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Provenance Study of Stony Samples by Multivariate Analysis

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Abstract

A number of 48 different specimens of stony specimens from historical buildings in Seville (south Spain), have been analyzed by Laser Induced Breakdown Spectroscopy and X-Ray Fluorescence, with the purpose of determine the provenance from which each sample was mined. Data reduction was performed using the Linear Discriminant Analysis, Principal Component Analysis and Soft Independent Modelling Class Analogy. The application of multivariate analysis allowed to recognize building materials and stones belonging to at six different quarries, also rejecting extraneous samples purposely added to check the discrimination capability.

Introduction

The even more rapid deterioration of facades in historical buildings and churches raises the issue of preserving originality and exterior aspect by proper interventions. The fulfilment of this requirement is facilitated by the determination of the geographic origin of the raw materials, which in the present study has been obtained by coupling fast physical and chemical analysis with multivariate analysis for data classification. As far as the historical buildings in the city of Seville is concerned, six quarries from Andalusia (South Spain) were considered representatives for the production sites and a provenance study was conducted on 48 specimens.

Literature studies give full evidence that the element composition in stony materials can supply a unique fingerprint to the purpose of provenance assessment [1, 2]. However the large variance observed in the elements' concentrations, often prevents the successful application of a few elements discrimination criterion, then requiring the use of multivariate statistical analysis. Here only spectrochemical techniques were used for samples' characterization, then their classification according to the provenance was attempted. To the purpose of reducing the problem size in terms of number of variables to be simultaneously measured, only 10 constituents were selected and used: Mn, Cr, Pb, Cu, Sr, Ti, Si, Mg, Fe and Ca.

Materials & Methods

XRF measurements were made by using an instrument equipped with a rhodium tube (Panalytical mod. AXIOS). The samples were grinded in an agata mortar and passed with a 50μm sieve, mixed with wax (6% w/w) and pressed at 20t for 60s.

LIBS measurements were made on cut and polished samples in air at atmospheric pressure. The experimental system was based on a Nd-YAG laser source (Quanta System mod. Handy) emitting light pulses at 1064nm with 10Hz prr, pulsewidth 8ns and energy 350mJ. The laser beam was focused by a 250mm planoconvex focal lens, producing an ablation crater with a diameter of 220 μm. The plasma emission was sent to a spectrograph (Jobin Yvon mod. Triax 550) equipped with a gated ICCD camera (Andor mod. DH534-18-F03). More details can be found in [3]. Optimal SNR on emissions of trace elements was obtained by fitting with a multi peaks model and the contribution from interfering elements was subtracted; spectral data were finally normalized to background emission. By following this procedure we obtained highly reproducible standardized measurements with reduced fluctuations to the external error sources.

The multivariate data reduction was performed using the SPSS statistical package and Matlab 7.1. A Principal Component Analysis was run on each class of objects; to refine the classification we used SIMCA trained on separate class model and then used as prediction tool. The criterion of similarity was based on the distance between the unknown measurement and each of classes representative; the sample was then assigned to the closest. To identify belonging to classes not considered in the training, we assumed that the distance from each class model had a normal distribution; the probability density function was evaluated and used to compute the probability of class membership: samples with an associated probability less than 10-6 remained unclassified.

Results

Classes with less than two samples were excluded (namely ANT and PUE quarries). We assumed that the reduction of the classes number did not influence the classification results, indeed ANT a PUE had the largest distance from Seville and their use is highly questionable. Linear Discriminant Analysis was applied to separate the building material samples according their petrographical description. Three linear discriminant functions were extracted and presented in Figure 1 as discriminant scores along the first two factors. Here we observe a clear distinction among {EST, CCA} and the couple {OCA, PCA}.The latter have indeed a similar petrographical classification partially explaining the observed overlap. A global PC analysis was run on LIBS measurements of the reference samples; since the intraclass variance is close to the distance of some classes, we had to resort to a more sophisticated approach. SIMCA was trained on separate reference classes, and then used as prediction tool for classification of unknown samples. The results of multivariate classification were compared with those based petrographical similarity. A number of 28 specimens had consistent classification, while 17 samples had a non consistent assignment.

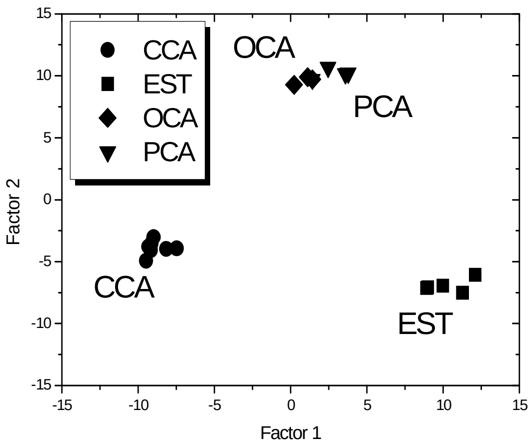

Fig. 1; LDA separate four classes each one representing a production site for stony materials

Conclusions

The application of multivariate analysis allowed to determine the geographical place of origin for historical building materials discriminating among materials of similar composition. The experimental technique is proven to be a powerful tool to rapidly collect and analyze - even in situ - valuable information of special interest to conservators and restorers, since considerable historical evidence can be drawn by the knowledge of material provenance.

References

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