Problems in Processing and Correlation of Data Relevant to the Study of Artworks

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Abstract

Starting from the Conference "State of the Art IX" on 2011 [1] the Diagnostic Laboratory for the Conservation and Restoration of the Vatican Museums works on a project dealing with the identification of unknown samples taken from drafts standardized binder mixed with pigments, in the round robin, which saw the participation of several national and international laboratories. Standard samples were prepared on glass plates and subjected to natural or accelerated aging in a climatic chamber with ultraviolet lamps. All real and standard samples were analysed by Fourier Transform-Infrared spectroscopy (FTIR), Gaschromatography/ mass spectrometry (GC / MS), PyrolysisGaschromatography/ mass spectrometry (PyGC / MS) and colorimetry.

Introduction

Multivariate statistical methods, being able to easily extract the maximum information from data, is particularly useful in case of studies related to Cultural Heritage [2] where the main problem rises from the often scarce significance of the sample that, in turn, depends on the obvious impossibility to dispose of enough samples, in enough high amount, coming from a correct "Experimental design". Further problems rise, especially for painted artworks, from the coexistence of different chemical elements, at different concentrations, that can lead to a difficult determination of those at very low concentration because their signals from instruments can be covered by the others (as an example using XRF, PIXE, SEM-EDS). Other difficulties come from the occurrence of complex chemical reactions between their components, as well as in consequence of ageing that, in turn, depend on the different environment in which they are located. The use of non-invasive and/or micro-destructive techniques seems to be a solution but their reliability and validity can be questioned when only one dataset is used. For example, if you determine Zinc in a painting attributed to the sixteenth century (Madonna of the Girdle), it means that it is a copy of the nineteenth century? If Pb is also present, it means that Zn is mixed with it so being a restoring pigment? If, through a stratigraphic approach, you verify that Zn is located in the preparatory layer, you could state that you are in presence of a false. When other data, such as other diagnostic results and historical sources who claim that the Pagans (XVI century) has painted a Madonna of the Girdle, assign the picture at the XVI century, it therefore evidences the random nature of the information acquired through the chemical composition of a single small sample. Finally, the possibility of obtaining quantitative data is strongly linked to the sample's homogeneity that generally lacks also in a same small crosshatch. It is therefore evident that "Sampling" plays an important role that must comply with the aesthetic and historical contents, and, above all, must ensure the physical integrity; this means that the lowest number of sample and lowest amounts of them must be carefully planned, taking into account the need for each of the inalienable analytical techniques, in order to have significant dataset. The best behaviour implies the use of standard procedures (i.e. Uni-Normal), but unfortunately they are scarce and, when existing, not followed at all.

Here we present a research based on a round robin project, started on 2011, in which the Diagnostic Laboratory for the Conservation and Restoration of the Vatican Museums collaborated with several national and international laboratories.

Materials & Methods

The project aims to the identification of unknown samples taken from specimens constituted of binder (linseed oil, rabbit glue, white or yolk egg, calcium caseate) mixed with pigments (white lead, "S. Giovanni" White, Cinnabar, Ochre, Malachite, copper acetate); the choice lies on the difficult identification of the pictorial medium in the presence of elements such as Pb, Cu, Fe and Ca, which may affect the analytical response. The standard samples consist of only binder (in number of 5) or pigment in binder (in number of 6), layered on 200x50 mm glass plates. 24 samples were sent to the 10 national or international laboratories for the round robin analysis while all the other samples were subjected to natural (in number of 24) or accelerated aging (in number of 24) by cycles in a climatic chamber with ultraviolet lamps. All samples were analysed by FTIR, GC / MS, pyGC / MS and colorimetry before, during and after aging.

The comparison of data coming from all the involved laboratories aimed to highlight the critical issues and challenges in the identification of binders. Depending on the skills of each laboratory, samples, identified only by acronyms, were sent IR, GC-MS, py-GC-MS, LC-MS, ELISA analyses.

Results & Conclusions

From FTIR analyses, carried out in 5 labs, the result is a low percentage of error, but only the class of the binder has been identified. In two cases the error was due to the presence of white lead that has distorted reading of the band of the ester carbonyl; on such bases in one of them a successive correction was done. GC-MS analysis (fig. 1), carried out in 3 labs, gave 80% corrected responses. In 1 case some errors were eliminated after the identification of the source, i.e. pollution problems. Py/GC-MS analyses, carried out in 5 labs, only a 16% of errors was evidenced, in between them the 17% were successively corrected by changing the pyrolysis system that resulted polluted. LC-MS/MS analyses evidenced a 54% of correct answers; a problem of carry-over, that led to identify the proteins of the milk in samples not containing it, was identified and eliminated by increasing the amount of enzyme used in the digestion of proteins. In the case of the ELISA method, for limits of the technique, it was not possible to identify the binder in all samples (with this technique is not determinable the presence of lipids); anyway a total correctness of answers was obtained highlighting the maximum efficiency of the analytical method based on immuno-staining. The higher percentage error was found in the analyses of the white lead in rabbit glue, of specimens with white and yolk egg, especially in the presence of white lead and yellow ochre, of white lead and "S. Giovanni White" in calcium caseate. This confirms that heavy metals, such as lead, affect the identification of the binder; the most frequent error was the confusion between albumen and casein with greater uncertainty in the identification in the case of egg (egg white or yolk).

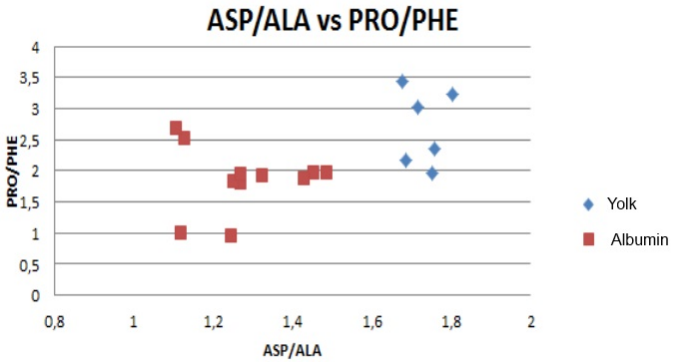

Fig. 1; TIC of aminoacids and 2D correlation

Results obtained in this round robin project evidenced the need of a multivariate treatment of data; really a research is running to optimize a method of statistical analysis (2D-Plot and PCA) using GC-MS data of protein binders to improve their identification (greater accuracy and sensitivity).

References

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