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Characterization of Black Pigment Used in 30 BC Fresco Wall Paint Using Instrumental Methods and Chemometry

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Abstract

Several commercial black pigments were characterized by means of thermogravimetry (TG) and allied techniques. These pigments were used to make standard frescoes. The latter were subjected to Raman and reflectance analysis. The results obtained, together with the TG data, were processed chemometrically and used to identify an analogous unknown standard, obtaining excellent results. The same colorimetric and reflectometric techniques, coupled with suitable chemometric techniques, were then successfully used to identify the type of black pigment present in an ancient Roman fresco of the Imperial Age.

Introduction

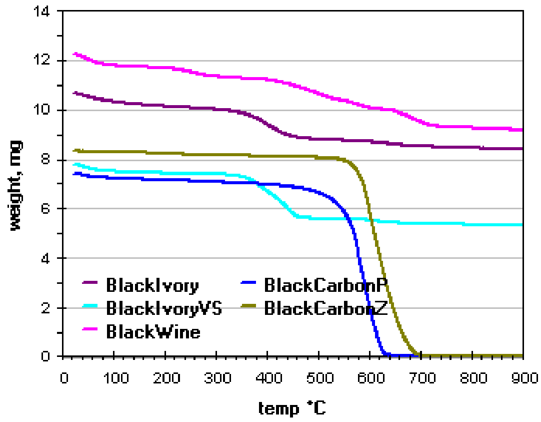
The aim of the present research was to identify the black pigment used in a Roman fresco dating to 30 B.C using a non destructive method. The application required comparison with pre-recorded reflectance spectra of standard plaster frescoes prepared ad hoc. For the preparation of these "standard frescoes" the previous characterization and authentication of utilised different commercial black pigments was necessary [1] and was performed by means of different instrumental techniques, in particular, thermogravimetry (TG-DTG). On the other hand, in order to characterize standard frescoes, TG, Raman micro-spectroscopy (Raman-μ S) [2] and colorimetry were used, while to identify the in situ Roman fresco, only colorimetry and reflectance spectroscopy it was possible to apply. Lastly, Multivariate Analysis techniques were used in order to compare all the available instrumental data.

Different types of black pigments were used to make the standard frescoes. These pigments were purchased over the counter in Rome and Florence in shops specializing in the sale of restoration materials; one black-ivory, two black-carbon and one black-wine pigments were used to construct the training set in the chemometric process; lastly, another black pigment, supplied to us probably only as black-ivory was considered and used for the "validation set".

Materials & Methods

The fresco we studied was found on the Palatine in Rome after the excavation of "Emperor Octavianus' house", in the room called "Augustus' studiolo". The TG curve printouts show the percent variation of the mass as a function of the temperature and the first derivative of this curve (DTG). These measures were carried out using a Mettler TG 10-TA thermobalance (Mettler Toledo, Swiss) with dynamic air, flow rate 10 ml/min, heating rate 10°C/min from 25 to 900 °C, balance sensitivity of 1 μg. For microspectroscopy the LabRam Infinity Raman microscope was employed (Horiba, Jobin-Yvon, USA) using a 25 mW He-Ne laser at 632.8 nm. The colorimetric spectrophotometer used was a Minolta CM2600d in the visible region, 400-700 nm, resolution 10 nm, using both D65 and D50 lamps. The spectra were transformed into L* a* b* and L* H* C* parameter using Minolta software. As expected, the low reflectance of black pigments does not allow a dominant wavelength to be found. For data analysis was used: Lotus spreadsheet 9.8 (IBM/Lotus, Usa); Past 2.01 (free version by Øyvind Hammer, Norvay); Datalab 2.7 (light version by H. Lohninger, Austria); Multivariate Analysis (an Excel ad-in by Prof. R. Brereton). Both colorimetric as well as Raman and TG data referring respectively to standard frescoes and to the black pigments tested, were digitized using modern software (WinDig), then processed using new exponential smoothing techniques to obtain more readable lines.

Results



To authenticate commercial pigments above all TG was used (see Fig. 1), which also allowed the activation energies of the oxidative sample step to be found. The Raman-μS technique proving to be a good tool [2] for recording the presence of any black carbon pigment in frescoes (even though the wavelength differences of Raman peaks of different black pigments we studied were found in practice not always well obvious). In fact, before identifying the black pigments used in an ancient fresco, it was necessary to know whether our methods and chemometrics techniques were capable of distinguishing some top-quality modern black pigments with which the standard frescoes were fabricated. Mainly two chemometrics methods was used, the Hierarchical Cluster Analysis (HCA) and Principal Components Analysis (PCA).

To check the validity of the analytical and chemometric procedures used, the second black-ivory pigment, supplied as only "probable" and considered by us as an unknown sample, was tested using the above three techniques and the results processed using the multivariate methods cited above. It was thus possible to corroborate the identification which may be considered as practically certain (confidence level 85 %). To characterize and identify in situ old Roman black pigment (30 b.C.) essentially the colorimetric technique was used. On the other hand reflectometric techniques, applied in the visible region (400-700 nm) was also used to identify the black pigment in the ancient Roman fresco, by comparing its optical reflectance spectrum with the spectra of well characterized commercial black pigments in the standard frescoes. The reflectometric and colorimetric data, that is the L*, a*, b* values, obtained by measurement in situ using Minolta software, were compared with those obtained from similar reflectometric and colorimetric measurements on standard frescoes and later, using the HCA representation of the colorimetric data, we were able to ascertain that the pigment of the old Roman fresco under test was probably a black wine pigment. However, in this case it was not possible to include in the data matrix both Raman and TG data, therefore identification had a confidence level of not more than 65 %.

Conclusions

In conclusion, TG seems to be the most useful technique to characterize and authenticate commercial black pigments, while, by using visible colorimetry and reflectance we were able to identify the ancient pigment in situ. Indeed, the very small difference between the reflectance spectra of ancient and commercial pigments is justified by the presence of wax (normally used in Roman frescoes to protect from moisture and to increase colour brightness) and by ageing. Of course in the lucky case in which all three techniques can be simultaneously applied, the identification is more simple and sure. The limitation of the present approach is due to the necessity to possess and previously record standard spectra as a reference tool. Furthermore, the commercial pigments that can be used to create such standard frescoes must be identified as "authentic" in the sense that they must have the true chemical-physical composition as those used for ancient pigments.

References

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