Talanta 154 (2016) 63–72

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Estimation of semiconductor-like pigment concentrations in paint mixtures and their differentiation from paint layers using first-derivative reflectance spectra

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ARTICLE INFO

Article history:
Received 8 November 2015
Received in revised form
10 March 2016
Accepted 15 March 2016
Available online 16 March 2016

Keywords:
Fibre-optic reflectance spectroscopy
First-derivative analysis
Function fitting
Deconvolution
Paint mixtures
Electronic-structure calculations
Vermillion
Red lead
Lead-tin yellow

ABSTRACT

Identification of the techniques employed by artists, e.g. mixing and layering of paints, if used together with information about their colour palette and style, can help to attribute works of art with more confidence. In this study, we show how the pigment composition in binary paint mixtures can be quantified using optical-reflectance spectroscopy, by analysis of the peak features corresponding to colour-transition edges in the first-derivative spectra. This technique is found to be more robust than a number of other spectral-analysis methods, which can suffer due to shifts in the transition edges in mixed paints compared to those observed in spectra of pure ones. Our method also provides a means of distinguishing paint mixtures from layering in some cases. The spectroscopy also shows the presence of multiple electronic transitions, accessible within a narrow energy range, to be a common feature of many coloured pigments, which electronic-structure calculations attribute to shallow band edges. We also demonstrate the successful application of the reflectance-analysis technique to painted areas on a selection of medieval illuminated manuscripts.

1. Introduction

Works of art have so far mostly been attributed to particular artists on the grounds of the artistic styles and colour palettes used. It is therefore important to understand the painting techniques used by artists on particular works under study. Artists used specific amounts of pigments to make paints with desired hues, and a painted layer could be a mixture of pigments or layers of one paint over another, producing wonderful optical effects to enchant their viewers. The proportions of pigments in a mixture, or the thickness of layers, can say much about an artist's technique. Having a precise knowledge of the working methods of an artist can aid in attribution, facilitate sympathetic restoration, and help to detect forgeries.

There is a growing need for techniques that allow analyses to be done onsite, and without having to remove samples from the artwork. Various non-invasive techniques, such as Raman [1–3], infra-red (IR) [4,5] and X-ray fluorescence (XRF) [6] spectroscopies, and micro-X-ray diffraction (XRD) [5], have been used to identify the pigments, and in some cases even the binders [7–9], in paint films. Fibre-optic reflectance spectroscopy (FORS) in the visible and near-IR range is another non-invasive method which is also robust in identifying pigments, and has shown promise in the identification of some paint binders [10–13]. Identification of pigments using techniques like FORS, XRF and Raman is in many ways, however, limited to identifying their presence, in the absence of stratigraphic information about the paint layers, as the spectra resulting from the absorption and scattering are invariably influenced by the surface texture of the paints, and possibly by complex layer structures consisting of paints, varnishes and/or support materials, depending on the layer composition and thicknesses. A lot of effort is thus being made to obtain more stratigraphic information, non-invasively, where possible [4,14,15].

FORS has been analysed quantitatively using the Kubelka-Munk (KM) theory of diffuse reflectance, or the so-called "two-flux" model, an approach widely used to study materials as diverse as paints [16,17], semiconductors [18], cosmetics on skin [19] and food [20,21]. In their review, Berns et al. [22] give a comprehensive summary of the various implementations of the KM theory. The most commonly-used is the "paint approach", where the spectrum of a paint mixture is modelled as a linear combination of the

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http://dx.doi.org/10.1016/j.talanta.2016.03.052

spectra of the pure components in the space of KM units. Dupis and Menu, in 2005, used these ideas to develop a method to identify the concentration of pigments in organic binding media [23]. It was later shown that KM theory could also be used to study paint mixtures [16]. Rodriguez and Fernandez (2005) further developed another interesting technique to characterise pigments in mixtures, using the second derivatives of reflectance spectra converted to KM units [24]. However, it has been reported that the usual solutions to the KM model did not yield satisfactory results in the identification of certain red pigments [16].

Various other techniques based on the derivatives of reflectance spectra have also been used for characterisation. Indeed, there exists an entire field of “derivative spectroscopy” [25–28] dedicated to the use of derivatives to extract maximum information from spectra. The most commonly-employed quantities are the heights of peaks in first- [16,29] or second-derivative spectra [24], which allow features in the reflectance spectra to be more easily identified, in part by discarding unwanted features such as a constant baseline shift. For example, first-derivative spectra have been used as a means to overcome spectral differences observed due to particle size and surface roughness [16]. The use of second and higher derivatives is often less preferable, however, due to the artefacts that may be present in such signals [26].

In the present work, we develop a procedure to deconvolute the peak features in the first derivatives of FORS spectra, corresponding to the colour-transition edges in the reflectance spectra, and show how the ratio of the areas under the characteristic peaks ascribed to different pigments can be used to quantify the composition of binary paint mixtures. This analysis of first-derivative spectra can also in some cases allow FORS data to be used to differentiate between pigment mixtures and paint layers. We also find that certain pigment mixtures lead to quantifiable blue shifts in the transition edges, which can be problematic for other analysis methods such as the “paint approach” variant of KM theory. As a proof of concept, we demonstrate the application of our method to the characterisation of red painted areas on two medieval illuminated leaves from the collection of the Fitzwilliam Museum, Cambridge, viz. MS McClean 79 (Book of Hours, Paris, c. 1405-1410; folios 11r and 71r) and MS 62 (Book of Hours, Northern France, probably Angers, c. 1431; folio 18 v) [30]. Finally, we employ electronic-structure calculations to investigate the origin of the complex structure of the colour-transition edges in three commonly-used coloured pigments, which appears to be a consistent feature of these systems.

2. Experimental

2.1. Sample preparation

All the pigments used in this study were purchased from Kremer Pigments, Inc. and used without any further processing. The grain sizes of the pigments as supplied were not specified. Gum arabic resin (Kordofan Grade) was imported from the Middle East via L. Cornelissen and Son, London, and the binder was prepared by dissolving the resin in water.

We considered paint mixtures containing three yellow and red pigments commonly used in medieval artwork, viz. lead-tin yellow (Pb_2SnO_4; LTY), red lead (Pb_3O_4; RL) and vermillion (α-HgS; VRM), as well as tints of LTY and RL with the white pigment, basic lead white ($2Pb_2CO_3$. $Pb(OH)_2$; LW). Paint films were made up in one of two ways: binary mixtures of LW/RL, LW/LTY, RL/LTY and RL/VRM were made with various pigment mass ratios (2:1, 3:2, 1:1, 2:3, 1:2), and we also made samples formed of superposed layers of pure paints of RL and LTY, and RL and VRM. For the latter, the thicknesses of the layers were not controlled, as is the case in real artwork samples.

The binder was prepared by dissolving gum Arabic in water until a suitable gum-like consistency was obtained, after which the concentration of the gum in water was kept fixed while preparing the paint samples. To prepare the paint mixtures, the two pigments (wt/wt) were first geometrically mixed, and a few drops of the binder added to obtain a paint of a consistent thickness. The paints were then brushed on to microscope glass slides and allowed to dry on the bench. To prepare the layered samples, paints of the pure pigments were prepared in a similar fashion to the mixtures, and the first layer painted onto a glass slide and allowed to dry for an hour before application of a second layer. One of each sample were prepared, but with a sufficiently large surface area that reflectance spectra could be recorded from multiple spots.

We note that these methods were chosen to mimic the techniques used by medieval artists as closely as possible, in line with the focus of this study on applications to conservation science.

2.2. Spectroscopy and data processing

Reflectance spectra were obtained using a FieldSpec 4 spectroradiometer (ASD Inc., USA), in the wavelength range of 350–2500 nm at a spectral resolution of 3 nm at 700 nm, and 10 nm at 1400 nm and 2100 nm. Before acquiring spectra, the instrument was calibrated using a 99% reflective spectralon standard (Labsphere). A minimum of three spectra were recorded from each paint sample, taken randomly from different spots on the film. We note that we did not attempt to collect spectra at a consistent working geometry; although the FieldSpec 4 has a suitable “contact-probe” accessory for doing so, it is not generally possible to use such a device to analyse cultural-heritage objects (including the manuscripts analysed in the present study) due to the risk of surface damage, and so we opted not to use it when collecting data from the model paint films, in order to emulate the same issues as would be present when analysing artwork samples.

The reflectance spectra were differentiated using a seven-point finite-difference stencil. The 350–750 nm colour-transition regions of the resulting derivative spectra were modelled as a sum of Gaussian peak functions, i.e.:

$$R'(\lambda)=\sum_{n}\frac{A_n}{\sqrt{2\pi}\sigma_n}\exp\left[-\frac{(\lambda-\mu_n)^2}{2\sigma_n^2}\right] \tag{1}$$

where λ is the wavelength and the sum runs over n peak functions with area A, central wavelength μ and bandwidth σ. The bandwidth is related to the full-width at half-maximum (FWHM) of the peak profile according to:

$$\mathrm{FWHM}=2\sqrt{2\ln 2}\,\sigma \tag{2}$$

The fitting procedure was implemented in the Python [31] programming language, using the Numpy [32] and SciPy [33] packages. For function fitting, we used the “minimize” routine available in SciPy 0.14.0, which implements the bounded L-BFGS-B algorithm [34,35]. We used the root-mean-square difference between the measured and fitted derivative spectra as the objective function to be minimised, and constrained the area and bandwidth to be ≥0. The parameters A_n, μ_n and σ_n for the spectra of the pure paints were fitted by eye and refined using the minimisation algorithm. Appropriate combinations of the optimised parameters for the pure paints were then used as the initial parameters for fitting the spectra of the mixtures and glazes.

The quality of the fits was verified by integrating the fitted derivative spectra to reconstruct simulated colour-transition edges. The arbitrary constant of integration – corresponding to a constant baseline shift in the measured reflectance spectra, which is effectively discarded during differentiation – was determined as