Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment
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8. Recommendations for further work on paint-based dosimetry and outlook

Although suggestions for further research and development are usually not included in a thesis such as this, the experience with exposure and analysis of the paint-based dosimeters, which has been gained in the ERA project allows the formulation of the recommendations and outlook presented in this chapter. The tempera paint-based dosimeters are now ready for further development and validation to make paint-based dosimetry a viable method for the evaluation of museum macro- and micro-environments on the large scale. The respective sections of this chapter present recommendations for the construction, readout, calibration and exposure of paint-based dosimeters.

It must be noted that some of the recommendations are currently being applied in a new project which aims at further development of paint-based dosimetry (MIMIC, Microclimate Monitoring in Cultural Heritage Preservation) [1, 2]. In addition, paint-based dosimeters which are similar to the ones used in the ERA project have been used in a study of the effects of laser cleaning of paintings in the framework of the European CRAFT-project "Advanced workstation for controlled laser cleaning of artworks" [3, 4].

8.1 Composition and size of the paint-based dosimeters

The test paintings used in the first field study of the ERA project were very large and their appearance was criticised by the management some of the museums where they were exposed [5]. In fact, the size and appearance of the test painting were the reason that the test painting in the Rijksmuseum Nightwatch room was placed where visitors could not easily see it. Reduction of the size of the test paintings will aid their acceptation by the museums and galleries. The size can be reduced by using smaller test strips. The recent application of fibre-optics in colorimetry [6, 7] allows smaller sample areas to be used for colour measurement. Very small samples can be analysed by DTMS and TGA. It must be stressed, however, that reduction in the sample size puts requirements on the homogeneity of the pigment/binder ratio of the paint systems. This applies for both surface and
bulk analysis. In the case of bulk analysis additional requirements are homogeneity of the paint layer thickness and reproducible sampling, so that the surface/volume ratio is constant for all samples. Hence, the preparation of the paint-based dosimeters must be standardised. This is an important reason to involve experienced industrial partners in the preparation of the test systems.

The present set of paint systems consisted exclusively of tempera paints with no or a single pigment. For future exploration of paint-based dosimetry it is recommended that the study be extended to a greater variety of systems, which include mixed pigments, varnished systems, other binding media, and various supports. After such an extended study, the most relevant and informative systems can be selected. The number of test systems in a test painting is then reduced so that the size of the test painting is reduced and the efficiency of paint-based dosimetry is improved.

8.2 Readout of the dosimeters

The robustness of paint-based dosimetry would not only benefit from standardisation of the paint formulation and preparation of the dosimeters, but also from standardisation of the readout of the dosimeters. Clearly, this applies for each of the techniques used to evaluate the changes of the physico-chemical properties of the dosimeters. As the work described here is restricted to the mass spectrometric analysis of the paint systems, the recommendations for readout of the dosimeters will focus on mass spectrometry.

In the methodology described in Chapter 2, samples are analysed integrally by DTMS. Hence, all components of the paint, lipids, proteins and (in)organic pigments, are subjected to analysis. As shown in Chapters 2 and 3, comparative DTMS analysis highlights the changes in the lipidic fraction of the paints. Lipophilic extraction of the paint samples before analysis by DTMS will further enhance the focus of the methodology on changes in the lipidic part. DTMS analysis of extracts has a distinct advantage in the case of systems that contain inorganic pigments, which may produce a great variety of interfering peaks upon pyrolysis, such as Naples yellow and lead chromate. It will also be advantageous for the analysis of paint systems such as the smalt tempera, which complicate the experimental process, in this case by the formation of glass on the filament of the DTMS probe. Preliminary tests with the light ageing series of the lead white tempera paint indicate that the discriminatory power of the lead white tempera paint system is greatly improved by analysis of dichloromethane/ethanol extracts of the exposed samples [4, 8]. The consistency of the results as
determined by the jack-knife method also increased upon extraction of the samples prior to analysis. In addition, the analysis of extracts instead of whole samples was found to cause less contamination of the instrument and require less instrument time. Although the preparation of the extracts introduces an extra, time consuming, step in the analytical methodology, it makes the practical methodology suitable for automation.

The analysis of the egg tempera binding medium can be focused on the glycerolipids by the use of other mass spectrometric ionisation techniques such as matrix-assisted laser desorption/ionisation (MALDI) and electrospray ionisation (ESI) which produce pseudo-molecular ions of triglycerides and phosphatidylcholines. Chapters 6 and 7 have shown that analysis of such ions by Fourier transform ion cyclotron resonance mass spectrometry (FTMS) yields highly detailed spectra, which allow identification of chemical changes on the basis of differences in exact mass. The MALDI-FTMS data allow quantification of the oxidative changes induced in a series of extracts of light-aged egg-only tempera samples by determination of the degree of oxygenation of the triglycerides and phospholipids (Chapter 6). Using ESI-FTMS both hydrolytic and oxidative changes in triglycerides can be identified (Chapter 7). Of the two ionisation techniques mentioned here, MALDI combined with time-of-flight mass spectrometry (ToF-MS) is currently used for high-throughput analysis, and probably the most suitable for automation. Although analysis of the extracts of paint systems by MALDI- (and ESI-) MS techniques implies loss of information on other lipidic components of the binding medium, such as cholesterol and mastic triterpenoids, the increase in information on the triglycerides and phosphatidylcholines is enormous. A Comparison of the assays will be necessary to determine which approach yields the most information.

Probably, the environmentally induced changes observed in the paint systems take place mainly in the top layer of the paint, close to the exposed surface. It is therefore likely that the sensitivity of paint-based dosimetry can be enhanced by focussing on the changes in the surface. Preliminary investigations aimed at the analysis of the surface of egg tempera paint systems by MALDI-ToFMS produced spectra of triglycerides and phospholipids [9]. The development of this methodology for the readout of paint-based dosimeters would only require standardisation of the matrix application and hence be very suitable for automation. It must be remarked however that this methodology would also make the systems more sensitive to contamination, because it is a surface analysis technique.
8.3 Calibration of the paint based dosimeters

As mentioned in Chapter 3, each of the tempera paints has a different starting point in its chemical state in terms of degree of oxidation and degree of hydrolysis. These differences, together with the varying degrees of catalytic action of each of the pigments on the environmentally induced chemical reactions constitute differences among the pigmented temperas in their response to the environmental factors. The dosimetric ranking results of nine different test systems presented in Chapter 4 clearly illustrate this. In principle, this phenomenon can be used to deconvolve the ageing processes that effect the chemical composition of the exposed dosimeters. In this way the chemical representation of the effect of the museum environment can be used to reconstruct the most important (major) characteristics of the museum conditions. The current calibration set is too small, however, to allow this deconvolution.

The level used for the artificial light ageing to obtain a calibration set of paint-based dosimeters was 18,000 lx. This light intensity is many times higher than actual light intensities in museums and galleries. For future work exposure at lower, more realistic levels is recommended, so that the reciprocity principle can be tested. This will contribute to the understanding of the results obtained on paint-based dosimeters.

If larger training sets, including a variety of or combinations of environmental factors, are used, then a better calibration can be obtained, and observed differences can be used to indicate which of the environmental factors dominates in causing the chemical change. The calibration of the tempera test systems against light was conducted at a low RH of 27-28%. Calibration at a range of (higher) relative humidity values would be useful. Moreover, given the dramatic changes observed in the dosimeters observed upon exposure to high NOx/SO2 levels, more detailed investigation of these pollutants is recommended. Exposure in the ERA project was at a single value of NOx and SO2 and it was performed in the dark. To provide more detailed information, calibration against a range of values of NOx and SO2 in combination with controlled light intensity, relative humidity and temperature would be advisable. In addition studies of the effects of CO2 and pollutants such as ozone on the dosimeters are recommended. Artificial ageing experiments involving atmospheric pollutants will be carried out in the MIMIC project.
A next step in the development of paint-based dosimetry could be a large-scale field exposure, which includes a range of sites with controlled and uncontrolled conditions and which would include measurement of relevant environmental conditions, including air quality, of the sites. Results obtained on field-exposed dosimeters could then be combined with records of the environmental conditions at the field sites. If the data set is large enough, data can be used as input for an expert system that correlates the results obtained on the exposed dosimeters with the conventional environmental data. Once the expert system is well trained, newly obtained dosimetric data on field sites can be put in and the expert system can be used to derive recommendations for improvement of the environmental conditions at these field sites (on the basis of the analytical/dosimetric results obtained on the paint-based dosimeters). It must be noted that the use of linear correlation methods such as principal component analysis and discriminant analysis will give rise to some fundamental problems in the correlation of the environmental factors with the dosimetric results. (It is for instance unknown whether the degree of change in paint shows a logarithmic, exponential or linear dependence of the number of visitors at a site, and hence it is not clear how the number of visitors should be specified in the data for linear correlation.) For this reason, it is recommended that non-linear correlation tools such as neural networks be explored for the development of expert systems. Clearly, the application of such tools can be used to identify correlated effects among the results of different analytical techniques.

The results of the three-months’ survey in the Rijksmuseum reported in Chapter 4 clearly show that exposure of the paint-based dosimeters for shorter periods than the nine months used in the first survey also leads to discrimination among the exposure sites. Three-months’ surveys can be used to study seasonal effects.

References


5  Hackney, S., Comment on mock paintings for dosimetry (1996) personal communication.


