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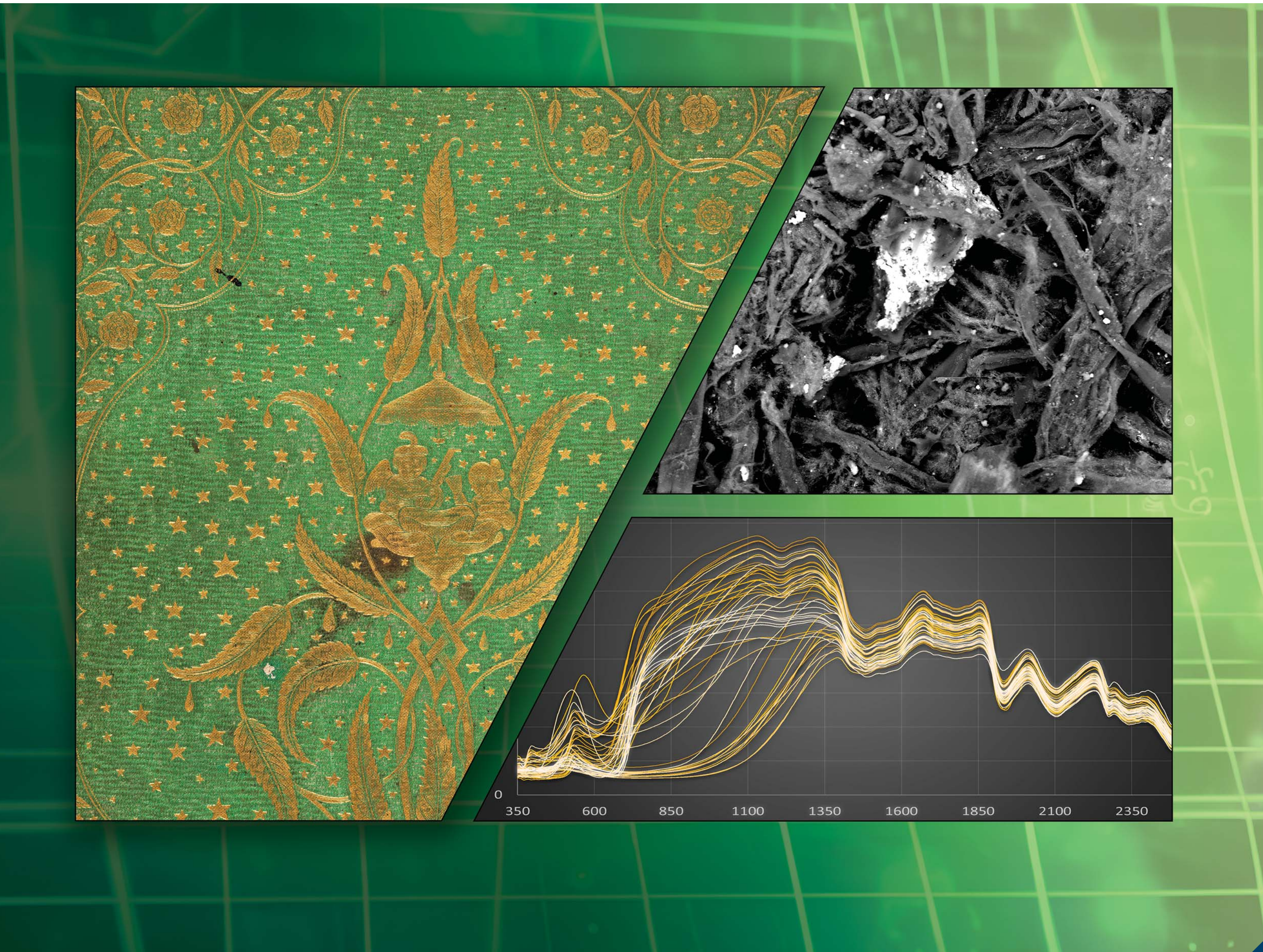

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TECHNICAL NOTE

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Detecting emerald green in 19thC book bindings using vis-NIR spectroscopy†

M. Pilar Gil, *[a] Elizabeth Henderson,[a] Jessica Burdge,[a] Erica Kotze‡[a] and William McCarthy ‡[b]

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Detection and identification of heavy metal-based pigments in 19th-century bookbindings is crucial to avoid human user exposure to toxic substances. Vibrant green bookbindings with arsenical emerald green are particularly problematic due to their friability. A pilot study at St Andrews University tested 800 green bookbindings for arsenic presence using visible near-infrared spectrometry, a technique not previously applied to the detection of heavy metals in bindings. The ASD TerraSpec Halo portable spectrometer that is normally used in geology to identify minerals in rocks, is used here to collect hyperspectral reflectance data between 350 and 2500 nm. Raman spectroscopy and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) are used here to validate hyperspectral test results. The study finds that bookbindings containing emerald green have a distinctive pattern in the visible part of the spectrum that is distinguishable from other green pigments. This finding opens up the possibility for all collecting institutions to test bindings for this toxic compound in a non-destructive, cost-effective and efficient manner.

Introduction

Historic pigments used to colour book covering materials are of growing interest to conservators and custodians of library, archive and museum collections. While pigments used in paintings and manuscripts have long been studied,[1] the inclusion of potentially harmful pigments in bookbindings poses a health risk during handling and is a new area of research.[2,3]

In 2019, the University Library of Southern Denmark reported on four 16th and early 17thC original parchment bindings with covers painted in arsenic-based green.[4] The arsenical element in the green paint was identified as orpiment (arsenic sulphide), and the purpose of its application was to disguise the written text on the reused parchment covers. Their research raised the concern that other similarly bound and treated volumes in collections may pose a risk of exposure and contamination. Increased awareness of the potential exposure to toxic pigments on elements of bookbindings that inevitably must be handled during access poses a challenge for libraries, curators, and conservators. Without conservation science support to test items in their collections, libraries have adopted a cautious approach to accessing potentially arsenic-containing items. This means erring on the side of caution, suspecting any green bindings produced within the timeframe associated with the use of arsenical pigments, and restricting access to any books that may fall into this category. While this will help to minimise any health and safety concerns, it is likely that many books identified as potential candidates will be unnecessarily isolated.

Since 2020, the department of conservation at the Winterthur Museum, Garden & Library in Delaware has been publishing research on the potentially toxic pigments used as colourants in 19th century bookcloth including arsenic, chromium, lead, and mercury.[5] Their research has indicated that production techniques may have an influence on the friability of finished bookcloths, particularly in starch-coated bookcloth colored with emerald green pigment (copper acetoarsenite). Particulates could offset onto skin from friable bookcloth or become airborne and then ingested or inhaled. As a result, there is an increased awareness of the potential hazard when handling green-coloured 19th century cloth bindings.[6]

Copper–arsenic pigments Scheele's green (copper arsenite) and emerald green (copper acetoarsenite) were some of the most desired pigments during Victorian times due to their vibrancy.[7] Their popularity and widespread use in many aspects of Victorian daily life led to a range of exposure routes, high levels of toxicity and the onset of non-specific symptoms that were dismissed or misinterpreted.[8,9]

Despite documented cases of death and poisoning, arsenic was pervasively used in 19th century Britain in the manufacture

[a]University Collections Division of the University of St Andrews Libraries and Museums, Library Annexe, North Haugh, St Andrews KY16 9WH, UK. E-mail: mpg6@st-andrews.ac.uk

[b]School of Earth & Environmental Sciences, University of St Andrews, Bute Building, Queen's Terrace, St Andrews KY16 9TS, UK

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‡ These authors contributed equally to this work.

of home goods and everyday objects while regulation to protect health was slow to be introduced.[10]

Not all 19th century green cloth-bound books contain copper–arsenic pigments. However, without an accessible tool to identify colourants in bookcloth, paper or paint, it is not possible to determine with absolute certainty, which green bindings are potentially toxic. Because of the dangers and risks associated with handling arsenic-containing books, some institutions have adopted a series of measures and protocols to protect workers and users, largely based on restricting access to all 19th-century green bindings.[11]

To date, techniques used to detect emerald green in book cloth have relied mainly on portable X-ray fluorescence (XRF) spectroscopy, as this is an *in situ*, non-destructive technique, which can determine elemental composition.[12] Additional techniques such as Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) have also been used to identify the molecular composition of book cloth to facilitate pigment characterisation. Synchrotron radiation X-ray absorption near edge structure (XANES) has been used to characterise the oxidation state of the pigments and, consequently, the mobility of the pigment and the presence of compounds resulting from the degradation of emerald green.[13]

However, such equipment requires specialised training and is prohibitively expensive for many institutions and collectors. In an effort to make the detection of emerald green in books more widely available, the University Collections Department of the University of St Andrews undertook an initiative to survey the green books in its rare book collections using visible and infrared light-based technology. This study reports on the results of this initiative, as well as the potential implications for developing and using the technology in the future.

Materials and methods

Books

The rare book collections in the University of St Andrews Libraries and Museums holds over 210 000 printed books dating from the fifteenth to the twenty-first centuries, of which approx. 103 000 were published between 1830 and 1900, the period examined in this report because it corresponds to the time in which emerald green was used.[14] Approximately 25% of these books have green covers.

For the purpose of this study, 800 books with green covers were subjected to non-destructive *in situ* testing using a portable visible near-infrared spectrometer. A subset of 170 books were further subjected to testing either by Raman spectroscopy (90 books), scanning electron microscopy with energy dispersive X-ray spectroscopy (24 books) or both (56 books).

Visible, near-infrared and short-wave infrared spectroscopy

In the context of cultural heritage, near-infrared spectroscopy has been used to identify pigments in easel paintings and to characterise the chemical and mechanical properties of paper-based collections.[15,16] To test its effectiveness in the identification of pigments in book covering materials, a portable instrument utilised in geology for the identification of minerals in rocks, the ASD TerraSpec® Halo Mineral Identifier, was used. This is a handheld near-infrared spectrometer with a visible near-infrared (VNIR: 350–1000 nm) and short wave-infrared (SWIR: 1001–2500 nm) range in a test area of 110 mm^2. The sampling was carried out with the sample being pressed against the sensor for analysis, so that no light other than that coming from the spectrometer could reach the sensor, and the TerraSpec® Halo test window was wiped clean with a lint-free tissue between samples. Calibration was performed using the white reference disc supplied by the manufacturer. During testing, at least two measurements were taken from the same book to ensure reproducibility of the measurements and assess if dirt, discolouration or differing print media created noise in the data set. To determine the reflectance and absorption characteristics of the book covering materials tested, the instrument readings were processed with the proprietary Halo Manager software and converted into binary ASD files. Spectra were analysed using SCIRO The Spectral Geologist (TSG) software.

Aside from guidelines for the safe handling of bindings containing arsenic compounds, no safety protocols are required to use this equipment. The light source is a filament bulb, and the instrument requires no special training or precautions for use.

Raman spectroscopy

To obtain a non-destructive detailed chemical and structural characterisation of the book covering materials, Raman spectroscopy measurements were performed with a Renishaw inVia Qontor confocal Raman microscope using a red 17 mW 633 nm HeNe laser and 1800 lines per mm diffraction grating. The defined spectral range was between 100 and 1300 cm^{-1}, with a resolution of 1 cm^{-1}. Raman spectra were collected in at least three different locations per book to ensure reproducibility of the measurements. The laser power was reduced by filters to avoid thermal photo-decomposition and degradation of the book cloth or paper, and the acquisition time and accumulations were defined for each sample to obtain a good signal-to-noise ratio. Wire 5.5 software (Renishaw) was used to remove cosmic rays and correct the baseline spectra. The evaluation and interpretation of the different Raman spectra obtained from the green books was performed by comparison with the data from reference libraries for the spectroscopic signature of pure pigments and minerals.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS)

High resolution and depth imaging of selected book cloth samples, as well as their composition and elemental distribution, was obtained using the JEOL model JSM-IT 200 with an accelerating voltage of 15 kV, under low vacuum conditions (30 Pa) and using a backscattered electron detector (BED-C). The book cloth fragments, measuring a few mm^2, were mounted on carbon tape and were not coated.

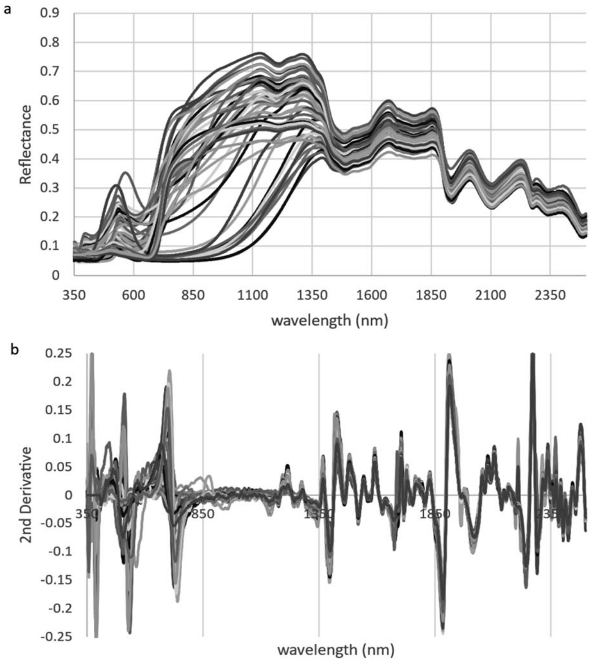

Fig. 1 (a) Reflectance spectra of 50 randomly chosen green book coverings; (b) reflectance values shown in (a) plotted as second derivative.

Results and discussion

Reflectance spectra of the green book cloth and paper covering material

A full set of spectral data for all the books analysed would be made available on request, but for ease of viewing Fig. 1(a) shows the reflectance spectra of 50 representative green books. There is a clear distinction between the VNIR (350–1000 nm) region of high reflectance variability and the highly uniform SWIR (1001–2500 nm) region. The SWIR spectral region shows the characteristic reflectance of the laminated board, millboard and cloth or paper cover material in which the book is bound, remaining constant for a given print medium and not changing as the inks change. The VNIR region corresponds to the reflectance of the colourant.[17] Fig. 1(b) corresponds to the same 50 books as the previous graph, but here the reflectance values are plotted as the second derivative, which allows the maxima and minima, as well as the concavity or convexity of the reflectance graph, to be more easily seen. This projection accentuates otherwise subtle features on the reflectance profile and allows characteristic profiles to be more readily identified, and therefore the differences between the books to be more easily distinguished. Hence forth, all the hyperspectral plots in this article will show reflectance as the second derivative.

Identification of emerald green containing book cloth

The database of arsenical books created and maintained by the team at Winterthur Museum, Garden & Library provided a good starting point for determining whether books in our collection could be used as a positive control.[18] Books in our study that had previously been confirmed as having emerald green were used as control specimens and their spectrum was compared to unknown books. Hyperspec data is routinely interpreted by comparing results to a spectra library of known minerals. In this study, the composition of pigments was unknown and not recognized by the TSG library.

One book in our collection matched a volume in the Winterthur database, albeit from a different edition: The Court Album: Fourteen Portraits of the Female Aristocracy, published in London in 1853 (Fig. 2). The book has a highly decorated, gilt-embossed green cloth cover which is very vivid in the centre, but has brown discolouration at the board edges and on the spine Fig. 2(a). It is well documented that emerald green darkens to brown copper sulphides when mixed with sulphur compounds from the atmosphere.[19] The visible, near and shortwave infrared spectrum for this book is shown in Fig. 2(b). To verify that we could detect and identify the presence of emerald green in these books, other techniques were used. These were either based on electronic transitions, such as Raman spectroscopy, which provides information about the molecular structure of the pigment, or on imaging and EDS, which provide information about the elemental composition and the location of the elements in the sample. The characteristic Raman bands at 136, 155, 175, 218, 243, 293, 295, 325, 369, 432, 487, 539, 842 and

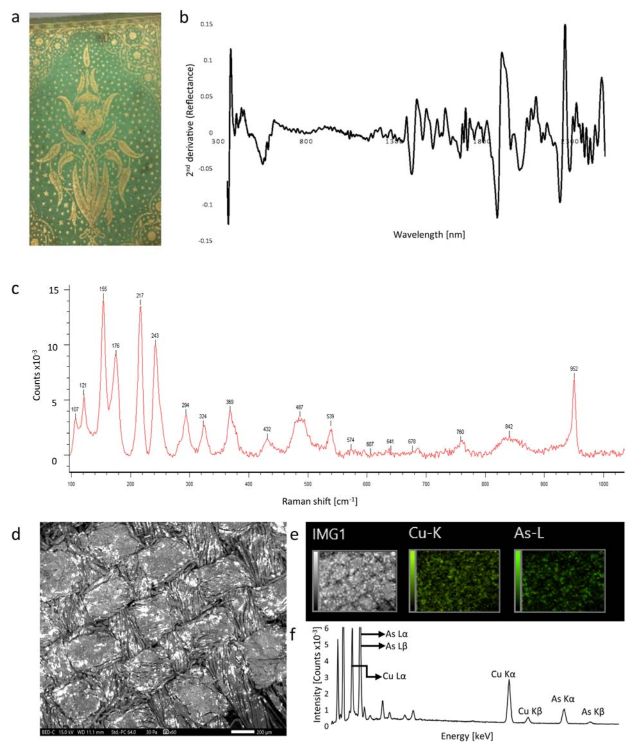

Fig. 2 (a) Photograph of book previously reported as containing emerald pigment: The Court Album: Fourteen Portraits of the Female Aristocracy, published in London by Davis Bogue in 1853, (b) its corresponding vis near-IR SWIR spectrum; (c) Raman spectrum of this book showing the characteristic peaks corresponding to emerald green; (d) EM image, (e) secondary electron image of the analysed area and the corresponding elemental distribution maps of Cu and As, (f) elemental map of the sample showing the peaks corresponding to arsenic and copper.

952 cm^{-1} in Fig. 2(c) confirmed the presence of emerald green in the book cloth as described in the Cameo Materials database.[20] The bright white spots on the book cloth fibres in the backscattered electron image Fig. 2(d) indicated the presence of heavy elements with large nuclei, which deflect incident electrons more strongly than lighter ones. One of these heavy metals could be arsenic, as can be seen on the SEM-BSE elemental map of arsenic shown in Fig. 2(e), with a similar distribution being observed on the map of copper. The energy emissions of Cu and As were translated into spectral peaks of varying intensity, directly proportional to the concentration of the elements in the sample Fig. 2(f); the elemental composition (atom%) for copper and arsenic was 5.15 and 5.02 respectively, an approximate 1 : 1 Cu/As ratio. This is in agreement with published data, which shows that the ratio of Cu to As in the XRF spectra of emerald green is approximately 1 : 1.[21]

Different pigment compositions result in clearly differentiated vis-NIR spectra

Comparison of hyperspectral measurement data collected from emerald green and non-emerald green containing bookcloths, confirmed that samples known to contain emerald green generate a spectrum readily distinguishable from samples that do not contain this pigment.

According to the published literature and our own unpublished data, more than 90% of the green books published during the 19th century contain lead, chromium or arsenic compounds. In these books, lead and chromium are usually present in the form of chrome green, a pigment mixture prepared with chromium yellow (lead chromate) and Prussian blue.[22]

The Fern Garden, (classmark rSB429.H5), a book published in London in 1872, was previously analysed by XRF and found to contain Pb and Cr, probably in the form of chrome green.[23] No arsenic was found on the book cloth. The presence of this book in our collection allowed us to use it as a negative control, and test if the resulting visible near-IR reflectance spectrum differed from that previously obtained from the book bound in emerald green containing cloth.

The Fern Garden is bound in the publisher's original gilt-decorated green cloth covers, with gilt-embossed title and author lettering on the spine and front cover, as shown in Fig. 3(a). The green is of a darker shade than that used in The Court Album: Fourteen Portraits of the Female Aristocracy, and there is no brown discolouration on the spine or edges. However, colour alone is not a good indicator of the presence of a particular pigment, as can be seen from the range of bookcloths and paper containing emerald green (Fig. S1†). Fig. 3(b) shows the superimposed visible-near IR-SWIR spectra of the two books (The Court Album in orange, The Fern Garden in black), with differences in reflectance in the 400–600 nm region and in the 1000–1300 nm range. As expected, the Raman spectrum of The Fern Garden shown in Fig. 3(c) does not present the characteristic Raman shifts of emerald green, but instead has peaks in the region of 340 cm^{-1} and 825 cm^{-1} which characterises lead(II) chromate ($PbCrO_4 \cdot PbO$).[24]

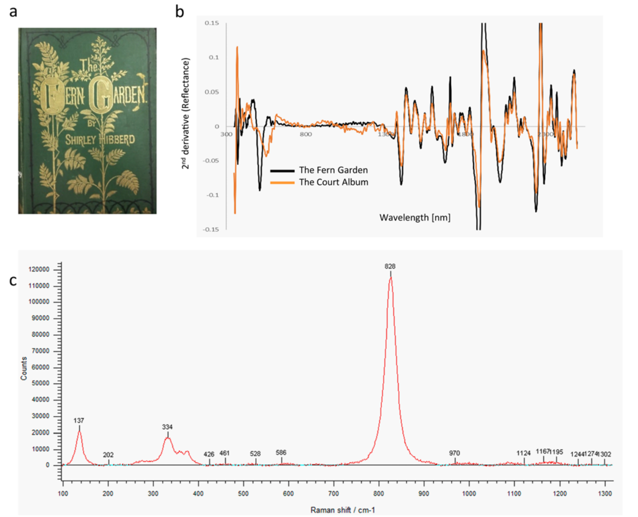

Fig. 3 (a) The Fern Garden: how to make it, and enjoy it, or, fern culture made easy by Shirley Hibberd. Published in London by Groombridge and Sons in 1870. (b) Visible near-IR SWIR spectrum of The Fern Garden (black) and The Court Album (orange). (c) Raman spectrum of The Fern Garden book cloth.

Fig. 3(b) shows a prominent reflectance feature at 475 nm in the sample containing chrome green, this corresponds to a trough in the sample containing emerald green. A similar observation can be made for the region around 560 nm that shows opposing reflection and absorption features for both bindings. These differences are observed in other books tested, allowing us to conclude that a different elemental composition results in a significantly different spectrum in the visible range.

Emerald green containing book bindings have a distinctive pattern in the visible spectrum

The marked differences between the spectra of the two books, particularly in the visible region, led us to search for a pattern, a distinctive fingerprint, exclusive to the book coverings containing emerald green, that would allow the pigment to be identified quickly, efficiently and in a safe and reliable way. Fig. 4 shows this distinctive pattern.

184 visible spectra randomly selected from the 800 green books tested, were plotted together with the 16 samples found to contain emerald green. The resulting plot, centred in the visible region (350 to 700 nm), is shown in Fig. 4(a). Within such a range of reflectance spectra, the subset of samples containing emerald green shows a high degree of uniformity characterised in the 470 to 565 nm range by negative values in the second derivative of the reflectance Fig. 4(b). Furthermore, all 16 samples show three distinct peaks at 574, 595 and 617 nm. A box and whisker plot was used to visually compare the two populations, the non-emerald green and the emerald green covering materials, and to understand the distribution of data points in both sample groups Fig. 4(c). The values in the graph represent the second derivative of the reflectance values obtained for each sample at the wavelength 515 nm, chosen because it is a midpoint in the region where the plot of the emerald green book covering shows high uniformity.

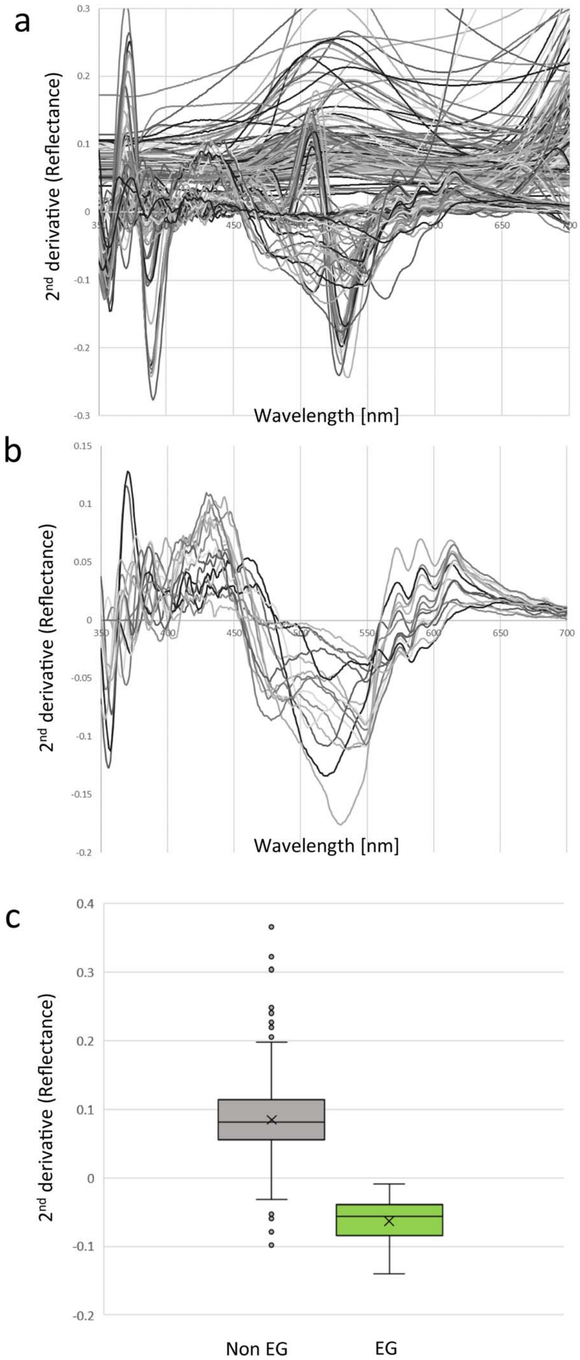

Fig. 4 (a) Graphic representation of the reflectance values – as a second derivative – of 200 green book covers. (b) Graph extracted from (a), in which only the reflectance values for the sub-group of books with the emerald green pigment in their cover are plotted. (c) Box and whiskers plot showing the distribution values of green books without emerald green (grey box) and with emerald green (green box).

Based on the plots shown in Fig. 4, we can conclude that books containing the emerald green pigment show a relatively uniform and distinguishable pattern of reflectance measurements from other green books that do not contain emerald green. This observation, which is immediately apparent when looking at the reflectance graph for the emerald green subgroup of books, is even more obvious when looking at the distribution of the values for the two groups of books in a box-and-whisker plot.

Even within the subgroup of the 16 emerald green books, four books on the list show differences in the slope of the graph and the wavelength for the minimum value of the second derivative of the reflectance. Fig. 5(a) shows the plots for 12 books, which have a minimum at around 550 nm and inflection points at around 480 and 510 nm. Fig. 5(b) corresponds to the plots of the four books with a minimum of the second derivative of the reflectance at about 520 nm and an inflection point at about 454 nm.

In one of the four books in this subset, the green paper containing emerald green was not on the covers, but in the printed wastepaper used by the binder to create the hollow spine. This paper, from a Victorian advertisement for a medical panacea called Dr J. Collis Browne's Chlorodine, has the peculiarity of having a coating which gives it a sheen (Fig. 5(c)). Indeed, all four books showing the characteristic pattern in the visible reflectance spectrum have coated green paper, giving them a sheen, which is absent in the other 12 books (see Fig. 5(c) and S1†).

The results shown in Fig. 4 and 5 confirm the suitability of the technique to detect emerald green pigment.

In general, book covers show differences in their surfaces that go beyond their colour. Surface coatings and finishes, bookcloth weave, decorative pattern and blind embossing as well as fading, accumulated surface dirt, abrasion and wear are all factors which may affect the light reflectance.[25] Despite these variables and even in samples with a glossy surface, the results obtained demonstrate that covering materials containing emerald green have a distinctive spectroscopic pattern not seen in materials without emerald green.

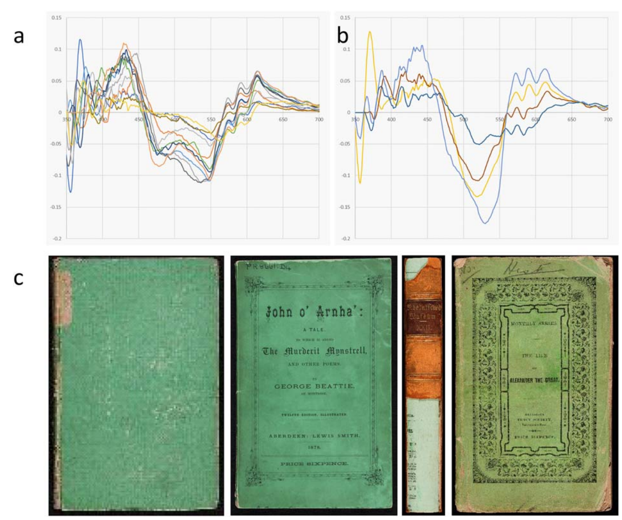

Fig. 5 (a) Graphic representation of the reflectance values – as a second derivative – of 12 green book covers containing emerald green pigment. (b) Graphic representation of the reflectance values – as a second derivative – of 4 green book covers containing emerald green pigment. (c) Images of the 4 books that correspond to the plots in (b).

Currently, the presence of the toxic compounds can only be confirmed using expensive laboratory equipment, limiting its use to relatively few institutions. The uniform pattern of spectra in the visible region observed for book covers containing emerald green opens the door to the development of a cheap and simple smartphone-based technique using the disordered optics approaches developed at the University of St Andrews.[26] Such a method has the potential for widespread global adoption to detect the presence of the toxic pigment.

Conclusions

This study demonstrates the use of vis-NIR spectroscopy as a rapid and safe method of detecting the presence of potentially toxic pigments used to colour bookcloth and paper in 19th-century bindings, particularly copper acetoarsenite or emerald green.

Using techniques based on visible and infrared spectroscopy, we detected a pattern in the reflectance spectrum of books containing emerald green pigment, allowing us to distinguish them from books without the pigment. This distinction is also possible even after considering differences in the surface of the books, such as those due to decorative embossing and cloth patterns, the accumulation of dirt and other changes to the covers due to ageing, and coatings and finishes of the bookcloth and papers.

Further research is currently underway to implement the observations presented in this study so that conservators, curators and collectors will be able to identify emerald green in books using a simple method that does not require specialist training or expensive equipment.

Author contributions

MPG: conceptual design, analytical strategy, selection of samples, data acquisition, data processing, analysis and curating, writing of original draft; EH: resources, funding acquisition, writing – review and editing; JB: funding acquisition, writing – review and editing; EK: conceptualisation, resources, funding acquisition, writing – review and editing; WMC: methodology, resources, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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