Chemometric Analysis of XRF Data and FTIR Investigations of Pigments Used in Religious Paintings – A Case Study

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Abstract

FTIR spectroscopy and X-Ray fluorescence were employed in conjunction with chemometrics in order to identify some pigments used in a religious painting. A chemometric treatment of the obtained data matrix through principal component analysis lead to a model based on six variables, explaining 88.8% variance and revealing the presence of three types of yellow pigments, two types of red pigments and the fact that the green pigment is a mixture of a yellow one with a blue one.

Introduction

In the cultural heritage area, non-destructive analytical methods are a must in the expertise of artefacts - usually high value masterpieces, religious items or archeological artifacts. Among these, X-ray fluorescence (XRF) gained a well established position due to its multiple advantages: it has a wide dynamic range, a high precision, supplying multi-element qualitative and quantitative information, being in the meantime relatively cheap [1, 2]. However, since generation of quite a high amount of data can be a drawback, complementary chemometric methods are necessary to extract meaningfull information. In such a context, our team focused on evaluation of some religious paintings by XRF in order to determine the elemental composition of the utilised painting as a first step for establishing recovering and preservation strategies.

Materials & Methods

Elemental analysis for P, S, Cl, K, Ca, Ti, Fe, Cu, As, Ag, Ba, Hg and Pb from the surface of a "St Nicholas" and „Jesus Christ" icons was accomplished by X-ray fluorescence (XRF) using a INNOV-X Alpha-6500 portable instrument. The FTIR spectra were acquired with JASCO 6100 FTIR spectrometer using KBr pellet technique. Principal component analysis and cluster analysis was accomplished using MatLab (The Mathworks, USA), after mean preprocessing of the data matrix.

Results

Principal component analysis (PCA) together with clustering were used in order to identify some of the painting materials used. PCA was performed using six variables (concentrations of Cu, Pb, As, S, Hg and Fe), leading to a model with two principal components, explaining 88.80% variance (Fig. 1).

Two different red pigments are present, clearly separated on plots: s1red and m-red (iron ochre $Fe_2O_3.H_2O$ and HgS). Green pigments (m2 green and m2 dark green) exhibit similar loadings on the

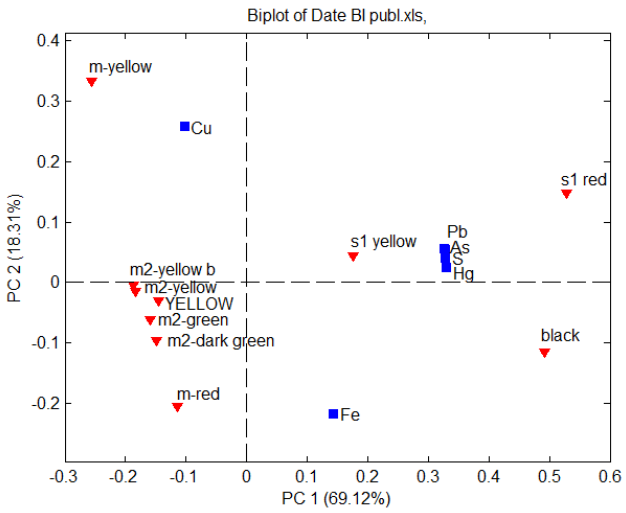

Fig.1: Biplot for the 5 variables model

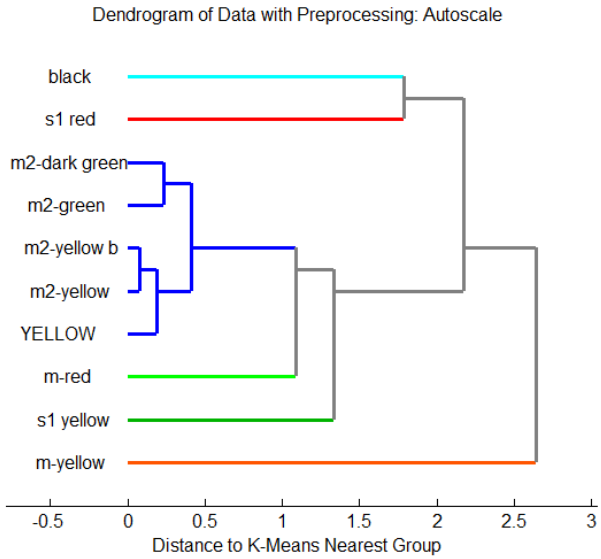

Fig.2: Dendrogram for K-means clustering

score plot, being close to the yellow ones; this can lead to the conclusion that green is a result of mixing the yellow pigments with a blue one. Cluster analysis was achieved by K-means clustering using Mahalanobis distance (Fig. 2), confirming the yellow and green samples'similarity.

Conclusion

By employing the XRF (and chemometry) and FTIR spectroscopy the painting materials for these two icons were identified: ground ($CaSO_4$), binder (egg yolk), pigments (iron red, Hg red, yellow (auripigment), Zn white and bronze powder. These two icons were painted in different historical periods due to the iron blue presence only in Jesus Christ icon. Hemp was employed as canvas. These data can be used in posterior interventions on religious paintings for their preservation and restoration.

Reference

1) K. Castro, S. Pessanha, N. Proietti, E. Princi, D. Capitani, M.L. Carvalho, J.M. Madariaga, Noninvasive and nondestructive nondestructive NMR, Raman and XRF analysis of a Blaeu coloured map from the seventeenth century, *Analand Bioanal Chem*, 391, (2008) 433-441.
2) A. Baciu, Z. Moldovan, I. Bratu, O.F. Marutoiu, I. Kacsó, I. Glajar, A. Hernanz, C. Marutoiu, Comparative Study of the Painting Materials of a Series of Orthodox Icons on Wooden and Glass Support from Transylvania, *Curr Anal Chem*, 6, (2010) 53-59.