Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 115 (2013) 617–628

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Evaluation of MidIR fibre optic reflectance: Detection limit, reproducibility and binary mixture discrimination

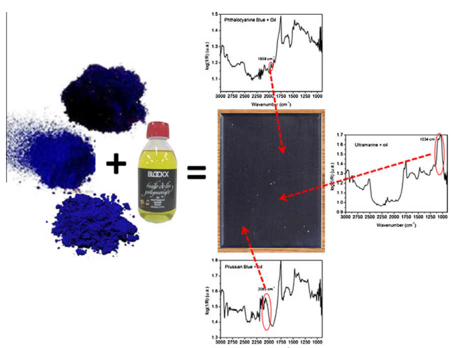
Clarimma Sessa, Héctor Bagán, José Francisco García *

Departament de Química Analítica, Universitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain

HIGHLIGHTS

- Detection limits for all the pigments are high for artworks characterisation purposes.
- Physical features of the artworks are important for characterisation using MidIR-FORS.
- Results dispersion is mainly affected by heterogeneity of the paint layers.
- Data pre-treatments reduce the instrumental/procedure variability.
- PCA and MidIR-FORS are able to discriminate between binary mixtures of oil paints.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 February 2013
Received in revised form 10 June 2013
Accepted 24 June 2013
Available online 3 July 2013

Keywords:
MidIR-FORS
FTIR
Paintings
Ultramarine blue
Prussian blue
Phthalocyanine blue

ABSTRACT

MidIR fibre optic reflectance (MidIR-FORS) is a promising analytical technique in the field of science conservation, especially because it is non-destructive. Another advantage of MidIR-FORS is that the obtained information is representative, as a large amount of spectral data can be collected. Although the technique has a high potential and is almost routinely applied, its quality parameters have not been thoroughly studied in the specific application of analysis of artistic materials.

The objective of this study is to evaluate the instrumental capabilities of MidIR-FORS for the analysis of artwork materials in terms of detection limit, reproducibility, and mixture characterisation. The study has been focused on oil easel painting and several paints of known composition have been analysed. Paint layers include blue pigments not only because of their important role along art history, but also because their physical and spectroscopic characteristics allow a better evaluation of the MidIR-FORS capabilities.

The results of the analysis indicate that MidIR-FORS supplies a signal affected by different factors, such as the optical, morphological and physical properties of the surface, in addition to the composition of materials analysed.

Consequently, the detection limits established are relatively high for artistic objects (Prussian blue – PB 2.1–6.5%; Phthalocyanine blue - Pht 6.3–10.2%; synthetic Ultramarine blue – UM 12.1%) and may therefore lead to an incomplete description of the artwork.

Reproducibility of the technique over time and across surface has been determined. The results show that the major sources of dispersion are the heterogeneity of the pigments distribution, physical features, and band shape distortions. The total dispersion is around 4% for the most intense bands (oil) and increases up to 26% when weak or overlapped bands are considered (PB, Pht, UM). The application of

* Corresponding author. Tel.: +34 934021281; fax: +34 934021233.
E-mail address: jfgarcia@ub.edu (J.F. García).

1386-1425/$ - see front matter
http://dx.doi.org/10.1016/j.saa.2013.06.088

different pre-treatments (cutoff of fibres absorption, Savizky–Golay smoothing algorithm, polynomial baseline offset, Standard Normal Variate algorithm – SNV) to the raw spectra allows improving these results to maximum values of 15%.

Finally, the capabilities of PCA and MidIR-FORS to discriminate between binary mixtures were tested. The results demonstrate that it is possible to differentiate mixtures depending on the range of concentration of their components, within specific limits of detection.

Introduction

An important characteristic of the artworks is their material heterogeneity [1]. The increase of the number of determinations is a common option to improve the representativity of the information obtained, but this approach is not favourable as it stands against the preservation of the physical integrity of these important objects [2].

Accordingly, science conservation fields are currently focusing on the development of non-invasive methods [3–7] to complement the classical techniques SEM–EDX, micro-FTIR, chromatographic, etc. [5,8,9].

The Mid-IR fibre optics coupled with Fourier transform infrared bench (MidIR-FORS) permits the performance of non-invasive reflection measurements. It is a promising technique, routinely applied [2] but its quality parameters, such as detection limit and reproducibility, have not been studied thoroughly for the specific application of artistic materials analysis [6,10]. It is important to underline that characterisation of minor components used in a piece of art is extremely useful, because these components may provide key information about the creation process and answer questions regarding conservation and restoration [3,5,11,12]. However, the use of a non-destructive technique such as MidIR-FORS implies some limitations. The signal obtained with Fourier infrared spectroscopy analysing a paint layer depends on the composition and concentration of the pigments and the binder, the absorption intensity, and the degree of overlap of the selected vibrations bands [13]. Moreover, the signal obtained with reflectance arrangement also depends on the particle size, the distribution of the pigments, the morphological and physical properties of the surface analysed [14], and the angle of the incident light as the penetration depth of the beam in the paint layer. Due to all of these factors, the main shortcoming of the technique is that reflection mode spectra can present odd distortions of band shape, position and intensity, implying that the interpretation of reflection spectra of unknown heterogeneous materials could be challenging [2,15].

Because of the non-destructiveness of the MidIR-FORS, a large amount of data could be obtained but the provided information is not easily interpretable. Accordingly, chemometric methods may be helpful tools to extract the information included in the recorded spectra. Among these methods, principal component analysis (PCA) allows reduction of the dimensionality of a series of data by transforming the set of original variables into a simplified group of variables named principal components (PCs), which represent the relevant information [1,10,16].

The objective of this study is to evaluate the instrumental capabilities of MidIR-FORS in the analysis of artwork in terms of detection limit, reproducibility, and capabilities to discriminate binary mixtures of inorganic pigments and colorants.

Despite of the general purpose of this study, the work has been focused on one of the most common types of artworks: oil easel paintings. The pigments included in the paint layers are blue and they have been selected not only by their historical use, but also because they present different physical, morphological and optical properties, as well as detection characteristics [13]. These factors permit to evaluate some of the variables that can affect the quality of spectra acquired.

Blue is a colour that has been included in art compositions since ancient times. This continuous use highlights the importance of blue pigments in the evolution of art history because they reflect the search to find new materials with equivalent or new chromatic properties that are more widely available and with a higher chemical stability. Azurite, lapis lazuli (natural ultramarine) and Egyptian blue were the most important blue pigments in antiquity. Since the eighteenth century chemical developments have yielded new, cheaper alternatives that include synthetic blues: Prussian blue (PB) [17–20] (1706), Ultramarine blue (UM) [17,21,22] (1828) and Phthalocyanine blue (Pht) [17,23,24] (1935). Several studies on these pigments have been published, and some reports stress the difficulties related to their identification when they are included in mixtures at low concentrations [11,13].

The information obtained for these pigments can be applied to address the expected limitations of MidIR-FORS when used to study other types of art objects [2].

Experimental

Materials

Pigments used in this study are presented in Table 1. The medium was a polymerised linseed oil purchased from Jacques Blockx trademark in Barcelona (Spain). A commercial canvas on a stretcher, prepared with a white ground (dimension 16×22 cm), was used as support.

Instrumentation

MidIR-FORS

Reflection FTIR spectra were recorded using a BOMEM MB^{-1}20 Fourier transform infrared spectrometer equipped with a Remspec mid-infrared fibre optic sampling probe. The spectrometer has a KBr beam splitter, a Glowbar source and a mercury cadmium telluride (MCT) detector refrigerated with liquid nitrogen.

The fibre optic probe is a bifurcate cable containing 19 chalcogenide glass fibres, each one with a diameter of 500 µm, seven of which carry the infrared radiation from the source to the sample, while the others 12 collect the radiation reflected off the surface.

The chalcogenide glass fibres allow the acquisition of spectra from 4000 to 900 cm^{-1}, except in the 2200–2050 cm^{-1} region due to the Se–H stretching absorption of the fibres. All FORS spectra were recording with 200 scans at a spectral resolution of 4 cm^{-1}.

Micro-FTIR

Analyses were performed with the same BOMEM MB120 Fourier transform infrared spectrometer equipped with a Spectra-Tech Analytical Plan microscope with a diamond cell as a sample holder. Spectra were recorded between 4000 and 350 cm^{-1} with a resolution of 4 cm^{-1} and an accumulation of 100 scans. Measurements were performed in transmission mode.

Infrared imaging

Reflection FTIR Imaging was performed with a Thermo iN10 MX spectrometer with a MCT detector. A computer controlled *x*–*y*