Investigation of the Degradation Mechanisms of Organic Materials: From Accelerated Ageing to Chemometric Studies

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Abstract: *The most common way followed for the determination of degradation mechanisms of organic materials is the application of physicochemical methods after accelerated ageing. The disadvantage of this practice is the inability to control the effect of the combination of degradation factors in real time and in real conditions as it happens in burial environment, in museum environment or in open-air conditions. In recent years it has been noticed a remarkable research activity towards the development of alternative decay determination methods in organic materials based on statistics (Chemometric studies). The discipline of Conservation of Antiquities and Works of Art has not developed yet its own statistic tools therefore it borrows the statistical methods used in social sciences and biosciences. One could claim that biostatistics is the most appropriate to answer the questions of the Conservators because faces similar "cases". At the same time it is necessary to establish a network of interested conservators/restorers and scientists and to build a central database containing all experimental data and software for all members of the network.*

Keywords: *Conservation, Organic materials, Chemometric studies.*

I. INTRODUCTION

Main concern of the Conservator's work is the safeguarding of the aesthetic, historical, structural and material integrity of the objects he/she conserves. This is achieved by the diagnosis of their state of preservation, by planning and applying the methods of preventive and interventive conservation. The cultural properties' integrated information content is related not only to their historical identity but also to the artefacts' technology, their material structure and their behavior towards the environment during natural ageing. The methods and the materials used in conservation should be compatible with the research that follows in order to highlight the historical identity of the cultural evidence. (E.C.C.O., 2002)

The investigation of the degradation mechanisms of the materials constituting the Cultural and Natural Heritage, despite the progress made, has a long way still to go. The most common way followed for the determination of these mechanisms is the application of physicochemical methods after accelerated ageing. The disadvantage of this practice is the inability to control the effect of the combination of degradation factors in real time and in real conditions as it happens in burial environment, in museum environment or in open-air conditions. This problem is getting even worse in the case of organic materials that are characterized by a variety in structure and composition, and that are extensively sensitive in many environmental factors, abiotic and – mainly– biotic.

The need for understanding the decay process - especially of these organic materials with industrial use (i.e. paper, wood) - resulted to the standardization of diagnostic techniques and of the accelerated ageing protocols (ASTM, 1993; ASTM, 1995; ASTM, 1996; ASTM, 2002a; ASTM, 2002b). Although this standardization, it is no coincidence that in recent years it has been noticed a remarkable research activity towards the development of alternative decay determination methods in organic materials based on statistics.

This method is based on statistical elaboration of analytical data from groups of existent objects and aims at the correlation of the factors that –potentially– are responsible for their decay and at the determination of the critical factor that can be considered as catalyst for their preservation (Malea, 1999; Larsen *et al*., 2002; Bechmann and Larsen, 2007; Zervos, 2007; Deselnicu, 2010; Malea, 2010).

II. METHODS

Statistics have been proved a useful tool for answering questions in many disciplines. In practice through an interactive process one studies the data in hand, examines it using some statistical method, decides to look at it another way by either transforming them, taking only a part of them or by even applying a different analysis method. Different methods are being used to bring out different aspects of the data, to ask and answer different questions about the "population" they came from and predict accurately future observations (make inference) by minimizing the time and effort needed. By using statistics the researcher has sound methodological tools that enable him to make accurate conclusions on the underlying process that generates the data itself (Berthold and Hand, 1998).

According to the generic definition, accepted by The International Chemometrics Society (ICS), chemometrics is *"…the science of correlating, by statistic-mathematic techniques, of measurements conducted on a chemical system process, its state being in given conditions or at a given time"*. Although the term of chemometrics has been introduced in 1972 (Wold, 1972), the operative definition of chemometrics, stated by practitioners, was established in 1986 and presented in the editorial from the first issue of Chemometrics and Intelligent Laboratory Systems Journal, in the following sentence: *"Chemometrics is that discipline in the field of chemistry which uses methods of mathematics and statistics to formulate or select experimental plans and procedures of physical-chemical analysis, in view of extracting maximum information by algorithmic processing of data obtained as a result of studies conducted at laboratory or industrial level"* (Deselnicu, 2010).

The objective of chemometric techniques is that of highlighting complex and non-obvious relationships ("hidden") between a large number of variables associated with studied systems, resorting to statistic-mathematic models capable of describing states of physical-chemical systems, at a given time or in their dynamic.

Techniques of modelling chemometric data can be classified into:

- *quantitative*, *regression techniques*, that provide numeric parameters of postulated models;
- *qualitative techniques*, *of recognising models/patterns/structures of multicriterial grouping of experimental data*, providing images and sometimes numerical indexes of similarity/dissimilarity, on the basis of which classes and/or filiations of studied systems or of states of a system going through a given process can be identified (Deselnicu, 2010).

The discipline of Conservation of Antiquities and Works of Art has not developed yet its own statistic tools therefore it borrows the statistical methods used in social sciences and biosciences. One could claim that biostatistics is the most appropriate to answer the questions of the Conservators because faces similar "cases" such as:

- Great number of data with many missing values
- Elaboration of data derived by small number of samples tested, in relation to the large number of variables (data), correspondingly to medical discipline when investigating rare diseases.

Missing data in clinical trials reduces the power of a study and is a major source of potential bias when interpreting study results, especially if the amount of missing data is substantial. There are many reasons for missing data. There is no universally acceptable method for handling missing data. When data are missing, any attempt to draw conclusions from a statistical analysis rests on untestable assumptions concerning the relationship between the missing (unobserved) data and the reasons why the data is missing (the missing data mechanism). The causes for missing data can be grouped into three different classes, depending on the relationship between the unobserved data and the missing data mechanism:

a) **Missing Completely at Random (MCAR).** MCAR means that the missing data mechanism is unrelated to the values of any variables, whether missing or observed. In other words when we say that data are missing completely at random, we mean that the probability that an observation (X_i) is missing is unrelated to the value of X_i or to the value of any other variables. Thus data on family income would not be considered MCAR if people with low incomes were less likely to report their family income than people with higher incomes. Similarly, if Whites were more likely to omit reporting income than African Americans, we again would not have data that were MCAR because missingness would be correlated with ethnicity. However if a participant's data were missing because he was stopped for a traffic violation and missed the data collection session, his data would presumably be missing completely at random. Also, data that are missing because a researcher forgot to perform a test are likely to be MCAR. Another way to think of MCAR is to note that in that case any piece of data is just as likely to be missing as any other piece of data. Unfortunately, most missing data are not MCAR.

b) **Missing at Random (MAR).** MAR means that the missing data mechanism is unrelated to the missing values but is related to either observed covariates or response variables. The data can be considered as missing at random if the data meet the requirement that missingness does not depend on the value of X_i after controlling for another variable. For example, people who are depressed might be less inclined to report their income, and thus reported income will be related to depression. Depressed people might also have a lower income in general, and thus when we have a high rate of missing data among depressed individuals, the existing mean income might be lower than it would be without missing data. However, if, within depressed patients the probability of reported income was unrelated to income level, then the data would be considered MAR, though not MCAR. Also, data that are missing because a subject is removed from a study based on a pre-defined clinical condition like an elevated blood glucose level are MAR.

c) **Non-Ignorable (NI).** NI is also known as **Missing Not at Random (MNAR).** It means that the missing data mechanism is related to the missing values. For example, if we are studying mental health and people who have been diagnosed as depressed are less likely than others to report their mental status, the data are not missing at random. Clearly the mean mental status score for the available data will not be an unbiased estimate of the mean that we would have obtained with complete

data. The same thing happens when people with low income are less likely to report their income on a data collection form.

A key distinction is whether the mechanism is ignorable (i.e., MCAR or MAR) or non-ignorable.

There are excellent techniques for handling ignorable missing data. A nice feature of data that are MCAR is that the analysis remains unbiased. We may lose power for our design, but the estimated parameters are not biased by the absence of data.

About the MAR data, the phraseology is a bit awkward because we tend to think of randomness as not producing bias, and thus might well think that Missing at Random is not a problem. Unfortunately is a problem, although in this case we have ways of dealing with the issue so as to produce meaningful and relatively unbiased estimates. For data that are missing at random, Chen and Little (1999, 2001) discuss methods for analyzing survival data with missing covariates. Little and Yau (1996) develops a multiple imputation method for intent-to-treat analysis of repeated measures data with drop-outs. The SAS code used to generate the multiple imputes in the example in this paper can be accessed by clicking on Little and Yau intent-to-treat code [1]. Little and Raghunathan (1999) compare maximum likelihood and summary measures approaches to longitudinal data with drop-outs in a simulation study. Likelihood-based methods for estimating the complier-average causal effects of treatments are considered in Little and Yau (1998), Yau and Little (2001). Ezzati-Rice *et al*. (1995) discusses a recent large-scale application of multiple imputation to a national survey. Little and An (2003) propose a robust likelihood-based method for multivariate data with missing values based on regressions on splines of propensity scores.

When we have data that are NI (or MNAR) we have a problem. The only way to obtain an unbiased estimate of parameters is to model missingness. In other words we would need to write a model that accounts for the missing data. That model could then be incorporated into a more complex model for estimating missing values. This is not a task anyone would take on lightly. See Dunning and Freedman (2008) for an example. Generally, the non-ignorable missing data are more challenging and require a different, more complicated approach. Depending on the data, this approach may include multiple imputation methods, survival analysis techniques, and pattern mixture models. For data that are not missing at random, Little (1993) discusses pattern-mixture models, a broad class of models that they do not require precise specification of the missing-data mechanism. Tang, Little and Raghunathan (2003) develop a pseudo-likelihood method for fitting no randomly missing data that avoids specifying the precise form of the mechanism. Little (1995) develops a model-based framework for repeated-measures data with drop-outs, and places existing literature within this framework.

Recently, in the United States, the Division of Behavioral and Social Sciences and Education under National Research Council of the National Academies have been working on a project "Handling missing data in clinical trials"[2]. The working group recently makes its report available. The report is titled: "The prevention and treatment of missing data in clinical trials" (National Research Council of the National Academies, 2010). Respectively we should link the cases of missing values met in Conservation of Cultural Properties with the missing data mechanisms. In example, missing data mainly of archaeological organic materials may due to loss of material, to insufficient or inadequate of diagnostic methods, or/and to incomplete documentation (loss of information) during the steps that take place between the excavation and the transportation to the Laboratory. We have to determine which of the above mentioned cases can be considered as MACR, MAR or MNAR.

Once the missing data has happened, there is no universal method to handle the missing data perfectly. The assumptions of MACR, MAR, and MNAR can never been fully verified.

Regarding the handling of the rare diseases, although there is no a single definition, the European Commission (Health and Consumer Protection Directorate-General) considers that a disease is rare if its prevalence is lower than 50 cases per 100,000 habitants. Hence, according to this definition, rare diseases will have very low observed cases in low populated areas. This definition could also be applied in archaeological organic materials that rarely can be found due to their vulnerability in degradation factors.

If the disease is rare, many areas may have zero counts, which will cause additional problems in the statistical analysis due to the large number of zeros that appear. Although standard methods could be used, care should be taken and other statistical methods that account for the excess of zeros may be required Lee et al. (2006).

Regarding the detection of disease clusters, many methods have been proposed so far and a comprehensive review can be found in Kulldorff (2006). The description of the geographical pattern of disease should be considered as a previous step to the detection of disease clusters. Regions of high risk will probably appear when displaying the relative risks in a map, but some other methods may be required to identify the actual location (and shape) of the clusters. Wakefield et al. (2000) describe some methods for the detection of disease clusters and show some examples of their use. Besag and Newell (1991) divide the types of methods for the detection of disease clusters in two groups: • *General methods* and • *Focused methods*. Another type of methods is that of *Scan methods*. Equally, relevant methods should be developed for the statistical elaboration of the data derived from organic materials. These data could be linked with “charts” of burial or museum environments.

The development of treatments for rare diseases can be challenging given the complexities and uncertainties regarding these diseases. To manage the effects of small patient populations and variable, irreversible disease requires the use of optimal statistical approaches, alternative study designs and for some diseases, the use of biomarkers. Industry, academia, the Food & Drug Administration, the National Institutes of Health, and other stakeholders must work together to develop strategies, policies and guidance to help improve the predictability and efficiency of the development process to enable more approvals for rare disease treatments. In other words, multidisciplinary research groups of experts in Conservation, in Material Science and in Statistics should be joined together in order to develop strategies, policies and methods of data elaboration of organic materials consisting our cultural heritage.

III. CONCLUSIONS

Statistics as applied in Chemometric studies opens new research horizons in the field of Conservation of Cultural and Natural Heritage and of Material Science, creating new perspective for the understanding of the materials' behavior –especially of the organic ones- under complex environmental factors. The results of statistics could then be used to create models of accelerated ageing for a better simulation of real condition effects. To achieve this, experts of statistics should develop statistical methods applied to conservation.

As stated by Larsen *et al*. (2002) a successful outcome will very much depend on the amount of data available for model building and the subsequent correlation analysis. It is important that many different techniques –advanced as well as simple- are applied to a large number of samples in different states of preservation. This will require extensive cooperation between both conservators/restorers and scientists, and an efficient flow of data and software between the different research groups. One way of achieving this may be, as in the case of IDAP (Bechmann and Larsen, 2007), to establish a network of interested conservators/restorers and scientists and to build a central database containing all experimental data and software for all members of the network.

The latter is enhanced by the very strong urge of E.U. for free access to results of research conducted in Europe.

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