



NIR, Thermogravimetry and Chemometrics, a Case Study: Burnt and Unburnt Human Bones

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Abstract

Twenty-four samples of human bones coming from four different necropolises (two in Italy and two in Sudan) have been investigated by Near InfraRed Spectroscopy (NIR) and Thermogravimetry (TG) coupled with Principal Component Analysis (PCA). Both data-blocks have been analysed individually and by a data-fusion method. The latter approach is the one provided the most relevant results, in fact, it allows realizing data show grouping tendencies according to both the funeral ritual bodies underwent and to their age.

Introduction

The investigation of biological findings unearthed in ancient cemeterial sites is a relevant topic because it allows unveiling information about ancient populations [1]. Among the different investigated aspects, the estimation of the age of archeological findings, and the disclosure of cultural behaviors of past populations are probably two of the main goals. In literature, several dating methodologies have been proposed (for example [2]), but, unfortunately, often they involve destructive techniques and they are relatively time-consuming. These aspects can be problematic, in particular considering the value some samples could have, or the reduced amount of available material.

As a consequence, in the present work, the possibility of developing a methodology which would allow the investigation of human biological findings without destroying a considerable amount of sample has been tested. For this purpose, Near Infrared spectroscopy (NIR) and Thermogravimetry (TG) have been coupled with Principal Component Analysis (PCA) [4]. Firstly, each data block (TG or NIR) has been individually analyzed by PCA and then, also a data-fusion approach, in order to see whether this could provide some additional information on the system under study, has been pursued.

Materials & Methods

Samples: 24 samples of human bones were available for the analysis. 12 fragments come from two necropolises in Italy (Cavo degli Zucchi and Elea Velia) and they are Pre-roman or Roman; samples belong to population that applied cremation during funeral rituals. The other 12 findings have been unearthed in two necropolises of the Middle-Nile region (Sudan); 4 from the Saggai site which are dated back to the Mesolithic and 8 have been deterred from the Geili necropolis; of these, 4 are Meroitic, and 4 are Christian. Sudanese samples did not undergo any cremation process.

NIR analysis: NIR spectra were collected by means of a Nicolet FT-NIR 6700 spectrometer, equipped with an integrating sphere and an InGaAs detector (Thermo Scientific, Walton, MA). The acquisition range was 4000-10000 cm^{-1} (82 scans, nominal resolution of 4 cm^{-1}). Four replicated spectra have been collected on each sample, switching side and orientation of fragments.

Thermal analysis: Thermal analysis was carried out on a Thermoscale Perkin Elmer Sistem 7/4 equipped with a P.E. 3700 Data Station (PerkinElmer, Waltham, MA). Bones were coarsely grinded

and the analysis was run under flux of oxygen (O₂) in the thermic range between 30 °C and 850 °C (heating rate 10 °C/min).

Results

As mentioned, all samples were analyzed by Thermogravimetry and by NIR spectroscopy. Then, data has been explored by Principal Component Analysis (PCA). Prior the creation of PCA models, different data-pretreatment have been tested on NIR (first and second derivative and Standard Normal Variate) and TG data (first and second derivative); independently of the preprocessing approach applied on signals, data has always been mean centered.

When PCA is calculated on TG data, it is possible to see a quite clear distinction among samples according to their age while when models are created on NIR spectra samples group according to the funeral ritual they underwent (burnt or unburnt).

In the second part of the work, the analysis has been focused only on the main TG losses (water, total collagen and carbonate mass losses) instead of using the entire TG signals. A Low-level data-fusion approach, applied combining the main TG losses with the principal components extracted from the model calculated on NIR spectra have been jointly analyzed.

The multi-block method resulted the most suitable in highlighting grouping tendencies among samples; in fact, as it can be seen from the scores plot displayed in Fig. 1, burnt bones fall at negative values for PC1, while the un-burnt at positive ones. Moreover, PC2 discriminates samples according to their age: Mesolithic present positive scores-values, burnt samples are close to zero and Meroitic and Christian samples present fall at negative PC2-values.

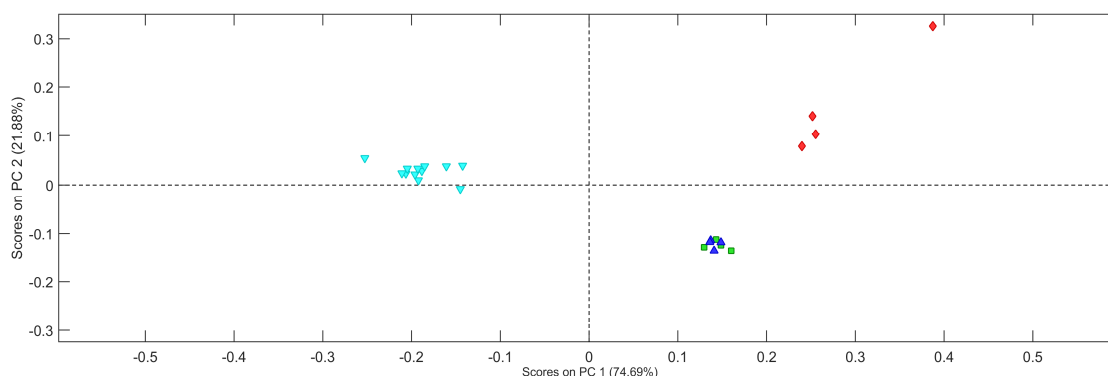


Figure 1 Low-Level data fusion approach- Scores plot: Legend: (Pre)Roman-cyan downward-pointing triangles, Mesolithic-red diamonds, Meroitic-green squares, Christian-blue triangles.

Conclusions

The proposed methodologies, i.e., the combination of NIR spectroscopy and TG with Principal components analysis resulted suitable approaches for the investigation of ancient human bones. The interpretation of individual models allowed discriminating two aspects: the age and the funeral ritual samples underwent. In particular, TG signals appeared suitable for the inspection of the first aspect, while NIR spectra for the second one. Anyhow, a low-level data fusion approach, aimed to the joint analysis of the main TG mass losses with NIR spectra resulted the most suitable approach to highlight grouping tendencies in data.

References

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