A Novel Reliability-Based Approach to Evaluate Painting Artworks Combining DRIFTS and PCA. Applications to Blue Pigments in Glue Tempera Painting

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INTRODUCTION.

The identification of pigments and binders is one of the most important tasks in the field of Painting Heritage. Most previous studies on characterization of historical paintings are based on separate and independent analyses of the different components, due to sample complexity (Edreira et al, 2001). Several analytical techniques have been used for this purpose, such as molecular vibrational spectroscopy, i.e. Fourier Transform Infrared spectroscopy in Transmittance mode (T-FTIR) (Manzano et al., 2000), Raman spectroscopy (De Oliveira et al, 2002), etc.

Vibrational techniques allow study of both organic and inorganic painting components. In the past, the T-FTIR technique was traditionally applied because sample preparation is simple and rapid; in addition it is a reasonably low-cost technique compared to other analytical methods. However, T-FTIR has limitations related to particle size (when minerals are present) and its negative effect in spectrum baseline, as well as the amount of sample analyzed. Therefore, the aim of this work is to apply and validate an alternative FTIR mode, DRIFTS (based on reflection measurements), to characterize paintings components.

The DRIFT technique is accepted as a very low impact method since only a very small quantity of powdered samples is needed (~ 5-10 μg). This makes it very attractive in the field of Painting Cultural Heritage, where non destructive techniques are preferred. Nevertheless, in the specialized literature only one article has been found regarding the application of DRIFT spectroscopy to characterize paintings components, providing a diffuse reflection FTIR spectral database of 25 dyes and pigments (Silva et al., 2006). Our work represents an advance in this research field, adding for the first time a factorial analysis such as Principal Component Analysis (PCA) to compare T-FTIR and DRIFTS spectra obtained from pigments and binders.

MATERIALS AND METHODS.

This paper describes the benefits of applying DRIFT spectroscopy compared to the use of T-FTIR spectroscopy to identify paintings components. As well, we demonstrate that the application of PCA to the acquired spectra is a powerful tool that allows separation of the different components according to their nature. To this end, three blue pigments, i.e. azurite ($Cu_3(CO_3)_2(OH)_2$), lapis lazuli ($Na_6Ca_2(Al_6Si_6O_{24})S_2$) and smalt (Co-K silicate glass), and the binding (proteinaceous) material rabbit glue were selected for analysis. Seven painting replica samples were prepared to emulate real paint layers as found in medieval artists' recipes. The first three replicas comprise each one of the three pure pigments, and the fourth replica the pure rabbit glue binder. The fifth, sixth and seventh replicas were prepared blending each pure pigment with the glue. To prepare the pure pigment samples, each pigment was blended with pure water until a dense paste was obtained. The pure binder sample was made by solving the pure glue with pure water and gradually heated in a bain-marie below 50ºC until a homogeneous mixture was formed. The pigment/glue mixture samples were prepared by blending the azurite with the glue as indicated in old recipes (Pacheco, 1990). Each replica sample was carefully spread out with a paintbrush in fine coats on a glass slide. Each coat was applied after the previous layer had dried to a constant weight. All samples were measured using T-FTIR and DRIFT modes. In both cases the spectra were registered from 400 cm^{-1} to 3999 cm^{-1} forming 3734 data points. Afterward PCA was performed separately on the spectral data from each technique to evaluate the capability of this multivariate tool to discriminate between different sample compositions.

RESULTS AND DISCUSSION.

The results of applying PCA to all spectral data are shown in Figure 1. It is observed that only when PCA was performed on DRIFT spectral data was a total separation of the different replica samples possible. Several IR regions were selected to perform the PCA analysis. The fingerprint IR region was tested due to its unique absorption pattern for every sample. The wavenumber interval 2100 – 3600 cm^{-1} was chosen by the results obtained in previous works (Manzano et al., 2008). These works evidenced that this IR region was the most informative when glue was present in the replica samples, thus it was also included to test in the present study. The other IR regions were selected from a visual analysis of the IR spectra, both T-FTIR and DRIFT. They were those with high spectral variability. Seven IR region were tested, and the fingerprint region of the DRIFT spectral data exhibited the best ability to clearly separate all the replica samples studied (see Figure 1a) into the plane of the two

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first principal components. With this approach, even the presence of glue in the replicates could be discriminated. When the fingerprint region of the T-FTIR was used to perform PCA, the seven samples were not perfectly separated (see Figure 1b). In this case, score plots of the azurite samples were grouped together without discriminating the presence of glue in the replicates. Score plots of smalt and lapis lazuli/glue replicate samples were likewise clustered.

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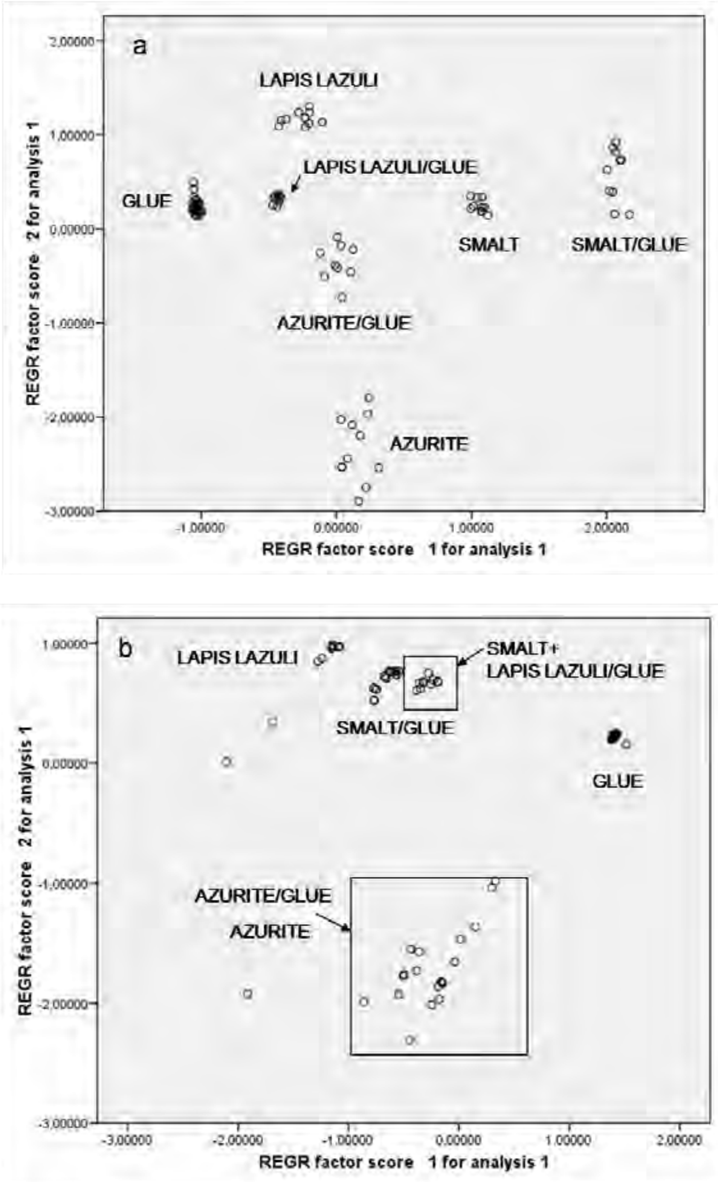

fig. 1*. PCA performed on the IR region between 600 cm-1 to 1450 cm-1 of all samples (pure samples and mixed): a) score plot of PC1 and PC2 from DRIFTS; b) score plot of PC1 and PC2 from T.*