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CMA4CH 2006 Lectures

Chemometrics as a Tool Investigating Environment and Cultural Heritage Problems

Introduction

In this lecture several applications of chemometrics to the elucidation of environmental and cultural heritage dataset are presented.

In particular, the arguments discussed, with some insights on the theoretical expects and limits of the applied chemometric tools are: the identification of environmental pollution profiles in the area of Alessandria [1, 2], the regionalization of the superficial waters in the same province, the modelling, by neural networks, of the emission profile of a large cement production plant, as function of process variables [3]; the use of multivariate statistics and control chart for monitoring the conservation state of different goods, for cultural heritage preservation [4, 5, 6, 7, 8, 9] and a provenance study of pottery pieces coming from the Novalesa abbey, in Piedmont [10, 11, 12].

Chemometrics in Environmental and Cultural Heritage fields

In our group Chemometrics has been applied to the elucidation of several problems in proteomics, as well as in environmental, cultural heritage, process optimisation, process control, food characterisation, analytical methods optimisation and validation, the calibration of a spectroscopic method, etc. BUT, what do proteomics has in common with food characterisation or the optimisation of a cement process? The answer is: the COMPLEXITY of the problems. This complexity is often related to the HIGH DIMENSIONALITY of the investigated system, either the number of variables like in the calibration of spectroscopic data and in proteomics, or the number of measurements, typical, for example, of environmental studies where the results of the automatic measurement tools are used and to the COMPLEX RELATIONSHIPS that often link the variables among them, the measurements (samples, objects) among them or the variables and the measurements. These relationships can sometime be not linear, which adds to the general complexity due to the high dimensionality. The increasing tendency of the complexity of the problems investigated in several fields is due either to the inner complexity of the problems or to the availability of instruments that produce huge amounts of data. The information produced by these

instruments and the inner complexity of the problems makes it natural for the researcher to look for some tools that permit a reduction of the problem dimensionality and a rationalisation of the relationships existing in the investigated system. This is the role of Chemometrics: essentially the role of a service discipline that permits to shed light on the investigated problem, offering tools that simplify the interpretation of the experimental results and offer privileged points of view of the investigated system, that often allow to solve the problem that is faced in turn.

In some scientific fields it would be impossible to make effective research without the aim of chemometric tools. As an example, in the present lecture, some application of chemometric tools performed by our research group in the University of Eastern Piedmont to environmental and cultural heritage problems shall be presented.

Examples of Environmental applications of Chemometric tools

The first examples report the study of the pollution sources in the Carlo Alberto channel in Alessandria province and the study of the superficial well water in the same province. In such studies, where there are both high dimensionality and complex relationships, the first and best tool is still PCA. By using particular scaling techniques to avoid spurious effects, like for example the data dependence on season, it has been possible to discover quite interesting relations and to identify some sources of pollution profiles, as well as the presence of some hot spot. In the latter case, for example, through the construction of a geographical map representing the first PCs, using Kriging mapping techniques, the presence of an unknown thermal source was discovered! A more refined application in both cases was the use of Self-Organising Kohonen maps, that provided the identification of some local similarities, that cannot be discovered using the usual clustering methods (e.g. agglomerative or divisive, as well as k-means based methods).

Another interesting application of chemometrics to environmental problems was the modelling of the emission of a large plant of BUZZI UNICEM, for the production of cement. These plant have often a sever effect on the environment, due to the wastes emitted by their oven. Both raw materials descriptors and process variables were used to predict the waste composition on a large time scale. The application of linear tools (OLS, PCR, PLS) proved not to be satisfactory, so back-propagation artificial neural networks were employed. The result showed that in spite of a very rough description of the process (the available data had not been designed for this purpose), for some noxious compounds a satisfactory predictive model could be built. This allows the change of the operative conditions of the production process to avoid the overflow of the law threshold for the specific compound, when necessary!

Examples of Cultural Heritage applications of Chemometric tools

In this specific area our research group has created a tool for monitoring the conservation state of cultural heritage goods by the application of surface spectroscopic methods, coupled to multivariate statistic and process control charts. The techniques has been applied with great success to wood goods, to paintings, fresco paintings and sheet, allowing the identification of the exact moment when an accelerated attack on the surface of the investigated object was applied, in order to simulate a natural degradation process. Humidity, UV light, acidic and basic attacks were investigated. The methodology allows also to obtain information on the nature and type of degradation process that is taking place, so permitting to design effective prevention actions, and eventually, also suggesting the best type of corrections or restorations required.

Another example was the study of provenance of several pottery samples discovered in the Novalesa Abbey, in Piedmont. Novalesa is important from a historical point of view, as it was one of the most important centre between France and Italy, for people crossing the Alps and

constituted, during the late middle age, an important centre for the preservation and irradiation of culture. The problem required first the optimisation of the analytical method, based on the dissolution of small pieces of the samples and their analysis by ICP-MS spectroscopy. This was performed by the modified simplex methodology, using a PCA based multicriteria target function. A decrease of 50% of the uncertainty of the experimental result was obtained, with respect to the standard setting of the ICP-MS instrument.

The provenance analysis was then performed by using both PCA, cluster analysis tools and Kohonen self-organising maps. In this way all samples could be assigned to a tentative class, that was successively validated and confirmed by the archaeologists.

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