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Differentiation of Roman *marmora* Samples Using NIR Spectroscopy and Chemometrics

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Abstract

NIR spectra were recorded for 13 different samples of *marmora* of different colours. After appropriate pre-treatment (SNV+ second derivative), the results were subjected to PCA treatment with a view to differentiating them.

Introduction

It is a fact that the word "marble", which derives from the Greek words "màrmaros", i.e. white stone, or "marmàreos", i.e. shiny stone, is today reserved for calcitic and/or dolomitic minerals that have been recrystallized as a result of regional metamorphism and that are extremely hard and have a completely white appearance. However, it is also a fact that the ancient Romans considered as "marmora" any hard and polishable stone and so not just the present-day white marbles but also a wide variety of hard, polishable but coloured stones. The large number of published studies on marbles [1] refer of course to the calcareous and dolomitic minerals, i.e. marbles in the modern sense that were used from ancient Greece onwards to shape countless inimitable statues.

For several years now, also our team has performed a number of studies [2-3] on calcitic or dolomitic marbles, in particular to test chemometric methods that, on the basis of experimental data obtained using chemical instrumental methods, would allow the classification of different types of ancient marble originating from the better known ancient quarries located in the Mediterranean basin [4]. The present research on the other hand focuses on the study of the stone materials that the ancient Romans referred to as "marmora" which include, as stated above, also materials of different colours of variable intensity ranging from black, to greyish, to green (also with yellow nuances), and to reddish. There is no lack of studies published on these stones although certainly fewer than those on calcitic or dolomitic marbles. Furthermore, some of these marbles have the appearance of somewhat dishomogeneous aggregates, especially when viewed close up, although when viewed from a certain distance they display a dominant colour. Also in the present research the aim was to use chemometric methods in an attempt to establish a classification of finds on the basis of experimental data obtained using instrumental chemical methods, in this particular case using near infrared reflectance spectroscopy (NIR).

Materials & Methods

Some 13 stone samples were tested, different in shape, size, and colour, originating from Italy, Africa and the Middle East (Asia). The names of all the samples tested are shown in the legend of Figure 1.

The NIR spectra were performed using an FT-NIR Thermo Finnigan 6700 spectrophotometer equipped with a halogen-tungsten lamp and an InGaAs detector, and operating in reflectance mode by means of an integrating sphere. For each spectrum, 82 scans were collected between 4000 and 10000 cm^{-1} at a nominal resolution of 4 cm^{-1}; the resulting signals were pretreated by SNV transform and second derivative (Savitzky Golay, with 2nd order polynomial and 19 points window) prior to chemometric data processing by Principal Component Analysis (PCA). Several reflectance spectra were performed and recorded for different points on the same sample. For the more homogeneous samples at least four spectra were performed and recorded, while a larger number were recorded for less homogeneous samples carried out on points of the sample that at first sight seemed to differ more from each other.

Results

PCA analysis carried out on the data set (4 components were selected, as suggested by cross-validation), evidenced, in many cases, well-defined clusters corresponding to the different *marmora* types. In particular, an evident separation was observed along the first component between "Africano", "Giallo antico", "Rosso antico" and "Cipollino" on the one hand and the remaining samples on the other. Moreover, the second component allowed "Breccia verde", "Breccia grigia" and "Granito grigio" to be identified (see Figure 1).

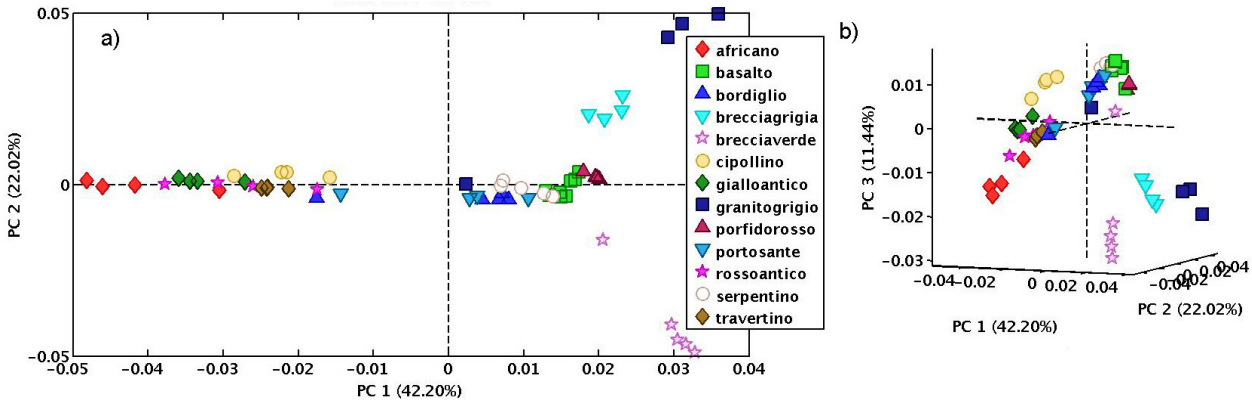

Figure 1 – Representation of the data onto the space of the first two (a) or three (b) PCs.

Inspection of the loadings allows the spectral regions which are most affected by the differences among the *marmora* to be identified and, as a consequence, could be promisingly thought of as being diagnostic for the different typologies. In particular, marmora lying at positive values of PC1 are characterized by higher absorbances in the regions 4243-4289 cm^{-1}, 4483-4497 cm^{-1}, 5001-5010 cm^{-1} and 5323 5334 cm^{-1}. On the other hand, samples lying at a lower value of PC1 present higher absorbances at 4179-4233 cm^{-1} and 4301-4314 cm^{-1}. Granito grigio and breccia grigia are characterized by higher absorbances at 7130-7201 cm^{-1} and 4385-4389 cm^{-1}, while breccia verde presents higher absorbances at 4397-4407 cm^{-1} and 7222-7255 cm^{-1}. All the main TG data were processed after autoscaling by Principal Component Analysis [7] for the purpose of demonstrating how thermal data alone, simply with the help of chemometric projection techniques, are sufficient to separate mortars belonging to frescoes of different ages into different clusters. Indeed, the representation of the samples onto the space spanned by the two significant principal components clearly evidences a separation between Roman and Renaissance frescoes, and also the subgrouping of the latter.

Conclusions

In this study, the potential of coupling NIR spectroscopy and chemometrics for the differentiation of coloured *marmora* samples has been demonstrated and spectral features corresponding to the different typologies have been tentatively identified.

References

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