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Benefits of applying combined diffuse reflectance FTIR spectroscopy and principal component analysis for the study of blue tempera historical painting

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ABSTRACT

This paper explores the application of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to the examination of historic blue pigments and blue tempera paintings commonly found on works of art. The discussion is mainly focused on the practical benefits of using this technique joined to principal component analysis (PCA), a powerful multivariate analysis tool. Thanks to the study of several replica samples that contain either pure blue pigments (azurite, lapis lazuli and smalt), or pure binder (rabbit glue) and mixtures of each of the pigments with the binder (*tempera* samples), different aspects of these benefits are highlighted. Comparative results of direct spectra and multivariate analysis using transmittance-Fourier transform infrared spectroscopy (T-FTIR) are discussed throughout this study. Results showed an excellent ability of PCA on DRIFT spectra for discriminating replica samples according to differing composition. Several IR regions were tested with this aim; the fingerprint IR region exhibited the best ability for successfully clustering the samples. The presence of the binder was also discriminated. Only using this approach it was possible to completely separate all the studied replica samples. This demonstrates the potential benefits of this approach in identifying historical pigments and binders for conservation and restoration purposes in the field of Cultural Heritage.

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1. Introduction

Scientific study of artwork is of interest in order to test the suitability of analytical techniques on matrices different from those classically examined. Historical paintings are often heterogeneous microlayered materials made of complex mixtures of inorganic and organic compounds applied on diverse supports, as for instance stone, canvas, wood and paper. Since ancient times, painters have tried out a variety of organic materials to mix with inorganic pigments. These components can be simultaneously present in different layers of paint

stratigraphy, making the recognition of paint constituents a difficult challenge for chemists [1–3]. The identification of pigments and binders when mixed is one of the most important tasks in the field of painting heritage, in order to establish suitable actions for both restoration and conservation and allow proper preservation.

Spectroscopic techniques offer great potential to solve many of the problems associated with the characterisation of the materials constituting works of art. Fourier transform infrared spectroscopy in its traditional mode of transmittance (T-FTIR) is particularly important because of the variety

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of information contained in the spectra – i.e. data of both organic and inorganic compounds – and because of its variety of possibilities for sample measurements. Therefore, T-FTIR spectroscopy has become one of the most important analytical techniques in the field of Cultural Heritage [4,5]. In addition, it is a reasonable low cost technique compared with other analytical methods. However, T-FTIR has limitations related to particle size (when minerals are present) and the negative effect on spectrum baseline. On the other hand, sampling restrictions imposed in artworks limit the amount of sample to work with, which in the particular case of T-FTIR technique makes it difficult to prepare the pellet and to acquire a standard spectrum. In the case of composite materials like ancient paintings, the interpretation of the T-FTIR spectra may be extremely arduous to resolve. By contrast, interesting results could be achieved by analysing the specimen in reflectance mode (diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy) though at present this technique has been scarcely used in Cultural Heritage [6] contrary to other scientific fields [7–9]. Recently, reflectance spectroscopy in the UV-visible region has shown to be useful for environmental monitoring conditions in museums [10,11].

DRIFTS refers to a particular FTIR sampling technique based on reflectance measurements [12]. The increasing application of DRIFTS is related to the development of optical devices using special attachments for standard spectrometers [13]. This technique is particularly useful in the investigations of powdered samples. Moreover, it is accepted to be a very low impact method since only a very small quantity of powdered sample is needed (~5–10 µg) unlike the T-FTIR mode (~30–50 µg) [14]. This makes it very attractive in the field of Painting Cultural Heritage, where non-destructive techniques and/or micro-destructive techniques are preferred. Nevertheless, in the specialised literature only one article has been found regarding the application of DRIFT spectroscopy to characterise paintings components, providing a diffuse reflectance FTIR spectral database of 25 dyes and pigments [6]. Thus, the present work represents an advance in this research field, since for the first time a study of the application of factorial analysis such as principal component analysis (PCA) is used to compare T-FTIR and DRIFTS spectral data obtained from historical pigments and binders. Application of chemometrics tools for the characterisation and conservation of Cultural Heritage is a well-established procedure [15]. Several works have recently demonstrated the usefulness of these approaches for calibrations [16], ageing detection [17–19], classification [20,21], and dating purposes [22].

This paper describes the benefits of using DRIFT spectroscopy versus T-FTIR spectroscopy, each joined with PCA as a tool in Heritage Science. Three blue pigments, i.e. azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), lapis lazuli ($\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_2$) and smalt (Co-K silicate glass), and rabbit glue as binder (proteinaceous medium) were selected to carry out this study since they have been widely used through historical epochs. Seven replicate samples, i.e. pure pigment samples, pure glue sample and pigment/glue mixture samples (*tempera* samples), were prepared and measured with both molecular vibrational techniques, i.e. T-FTIR and DRIFT, which allowed direct evaluation of the obtained spectral data. Comparative discussion of the direct spectra obtained by both spectroscopic modes is discussed

throughout this work. PCA was performed separately on the spectral data from both FTIR modes to evaluate the capability of this multivariate tool to discriminate between different sample compositions. Only when the PCA was performed on the spectral data from DRIFT, it was possible to successfully discriminate all replicate samples by their composition.

2. Experimental

2.1. Reagents

Reagents were chosen based on their widespread use through history, in particular during the Middle Ages and Renaissance. Azurite is a non-expensive hydrated copper carbonate mineral of composition $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. It was the most important pigment in European paintings until near the end of the 17th century. Azurite has a bright blue colour that sometimes resembles lapis lazuli, and the two were often confused [23]. In addition to azurite, by far the most important blue in the Middle Ages was lapis lazuli. This vivid rich blue pigment is made by grinding the semi-precious rock lapis lazuli whose main constituent is the mineral lazurite ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$). The first noted use of the stone as pigment was in 6th- and 7th-century AD cave paintings in Afghan temples. Lapis lazuli pigment found its most extensive use in 14th and 15th centuries, illuminating manuscripts and Italian panel paintings, often reserved for the cloaks of Christ and the Virgin. It is famous for having been the most expensive pigment [23]. Smalt is an artificial pigment made of fine to coarsely ground potassium cobalt glass. The blue colour is due to small amounts of cobalt added as cobalt oxide during manufacture. Since ancient times, smalt was used to colour and decorate glasses, though powdered cobalt glass was also employed as pigment. Smalt was an important pigment in European oil paintings. In Italy it was little used in the 14th and 15th centuries but became a substitute for azurite and lapis lazuli in the 17th century [24].

The azurite and smalt pigments were purchased from Kremer Pigments GmbH & Co. KG (Madrid, Spain). Pigment references are: 10,200 natural azurite (CI: PB 30.77420) with particle size 0–120 µm, and 10,010 blue smalt (CI: PB 32.77365) with particle size 0–80 µm. The lapis lazuli was supplied by Caremi Pigmentos (Sevilla, Spain). Pigment reference is natural Lapis lazuli Afghanistan, medium blue.

The standard protein binder selected was rabbit skin glue (collagen). This binder has been used since ancient times, mostly in traditional woodworking, gilding and paintings due to its high strength, viscosity and elasticity. It was purchased from Sigma (Barcelona, Spain).

Potassium bromide was used as a non-absorbing reference material for the spectroscopic background measurement. It was purchased from Merck (Damstadt, Germany).

2.2. Replica samples

Seven painting replica samples were prepared to emulate real paint layers according to old master recipes to obtain standards similar to those used by medieval artists [25]. The first, second and third replicas comprise each of the three pure pig-

Table 1 – Replica sample composition.

Replica sample	Binder	Pigment
Pure samples		
1	–	Azurite
2	–	Lapis lazuli
3	–	Smalt
4	Rabbit glue	–
Tempera samples		
5	Rabbit glue	Azurite
6	Rabbit glue	Lapis lazuli
7	Rabbit glue	Smalt

ments (azurite, lapis lazuli and smalt), and the fourth replica the pure rabbit glue binder (Table 1). Preparation of the pure pigment samples was as follows: 5 g of powder pigment was formed as a crater-shaped mass and six drops of pure water (total volume of 30 μL) were added until a dense paste was attained. Then, four layers of the obtained paste were sequentially spread out with a paintbrush in fine coats on a glass slide. Each layer needs to dry thoroughly before applying the next. This is the traditional way to obtain an opaque painted layer and to guarantee full luminosity of the colour, otherwise it immediately appears dead. The pure binder sample (fourth replica) was prepared as follows: 10 g of rabbit glue was diluted 10% in ultra pure water (MILIQ) by gently adding the glue to the water during 24 h, and stirring periodically. Next the obtained blend was gradually heated in a bain-marie below 50 °C to obtain a homogeneous mixture. Then the glue was carefully spread on a glass slide with a paintbrush in six successive fine coats, each applied after the previous layer had dried to a constant weight using a gel air dryer system.

The fifth, sixth and seventh replicas include mixtures between glue and each of the pure pigments, i.e. azurite, lapis lazuli and smalt, thus blue tempera replicate samples were obtained. They were prepared by blending the pigment with the glue – both components elaborated as above – in a ratio 5.2:1 (w/v) (Table 1). Next, mixtures were spread on glass slides in three fine coats. This procedure was adapted to emulate real paint layers as found in ancient paintings. *Tempera* is a painting method in which finely ground pigments are mixed with a solidifying proteinaceous binding agent, such as egg, animal glue and casein [26]. Well known from antiquity, *tempera* was the exclusive panel medium in the Middle Ages and the early Renaissance, and in Italy it was not supplanted by oil until ca.1500.

2.3. Instrument and software

The FTIR spectra were collected using a NICOLET spectrometer 20SXB, working in transmission mode (T-FTIR) and diffuse reflectance mode (DRIFT). The instrument was connected to a Pentium 200 and the instrument software was OMNIC v 4.1, running under Windows 2000 Professional (Microsoft Corporation, USA).

The T-FTIR spectra were registered from 3999 to 400 cm^{-1} with a resolution of 2 cm^{-1} and 200 scans. Each replica sample was characterised by 10 T-FTIR spectra, except the pure glue replica sample (25 T-FTIR spectra). These spectra were obtained from KBr pellets prepared by homogeneously mixing

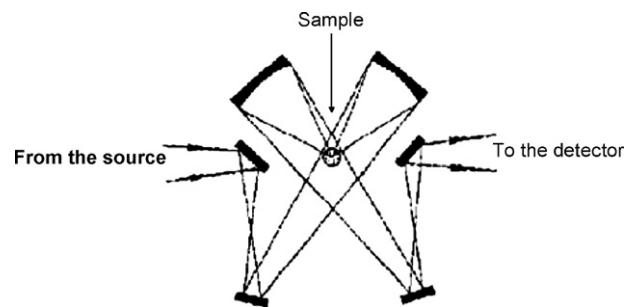


Fig. 1 – Sample compartment and optical accessories for measuring diffuse reflection in the spectroscopic equipment.

aliquots removed from seven random locations on the glass slide (KBr in 1%). In this way, T-FTIR spectra were independent from the position where the powder micro-sample was taken from the glass slide. Baseline correction was performed in all T-FTIR spectra.

In order to better discriminate the Fresnel reflectance, the SPECTRA-TECH attachment Model COLLECTOR (Sutton, Surrey, England, SM1 1TH) was used to measure the diffuse reflectance in the FTIR spectrometer. This optical accessory uses a focusing mirror to collimate the beam on the sample surface and collect the IR energy (Fig. 1). Aliquots were also taken from seven random places from each replica sample and later mixed with the potassium bromide used as diluent and for the background spectra. The mixture (5% in KBr) was placed in a micro-sample cup (3 mm diameter). In this case, the sample consumed in the preparation of the KBr medium is reduced compare to that required for T-FTIR analysis, using only 1–5 μg of powder sample. For comparison purposes, DRIFTS spectra were scanned at the same experimental conditions (resolving power 2 cm^{-1} and 200 scans) as in transmission mode. Likewise each replica sample was characterised by 10 DRIFT spectra, except for pure glue replica sample (25 DRIFT spectra). These spectra were converted to Kubelka–Munk units [12].

Chemometric data analysis was done using Statistical Product and Service Solutions program (SPSS, for Windows Ver. 15, USA) and Excel 2000 (Microsoft Corporation, USA).

3. Results and discussion

3.1. Direct spectrometric analysis

Scientific examination and comparative investigation of historical pigments in the laboratory is fundamental to further analyse and understand real painted artworks, in addition to be of particular usefulness for conservators. Furthermore, knowledge of the properties of ancient pigments and their response and sensitivity to specific spectroscopic methods are relevant in Science Heritage. In this context, the three blue pigments, i.e. azurite, lapis lazuli and smalt were investigated by means of diffuse reflectance infrared spectroscopy (DRIFTS) and transmittance Fourier transform infrared spectroscopy for comparison purposes.

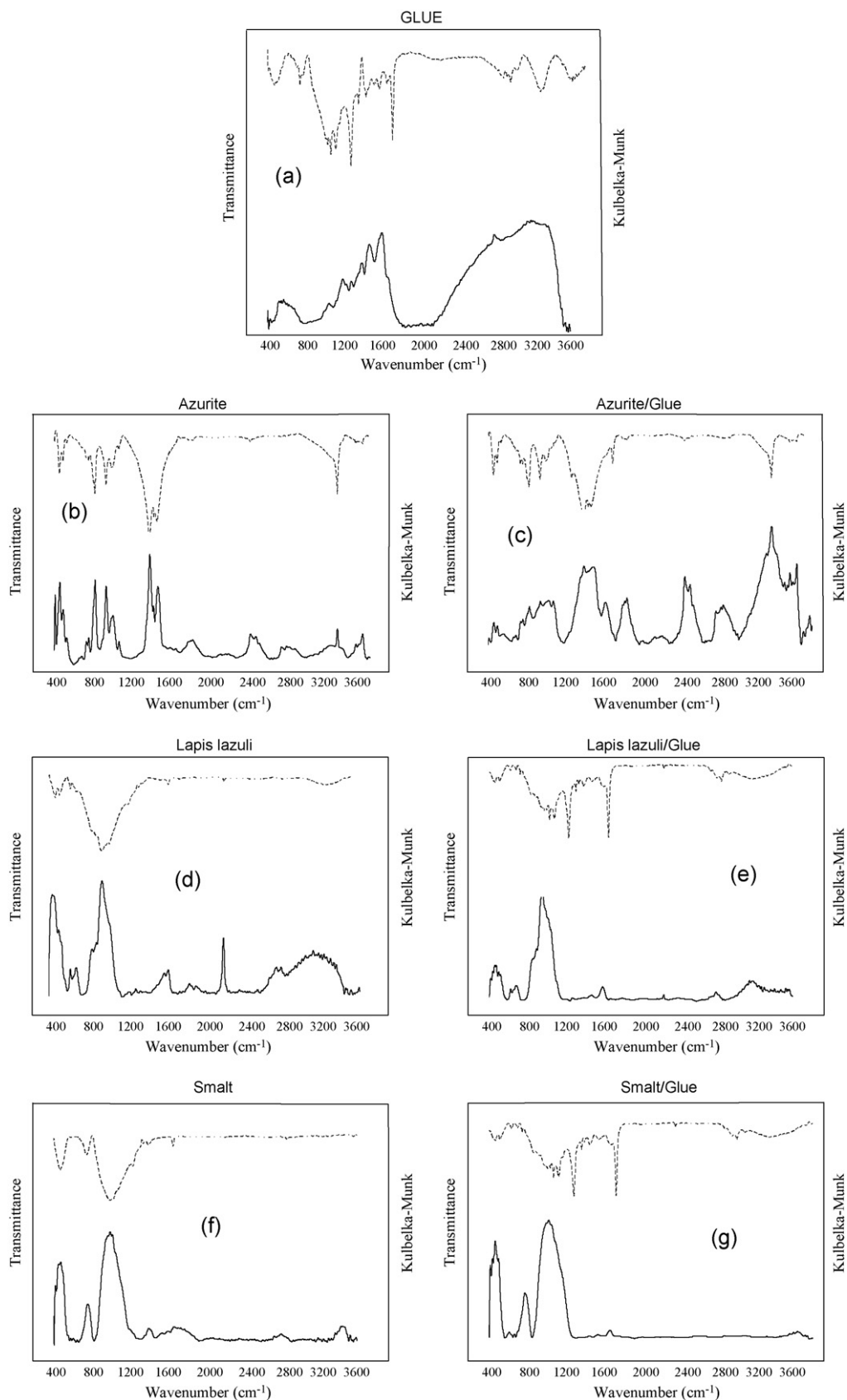


Fig. 2 – DRIFT (lower) and T-FTIR (upper) spectra of the seven replica samples: (a) pure glue (collagen), (b) pure azurite, (c) azurite/glue, (d) pure lapis lazuli, (e) lapis lazuli/glue, (f) pure smalt, and (g) smalt/glue.

Table 2 – Main IR absorption bands of the blue pigments and their temperas for identifications purposes.

Replica sample	Description	Vibrational wavenumber (cm ⁻¹)	
		T-FTIR	DRIFT
Pure rabbit glue	Collagen	700 (δ (NH) wagging band) 1290 (amide band II) 1730 (amide band I) 3310 (N–H stretching mode)	680, 3000 [31]
Pure azurite	Cu ₃ (CO ₃) ₂ (OH) ₂	840 (carbonate stretching [28]) 1430 (carbonate stretching [28])	840 (as in T-FTIR) 1430 (as in T-FTIR)
Azurite/rabbit glue	Cu ₃ (CO ₃) ₂ (OH) ₂ /collagen	840 (carbonate stretching [28]) 1430 (carbonate stretching [28])	840 (as in T-FTIR) 1430 (as in T-FTIR) 1890, 2510, 2890
Pure lapis lazuli	Na ₈₋₁₀ Al ₆ Si ₆ O ₂₄ S ₂₋₄	460 (O–Si–O deformation mode [29,30]) 990 (O–Si–O anti-symmetric stretching mode [29,30])	460 (as in T-FTIR) 990 (as in T-FTIR)
Lapis lazuli/rabbit glue	Na ₈₋₁₀ Al ₆ Si ₆ O ₂₄ S ₂₋₄ /collagen	460 (O–Si–O deformation mode [29,30]) 990 (O–Si–O anti-symmetric stretching mode [29,30]) 1290 (amide band II) 1730 (amide band I)	460 (as in T-FTIR) 990 (as in T-FTIR)
Pure smalt	Potassium silicate glass with some cobalt oxide	480 (O–Si–O deformation mode [29,30]) 1030 (O–Si–O anti-symmetric stretching mode [29,30])	480 (as in T-FTIR) 1030 (as in T-FTIR)
Smalt/rabbit glue	Potassium silicate glass with some cobalt oxide/collagen	480 (O–Si–O deformation mode [29,30]) 1030 (O–Si–O anti-symmetric stretching mode [29,30]) 1290 (amide band II) 1730 (amide band I)	480 (as in T-FTIR) 1030 (as in T-FTIR)

Fig. 2 shows simultaneously both the DRIFT (lower) and the T-FTIR (upper) spectra of the seven replica samples. The main vibrational wavenumbers observed in all these spectra are recorded in Table 2.

For the replica samples studied in the present work, the comparison of the DRIFT spectra with the T-FTIR in terms of baseline shows no clear advantage of one technique over the other, since the quality of both type of spectra were similar for both pure replica samples and tempera replica samples. The position of the absorption bands was also similar in DRIFT and T-FTIR spectra, except in the case of pure glue replica sample. However, the relative intensity of the bands was clearly different, being more intense in the case of DRIFT spectra, particularly the secondary absorption bands [27]. This characteristic of DRIFT spectra, i.e. the most prominent vibrational bands, reveals this technique more suitable for purposes of identification and characterisation of pigments, both when pure or mixed with binder.

Specifically, pure azurite presents bands at 1430 and 840 cm⁻¹ that can be assigned to carbonate stretching [28] and a band at 3430 cm⁻¹ related to the O–H stretching mode (Fig. 2b). Pure lapis lazuli and pure smalt present two prominent and specific bands that can be used as markers for the silicate group [29,30]. The observed bands at 460 and 480 cm⁻¹ respectively are related to the (O–Si–O) deformation mode, whereas the bands at 990 cm⁻¹ (lapis lazuli) and 1030 cm⁻¹ (smalt) are assigned to the (Si–O–Si) anti-symmetric stretching mode.

DRIFT and T-FTIR spectra for the pure glue replica samples were not entirely complementary (Fig. 2a). T-FTIR showed a

prominent amide band I at 1730 cm⁻¹ and the combined N–H deformation and C–N stretching vibration, the amide II of the secondary amides, at 1290 cm⁻¹ [31]. The band at 3310 cm⁻¹ was assigned to the N–H stretching modes. In addition, there is a very wide δ (NH) wagging band at around 700 cm⁻¹. DRIFT spectra showed two wide bands in accordance with previous work [31] located at around 1680 and 3200 cm⁻¹.

The presence of glue in the replica pigment samples introduced several changes in both types of spectra, DRIFT and T-FTIR. The T-FTIR spectra of azurite when pure or mixed with glue were similar, with only a small band at 1730 cm⁻¹ (the amide band I) indicating the presence of the binder. Lapis lazuli and smalt glue tempera samples can be distinguished from their corresponding pure replica samples by the amide bands I and II in the T-FTIR spectra (1730 and 1290 cm⁻¹, respectively) attributed to the presence of glue. These bands were not detected in the corresponding DRIFT spectra. By visual examination of the lapis lazuli and smalt DRIFT spectra – the two silicate-based pigments – it was not possible to distinguish the presence of glue in the replica samples. In the case of azurite, the presence of glue in the replica sample could be detected mainly by means of the DRIFT spectra, since bands at around 1890, 2510, 2890 and 3430 cm⁻¹ increased their relative intensity with respect to the corresponding DRIFT spectra of the pure azurite samples.

Consistent with these results, direct analysis of the spectra obtained by the two spectroscopic FTIR modes showed that DRIFT spectra better identify pigments, both when pure or mixed with binder. This ability was also extended to the identification of the glue when mixed with azurite. This information

is relevant since it will permit further investigation of the azurite/glue interaction by DRIFT spectra. Nevertheless in the case of the silicate-based pigments (lapis and smalt), T-FTIR better identified the presence of glue. As is usual in Heritage Science due to the complexity of the samples analysed, a combination of analytical techniques provides better and more complete information [32].

3.2. PCA analysis on DRIFT and T-FTIR spectroscopic data

Chemometric evaluation of spectral data is well accepted as a powerful tool for different purposes, including sample identification and recognition [33]. Among the different chemometric tools, PCA is a powerful data-mining technique that reduces data dimensionality obtaining more interpretable representation of the system under investigation [34,35]. In addition, valuable information about the most important variables involved in the process studied is also obtained.

In this work aimed at evaluating the ability to extract information from DRIFT and T-FTIR spectral data, PCA was performed separately on each. Thus, a matrix was built for each type of spectral data, DRIFT and T-FTIR, which includes the seven replica samples. In this way, for multivariate analysis each matrix was formed by 85 IR spectra, since each sample was characterised by 10 FT-IR and 10 DRIFT spectra (except pure glue replica samples characterised by 25 spectra of each IR mode). The PCs were obtained using both the covariance data matrices (scaling by mean-centered data) and the correlation data matrixes (scaling by unit variance). Similar to previous work [19,36], results were better when PCA was performed on correlation data matrices, so the results shown and discussed here correspond to autoscaled data. A simple centring data procedure is often adopted for spectral data [18,37] because the commonly applied autoscaling procedure assigns the same relevance to each IR spectral region. Thus spectral regions with small variation – no relevant IR bands – can acquire the same importance as large IR bands related to important functional groups. This problem was avoided in this work because only IR regions containing absorption bands were selected to apply PCA (not the whole IR spectrum). The IR regions selected to perform the multivariate analysis are

Table 3 – IR regions studied by PCA.

IR intervals (cm ⁻¹)	
600–1200	Fingerprint
1200–2000	Azurite band
2100–2700	Azurite band, lapis lazuli band
2100–3600	Glue most informative IR region ^a

^a From previous work [19,36].

shown in Table 3. PCA was performed independently on these IR regions. The fingerprint IR region was tested due to its unique absorption pattern for every sample. The wavenumber interval 2100–3600 cm⁻¹ was chosen according to results from previous work [19,36]. These studies found this IR region quite informative when glue was present in the replica samples, thus it was also tested in the present work. The other IR regions were selected from a visual examination of the IR spectra obtained with both T-FTIR and DRIFT, where an absorption band was observed.

The highest quality information for the two FTIR modes was obtained using the IR region in the wavenumber interval 600–1200 cm⁻¹, the fingerprint region. The main absorption bands of the two silicate-based pigments (lapis and smalt) are also found here. PCA on the wavenumber interval 1200–2000 cm⁻¹ allowed separation according to chemical class, that is, glue, azurite (pure and mixed with glue) and the silicate-based pigments (pure and mixed with glue). This result is justified since absorption bands of azurite that separate this pigment from the others compounds are found in this IR region. The wavenumber interval 2100–2700 cm⁻¹ also separated the replica samples, although less clearly, despite containing information on the absorption bands of azurite and lapis lazuli. The last IR region tested, 2100–3600 cm⁻¹, showed the ability to separate replica samples, but again less clearly than the fingerprint region. The results of the corresponding PCA in terms of explained variance (%) and cumulative explained variance (%) for each FTIR mode, and for the two IR regions with the best ability to discriminate samples are shown in Table 4.

The results obtained by applying PCA separately on the DRIFT and T-FTIR spectral data in the fingerprint region are summarised in Figs. 3 and 4. These figures show the score plot

Table 4 – PCA performed on DRIFT and T-FTIR spectral data.

IR region	PC	DRIFT		T-FTIR	
		Variance account (%)	Variance accumulated (%)	Variance account (%)	Variance accumulated (%)
600–1200 cm ⁻¹	PC1	59.3	59.3	58.1	58.1
	PC2	23.0	82.4	34.3	92.4
	PC3	13.0	95.4	4.0	96.4
	PC4	2.4	97.8	2.0	98.4
	PC5	1.1	98.9	0.9	99.3
2900–3600 cm ⁻¹	PC1	58.9	58.9	47.4	47.4
	PC2	21.5	80.4	25.2	72.6
	PC3	9.9	90.4	11.1	83.6
	PC4	6.0	96.4	6.6	90.2
	PC5	1.5	97.9	5.2	95.4

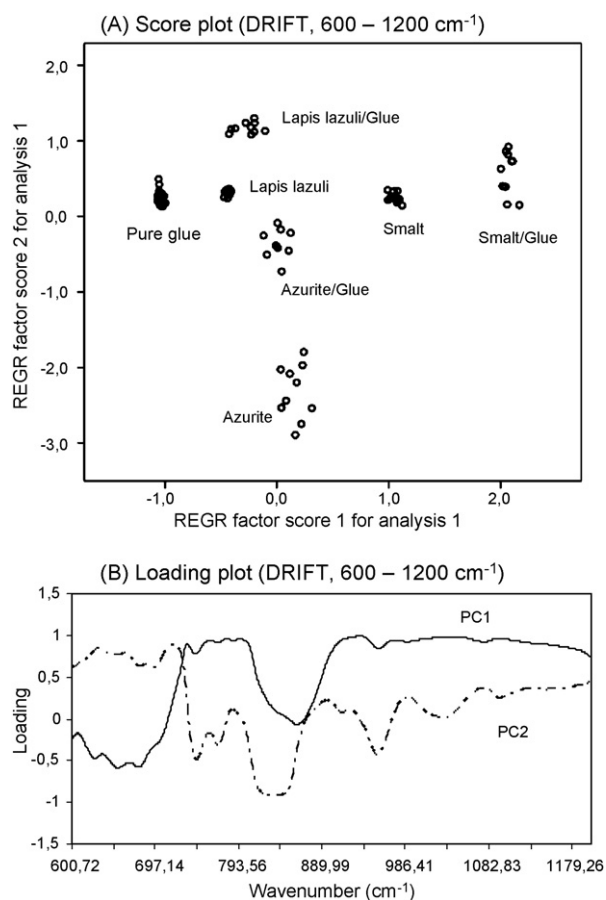


Fig. 3 – Results of the PCA performed on the DRIFT spectral data using the IR wavenumber interval 400–1200 cm^{-1} (fingerprint): (A) score plot (DRIFT, 600–1200 cm^{-1}) of PC1 and PC2; (B) loading plot (DRIFT, 600–1200 cm^{-1}) of PC1 and PC2.

of all the replica samples in the plane of the two first principal components, PC1 and PC2. The loading plot of the two first PCs is also included for each spectroscopy mode.

In the case of DRIFT spectral data (Fig. 3), seven clusters were clearly distinguished, according to replica sample composition. The score plot shows the most positive values on PC1 for smalt/glue replica samples, followed by pure smalt, with the most negative values for glue replica samples. The lapis lazuli/glue sample scored highest for PC2, followed by pure lapis lazuli, with the most negative scores for pure azurite. These results, combined with the analysis of the loading plot, suggested that the spectral variability explained by PC1 (59.3% of the total variance) was mainly related to the presence of the pigment smalt in the replica sample. The main absorption band of the smalt pigment was located in the wavenumber interval with the highest loading values for PC1 (900–1200 cm^{-1}), as well as its characteristic absorption band at 780 cm^{-1} (734–806 cm^{-1}). This behaviour of the replica samples allowed separation of the smalt pigment from its mixture with glue, since the presence of glue increased the absorption bands in those regions. In contrast pure glue exhibited the smallest absorption in those IR regions. The loadings for PC2 (23% of the total variance) indicated that a large frac-

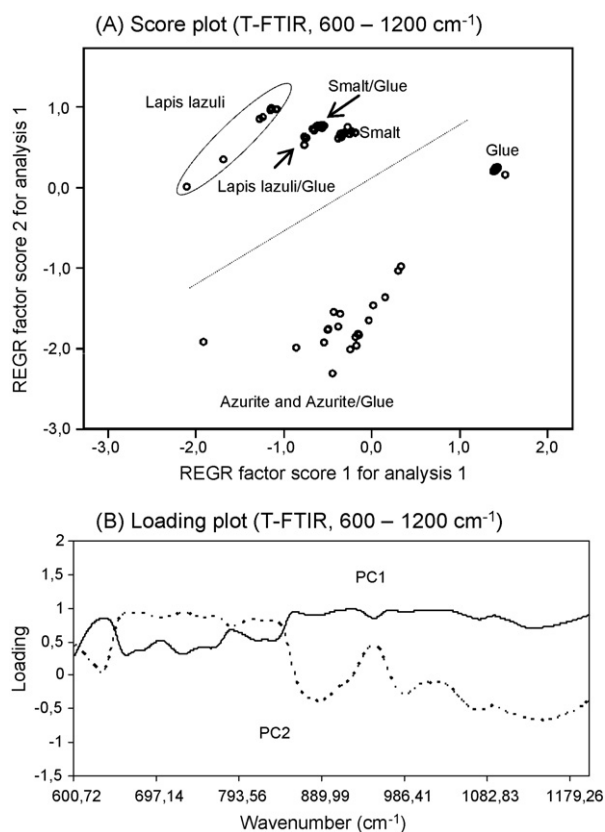


Fig. 4 – Results of the PCA performed on the T-FTIR spectral data using the IR wavenumber interval 400–1200 cm^{-1} (fingerprint): (A) score plot (T-FTIR, 600–1200 cm^{-1}) of PC1 and PC2; (B) loading plot (T-FTIR, 600–1200 cm^{-1}) of PC1 and PC2.

tion of spectral variability was due to the spectral region 600–734 cm^{-1} , where an absorption band of lapis lazuli at 660 cm^{-1} was located. Again, the presence of glue in the replica samples produces an increment of the characteristic absorption bands of the silicate-based pigment lapis lazuli, and this fact was correlated with the highest scores for PC2 for this replica sample. Therefore, it was possible to perfectly group replica samples of lapis lazuli with and without glue in two well-separated clusters. The pure azurite replicate samples presented the most negative score for this PC2. The negative loadings for the wavenumber interval 820–852 cm^{-1} suggested that the absorption band of azurite at 840 cm^{-1} determined separation along this PC2. In the case of azurite, the presence of glue in the replica samples decreased the absorption in this IR band, with scores shifted to more positive values.

In a similar way, PCA was performed on the T-FTIR spectral data, to evaluate whether the difference due to the diverse sample composition could be detected as in the case of DRIFT spectral data. Fig. 4 shows clearly a lesser capability of this approach to discriminate sample composition since five clusters instead of seven were distinguished in the score plot in the plane of the two first PCs (92.4% of the total variance). The replicate samples containing azurite (pure or mixed with glue) were separated from glue and from a cluster formed by all replica samples containing silicate-based pigments (pure or

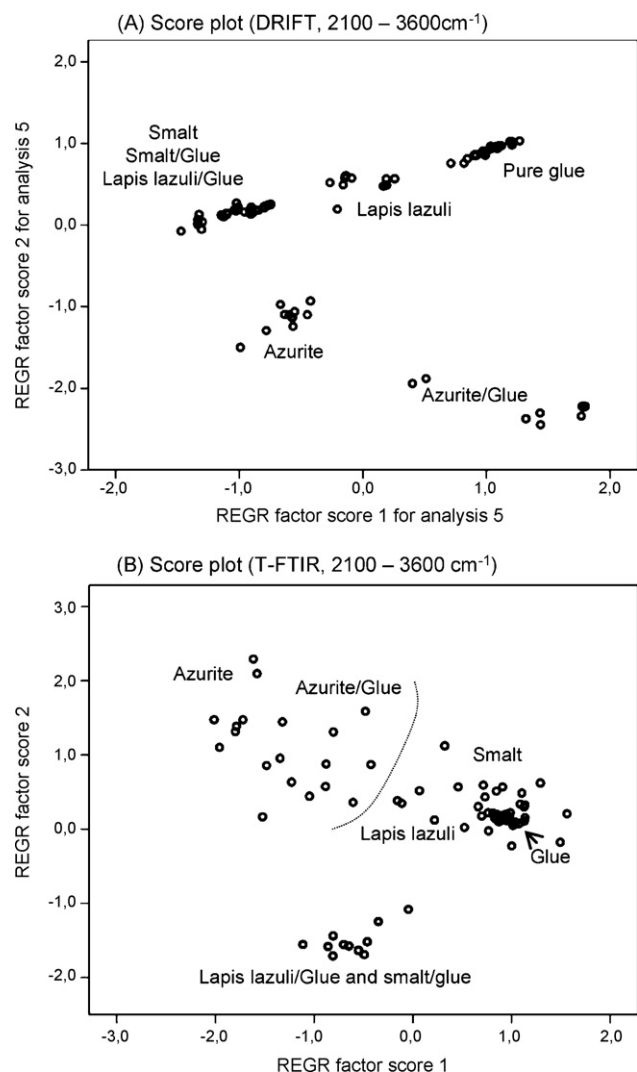


Fig. 5 – Score plot of PC1 and PC2 of the replica samples using the IR region between 2100 and 3600 cm⁻¹: (A) DRIFT spectral data, score plot (DRIFT, 2100–3600 cm⁻¹); (B) T-FTIR spectral data, score plot (T-FTIR, 2100–3600 cm⁻¹).

mixed with glue). An in-depth analysis of this cluster showed the separation of the pure lapis lazuli and pure smalt samples. Nevertheless when glue was present in the sample, the two silicate-based pigments were not distinguished. In addition, the loading values for PC1 were quite similar, making their interpretation difficult.

The results of applying this approach in the other IR region previously cited were less conclusive, particularly when the T-FTIR spectral data were used. As an example, Fig. 5B represents the scores of the first two relevant PCs for both FTIR modes in the wavenumber interval 2100–3600 cm⁻¹. The capability of clustering samples by composition was again clearly better when DRIFT data were used (Fig. 5A). In this case, samples were grouped in five clusters: pure azurite, azurite/glue, pure glue, pure lapis lazuli and a cluster containing pure smalt, smalt/glue and lapis lazuli/glue. In the score plot for the T-FTIR data, only replicate samples containing glue mixed with the silicate-based pigments (lapis lazuli and smalt) were clearly

separated from the rest of the samples that grouped in a large cluster. The distribution of the samples in this cluster was as follows: pure azurite with the most negative scores for PC1, azurite/glue samples were shifted to more positive values, and pure smalt, pure lapis lazuli and pure glue had the highest scores. Thus, only PCA performed on DRIFT spectral data in the fingerprint region enabled the discrimination of all replicate samples.

Based on these results, it can be concluded that the application of PCA to DRIFT spectra represents an improvement over the same approach using T-FTIR. The presence of the most prominent vibrational bands in the DRIFT spectra, in addition to permitting direct analysis for identification purpose, also benefits the application of data exploration techniques like PCA.

4. Conclusions

For the conservator concerned with the identification of materials, concretely blue pigments and their corresponding temperas, PCA performed on DRIFT spectral data has marked advantages when compared the results obtained with the same approach but using T-FTIR spectral data. Multivariate analysis of DRIFT data demonstrated better ability to discriminate replica samples according to known composition. Moreover, it was possible to group in different clusters samples that differed only in terms of the presence of glue. This is the first attempt to use this approach in Heritage Science, and the results are very promising to identify pigments and temperas used in historical paintings.

Regarding direct analysis of DRIFT and T-FTIR spectra, the complementary use of both spectroscopic modes are highly recommended. Pigment identification in art paintings will certainly benefit from the use of DRIFT spectra since these are easier to interpret. The presence of glue in tempera can be confirmed by the occurrence of several characteristic absorption bands in the corresponding T-FTIR spectra.

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