Different Types of Marble Classification Using Thermal Analysis and Chemometry in Order to Identify Provenance

T. Gatta, E. Gregori, F. Marini, M. Tomassetti, G. Visco
Chemistry Department, University of Rome "La Sapienza", P.le. Aldo Moro 5, Rome, Italy

Abstract

Thermal analytical characterisation of several marbles frequently used in ancient times for artistic or decorative purposes was performed in support of the work of historians and restorers. The data were obtained using TG, DTG and DTA (Thermogravimetry, Differential Thermogravimetry and Differential Thermal Analysis). The data have already proved after subsequent chemometric elaboration in the identification of a small number of archaeological finds.

Introduction

Marble is certainly the best known and the most frequently used stone in sculptural masterpieces owing to its brightness, translucency, ease of working and polishing, and above all the ease which extremely smooth surfaces of great beauty can be obtained. A wide variety of marbles has been available in the Mediterranean basin for over two millennia. The identification of pure white marbles of Italian, Greek, Turkish, Spanish or other origin, as well as their use in archaeology and art, is the subject of study by a number of scientists. To classify the provenance of a marble object is therefore not an easy task. In the past, numerous methods have been tried to solve this problem: macroscopic examination, mineralogical and petrographical identification; X-ray diffraction, X-Ray fluorescence spectroscopy, atomic absorption spectroscopy, neutron activation analysis, mass spectrometry and electron spin resonance spectrometry. A thorough scientific investigation is usually necessary in order to support and complete the work of historians and restorers. In practice, a knowledge of the chemical properties and the composition of the different types of marble enables identification and facilitate comparative study. Once the type of marble used to make the artistic artefacts under study has been identified, an attempt can be made to solve the problems related to restoration and conservation. The demand for a rapid instrumental chemical method has increased in recent times. Consequently in the present study, the research involved only rapid methods, namely thermogravimetry, differential thermogravimetry, and differential thermal analysis as well as classical chemometrics methods (PCA, PCoA and so on).

Materials & Methods

Thermal Analysis (TG, DTG, DTA): for TG and DTA analysis a Dupont TGA 50 thermobalance connected to a PC running Du Pont 2000 data processing software, (Du Pont Inc. USA) was used. About 15 mg of gently ground marble specimens were subjected to analysis on a platinum plate heated over the 35-1000 °C range (at a 10 °C/min heating rate) under a 100 mL/min airflows.

Chemomety: different software was used, first to obtain curves, after for interpolation, smoothing and calculation of peaks and inflection points and finally for chemometrics. Was used, WinDig, XLXtrFun, WinIdams, MVSP, Past, Scout 2008, MVA add-ins for Excel, Aproximator and some hand made routines in Matlab and Octave, all on XP OS environment.

Samples tested: the marble samples used for references purposes in the present work were taken directly from their respective quarries with aid of archaeologist. For the sake of simplicity they have been classified by country of origin.

Results

In the last few years our research group has tackled this problem on at least two occasions. Initially [1] the approach involved analysing samples of the most significant marbles used in ancient times and originating from the Mediterranean Basin. Several different instrumental techniques were

used, such as Atomic Emission Spectroscopy, Inductively Coupled Plasma Emission, X-ray diffractometry and thermoanalysis. The huge quantity of data obtained in this way, processed using classical chemometric methods, have produced relatively interesting results. Nevertheless, this approach involves carrying out a large number of analyses and collecting and classifying huge amounts of data. Recently, our research carried out for various reasons on different materials contained in archaeological finds and cultural assets and performed using thermoanalytical techniques (TG, DTG and DTA) [2], showed that these techniques, above all if the data thereby obtained are suitably processed, can by themselves help solve the many problems surrounding the dating or origin of archaeological material. This led us to carry out further research on the problem of the provenance of the marble using exclusively (but all) the data obtained from the TG curves [3].

Of course, this approach substantially narrows the information down to a single type of data, albeit abundant, as in practice all the values composing a thermogravimetric curve are used. For this reason their chemometric treatment is affected by the difficulty encountered in separating the 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 has 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 "rough" curves have been considerably refined and have now become much more reliable thanks to the new mathematical processing methods introduced and the new instrument software used in modern thermoanalytical apparatus. In the present note we processed the data obtained from TG, DTG and DTA analytical techniques. From them, we extracted the values referring to peak temperatures and mass variations of the main thermogravimetric steps and TG residues at 1000 °C (see a typical example in Fig.1). To this may be added the area's values of the principal DTA peaks and above all the activation energy values of the principal TG-DTG processes computed using the so called Widen and Widmann method [4].

Currently, the main effort by our group is directed towards selecting the minimum number of these variables needed to obtain the best chemometric separation of the different types of marble considered. The preliminary results obtained so far already seem to be Very encouraging.

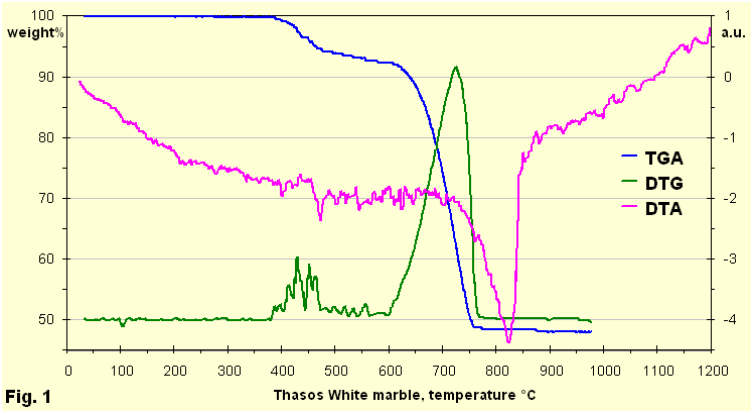

Fig. 1

Conclusions

Using thermoanalytical methods alone, which affords considerable savings in terms of time and resources and the classical chemometric methods of data processing, some success was obtained in solving the longstanding problem of developing a simple, rapid, innovative and cheap method to determine the provenance of the principal Mediterranean Basin marbles used since ancient times to create the most important marble artworks found today in international museums.

References

1) L. Campanella, E. Gregori, M. Tomassetti, G. Visco, Identification of different type of imperial age marble finds using instrumental chemical analysis and pattern recognition analysis, *Ann. Chim.*, 91(11-12), (2010) 701-718

2) G. Visco, E. Gregori, M. Tomassetti, L. Campanella, 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, *Microchemical J.*, 88(2), (2008) 210-217

3) L. Campanella, C. Costanza, M. Tomassetti, S. Vecchio, Kinetic processing of thermoanalytical curves of cellulose sample and finds assessment of possibile archeometric application, *Curr. Anal. Chem.*, 6(4), (2010) 260-268

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