed with the notation "Indian Miniatures 17th–18th century," although recent scholarship has suggested that it might be from the 18th or 19th century. A full palette study was conducted to determine if any date-marker pigments were present that could enlighten the dating of the object. The long wavelength UV-induced visible fluorescence image shown in the lower half of Fig. 3 indicates that a brightly fluorescing pigment is used for the yellow borders, yellow details, and in the green background throughout the work. Raman analyses were undertaken in these areas, and the exact analysis locations are indicated in the Figure with numerals.

Fig. 4(a) shows the Raman spectrum of the yellow border collected using 785 nm laser excitation. The spectrum corresponds

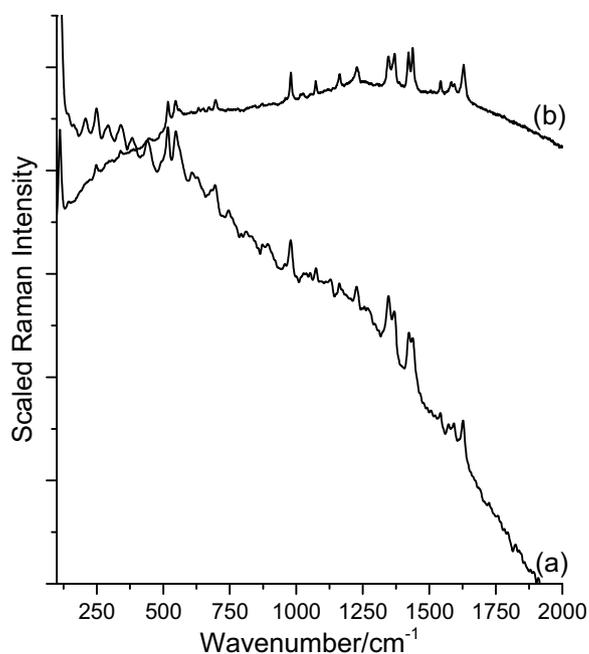


Fig. 4. Raman spectrum of (a) the yellow colorant in the border of page 5 of the illustrated Hindu manuscript shown in Fig. 3 compared to (b) the authentic Forbes collection Indian yellow. The spectra were collected using 785 nm excitation.

well to Fig. 4(b) a high resolution spectrum also attained using 785 nm excitation of the Forbes collection sample of authentic Indian yellow. The analysis of the green background area also revealed the use of Indian yellow, this time mixed with the blue pigment indigo. These spectra now represent the first direct



Fig. 3. Color corrected visible (top) and UV-induced visible fluorescence (bottom) images of pages 4 and 5 of an illustrated Hindu manuscript (IMA#69.25.1, Gift of the Alliance Rental Gallery Fund). Black numeric notations mark the locations of in situ, nondestructive Raman analyses that identified authentic Indian yellow pigment. Photos courtesy of IMA conservators Fiona Beckett and Erica Schuler.

identification of genuine Indian yellow in a museum artwork using Raman spectroscopy and highlight the ability of widely available dispersive Raman instruments to capture good quality spectra of the pigment from realistic samples. Aside from Indian yellow and indigo, Raman analysis also showed the presence of vermilion (HgS), lead white ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ), and carbon black (C) pigments. The silver foil used for the throne yielded the spectrum of romarchite (SnO) with principle bands at 115 and  $213\text{ cm}^{-1}$ , suggesting the use of tin leaf that has tarnished, while the gold crowns gave no Raman signal. Subsequent analysis of these metallic gildings by x-ray fluorescence analysis confirmed their assignments to tin and gold, respectively. Unfortunately, all of these materials have been available since the 17th century to the present and therefore do not refine the dating of the manuscript. However, the presence of genuine Indian yellow does allow one to assume with some confidence a creation date prior to the advent of the 20th century after which the availability of this pigment would have been in steep decline.

#### 4. Conclusions

New reference data for the Raman spectrum of genuine Indian yellow pigment facilitate the identification of this colorant on Asian and European artworks for studies related to pigment usage, conservation, authentication, and technical art history. A re-examination of the previous identifications of Indian yellow on museum collections based on earlier erroneous reference data, now known to be the modern dye tartrazine, demonstrates the potential role of this non-invasive technique to resolve questions of authenticity and alteration. The new data presented here correct previous inaccurate statements about the ability of dispersive Raman spectrometers, now common to many museum and forensic laboratories, to collect high quality spectra of Indian yellow at excitation powers suitable to the safe examination of valuable cultural patrimony. When modern imitations for Indian yellow are used in an original artwork or in the creation of a forgery of an historic object, numerous date-marker pigments can be easily identified by Raman spectroscopy to assist in providing a *terminus post quem* for the piece. For the first time, authentic Indian yellow has been identified nondestructively using Raman microscopy on a museum artwork, providing additional evidence of its originality and likely manufacture prior to the 20th century when the pigment became unavailable to artists.

#### Conflict of interest

The author declares that he has no conflict of interest.

#### Acknowledgements

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