Damage assessment approaches for organic materials in art: simple tests or sophisticated analyses?

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Summary

When damage assessment requires the withdrawal of a sample from an object, then the sample size is generally accepted to be a critical factor, as it can be destructive to the object. Less criticism is displayed when it comes to considering the amount and detail of information to be gathered on objects or samples, especially when dealing with organic materials. The best ratio between information quality and sample size is obtained in this case by the application of sophisticated analytical techniques on micro samples. Simple tests involve lack of detail, error, and the risk of failure, to such an extent that their use on objects of art and culture should not be promoted. Hence, the best approaches for damage assessment are those that combine the professional skills of both conservators and scientists. This is clearly illustrated by the outcomes and spin-offs of European RTD projects, in which end-users have played an active role.

Introduction

The withdrawal of samples from an object of art or culture inevitably implies some kind of mutilation, even when executed in an inconspicuous area or when dealing with minute samples. Such handling should therefore be called destructive to the object, independent of what will further happen with that particular sample.

On the other hand, there are analytical techniques available which may be applied directly to the object, without the removal of a sample being required. These techniques are often referred to as non-destructive or non-invasive to the object. However, from a scientific point of view, any interaction between a material and an analytical vehicle, such as a beam of particles or electromagnetic radiation, is unlikely to leave that material unaltered after the interaction, especially when considered on the molecular level. This observation creates a distinction between object and material when discussing the destructive nature of an action such as sampling or analysis. Moreover, such so-called non-destructive techniques are almost exclusively applied to inorganic materials (DEMORTIER, 2000).

In many cases, the complex combinations of organic and inorganic materials in objects of art and culture will require the removal of samples for adequate analysis. In these cases, a low level of destructivity in an analytical technique should be highly preferred in order to allow for subsequent analysis of the same sample, necessary to elucidate the sample's composition. Such an approach combines destructivity (withdrawal of a sample) and non- (or low-) destructivity (preservation of sample integrity).

Things get even more complicated when dealing with terms such as simple tests and sophisticated analyses. The former are thought of as evaluation tests, developed by scientists to meet the needs of people directly involved with the conservation of objects. The emphasis lies on the simple and safe execution of a measurement for performing a condition evaluation on objects or samples to allow visual or, at best, microscopic observations of the test result. The latter cover analyses, executed with instruments displaying ever-increasing accuracy in terms of sensitivity and resolution, leading to lower sample consumption and higher detail of data. There is no doubt that the instruments involved must be handled by trained staff in dedicated laboratories.

This paper aims to discuss simple and sophisticated approaches for the evaluation of damage to objects, mainly composed of organic materials or specifically following parameters derived from organic components. This discussion will be carried out according to the following parameters: the destructivity of sampling and analysis, the resources required to perform the job, the risks of failure that have to be taken into account, and the ratio of information obtained over the level of destruction.

Approaches to measuring past and future damage

From the moment of its creation, an object starts to age. Ageing as such is a process resulting from damage brought about as a consequence of production technology, environmental conditions, handling and repair. When the condition of such an aged or damaged historic(al) object or of one or more of its constituent materials has to be evaluated, analysis has to be executed, and representative parameters for the description of damage have to be developed and interpreted. Since the object itself is the only product available for such an evaluation, the destructivity of sampling and of the analytical approach will be important parameters to take into account.

On the other hand, it would be interesting to try to estimate any future proliferation of damage occurring as

a consequence of production technology, environmental conditions, handling and repair. To this end, damage monitoring systems may be developed, allowing for both a quick response to a jeopardizing condition and a more liberal position with respect to sample consumption and analytical approach in terms of destructivity, since the object is not directly involved anymore. Since alertness becomes the most important feature, simplicity of approach becomes prevalent.

In this paper, I will discuss only those approaches needed to assess past damage or actual conditions and, hence, involving only measurements that interact directly with the object.

Assessment of damage through analysis of historic(al) materials

Condition evaluation of vegetable tanned leather

Vegetable tanned leather is a complex material, displaying a large variety of products used in the course of history. From several European research projects, methods for its condition assessment have been developed. These rely upon simple tests as well as sophisticated analyses (LARSEN, 1994, LARSEN, 1996a).

The simple fibre quality assessment test involves scraping a leather sample with the blunt edge of a scalpel and evaluating the visual/microscopic aspect and coherence of a representative amount of fibres in the scrapings. The precision of the result is limited by the availability of reference leathers, with different and known states of degradation (determined by instrumental analyses). Five reference leathers were used in the current test procedure. This may lead to an amount of information limited to a fibre quality ranking from 1 to 5, which is to be extended to 9 rankings when taking into account interpolations. The quality of the testing procedure has been evaluated by having the test executed by the partners of the European research consortium and by conservation students. The result of the assessment trial was said not to be very positive because the reproducibility turned out to be lower than 61% and 80% when dealing with artificially aged leathers, when taking into account 9 or 5 rankings, respectively. The reproducibilities obtained with naturally aged leathers were lower than 79% when 5 rankings were taken into account (LARSEN, 1996b).

A widely used parameter for measuring the condition of leather is the shrinkage temperature (Ts), representing the temperature at which leather has to be heated in an aqueous environment in order to lose its characteristic tridimensional fibre network construction. The loss of this structure causes the leather to shrink. The Ts of leather falls with increasing deterioration. For vegetable tanned leather, it may vary from over 80°C to below room temperature. The test is described in a standard (ISO 3380), and may be used for damage assessment purposes, when slightly adapted. The adapted test requires a leather strip of 2×20mm, to be fixed at one end to the bulb of a thermometer. This is then heated in a beaker filled with water, on an electrical hotplate. Shrinking starts when the leather strip starts curling up and ends when curling stops. The corresponding temperatures are read from the thermometer. The precision of the measurement of Ts depends on the precision of the thermometer and must not be regarded as better than 1°C. The accuracy is a function of the skills of the observer in determining the start and end of the curling, and of the inherent leather heterogeneity, and should not be estimated better than 5°C. The information gathered is Ts and ΔTs, detailed as its onset and interval, respectively.

Thanks to three European research projects, a new method could be developed for the measurement of the shrinkage temperature of leather and parchment in very small samples: the micro hot table technique (MHT) (LARSEN, 1994, LARSEN, 1996a, LARSEN, 2002). The test is based on exactly the same physico-chemical phenomenon as the one explained above, but it only requires a sub-mg amount of corium fibres. These are then heated in a thermostatically controlled heating cell and their behaviour is observed by a microscope and is video-recorded. Since crucial observations need not be made in real time anymore, precision is dramatically enhanced and may be as good as 0.1°C. The accuracy was claimed to be 2°C (LARSEN, 2000a). The result of this kind of observation is a combination of 5 different shrinkage intervals, describing not only the actual shrinkage temperature (Ts) but also giving valuable information as to the heterogeneity of the leather involved.

Other methods for the evaluation of the condition of vegetable tanned leather refer to more specific material analyses, mainly focussing on the major protein collagen (LARSEN, 1989), and on tannin and acidity (WOUTERS, 1994, WOUTERS, 1996a, WOUTERS, 1996b). Calibrated amino acid analysis of leather collagen allows the calculation of a parameter which describes the oxidative alteration of this protein: the B/A ratio. In this parameter B represents the sum of the molar fractions of the basic amino acids lysine, hydroxylysine and arginine, and A the sum of the molar fractions of the amino acids aspartic and glutamic acid. B/A is around 0.69 in new hide collagen and may fall to below 0.50 by natural or artificial ageing. Hence, this parameter indicates specifically oxidative alterations. But this can be done in a reliable way and on a sub-mg amount of fibres only if high-sensitivity and high-precision amino acid analysis

and data treatment equipment are available. The overall precision of the B/A parameter must be estimated at around 3%. Besides B/A, the complete amino acid composition, including degradation products, may be established by this kind of analysis (LARSEN, 1996c).

The most challenging application of sophisticated analyses may be found in a combination of two essential parameters: Ts as determined by the micro hot table technique and B/A, calculated from calibrated amino acid analyses and both obtained from sub-mg amounts of sample. A graphical representation of both parameters was established for parchment and may be further adapted for vegetable tanned leather. It leads to the establishment of 4 probability areas representing, respectively, no appreciable degradation (a combination of high Ts and high B/A), mainly hydrolytic breakdown of collagen (a combination of low Ts and high B/A), mainly oxidative alterations (a combination of low Ts and low B/A) and mainly cross-linking (a combination of high Ts and low B/A) (LARSEN, 2000b).

The discussion of the condition evaluation of vegetable tanned leather is summarized in Table 1. There is a clear evolution to be seen from simple tests (fibre coherence) to sophisticated analyses (combining Ts and B/A) in terms of decreasing sample size, increasing resources (human and financial) and increasing analytical detail. There is no doubt that the most complete picture referring to damage assessment of vegetable tanned leather, involving the smallest possible amount of sample, is obtained by combining micro measurements of Ts and B/A, further completed by specific analyses for tannin and acidity.

Assessment of acidity in paper

Deterioration of paper by metal-tannate (iron-gall) inks is largely a result of acid hydrolysis and oxidation of cellulose through the catalytic action of iron(II)-ions or other transition metal ions being present. Any successful chemical inhibition of iron gall ink corrosion on paper therefore must involve deacidification, as well as inhibition of the catalytic action of transition metal ions. The efficiency of a paper splitting conservation treatment, involving the introduction of an alkaline reserve in the interleave of a model paper written on with irongall ink, was investigated by subjecting this paper to cycles of dynamic artificial ageing. 'Simple' surface acidity measurements were performed by means of non-bleeding pH indicator strips (Merck 9542, Merck 9543). Alternatively, pH measurements of extracts were performed in a way equivalent to ISO 6588, cold extraction. Samples of around 3mg were cut out of the inked sheets and were extracted in 150μl of MilliQ water for 1 hour and the pH was measured with a Minitrode-electrode (Hamilton). On some occasions, micro samples (diameter 0.7mm) of around 40μg were drilled out of the sheets (WOUTERS, 2002) and were measured with a micro-extraction and micro pH-measurement technique (Model 98-10 micro-pH-electrode, Orion) (SAVERWYNS, 2002). pH measurements were performed either at an ink spot, or close to it (a distance of less than 2mm) or far away from it (a distance of at least 20mm). Ageing caused all pH's to drop, but the pictures shown by surface and extraction measurements were significantly different. Some of the results are represented in Figure 1.

The surface pH as measured on an inked area with pH indicator strips gradually and dramatically dropped over the ageing period considered. However, the extracts of inked area samples tended to stabilise pH initially (up to 12 days of ageing) but dropped dramatically thereafter. Similar behaviour was recorded for samples taken close to inked areas, although the fall in pH was less dramatic than that of the inked area. Apparently, the alkaline reserve present in the core adhesive and the interleaving paper played a pH stabilising role in the whole paper sandwich (as measured by the extraction method), until the alkaline reserve was consumed by acidification (after 12 days of ageing). Moreover, it seems that the

Table 1. Approaches for the condition evaluation of leather and parchment.

Approach	Size of sample	Detail of data	Resources required	Risk of failure	Ratio information/ destruction
Fibre coherence	Macro	Low	Low	High	Low
Ts (standard)	Macro	Low	Medium	Medium	Low
Ts (MHT)	Micro	High	High	Low	Medium
Ts + B/A	Micro	Very high	Very high	Low	High

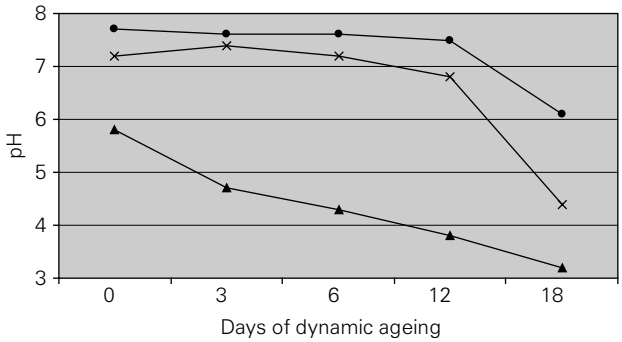

Figure 1. Evolution of pH of iron gall inked paper, as a function of dynamic artificial ageing; ▲: surface pH measured on an ink spot; ×: micro extraction pH of paper in the ink spot; ●: micro extraction pH of paper close to ink spot.

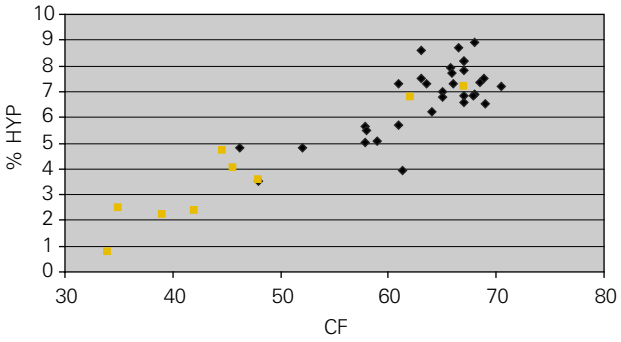

Figure 2. Determination of the nature of the proteinaceous modifier in Baroque artificial marble; % HYP: relative amount of hydroxyproline in the total amino acid composition; CF: collagen factor; ■: coloured layers; ■: white layers.

pH stabilisation of the sandwich could not prevent the fast and serious further acidification of the inked paper surface (as measured by the surface method). In this case, it must be stated that neither of the approaches for the evaluation of paper acidification created a complete picture of events. Both must be considered as complementary (BANIK, 2002). Moreover, it is only the combination of both that allows interpretations which have direct consequences for paper conservation. Indeed, it follows from these measurements that the introduction of an alkaline reserve containing interleave poses no guarantee for the future of the original paper, when written with acid iron gall ink. Suggestions for improvements of this particular conservation treatment should involve other materials for creating an alkaline reserve, or another method for their application.

Presence and composition of proteinaceous materials

Proteins as such may be detected in micro-samples by techniques involving the development of specific colour or fluorescence, or displaying amide band-specific spectroscopic features. However, more information may be gained from approaches which imply the determination of the amino acid composition, including the detection and quantification of degradation products, and statistical treatment of the results. High performance chromatographic techniques combined with high sensitivity detection systems may contribute to the damage assessment of proteinaceous materials, requiring not more than 1μg of protein.

In an example to be discussed, the added value offered by a combination of high performance liquid chromatography and fluorescence detection of amino acids (HPLC-FLUO) revealed technological features and predicted the future ageing of artificial marble. This work was performed in the framework of a European research project (WITTENBURG, 1999).

Figure 2 presents a combination of parameters used to describe the provenance of the proteinaceous modifier in artificial marble: the collagen factor (CF) and the relative amount of hydroxyproline (%hyp) (WOUTERS, 2000). The combination of both allows the discerning of two groups of proteinaceous modifiers, one representing pure collagen (gelatin) characteristics and one indicating the admixture of another protein. Interestingly, it appeared that the protein mixture was used in those cases where artificial marble with a white colour had to be produced. This feature may have implications on ageing and on the conservation of the historical marble, and would not have been revealed by simple protein detection methods.

Monitoring of damage in historic tapestries (MODHT). A new European research project: simple tests or sophisticated analyses?

The MODHT project will run in the 5th Framework Programme, from 1 April 2002 till 31 March 2005. Tapestries woven in renowned European centres from the 15th to the 18th centuries are among the most valuable testimonies of European cultural heritage. Their survival, however, is jeopardised by the degradation processes operating in the coloured fibres and the metal threads. The project seeks to improve the care and protection of these tapestries through a better understanding of the materials and techniques used in their construction and of the mechanisms leading towards their degradation at the molecular level. These objectives will be achieved by the preparation of model tapestries according to traditional techniques, by analysing samples from historic tapestries in collections in Northern and Southern European locations and by the use of an integrated analytical approach to obtain risk assessment parameters. The results obtained with sophisticated analytical techniques will be compared with the vi-

sual appearance and conservation history, and are supposed to lead to an early warning system and, hence, to a better future conservation strategy of the tapestries. To this end the consortium is composed of natural scientists, curators and art historians. The choice for an assessment approach involving sophisticated analyses is justified by the goal to be reached: an early warning system, based on scientific analyses and observation.

Conclusions

Damage assessments involving sampling of historic(al) objects may be performed following two approaches: simple tests or sophisticated analyses.

From the examples it appears that simple tests often require a low input of resources (both human and financial), but that the risk of failure must be estimated to be high. This is mainly due to the fact that there should be a firmly established correlation between the test procedure, its output and damage, and that both systematic and accidental errors should be taken into account. Contrary to what one would expect, simple tests require much experience, yet they are executed on an accidental basis in most cases.

Sophisticated analyses imply a high input of financial resources, because expensive high-performance instrumentation is involved. However, the risk of failure is low and errors and failures are more easily discovered by appropriate data treatment and databank matching procedures. The information obtained is much more detailed in most cases, as compared to that obtained from simple tests.

The fact that conservation/restoration and scientific analysis are two completely different fields is not a new notion. However, it would be wrong for people having to take active care of our cultural heritage to avoid 'heavy' scientific approaches for problem-solving purposes, or to prefer to replace them with 'simple' tests. Preference should be given to convey appropriate responsibilities to people working in their specialised fields, where they are at their best. The observations and approaches of both restorers/conservators and scientists must be combined in order to produce a damage assessment report which is mutually clear and understandable.

Appropriate interaction between disciplines may be catalysed by the use or creation of forums, where people can meet and discuss in a dedicated way. The examples shown in this paper clearly indicate that former European research projects have played an important role in this respect, by bringing together scientific researchers and end-users, as well as by creating damage assessment approaches which are readily applicable in other fields. Other international forums should be used as well, such as triennial meetings organized by the International Council of Museums – Committee for Conservation (ICOM-CC) and biennials provided by the International Institute for Conservation (IIC).

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