Counterfeit on Roman Imperial Statue: Pattern Recognition Helps Diagnostic Performed with ICP and TG of a Torso and a Head of One Marble Sculpture

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Abstract

The correct assignment of the provenance of marbles used for ancient artifacts [1] provides valuable/useful information for their historic study. Knowing the ancient quarrying areas can resolve some problems, as associating broken or separated fragments or identify restorations or additions.

On the other side, transport of marble from far quarries (Spain, Turkish, e.g.) and find famous sculptors was quite expensive, for this reason many statues were reused cutting away the head and substituted with a new one, especially during the end of Roman age. On the other hand this custom continued about until the modern age.

Chemical and physical technique are available to obtain classification and counterfeit analysis if supported by multivariate analysis, applied this time to a female figure of Imperial Age.

Fig. 1; Female figure, probably I century b.C.. The head and body are different marbles

With this work we checked the possibility to obtain classification of marble, using chemometry and two different instrumental techniques, as Inductive Coupled Plasma Spectrometry and Termogravimetry analysis. Chemometrics are hyphenate, firstly to obtain variable selection on weight loss vs temperature (temp.) and after for visual classification of 22 samples (head and torso, 3 ancient marble, 17 single sample from quarries) obtaining a well recognisable classification.

Introduction

Many scientific methods can be used in order to distinguish marble artifacts and quarries. Often a single technique is not useful for clear characterisation-classification of white and coloured marbles, but multivariate analysis after several instrumental analysis can be the solution. This is the main topic of this Meeting and this research is a fulfil application.

The approach on marble artistic artifacts is the cations analysis by ICP after simple pre treatments; with modern equipment are necessary only a few grams of finds. An other useful technique is the TG, in carbonaceous stones this can product a "fingerprint" of sample with accurate selections of operative parameters with several mg of sample.

(Un)fortunately both techniques furnish a lot of information for each sample: with ICP we can make determination of main components (Ca, Mg, ..) up to the minor and trace elements (Ti, Sb ...); with TG, a single thermogram is composed by 1000 or 2000 values but many bringing the same information. Chemometrics can help the researcher to select useful variables able to classify the samples remembering the fundamental objectives, specificity and/or selectivity.

Among statistical and chemometrics tools we select the Principal Components Analysis for their simplicity, for this reason we worked for long time in scaling and variable selection before visual classification.

Materials & Methods

The TG was carried out on heating range, 35-1000 °C with raising of 10 °C/min and airflow of 100ml/min, starting from 15-20 mg of sample, using Du Pont TGA 50 thermobalance, connected to a PC running Du Pont 2000 data processing software. The ICP analysis was performed on about 200 mg of sample accurately weighed and dissolved, in ultrapure nitric acid and hydrogen peroxide, using a microwave digester. The solutions were filtered, diluted to 50 ml with ultrapure water. For both techniques, three repetitions are carried out in different day and mediane values were used. Three software were used for elaboration: firstly Lotus 123 v.9.8, useful for spreadsheet, matrix calculation and charts; VParvus (from Prof. Forina of Genoa, Italy) for chemometry; and MVSP (Kovach Computing, U.K.) for calculation and graph.

The chemometrics were applied two times, firstly with a method often used for "wavelength selection" on TG to find 4 temp./mass loss % useful for classification (406, 555, 698, 738 °C), and then on a matrix of 7 cations (Ca, Mg, K, Al, Fe, Sr, Mn) and the already mentioned 4 temp..

Results

We have analysed: 17 marble samples, from different quarries of Italy, Greece, Turkish; 5 samples from ancient artifacts of same historical age, included the two samples, aim of this research, from the head "testa" and the back "dorso" of draped female statue, see fig. 1.

In a previous work [2], we used 5 cations, 2 temp. and mass loss residue as variables. For this work we choose to use the TG data for 33% of variables (4 temp.), and the remain 66% from ICP.

Firstly, one matrix of 22 columns, marbles, and 951 row, the weight loss %, were obtained. Then the matrix was scaled by row centering. This matrix was used twice, to calculate the two maximum spreads by row obtaining the first 2 temp. (698 and 738 °C), and to make the first PCA analysis. After autoscaling, from PCA we selected the objects (temperature!) with largest value for PC1 and 0 for PC2, and with largest value for PC2 and 0 for PC1 obtaining the other two temp. (406 and 555 °C).

The new matrix 11x22 was autoscaled and after PCA analysis we obtained the fig. 2 with well definite visual classification. The specificity for Italian marbles (green square) is good with inclusion of Ephesus only.

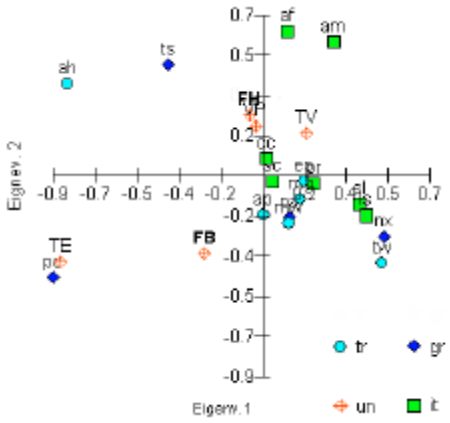

Fig. 2; PCA scores, after autoscaling, 4 TG mass loss % and 7 cations as variables. FB= back and FH= head of female figure

Conclusions

ICP, TG, a good use of scaling, and recursive use of PCA can produce a useful visual classification. In this study the marbles of "testa" and "dorso" of the draped female figure were recognised different, the head is probably an Italian marble. A historical reference about the use of Pentelic marble in "Tempio Rotondo" in Rome is confirmed by Fig. 2, see pe-TE

Unfortunately the 17 analysed marble are "know" with 95% of confidence and also we have only ONE sample for each quarry with the well know problem on quarry homogeneity.

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References

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