NEW FORMAT TO IDENTIFY THE PROVENIENCE OF DIFFERENT TYPES OF MARBLES USED TO MAKE ARTISTIC ARTEFACT

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The classification of the provenance of marble samples used to make artistic artefacts is not a easy task, therefore over the last few years our research group has tackled this problem on at least two occasions. Initially (Campanella et al., 2001) the approach, involved analysing samples of several significant marbles used in ancient times and originating from the Mediterranean basin, and the study was carried out using several different instrumental techniques, such as Atomic Emission Spectroscopy, Coupled Plasma Emission, X-ray diffractometry and Thermal Analysis. The huge quantity of data obtained in this way, processed using classical chemometric methods, has produced relatively interesting but certainly not exhaustive results. In addition, this approach involves the necessity of carrying out a large number of analyses and collecting and classifying huge amounts of data. Recently (Campanella et al., 2010), our research, carried out for various reasons on different materials of which different archaeological finds and cultural assets, were composed and performed using thermal analytical techniques, i.e.Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Thermal Analysis (DTA), showed that these thermal techniques, above all if the data thereby obtained were suitably processed, can alone solve many problems surrounding the dating or the origin of archaeological material. This led us to carry out further research, described in a previous paper (Visco et al., 2008), on the problem of the provenance of the marbles using exclusively (but all) the data obtained from the TG curves. Of course, this approach substantially narrows the information down to a single type of data, albeit abundant, as in practice all the raw values making up a thermogravimetric curve were used. For this reason their chemometric treatment was affected by the difficulty encountered in separating the TG data that actually contain information from redundant data that only represent "noise". An additional problem was represented by the loud instrumental noise that inevitably affects the data obtained using these techniques. Consequently, this meant that the results obtained following this type of approach did not live up to expectations. As we have seen, however, in recent times the thermoanalytical data obtainable by processing the "raw" curves have been considerably refined and have now become much more reliable thanks to the new mathematical processing kinetic methods introduced and the new software used in modern thermoanalytical apparatus. In the present communication therefore we first of all processed the main data obtained using TG, DTG and DTA thermal analytical techniques of several standard reference marbles, than a small number of unknown marble samples (a representative example is reported in Figure 1). From these, we extracted the values referring to true peak temperatures and mass variations of the main thermogravimetric steps and TG residues at 1000 °C. Subsequently, to these values were added the values of the principal DTA peak temperature and above all the activation energy Ea and the log A (A=Arrhenius pre-exponential factor) values of the principal TG-DTG thermal step, evaluated by processing thermogravimetric data using the so-called Wyden and Widmann method (Wyden and Widman, 1979). These data constitute the minimum set of variables that can be extracted from the thermal profiles in order to characterize the marble samples in order to differentiate them. Finally to investigate the relations and the similarities among the different marbles, Principal Component Analysis was applied to all the data after autoscaling. Shortly results of the present investigation showed as the thermal analysis coupled to Principal Component Analysis provides a valuable tool for characterizing ancient marbles, evidencing the similarities and dissimilarities among the investigated samples. In particular, it allows the differences between a set of marbles chosen as references to be highlighted and interpreted in terms of the experimentally observed thermal transition. Moreover, since the main aim is to verify whether unknown samples could be attributed to any of the marble types chosen as reference, the proposed chemometric approach reported in this investigation seems to have several advantages with respect to the previously described approaches (Campanella et al., 2001; Visco et al., 2008). First of all, the consistency between the attribution of the only known test sample and its real origin suggests that the proposed approach is likely to provide accurate results. Additionally, the possibility of using standard diagnostics for the identification of outlying samples proved to be particularly useful in detecting marble samples which do not correspond to any reference material and therefore prevents incorrect interpretations and assignments being made.

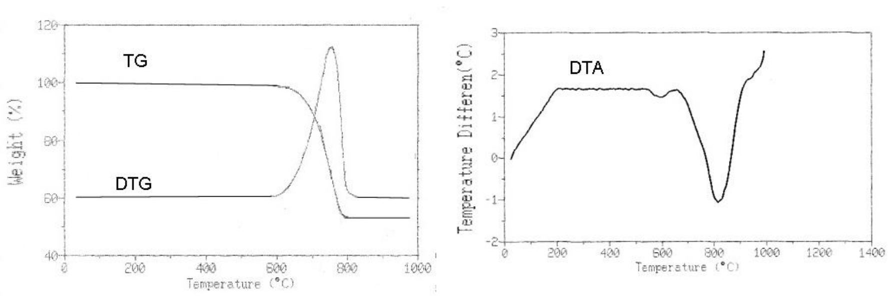

Fig. 1. Typical TG, DTG (left) and DTA (right) curves of a marble sample.

References

Campanella L, Gregori E, Tomassetti M, Visco G., 2001. Identification of different types of imperial age marble finds using instrumental chemical analysis and pattern recognition analysis. *Ann Chem- Rome*, 91(11-12)**:**701-718.

Campanella L, Costanza C, Tomassetti M, Vecchio S., 2010. Kinetic processing of thermoanalytical curves of cellulose samples and assessment of possible archeometric applications. *Curr Anal Chem*, 6(4)**:** 260-268.

Visco G, Gregori E, Tomassetti M, Campanella L., 2008. Probably counterfeit in Roman Imperial Age: pattern recognition helps diagnostic performed with inductive coupled plasma spectrometry and thermogravimetry analysis of a torso and a head of Roman age marble statue. *Microchem J*, 88(2):210-217.

Wyden H, Widman G., 1979. Kinetic evaluation of TG measurements with multiple regression. *Experientia, Supl. 37 of Angew Chem Thermodyn Thermoanal*, 37: 284-290.