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Image Processing and X-Ray Fluorescence Analysis for Pigment Identification

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Abstract

This study utilized image processing, X-ray fluorescence and principal component analysis (PCA) to characterize pigments in watercolour mock-up paintings. This was accomplished by using a portable digital microscope with 200x magnification and a portable X-ray fluorescence (PXRF) instrument. Experimental results have shown that image analysis can conduct to a better interpretation of the analytical data.

Introduction

In recent years, the analysis of paintings is widely performed noninvasively using handheld X-ray fluorescence devices [1-2]. Unfortunately, this analysis is subject to many errors and misinterpretation without a closer examination of the analysed areas at high magnification and other complementary techniques. For example, Pb, Zn or Ti identified with PXRF on paintings could indicate not only a white pigment, but also other pigments. Using only the PXRF technique it would be difficult to find out which pigment is present in the analysed area or if it is a mixture of pigments. [3-5]. The intention of this study is to show the advantage of using image analysis for XRF data interpretation.

Materials & Methods

28 pigments from Kremer Pigmente (set no. 14251) were applied with gum Arabic (Kremer 63320) on Fabriano Artistique 300 g/m^2 acid free paper. For each pigment several images were taken with Dino-Lite AM311s digital microscope (from AnMo Electronics Co., Taiwan) 640x480 resolution, 40 - 200x magnification. An ambient light block adaptor was used for eliminating ambient light and a diffuser to help spread light evenly. The PC monitor was calibrated with Spyder 3 (Datacolor, USA). PXRF data was acquired with a handheld Innov-X Alpha series (Woburn, USA), W anode, 35 kV, 40 μA. The photomicrographs and XRF data were used to build a test set for pigment characterization. Data analysis was performed by means of Matlab software (version 7.10, The Mathworks Inc., USA).

Results

PXRF, combined with image analysis, and associated with statistical analyses of data has been applied to characterize pigments in watercolor painting. Preliminary results were obtained for a collection of swatches with blue Kremer pigments mixed with gum Arabic solution and applied on Fabriano paper. Four images of different areas of the painting have been captured with Dino-Lite digital microscope, at 200x magnification. The Matlab software was used for converting RGB images of the pigments to CIELAB coordinates and for obtaining the ΔE values, calculated for every pixel in the test set using as standard the L*a*b* colour average value of a selected area

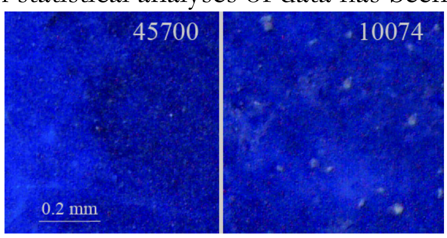

Fig. 1; Photomicrographs of cobalt blue dark $(Co,Zn)_2SiO_4$ (left) and copper barium silicate (right) with gum Arabic on paper.

in the image of an unknown pigment. ΔE is calculated as follows:

$\Delta L^* = \text{LChannel} - \text{LStandard};$

$\Delta a^* = \text{aChannel} - \text{aStandard};$

$\Delta b^* = \text{bChannel} - \text{bStandard};$

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

The software can find all pixels within a specified ΔE, closer to the colour of the unknown pigment, thus different pigments could be found by matching colours in the test set. The list of the possible pigments can be reduced with this preliminary image analysis by choosing a lower ΔE value.

An example for a cobalt blue dark pigment (45700 Kremer) is presented below. By selecting an area on the test image of this blue pigment, the software showed two matching pigments, for a maximum of ΔE = 3, cobalt blue dark (45700 Kremer) and copper barium silicate (10074 Kremer) (Figure 1). This indicates that these two pigments have similar colour. Using this test, other nine cobalt-containing pigments and four copper-containing pigments from our test set were excluded from the possible pigments list. The PCA of the XRF dataset revealed the different elemental composition of the pigments (Figure 2). We can see from the PC2 – PC3 scores plot that the pigment 10074 is present in the group of copper-based pigments, whereas the matching pigment, with similar color, 45700, is situated on the left side, in the group of cobalt-based pigments; the first three PCs explained 74.5% of data variance (Figure 2a). The pigment 45700 could be found at negative PC2 and positive PC4, where are located pigments characterized by strong signals for Co and Zn, as PC loadings indicate (Figure 2c). Similar results have been obtained for mixtures of pigments containing cobalt blue, the areas of pigments being identified using a microscope with a higher magnification (500x).

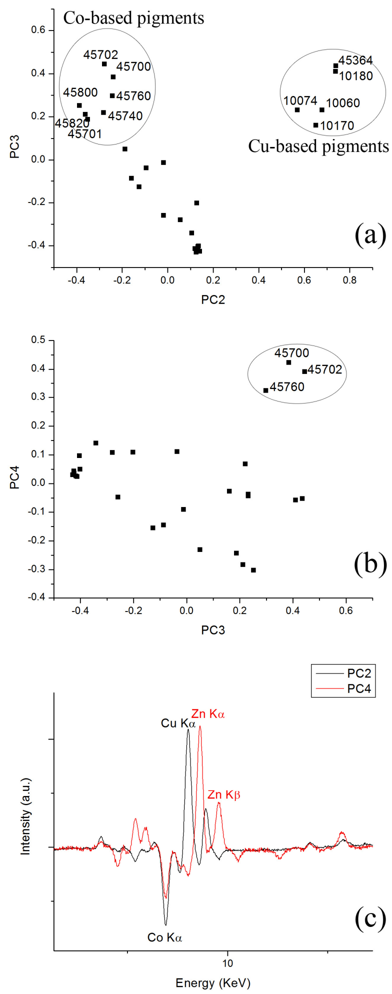

Fig. 2; Scores plot of PC2 (20.2%) versus PC3 (16.7%) showing a good separation of copper-based (right) and cobalt-based pigments (left) (a); from the 3rd and 4th PC we can see a group of three pigments (45700, 45702 and 45760) with positive score in PC4 that indicate a high Zn content (b); PC2 loading shows the K lines of copper (+) and K line of cobalt (-), while PC4 loading shows the K lines of zinc (+) and the K line of cobalt (-) (c).

Conclusions

The results of any XRF analysis should always be interpreted in conjunction with image analysis of the paintings. Although image analysis is not sufficient for pigment identification, it is very useful for XRF data interpretation. This method is most successful on unaltered, one-layer pigment watercolour paintings. Further study is necessary to take into consideration paintings with multi-layered pigments, different painting techniques and the effects of ageing process on painting.

References

1) A. Adriaens Non-destructive analysis and testing of museum objects: An overview of 5 years of research, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 60 (12), (2005) 1503-1507
2) G. Bitossi, R. Giorgi, M. Mauro, B. Salvadori and L. Dei Spectroscopic Techniques in Cultural Heritage Conservation: A Survey, *Applied Spectroscopy Reviews*, 40 (3), (2005) 194
3) T. Čechák, J. Gerndt, L. Musílek, I. Kopecká, Analysis of fresco paintings by X-ray fluorescence method, *Radiation Physics and Chemistry*, 61 (3–6), (2001) 717-719
4) Z. Szökefalvi-Nagy, I. Demeter, A. Kocsonya, I. Kovács, Non-destructive XRF analysis of paintings, *Nuclear Instruments and Methods in Physics Research B*, 226 (1–2), (2004) 53-59
5) P.H.O.V. Campos, E.A.M. Kajiya, M.A. Rizzutto, A.C. Neiva, H.P.F. Pinto, P.A.D. Almeida, *Radiation Physics and Chemistry,* 95, (2014) 362-367