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Thermochimica Acta 365 (2000) 1–23

thermochimica acta

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Dosimetry of paintings: determination of the degree of chemical change in museum-exposed test paintings by mass spectrometry

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Abstract

Painted works of art are constantly exposed to and affected by their environment. The chemical, mechanical and visual characteristics of paintings are subject to changes. The paintings themselves can be seen as dosimeters that integrate the effect of their environment. In the present research, mock paintings are used as dosimeters to integrate the overall effect of the museum environment on the paint in a given time span. Direct temperature resolved mass spectrometry (DTMS) and the multivariate technique of discriminant analysis are used to compare the chemical composition of mock paintings exposed in five different museums in Europe. Changes observed on laboratory-exposed (light, temperature and a mixture of nitrogen oxides and sulphur dioxide) dosimeters serve as the calibration set. The methodology applied to derive chemical information from the dosimeters is presented here. The results obtained on the exposed mock paintings show that the principle of paint-based dosimetry works. Other factors than light alone are found to play an important role in environment-induced deterioration.

Keywords: Environmental monitoring; Museum environment; Mass spectrometry; Multivariate analysis; Dosimetry

1. Introduction and rationale

Objects stored or displayed in museums and galleries are constantly subject to decay. The environment in the interior of a museum or historic building and the microclimate surrounding the object constitute a complex set of multivariate factors, which determines the nature and rate of decay. Depending on the materials present and provided the environment is understood, skilled and informed conservators can retard to some extent the rate of deterioration of works of art. This can be achieved in a number of ways, for instance, by controlling factors such as the temperature and relative humidity of the air. Much effort and expense in major museums is directed towards standardising environmental conditions surrounding works of art. Maintaining a stable microclimate around a work of art, for instance, is probably the most effective method of protection, but widespread adoption of such methods will not occur until confidence is fully established and that will depend on a detailed understanding of the mechanisms of degradation due to environmental factors. On the other hand, not all art is well protected. Works of art are often stored in rooms with no climate control. Art on display in public buildings, historic buildings, palaces, churches and chapels is exposed to much larger environmental fluctuations. In particular, where paintings are hung directly on external walls, large temperature and humidity fluctuations give rise to gradients, which

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0040-6031/00/$ – see front matter
PII: S0040-6031(00)00609-2

affect the mechanical and chemical stability of the paint films. This may even lead to migration of organic constituents and cause blanching phenomena (e.g. in paintings by Stanley Spencer in the Sandham Chapel). Such conditions require repeated interventions by trained conservators, which does not improve the condition and the overall stability of the art works.

The quality of the museum environment determines the rate of chemical and physical changes in paintings. Important factors are temperature, relative humidity, concentration of air pollutants, light intensity and wavelength distribution [1]. Painted works of art on display in museums are inevitably subject to changes as time progresses. Such changes include not only discoloration of the varnish, but also discoloration of pigments and degradation of the binding medium. For example, Bacci et al. [2] have observed noticeable colour change in the "Predela della Trinità" by Luca Signorelli (1445–1523) on display in the Uffizi Gallery after a period of 66 months of regular exhibition to the public in the environmentally controlled Leonardo room.

1.1. Model studies and monitoring

In conservation science, considerable attention is given to model studies on the effects of these environmental factors on artists' materials. Erhardt et al. [3] have investigated the effect of relative humidity changes on wooden panels and attempted to establish allowable relative humidity fluctuations. They have also determined expansion coefficients for typical layers in panel paintings, such as lead white oil paint, gesso and hide glue. This work has had a catalytic function in the development of thoughts on the issues of modelling painting behaviour and the establishment of new guidelines for museum conditions. Saunders and Kirby [4] have investigated light-induced damage to a variety of pigments. In their study, some pigments followed the reciprocity principle for light exposure, i.e. the degree of deterioration was determined by the product of exposure time and light intensity. In some cases, however, the principle was not applicable. To our knowledge apart from our own efforts in the Scicult project (partly published in [5]), no molecular model studies of light-induced deterioration of natural binding media have been carried out.

Already in 1850, the famous chemist and physicist Michael Faraday rang the alarm bell for the effects of sulphur dioxide on works of art, and suggested measures for the protection of paintings. More recently, Baer and Banks [6], and Brimblecombe [7] have drawn the attention of conservation science and atmospheric scientists for the effects of air pollutants on museum objects. Not only did these authors discuss the potential effects of pollutants that are imported into the museum from outside, such as nitrogen oxides and sulphur oxides, they also mentioned pollutants of typical indoor origin, such as formaldehyde from wood and wood composites, and other building materials. Comparison by Baer and Banks [6] shows that many standards for levels of pollutants can be applied, but these are rather arbitrarily determined. The effects of air pollutants such as nitrogen oxides (NO_x and atmospheric nitric acid) [8], sulphur oxides [9], peroxyacetyl nitrate [10] and ozone [11–13] on organic dyes have been studied extensively by Grosjean et al. [14] and molecular changes have been identified mainly by mass spectrometric studies.

Monitoring of pollutants in the museum environment has received more and more attention since the 1980s. The internal environment of the Tate Gallery, for instance, has been studied extensively, and concentrations of nitrogen oxides and sulphur oxides in this museum have been determined using various methods [15]. Hisham and Grosjean [16] have studied the indoor and outdoor levels of nitrogen dioxide, nitric acid, and peroxyacetyl nitrate in nine Southern California museums. These studies clearly point at diurnal and seasonal variations in the levels of pollution. Variations in the values of relative humidity and temperature were investigated in a study of a museum microclimate in Padua by Camuffo and Bernard [17]. The values were found to fluctuate considerably with season and the time of the day. Within the framework of the Uffizi Project [18], a comparative study of the air quality in two rooms of the Uffizi Gallery, Florence, Italy has been carried out by Bernardi and Camuffo [19]. In their survey, the temperature and relative humidity distributions were studied in detail. Attention was also paid to particulate air pollution. Also within the Uffizi Project, De Santis et al. [20] have carried out monitoring of gaseous air pollutants, sulphur dioxide, nitric acid, nitrous acid and ozone. In this study, indoor and outdoor values were compared. At another site, this group investigated the relationship between indoor and outdoor levels of pollution [21]

showing that the indoor levels of air pollution were greatly influenced by the magnitude of automotive traffic and by the weather conditions. A recent book by Camuffo [22] discusses in detail many physical factors that play a role in the microenvironments that surround objects of cultural heritage. It also deals with methods for monitoring of the microclimate.

1.2. Why paint-based dosimetry?

The internal environment is subject to fluctuations. Monitoring the quality of the museum environment by separate measurement of the individual factors that determine the museum environment at a particular point in time, however valuable, does not necessarily yield an accurate assessment of the potential damage to the art on display. Using dosimetry, factors that are not constant can be integrated over a longer period in time. Several dosimeters have been developed for specific purposes. Tennent et al. [23] developed an integrating dosimeter for ultraviolet light using the absorbance of a phenothiazine-doped PVC films which increases proportionally with the dose of UV light received by the foil due to transformation of the UV-sensitive phenothiazine. More recently, Leissner et al. [24,25] developed a dosimetric glass sensor that degrades as a function of the total experienced acidity during its exposure. Johansson et al. [26] developed a dosimetric system using metal strip to measure corrosivity in indoor environments.

Studies of the local museum environment mostly focus on a number of preselected factors, such as RH, temperature, light intensity and wavelength distribution, or the monitoring of specific air pollutants, such as sulphur dioxide, nitrogen oxides and peroxyacetyl nitrate. A major disadvantage of such separate measurement of environmental variables is that unexpected or exceptional factors can easily be overlooked. For example, during a routine conservation survey of the collection of the Herbert F. Johnson museum of Cornell University, an oily layer was discovered on many objects and display cases [27]. Mass spectrometric analysis of the material revealed that diethylaminoethanol (DEAE) had formed the oily layer. The volatile DEAE had been introduced into the museum environment by an open steam humidification system in which it was used as a corrosion inhibitor. Environmental monitoring by measurement of the concentrations of air pollutants can be compromised because some sources introduce a great variety of pollutants into the museum environment. Visitors, for instance, do not only change the relative humidity of the museum environment, they also change the chemical composition of the museum air as they release a wide range of organic compounds and inorganic gases [28].

A phenomenon that is generally ignored in conservation science is that the effect of one factor may be greatly influenced by another. Some processes are inhibited by certain conditions, others are enhanced. Hence, the effect of the environment on a painting cannot be considered simply as the sum of all the active agents of which it is composed. Rather, it must be regarded as a complex convolution of interacting factors. Therefore, monitoring the quality of the museum environment by separate measurement of the individual factors that make up the museum environment, however valuable, does not necessarily yield an accurate assessment of the damage done to the works of art on display.

Although the paintings themselves can be considered as dosimeters integrating all the effects of the environment, the deterioration in the conditions of paintings cannot be measured easily. In the ERA project [29,30], mock paintings with relevant materials take over this role and serve as dosimeters in which the compositional changes are related to environmental quality. Model paint systems have been prepared and exposed to extreme environmental conditions and to museum environments. Changes of the paints used in the mock paintings have been studied on the macroscopic, mesoscopic and molecular level by thermal and dynamic mechanical techniques (TGA, DMTA and DSC) [31], spectroscopic techniques (VIS and NIR) [32] and mass spectrometric techniques. This paper focuses on the molecular studies carried out using mass spectrometry, and presents the methodology in the development of a paint-based dosimeter for environmental conditions.

1.3. Composition of the test systems based on egg tempera paint

Traditionally, paintings have been made with natural products, such as drying oils, eggs, terpenoid resins, and natural glues. In the first stage of the

development of a paint-based dosimeter for museum conditions, egg was selected as the binding medium, because it is the richest binding medium with respect to the variety of compounds and compound classes. The chemical composition of an average chicken egg as relevant to tempera painting is discussed in detail elsewhere [5,33]. Eggs contain a large fraction of proteinaceous material. Proteins can undergo many alteration reactions, such as oxidation, β-elimination, alkylation and deamidation taking place on the amino acid residues, and cleavage of the peptide bonds. An overview of possible alteration reactions that proteinaceous materials can undergo is given by Boon et al. [5]. The second most abundant class is lipids, comprising cholesterol and glycerolipids, triglycerides and glycerophospholipids. These compounds can undergo oxidative reactions leading to a great variety of oxidation products depending on the degree of oxidative stress. Cholesterol, for instance, has many reactive sites, and many cholesterol alteration products are known in literature [34–38]. Egg glycerolipids contain singly and multiply unsaturated fatty acid residues that all have their own reactivity towards oxidative stress. Depending on their degree of unsaturation, multiple oxygenation can occur, eventually leading to chain shortening [39]. Furthermore, triglycerides are sensitive to hydrolysis, ultimately leading to the formation of free fatty acids and glycerol.

Resin mastic (chemically consisting of a mixture of triterpenoids and a polymeric fraction) was added to the egg binding medium for two reasons. First, it enhances the adhesive properties of the binding medium so that the paint adheres well to the relatively smooth surface of the inert Melinex® support. Secondly, it provides for another compound class that is not present in egg and it may provide potential marker molecules for processes that occur in terpenoid resins. Many components of mastic are known [40] and the ageing of triterpenoids is studied at our institute [41,42]. A mixture of egg and resin has been used in Italian painting practice [43].

Added to the binding medium were inorganic pigments containing a variety of metal ions, such as basic lead carbonate, azurite (basic copper carbonate), smalt (glass sintered with cobalt oxide), lead chromate, sienna (a mixture of [α]-goethite, FeOOH and, [α]-haematite explanation: [α]-haematite is Fe_2O_3), Naples yellow (lead antimonate), and vermilion (mercuric sulphide). Paint systems were also prepared that contained organic pigments that are known to be sensitive to photodegradation and to oxidative air pollutants. These systems include indigo, curcumin and alizarin tempera.

The development of a paint-based dosimeter for environmental conditions has been pursued in two phases. Firstly, the concept was tested using artificial exposure, such as accelerated artificial light ageing and exposure to high concentrations of air pollutants. In the second phase, test systems were exposed at selected museum environments. The exposure time is determined based on artificial light ageing results. The light ageing results serve as a calibration set, in this phase, for comparison of the field exposure results.

1.4. Design and exposure of the mock paintings

Mock paintings were prepared that consisted of unexposed strips of the aforementioned formulations, mounted on a black background. Fig. 1 shows the design of these mock paintings. Test paintings that were made according to this design were exposed at seven sites. These include major art galleries where the local environment was controlled (RH and *T*), such as the Nightwatch room in the Rijksmuseum (Amsterdam, the Netherlands), the Tate Gallery (Glore gallery, UK), and the Uffizi (Leonardo room, Italy), and two uncontrolled sites, viz. Sandham Memorial Chapel at Burghclere (UK) and the Alcázar in Segovia (Spain). An additional test painting was placed in the storage facility of the Rijksmuseum (Depot ''Oost''). This test painting is shown in Fig. 2. The environmental conditions of these field sites are discussed in detail by Odlyha et al. [44] and by Bacci et al. [45] in this issue. One test painting was stored at the FOM Institute for Atomic and Molecular Physics, under exclusion of oxygen and light.

1.5. Analytical methodology

The analytical methodology applied to obtain dosimetric results from the test systems is schematically shown in Fig. 3. After exposure of a test system to the museum environment or to laboratory ageing conditions, small samples are taken from a test system that can be processed directly when DTMS is applied. The DTMS methodology allows the analysis of particulate

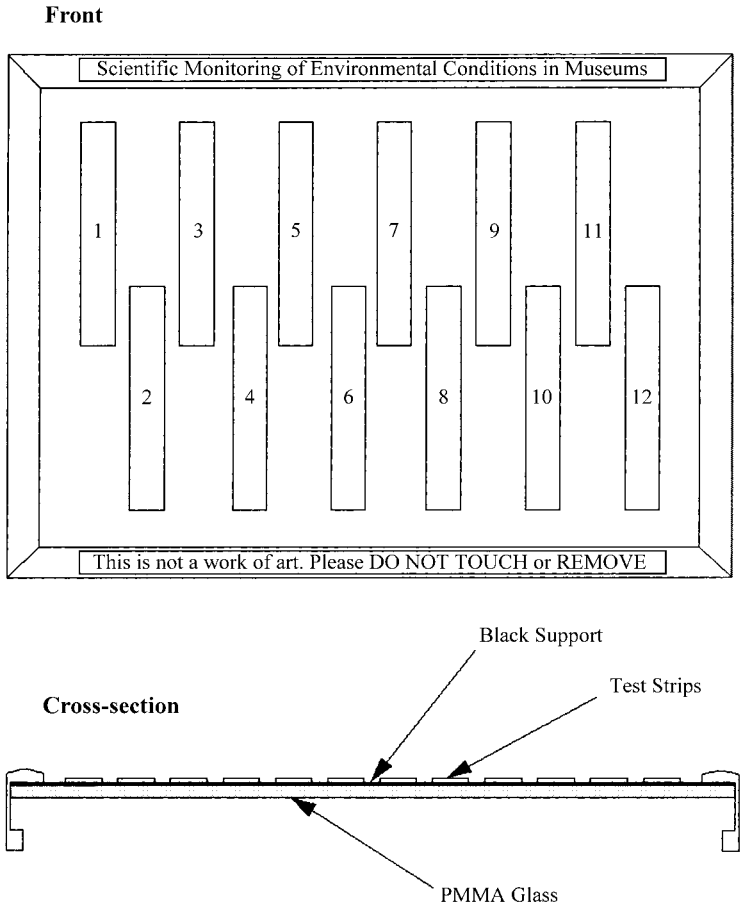

Fig. 1. Design of the mock painting with dosimetric test strips. The following paint systems were used: (1) unpigmented egg; (2) unpigmented egg+mastic; (3) lead white; (4) lead chromate; (5) curcumin; (6) sienna; (7) vermilion; (8) alizarin; (9) azurite; (10) smalt (cobalt glass); (11) mastic resin; (12) Naples yellow (lead antimonate). Strips (65×9 mm^2) of the tempera paints on Melinex® were mounted on a black support and framed.

material on an analytical probe. Information is obtained on volatile matter in vacuo such as lipids, sterols and organic dyes at low analysis temperatures. Information on polymerised substances or materials with strong chemical bonds, e.g. metal-bonded organic networks, is obtained at higher temperatures. At the highest temperatures, information on metals and inorganic salts is obtained. Thus, a DTMS analysis provides mass spectrometric information on a wide variety of compounds in one analytical run. A detailed description of the technique is given by Boon [46].

Analysis of the large number of test systems that were aged under the different conditions results in an enormous data set. For example, each DTMS run consists of 120 scans over a mass range from 20 to 950 amu. Analyses were performed in triplicate. Samples of field dosimeters always have to be compared with the control test system and the set of laboratory light aged test systems. Hence, rigorous data reduction methodology must be applied to visualise and quantify the extent to which the dosimetric test system had changed chemically as a function of environmental exposure. As a first step in data reduction, the spectra obtained in the DTMS run were summed. Then, discriminant analysis (DA) was performed on the summation spectra to estimate analytical

Fig. 2. Photograph of a test painting (in circle) on the storage rack of the Rijksmuseum Depot "Oost".

reproducibility and perform the data reduction. Field site data are mathematically compared with the light ageing data to derive a quantitative number on the environmental stress experienced.

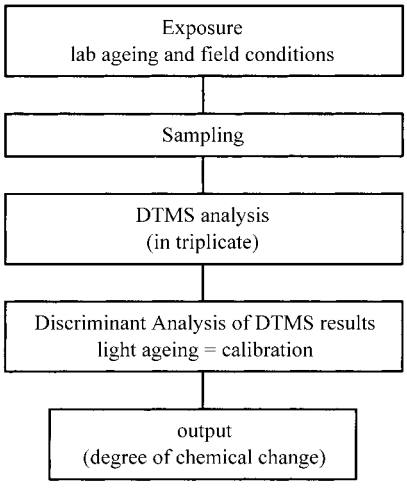

Fig. 3. Analytical methodology flow chart for evaluation of chemical changes using DTMS and DA.

2. Experimental

2.1. Paint formulation and preparation of the test systems

The tempera binding medium was prepared by Roberto Belucci (restorer at the Opificio delle Pietre Dure, Florence, Italy) following mostly the recipe reported in *Il libro dell'arte* by Cennino Cennini [47]. The yolk was separated from the white of an egg. The egg white was beaten so that a layer of foam formed on the liquid. After the egg white was left to stand overnight, the foam was separated from the liquid part of the egg white and discarded. The yolk was mixed with the remaining part of the egg white. To the egg were added three drops of apple cider vinegar and a solution of mastic in white spirit (Zecchi, Florence, Italy), half the volume of the mixed egg. When pigmented tempera was prepared, the pigment was first ground with a few drops of water. Then the tempera binding medium was added, in some cases under addition of a few more drops of water to keep the paint easy to spread. The paint system was deposited on a sheet of Melinex® using a Byk Gardner

(Geretsried, Germany) film applicator at 200 μm wet layer thickness. The paint was allowed to cure for a period of 3 months before it was subjected to artificial light ageing.

2.2. Artificial light ageing of the test systems

Light ageing was performed in an ageing facility at the Tate Gallery (London). Samples were exposed in the light-box for 4, 8, 16, 32 and 64 days. The ageing facility uses six Philips TLD94 58 Watt daylight rendering fluorescent tubes. They are filtered with a Perspex VE ultraviolet filter which has a cut-on wavelength at about 400 nm. The tubes are changed regularly to maintain a constant sample illuminance of about 20 klux. Cooling fans maintain the temperature at 4–5°C above ambient, and 5–10% below ambient relative humidity. Effectively, this yielded average values of 28–29°C and 27–28% relative humidity when the ageing was carried out. Light intensity during the exposure of the tempera test systems was 18 000 lux.

2.3. Thermal ageing

Thermal ageing was also carried out at the Tate Gallery. The samples were placed in an oven that maintained the temperature at 60°C and relative humidity at 55%. No light was admitted into the oven. The samples were exposed for 7, 14 and 21 days.

2.4. Exposure to SO_2 and NO_x

Exposure to air pollutants was carried out at TNO (Delft, the Netherlands). The experimental set-up was used previously for the exposure of paper to air pollutants, and a detailed description is given by Havermans [48]. Samples mounted on A4 size PMMA plates were placed in a gas chamber situated inside a climate chamber. During exposure, the climate chamber maintained the temperature at 23°C and relative humidity at 55%. No light was admitted into the exposure chamber. Flows of SO_2, NO_x, and air were tuned continuously so that the overall concentrations of SO_2 and NO_x in the gas chamber were approximately 10 and 20 ppm, respectively. Unlike light and thermal ageing, where samples were exposed for a range of times, the samples were exposed to NO_x/SO_2 for a single fixed period of 4 days. Effectively, the average concentrations of SO_2 and NO_x were 10.2 and 16.7 ppm, respectively, during exposure.

2.5. Direct temperature resolved mass spectrometry (DTMS)

Although the sensitivity of the DTMS method allows analysis of samples that are much smaller, for the analysis of the dosimetric test systems samples of approximately 1 mg were scraped off the Melinex support and homogenised into ethanol (∼100 μl). The exact sample size and volume of the ethanol added varied with the composition of the tempera test system, i.e. the pigment-volume concentration. Aliquots of 1 μl of the sample suspension was deposited on the 0.1 mm diameter, platinum/rhodium (90:10) filament (Drijfhout, the Netherlands) of the DTMS probe. DTMS analysis was performed on a JEOL SX 102A double focusing mass spectrometer with B/E geometry. In the ion source of this instrument, the wire was resistively heated by ramping the current at a rate of 0.5 A/min. Using this ramp, the temperature was linearly increased from ambient to approximately 800°C in 2 min. Desorbed and pyrolysed material was ionised by 16 eV electron impact ionisation. The mass spectrometer was scanned over a m/z range of 20–1000 using a 1 s cycle time. Samples were analysed in triplicate for DA, and the spectra were summed over the TIC.

2.6. Discriminant analysis (DA)

Mass spectra were numerically analysed by DA with the FOMpyroMAP multivariate analysis programme, a modified version of the ARTHUR package from Infometrix (Seattle, WA; 1978 release) and with the FOM developed Matlab® (The Mathworks, Natick, MA) toolbox ChemomeTricks. DA, as applied here, is a double stage principle component analysis (PCA) technique [49].

There are a few requirements that have to be met in order to perform DA successfully. Data on a test system must be available in at least duplicate before DA can be performed. In the present research, results of triplicate measurements were subjected to DA. Furthermore, the application of the DA to evaluate the chemical change in the dosimetric test systems

requires that all samples be measured within a single day to minimise variance due to variance in the operation of the mass spectrometer.

3. Results and discussion

3.1. Qualitative description of chemical changes in tempera test systems

Water, proteins and lipids are the main constituents of an egg. The chemical composition of an average chicken egg as relevant to tempera painting is discussed in detail elsewhere [5,33]. Oxidised lipids, mastic and polymerised proteinaceous material are the components of aged tempera paint in our tempera test systems. Of these components, the lipid and mastic fraction is detected with greatest sensitivity by DTMS. Due to their polymeric nature, proteins are not detected as intact molecules, but are pyrolysed to fragments of lower molecular weight. The proteinaceous fraction is observed at lower sensitivity compared to the lipid components because the yield from pyrolysis is relatively low compared to the more quantitative desorption of apolar substances.

3.1.1. Unpigmented tempera

Fig. 4A shows the DTMS summation spectrum of the unpigmented tempera control sample. There are

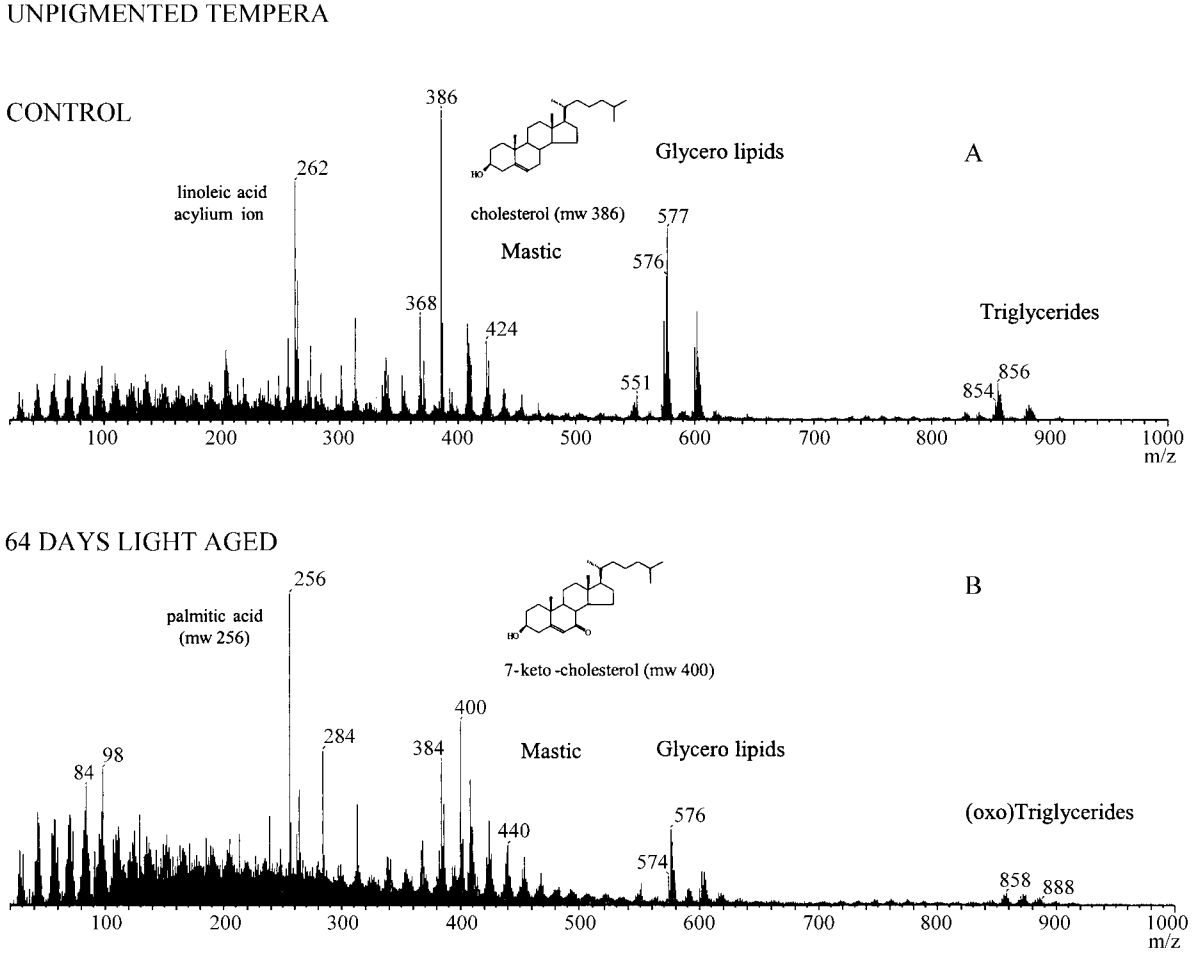

Fig. 4. DTMS summation spectra of unpigmented tempera control (A) and unpigmented tempera light aged 64 days (B).

three important mass peak windows in which components of the binding medium are observed. Triglyceride mass peaks are present between *m/z* 830 and 900. The cluster between *m/z* 852 and 862 represents the triglycerides consisting of 55 C-atoms (C55-TGs), and the cluster at *m/z* 876–890 triglycerides consisting of 57 C-atoms (C57-TGs). Diglycerides and fragments of triglycerides (TGs) and phospholipids show mass peaks between *m/z* 540 and 640. In the range from *m/z* 350 to 500, mass peaks from mastic are detected together with peaks originating from cholesterol (*m/z* 368 and 386). In the lower mass range, fragment ions from di- and tri-glycerides, ions from fatty acids and dicarboxylic acids, and ions from pyrolysis products of (pre)polymeric compounds are observed. The peaks at *m/z* 262 and 264, e.g. originate from acylium ions that are formed as fragments of glycerolipids which contain linoleic and oleic acid residues, respectively. Peaks at *m/z* 262 and 264 are also observed in the spectra of free linoleic and oleic acid [50].

Fig. 4B shows the DTMS spectrum of unpigmented tempera artificially light aged 64 days. Comparison with Fig. 4A shows that linoleic (*m/z* 262) and oleic (*m/z* 264) acid residues are drastically depleted upon exposure to light, as indicated by the decrease of the relative intensities of the peaks. Linoleic acid residues decrease more than oleic acid residues. Increased intensities of peaks at *m/z* 84, 98 and 152 are ions indicative of dicarboxylic acids formed by oxidative cleavage of unsaturated fatty acid moieties. The unresolved peak pattern between *m/z* 100 and 300, especially in the high temperature window of the data, is indicative of polymeric networks that break down upon pyrolysis. Free palmitic and stearic acid are formed upon ageing due to hydrolysis of glycerolipids, as indicated by an increase of the peaks at *m/z* 256 and 284, respectively. Increased intensities of *m/z* 384, 400, and 402 relative to *m/z* 386 indicate oxidation of cholesterol to cholestenone (*m/z* 384), 7-ketocholesterol (*m/z* 400), and 7-hydroxy-cholesterol (*m/z* 402). The formation of these compounds has been confirmed by GC-MS analyses [5] and by DTMS-MS studies [51].

Focusing on the relative intensities of the peaks at *m/z* 854, 856 and 858, a decrease can also be observed in *m/z* 854, the molecular ion of a fourfold unsaturated C55 triglyceride, and *m/z* 856, a triply unsaturated C55 triglyceride. This indicates that the degree of unsaturation determines the degree to which some of the triglycerides are depleted. Furthermore, in the triglyceride mass window of the light aged sample, a cluster appears between *m/z* 860 and 875. The mass difference between the most abundant triglyceride peak in unaged tempera (*m/z* 856) and the most abundant peak in the light aged sample (*m/z* 872), viz. 16 amu, suggests that insertion of oxygen has taken place. The novel technique of matrix-assisted laser desorption and ionisation Fourier transform mass spectrometry (MALDI-FTMS) was applied to study the changes in the TGs in more detail [52,53]. The high resolution of the MS data obtained by this technique allowed unequivocal determination of the elemental composition of triglyceride ageing products and unambiguously demonstrates that light ageing induces oxygenation of the unsaturated TGs.

Table 1 summarises the attribution of the most important peaks in the DTMS spectra of fresh and aged unpigmented tempera. The first column shows the *m/z* value, the second the mass spectrometric interpretation and the third column shows the molecular origin of the compound or the compound class.

3.1.2. Lead white pigmented tempera

Fig. 5A shows the DTMS spectrum of an unaged lead white pigmented test system. Due to the high pigment concentration, the peaks in this spectrum at *m/z* 206–208 and 44, which originate from the lead white pigment itself, are plotted off-scale. Comparison of the DTMS spectrum of the unaged lead white pigmented tempera with that of unaged unpigmented tempera shows that some alteration of unsaturated triglycerides has already taken place in the curing stage of the lead white tempera. Early metal catalysed oxidation reactions in the dark are evidenced by lower relative intensities of the peaks at *m/z* 854, 856, 262 and 264 and the presence of a small cluster at *m/z* 866–876. Oxidation of cholesterol is also taking place in the curing stage. Furthermore, in the unaged lead white tempera, free fatty acids such as palmitic acid (*m/z* 256) and stearic acid (*m/z* 284) are observed with higher relative abundance than in the unpigmented equivalent. This is interpreted as hydrolysis of glycerol ester moieties in phospholipids and di- and triglycerides. The formation of free fatty acids is also observed in DSC results [54,55] where a low temperature peak/shoulder develops upon light exposure.

Table 1
Characteristic peaks in DTMS spectra

m/z	Interpretation	Compound class of origin
84	Fragment of dicarboxylic acids	Glycerolipids aged
98	Fragment of dicarboxylic acids	Glycerolipids aged
99	Side chain fragment ion of 3-oxo-25,26,27-trinordammarano-24,20-lactone	Mastic triterpenoids (aged)
109	Side chain fragment ion of hydroxydammarenone	Mastic triterpenoids
143	Side chain fragment ion of ocotillone	Mastic triterpenoids (aged)
152	C9 dicarboxylic acid diacylium ion	Glycerolipids aged
203	Pentacyclic triterpenoid fragment ion	Mastic triterpenoids
205	Pentacyclic triterpenoid fragment ion	Mastic triterpenoids
248	Fragment ion of oleanoic acid	Mastic triterpenoids
256	Palmitic acid	Glycerolipids
262	Linoleic acid acylium ion	Glycerolipids
264	Oleic acid acylium ion	Glycerolipids
284	Stearic acid	Glycerolipids
313	Palmitic acid monoglyceride fragment	Glycerolipids
338, 339	Oleic acid monoglyceride fragment	Glycerolipids
341	Stearic acid monoglyceride fragment	Glycerolipids
368	Cholesterol–H_2O (cholestadiene)	Sterols
382	Cholestadienone	Sterols aged
384	Cholestenone	Sterols aged
386	Cholesterol	Sterols
400	Hydroxycholestenone	Sterols aged
402	Hydroxycholesterol	Sterols aged
408	28-nor-olean-17-en-3-one	Mastic triterpenoids
414	3-oxo-25,26,27-trinordammarano-24,20-lactone	Mastic triterpenoids (aged)
426	Dammaradienol (3β-hydroxy-dammara-20,24-diene)	Mastic triterpenoids
439	Ursonic and oleanoic acid	Mastic triterpenoids
454	Ursonic and oleanoic acid	Mastic triterpenoids
468	Oxo-ursonic and -oleanoic acid	Mastic triterpenoids
546–550	C35 diglyceryl ions (2–0 unsaturations)	Glycerolipids
572–578	C37 diglyceryl ions (3–0 unsaturations)	Glycerolipids
600–606	C39 diglyceryl ions	Glycerolipids
852–862	C55 triglycerides (5–0 unsaturations)	Triglycerides
866–876	Oxygenated C55 triglycerides	Triglycerides (aged)
878–890	C57 triglycerides (6–0 unsaturations)	Triglycerides
892–906	Oxygenated C57 triglycerides	Triglycerides (aged)

The spectrum of 64 days light aged lead white test system (Fig. 5B) indicates that light ageing leads to the formation of similar reaction products as observed in the corresponding light aged unpigmented test systems, albeit at a higher reaction rate. This is deduced from the relative intensities of *m/z* 854, 856 and 858, which point to a lower degree of unsaturation in the di- and tri-glycerides for the light aged lead white tempera (64 days) as compared to the unpigmented equivalent. Furthermore, the intensity of the cluster of peaks from oxygenated triglycerides (*m/z* 866–876) has increased.

3.1.3. Azurite pigmented tempera

The spectra of unaged and 64 days light aged azurite pigmented test systems are shown in Figs. 6A and B. Azurite, a basic copper carbonate, decomposes and forms carbon dioxide at high temperature. The resulting *m/z* 44 dominates the spectra. Copper is not observed in the DTMS spectra of azurite tempera. Comparison of the spectrum of unaged azurite tempera with that of unaged unpigmented tempera strips shows that the effect of addition of azurite to the binding medium leads to severe changes in the curing stage. These changes are due to metal catalysed oxidation of

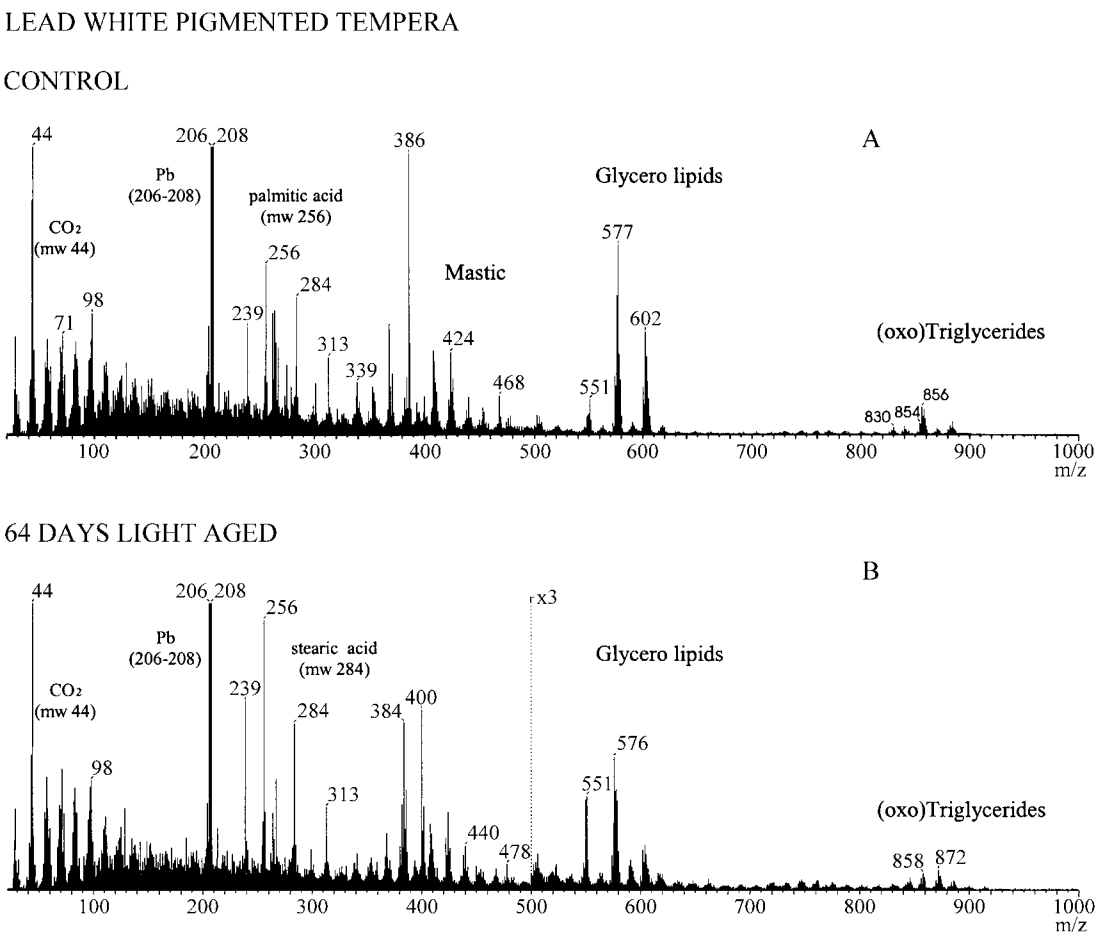

Fig. 5. DTMS summation spectra of lead white tempera control (A) and light aged 64 days (B).

the binding medium. Unlike lead white pigmented test systems, free fatty acids are not observed to a great extent in azurite test systems. Copper catalyses oxidation but does not affect the stability of the ester bonds in the triglycerides and phospholipids, to such a great extent as lead white. Comparison of the unaged with the 64 days light aged azurite test system suggests that the lipid fraction of the paint undergoes only minor additional changes upon light ageing, such as further oxidation of cholesterol.

3.2. Description of chemical changes in light aged test systems by DA

The analytical results discussed above show that many processes in the test systems can be retrieved by DTMS. Since the DTMS spectra of the tempera dosimetric systems contain many mass peaks, quantification of the changes using peak ratios alone is insufficient. The multivariate technique of DA was used to compare the spectra, determine the analytical reproducibility, and derive relevant sets of correlated mass peaks, which describe the changes quantitatively in the mathematical form of discriminant function scores.

In the case of the DTMS and DA of a light ageing series of a tempera test system, an increase in the degree of chemical change with ageing time can be expected. Fig. 7 shows the result of DA of DTMS data from a light ageing series of unpigmented tempera strips. The abscissa represents the ageing time (days), while the ordinate represents the score on the first

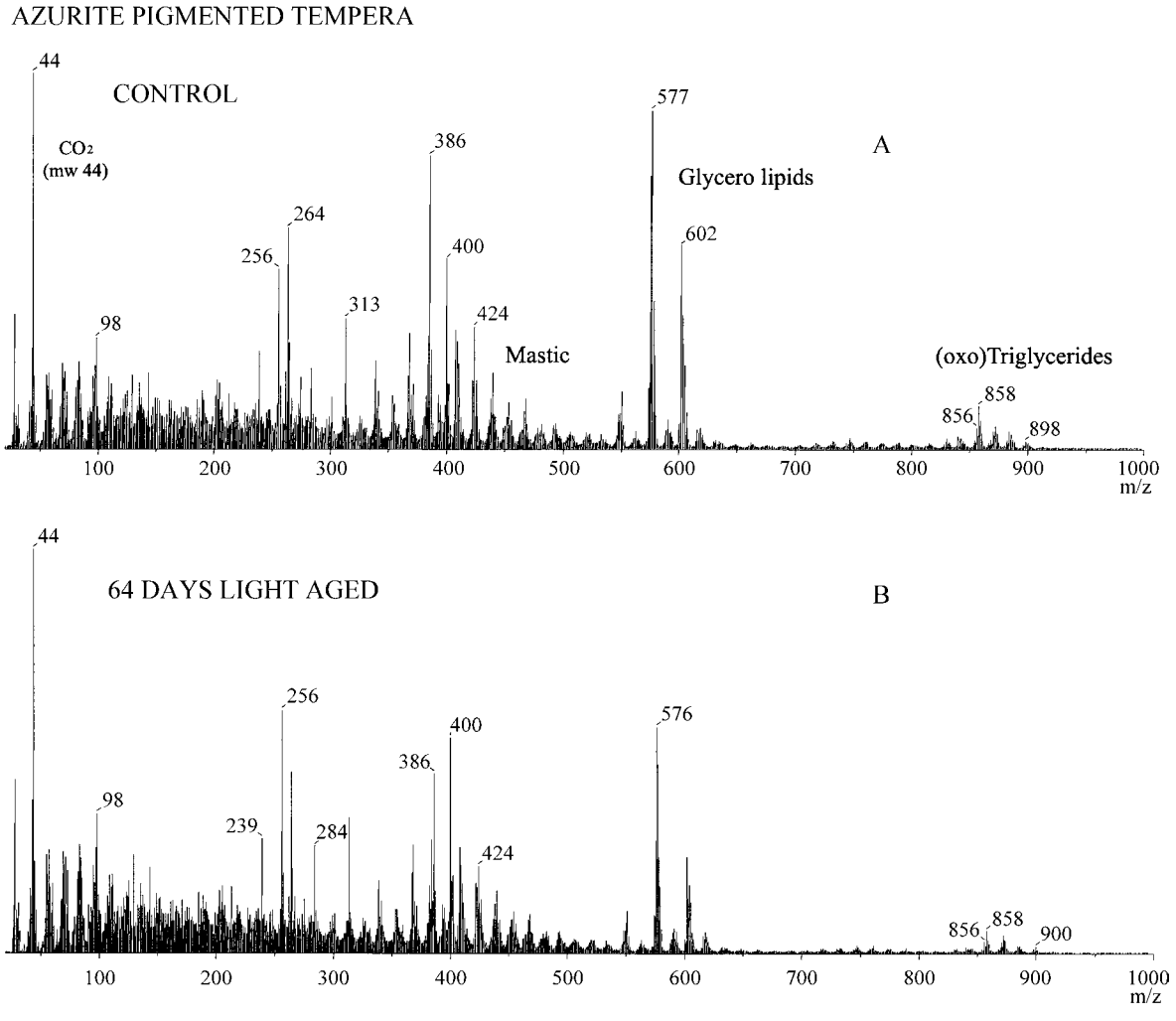

Fig. 6. DTMS summation spectra of azurite tempera control (A) and light aged 64 days (B).

discriminant function. The spreading in the data is indicated with the grey band. This figure demonstrates that the light ageing of an unpigmented test system takes place very quickly in the first days of exposure. At longer exposure times, the process proceeds at a much lower rate and the degree of chemical change appears to plateau. These observations agree with classical kinetic considerations that predict that reaction rates decrease as time progresses due to diminishing concentrations of reactants. By performing an inverted standardisation procedure on the loadings of the *m*/*z* values of the discriminant functions, the so-called discriminant mass spectra can be derived, these indicate which *m*/*z* peaks increase or decrease as a function of the ageing time. In this way, discriminant function data can be interpreted chemically.

Fig. 8 shows the first discriminant function (DF1) mass spectrum from the light ageing series of unpigmented tempera. Peaks in this figure that decrease in relative intensity upon exposure are plotted as negative peaks, whereas those that increase as a function of light exposure are positive peaks. The DF1 spectrum, therefore, indicates the following: a decrease in triglycerides with unsaturated bonds (*m*/*z* multiplets at 856 and 882); a decrease in mastic pentacyclic triterpenoids (*m*/*z* 454, 439, 426, 248, 203) [42], and a

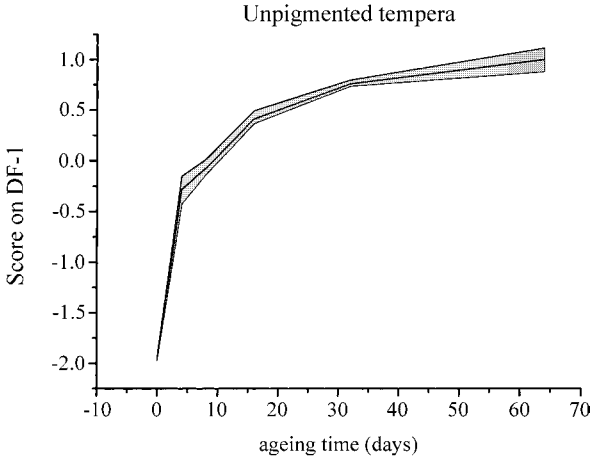

Fig. 7. Light ageing curve of unpigmented tempera obtained by DTMS and DA. The outer lines of the graph are the minimum and maximum and the inner line is the average of three results.

decrease in C18:2 fatty acyl moieties (*m/z* 262) and cholesterol (*m/z* 386 and 368). Light-induced oxidation is exemplified by: an increase in oxidised triglycerides (872 and 898); high intensity peaks for oxidised cholesterol at *m/z* 400 and 384; and the appearance of mass peaks for palmitic acid (*m/z* 256), stearic acid (*m/z* 284), and azelaic acid (*m/z* 152 and 98).

As many environmental factors interact in a museum environment, the changes in the chemical composition of a test system exposed in a museum cannot simply be seen as due to one process alone, but is an integration of a number of processes. The extent to which the processes have proceeded is a function of the different environmental factors. For example the presence of air pollutants such as nitrogen oxides and sulphur oxides in the museum atmosphere, leads to oxidation of organic materials. Moreover, acidifying air pollutants in combination with high relative humidity accelerate hydrolytic processes, especially in the presence of higher temperatures.

The following example shows that different processes of chemical change can be identified in the tempera dosimetric test systems. In this case, the processes are determined by the pigments rather than by different environmental factors. DTMS data of the light ageing series of unpigmented, lead white pig-

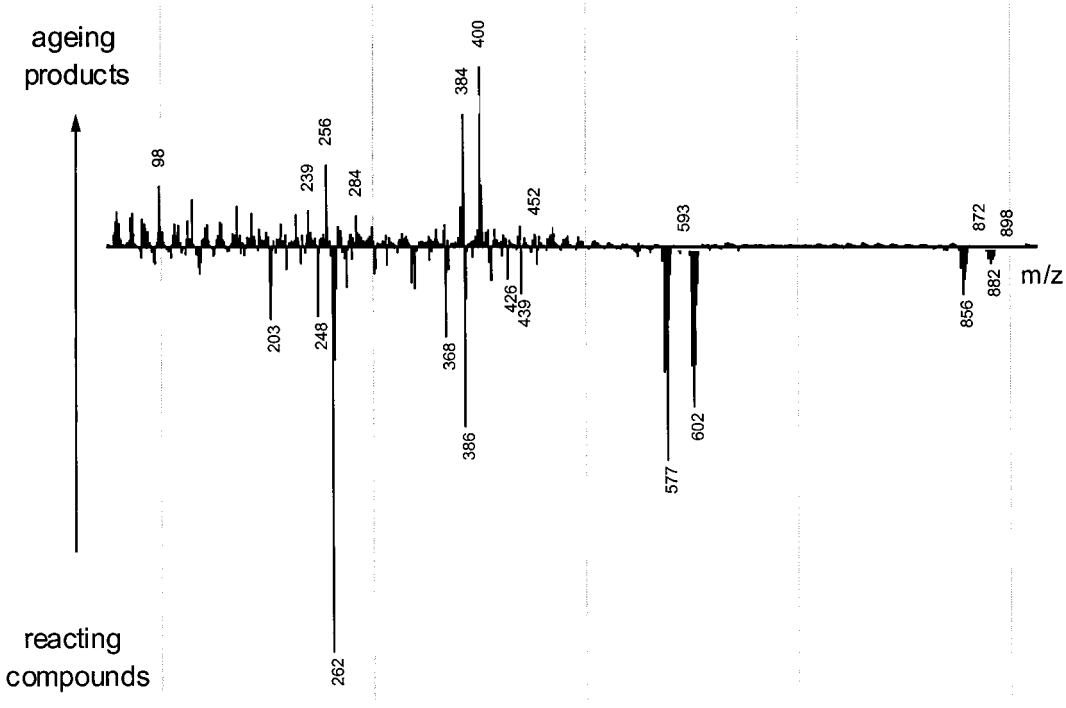

Fig. 8. Discriminant mass spectrum (first) for light aged unpigmented tempera.

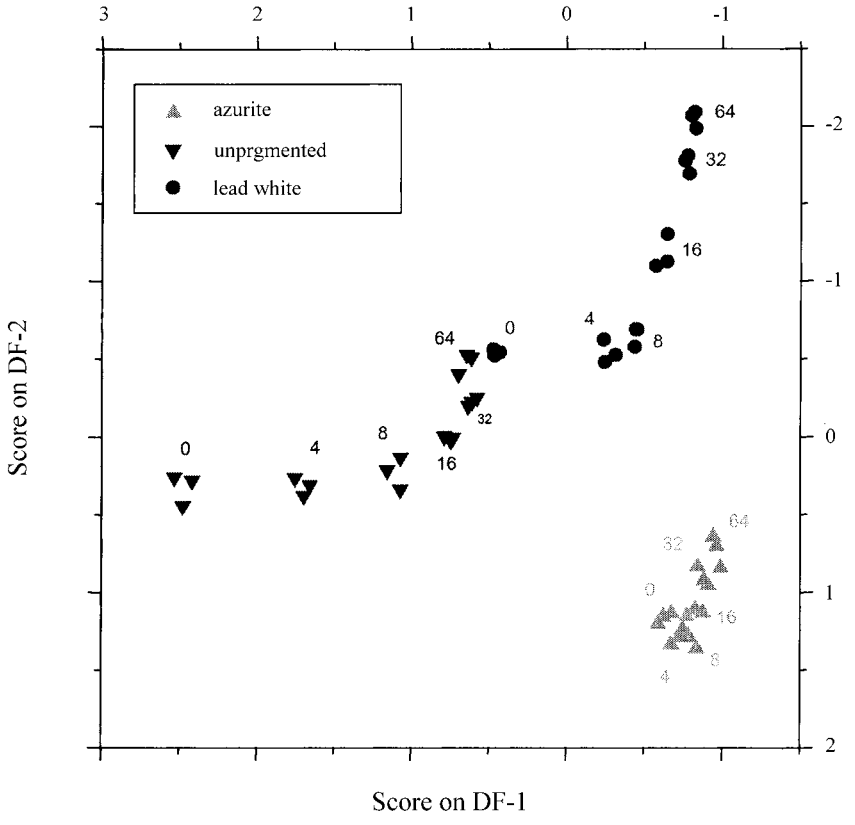

Fig. 9. Map of scores on the first two discriminant functions for light ageing series of unpigmented, lead white pigmented and azurite pigmented tempera.

mented and azurite pigmented test systems were subjected to DA. Two different types of chemical reactions were detected.

Fig. 9 shows plots of the data points obtained on the test systems as co-ordinates in the score map of the first discriminant function (DF1) and the second discriminant function (DF2). The geometric distance between the data points is a measure of the difference in chemical composition. Two ageing phenomena are observed and interpreted as due to (1) oxidation and (2) hydrolysis of ester bonds in the glycerolipids and in the protein lipid network polymer [5]. DF1 (oxidation) separates unpigmented test systems from lead white and azurite pigmented ones. DF2 (ester bond hydrolysis) separates lead white pigmented from azurite pigmented tempera. The series of aged azurite pigmented tempera data points is less resolved, because most of the chemical changes had already taken place during the curing stage in the dark.

Figs. 10A and B show the corresponding discriminant mass spectra of the first (A) and the second (B) discriminant function. The first discriminant mass spectrum suggests that the process represented by the horizontal axis mainly involves oxidative processes, as indicated by *m/z* 386 (cholesterol) being plotted as reacting compound and *m/z* 384 and 400 (cholesterol oxidation products) as ageing products. Oxidation is also indicated by the positions of intact TGs and oxidised TGs. The discriminant mass spectrum of the vertical axis shows di- and tri-glyceride peaks (*m/z* 570–620 and 850–900) on the side of the reacting compounds and peaks at *m/z* 239, 256, 267, and 284 on the product side. This is interpreted as de-esterification of glycerolipids to form free fatty acids or fatty acid salts with the metal cations. Hence, the data indicate that hydrolysis of ester bonds is an important process during light ageing of lead white pigmented tempera. The map also indicates that the

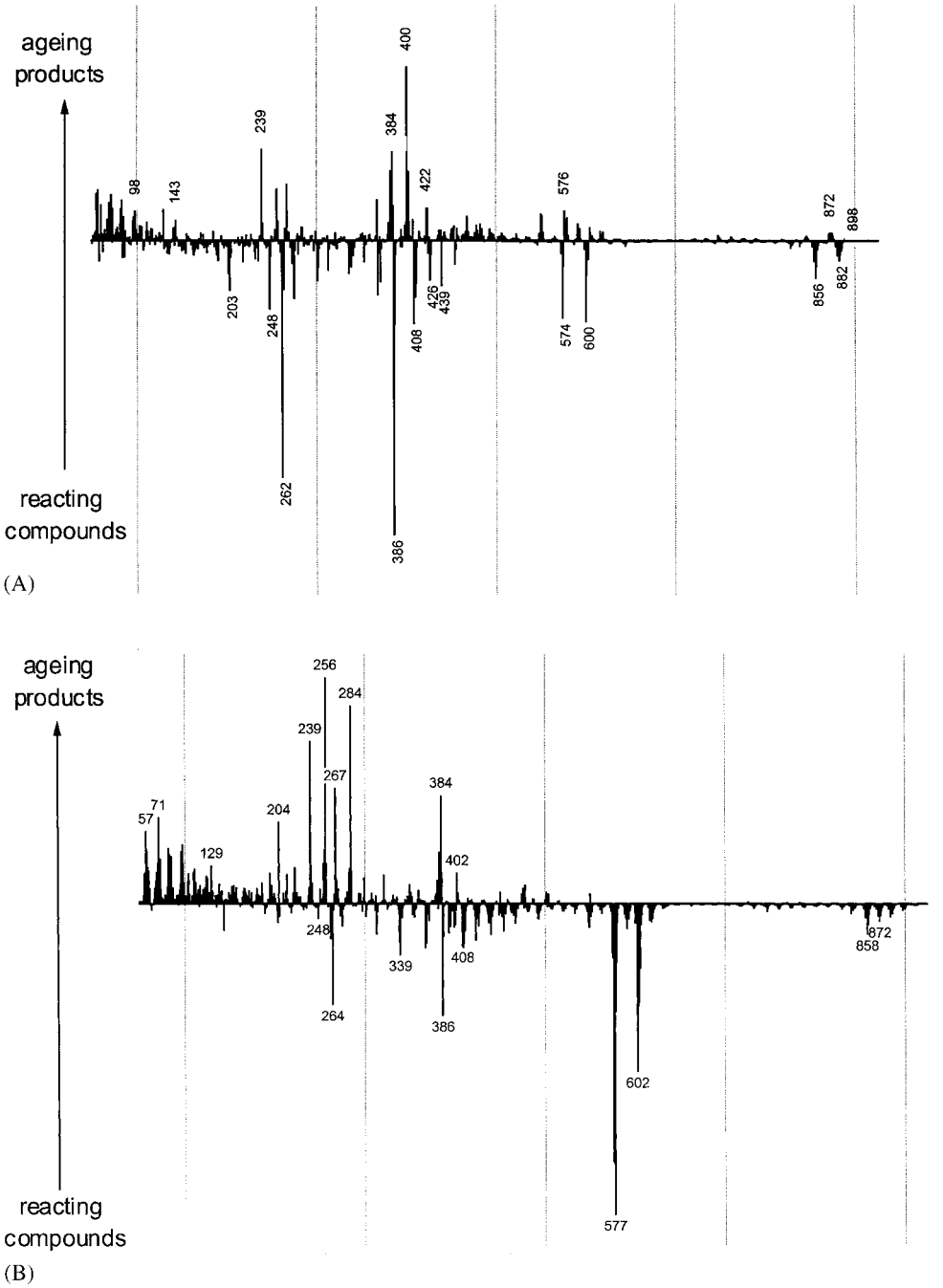

Fig. 10. (A) First discriminant mass spectrum for light ageing series of unpigmented, lead white pigmented and azurite pigmented tempera; (B) second discriminant mass spectrum for light ageing series of unpigmented, lead white pigmented and azurite pigmented tempera.

degree of oxidation of the binding medium of azurite pigmented tempera is very high, but that the degree of hydrolysis is relatively low compared to lead white pigmented systems.

These data clearly show that DTMS and DA can be used successfully to bring the different processes into focus that take place in the tempera dosimetric test systems. Hydrolytic and oxidative processes in the test systems induced by environmental factors are important tracers of the degradation processes. Tracing these phenomena in the field-exposed dosimetric test systems will give important indications on the quality of the exposure environment. A low severity environment should lead to chemical changes that correspond to only a few days of light ageing induced change under lab conditions. High severity environments on the other hand may lead to a degree of chemical change in the test systems considerably stronger than that seen in the 64 days light ageing experiments.

3.3. Effects on the chemistry of the test systems by exposure to NO_x and SO_2

In order to test the sensitivity of the dosimetric test systems to air pollutants, all tempera test systems prepared were subjected to a period of exposure lasting four days to evaluate the effects of exposure to NO_x and SO_x. DTMS was used to investigate the chemical changes in the lipid marker compounds.

Fig. 11 presents a discriminant function score map of a comparative study of controls, 21 day thermally aged, 16 and 64 days light aged and NO_x/SO_2-exposed unpigmented tempera dosimetric test systems by DTMS. The study was designed to probe the data set for differences in effects of thermal ageing, light ageing and ageing due to noxious gases. The 16 days light aged, 21 days thermally aged, the NO_x/SO_2-exposed and the control sample defined the training set. The 64 days light ageing results were used as test set. The geometric distance between controls (only curing) and 21 days thermal ageing is relatively small compared to the effect of light ageing. The conclusion can be drawn that thermal ageing effects (in the dark) on the lipids and mastic in the binder are small. The chemical effect of the noxious gases on the lipid fraction of the binding medium is similar to the effects of light ageing because triglycerides and sterols are oxidised. However, differences between the two conditions are detected in the second discriminant function DF2. The mass spectral data in DF2 indicate that the oxidation of sterols is less severe under NO_x/SO_2 conditions but that hydrolytic processes affecting the ester bond are more prominent. Incorporation of SO_2 in the form of sulphates or sulphonic acids is also evident from ions at m/z 64 which are due to pyrolytic elimination of SO_2 from the samples [56]. The presence of sulphates in the NO_x/SO_2-exposed unpigmented tempera test system was confirmed by FTIR spectroscopy [54]. Further comparative studies of the different tempera test systems have shown that NO_x/SO_2 effects are detected with good sensitivity in lead white, smalt, sienna and alizarin test systems.

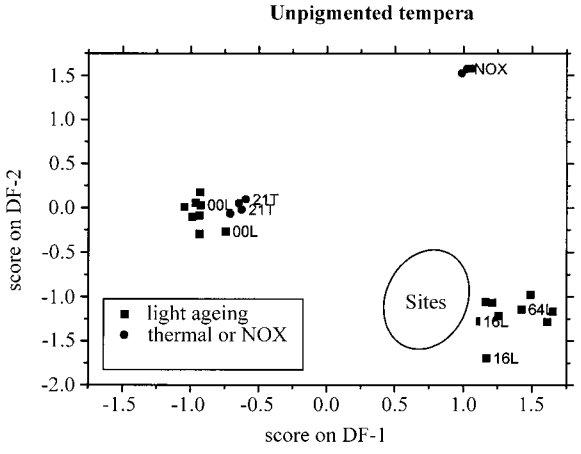

Fig. 11. Map of scores on the first two discriminant functions for light aged (16L), thermally aged (21T) and NO_x/SO_2-exposed unpigmented tempera test systems.

3.4. DTMS studies of selected dosimetric test systems from the field sites

As mentioned in Section 1, mock test paintings were exposed at a selection of seven different sites, consisting of controlled (Tate, Rijksmuseum, Uffizi) and uncontrolled sites (Sandham Chapel and Alcázar). Control in this context means that the relative humidity and temperature are set by air conditioning systems. Furthermore, at controlled sites illuminance levels are such that the annual dose of illumination is below the generally accepted value of 650 klux h for museum exposure of paintings [1]. At the uncontrolled sites, the light levels are expected to exceed those

values, and hence more drastic chemical changes in the test systems can be anticipated. On top of that, other environmental factors, such as variations in relative humidity, temperature and air pollution also contribute to the chemical changes in a test system. A detailed description of the field sites is given elsewhere in this issue by Odlyha [44] and Bacci et al. [45].

The question was tested whether dosimetric test systems from field sites were similar to those subjected to the laboratory conditions of thermal ageing, light ageing or noxious gas exposure, respectively. The DTMS after DA with a training set consisting of controls, thermally aged (21 days), NO_x/SO_2 and 16 days light ageing of the unpigmented tempera dosimeters shows that field site-exposed dosimeters plot in the area of light aged test systems of 8–16 day exposure. This implies that the chemistry at the field sites resembles mostly that of light ageing (vide infra).

This observation was used to define a protocol for the comparison of field-exposed dosimeters. The DTMS data from the light ageing under laboratory conditions during 4, 8, 16, 32 and 64 days were used for calibration. DA was performed with the artificially light aged test systems as the training set in order to calculate a multivariate solution space in which the geometric position of the DTMS data of field-exposed dosimeters was interpolated (i.e. field site data were included as a test set). The following example illustrates the approach and discusses results on the field-exposed unpigmented tempera test systems. Fig. 12 shows the scores on the first discriminant function for the field-exposed unpigmented dosimeters. The light ageing data, the data from NO_x/SO_2 and from the control sample for field exposure (FOM; stored under dark and oxygen-free conditions in a copper lined anticorrosive bag) are given for comparison. As might be expected, field-exposed test strips from the uncontrolled environments (the Alcàzar and Sandham Chapel) indicate a stronger chemical change than dosimeters exposed in the controlled museum environments. The result of the Rijksmuseum Depot ''Oost'' sample is remarkable because this dosimeter shows considerable chemical change, although it was exposed in the painting storage facility where light intensity is very low. It indicates that other factors than light intensity alone play an important role in environment-induced chemical processes.

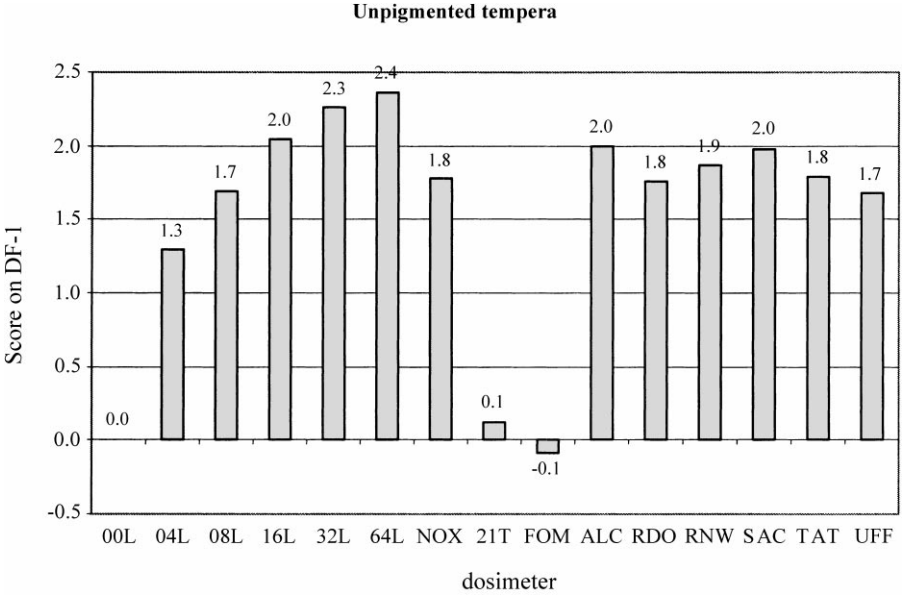

Fig. 12. Comparison of the scores on the first discriminant function (DF1) of laboratory aged and field-exposed unpigmented tempera dosimeters. The light ageing series defined the training set for DA. Discriminant scores are normalised so that the score of the control for light ageing (00L) is zero. Legend to field sites FOM, control dosimeter stored under exclusion of oxygen; ALC: Alcázar; RDO: Rijksmuseum Depot ''Oost''; RNW: Rijksmuseum Nightwatch; SAC: Sandham Chapel; TAT: Tate Gallery; UFF: Uffizi.

In the ideal situation, the dosimetric test systems would be calibrated against all (combinations of) environmental factors. This, however, would require an extensive data set that would have been far too large for the explorative character of the ERA project. Therefore, the light ageing set was used for calibration of the degree of chemical change in the field-exposed dosimeters. This approach can only yield valid results if the chemical processes that take place during natural ageing at the field sites closely resemble those that take place during light ageing. Hence, it is important to compare the nature of the chemical change in the natural ageing process with that of the light ageing process. DA with both the light ageing and the field site DTMS data in the training set was used to determine whether the processes that occur during the light ageing differ substantially from those taking place during field exposure. This was done for the unpigmented tempera dosimetric test systems. Fig. 13A shows the map of the scores on the first discriminant function plotted against those on the second discriminant direction. The relative significance of the discriminant functions indicated along the axes is 88% (DF1) and 11% (DF2). A deviation of the score on DF2 (the ordinate) is far less important than the score on DF1 (the abscissa). This demonstrates that field site exposure in the museums is expressed by the same molecular characteristics as the light ageing.

In the case of the lead white pigmented test systems, however, a difference is observed between artificial light aged and the majority of the field site-exposed dosimeters. The map of the scores on the first two DFs for the lead white temperas is shown in Fig. 13B. The first DF separates the light aged systems from the field-exposed systems, with the exception of the Tate Gallery-exposed dosimeter. Chemically, the differences are caused by a stronger presence of lead soaps, and the cholesterol oxidation products with molecular weights of *m/z* 382 and 400 (cholestadienone and 7-hydroxy-cholestenone) in the field-exposed systems. Furthermore, the mastic-derived ageing product 3-oxo-25,26,27-trinordamarano-24,20-lactone (*m/z* 414) [41] is more abundantly present in the field-exposed dosimeters. Additional processes occurring during field exposure of lead white tempera compared to light ageing are the occurrence of other sterol oxidation products and more prominent hydrolysis of glycerolipids.

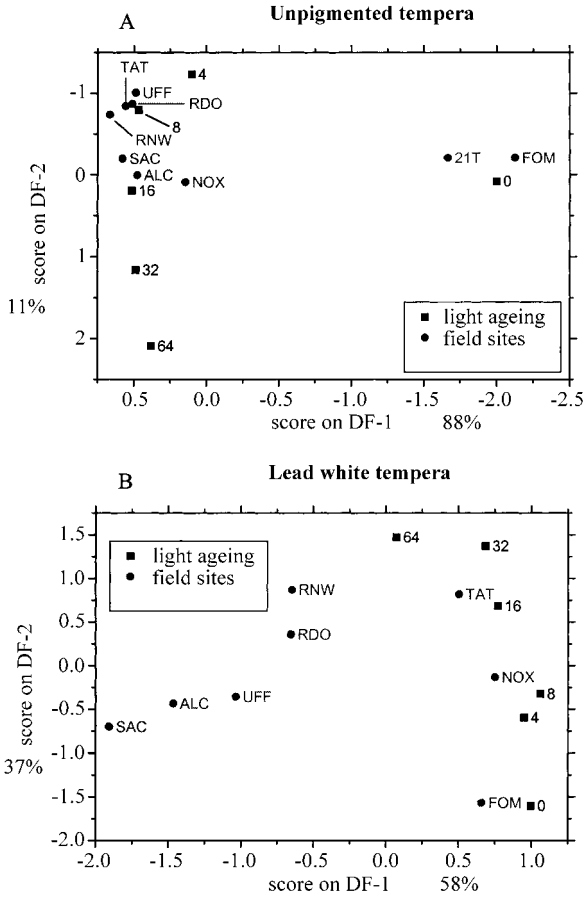

Fig. 13. Map of scores on the first two discriminant functions for artificially light aged and field-exposed unpigmented (A) and lead white tempera test systems (B). Both the light ageing results and the field exposure results were included in the training set.

Figs. 14 and 15 show the degree of chemical change in the laboratory aged and field-exposed dosimeters of the lead white pigmented and sienna pigmented dosimeters, respectively. As expected, the degree of chemical change in the artificially light aged dosimeters shows a positive correlation with exposure time for both these systems. The degree of chemical change in the lead white pigmented tempera control test strip that had been stored under exclusion of oxygen and light (FOM) is negligible. This also holds for the sienna tempera dosimeter that was stored under these conditions. The dark storage room in the Rijksmuseum Depot (RDO) has again a relatively high degree of chemical change and is in this respect comparable

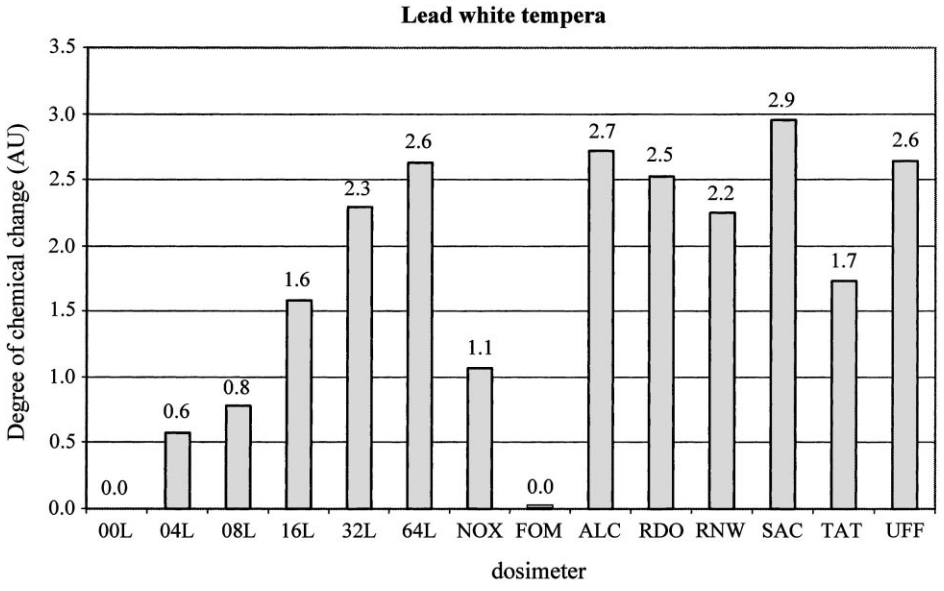

Fig. 14. Comparison of the degree of chemical change of artificially light aged and field-exposed lead white tempera dosimetric test systems. The degree of chemical change is the score on the first discriminant function after DA of the DTMS spectra (with the light ageing data in the training set). Discriminant scores are normalised so that the degree of chemical change in the control for light ageing (00L) is zero.

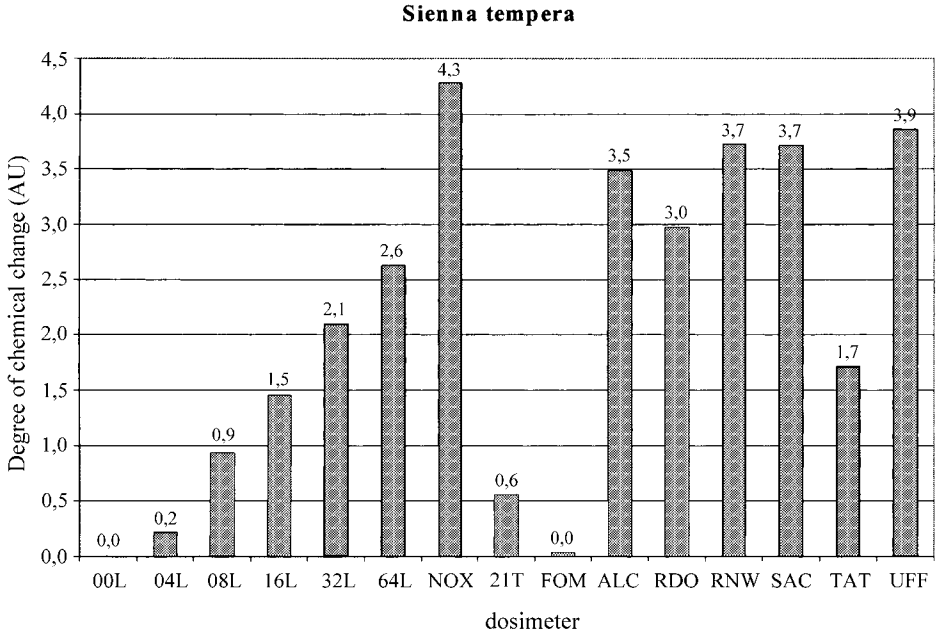

Fig. 15. Comparison of the degree of chemical change of artificially light aged and field-exposed lead white tempera dosimetric test systems. The degree of chemical change is the score on the first discriminant function after DA of the DTMS spectra (with the light ageing data in the training set). Discriminant scores are normalised so that the degree of chemical change in the control for light ageing (00L) is zero.

to the unpigmented dosimeter. This suggests that there is an unknown oxidising agent active in the dark, which contributes to a chemical change comparable to very strong light ageing. In both cases, the lowest degree of chemical change is found in the Tate Gallery dosimeter. This is consistent through all tempera dosimeters that are pigmented with inorganic pigments. This effect is attributed to the fact that the Tate Gallery is the best controlled field site in terms of temperature and relative humidity and that it is the only field site where carbon filters are used in the air inlet system. For the lead white dosimeters, the highest value is found for the Sandham Chapel, which is the site with the highest relative humidity. In the case of the field-exposed sienna dosimeters, the Uffizi Gallery shows the highest degree of chemical change. The fact that this is not the case for the lead white dosimeter, suggests that the sienna dosimeter detected an additional contribution to the environmental ageing stress in the Uffizi Gallery. An indication for a significant role of air pollutants comes from the experiments with nitrogen oxide and sulphur dioxide atmospheres in the dark. Clearly, both systems respond to exposure to these air pollutants. However, the NO_x/SO_2-exposed lead white tempera shows a degree of chemical change that is comparable with more than 8 days light ageing (i.e. a light ageing equivalent of more than 8 days), whereas the NO_x/SO_2-exposed sienna tempera dosimeter shows a light ageing equivalent much greater than 64 days. Apparently, the sienna dosimeter is much more sensitive as a ''detector'' for air pollution than the lead white dosimeter.

3.5. Extrapolation to museum exposure years

Referring to the dosimetric results obtained on the field-exposed unpigmented tempera dosimeters, it must be noted that even the ''best'' field sites, i.e. the ones with the smallest chemical change, show effects which are comparable with those observed upon 8 days of artificial light ageing. In the case of the lead white tempera, all dosimeters score higher than 16 days light ageing, and the worst site shows a chemical change that is larger than the effect of 64 days light ageing. The field-exposed sienna tempera dosimeters show light ageing equivalents of more than 64 days for all except the best site. Using the reciprocity principle [4], this value of light exposure can be related to the number of years of exposure in a museum. The reciprocity principle states that the product of light intensity and exposure time determines the amount of damage to an object. Thus, 8 days of artificial light ageing at 18 klux is 3.5 Mlux h by reciprocity. This value exceeds the generally accepted annual dose of illumination of 650 klux h [1] by more than a factor of 5.

The discrepancy between the actual effects of exposure to the museum environment observed and the theoretically expected value based on the reciprocity principle for light ageing may be explained in two different ways. Firstly, the assumption of the reciprocity is not valid because there are many factors that may affect the reciprocity principle (see [57]). The following factors may explain the relatively strong effects at lower light intensities. In several cases of radical initiated oxidative processes, the oxygen uptake is proportional to the square root of the light intensity. The depth of penetration of the light may vary when a layer of radiation absorbing material is formed on the surface. This factor becomes particularly relevant to the validity of the reciprocity principle when light intensities are so high that they allow two-photon processes to occur (very unlikely at 18 000 lux light intensity). Furthermore, the moisture content may affect the rates of light-induced processes. In the present experiment, moisture content may have played an important role; the artificial light ageing experiments were carried out at relatively low relative humidity (27–28%) and in many cases, the relative humidity at the field sites was found to be much higher.

On the other hand, if the reciprocity principle is valid, the extreme effects cannot be explained when exposure to light is seen as the most important factor in ageing. Hence, the effects must originate from other factors that strongly contribute to the environmental stress (expressed as chemical change in the multivariate space) detected by the dosimeters. The composition (or reactivity) of the museum air may be such a factor. Air pollution, either diffusing into the museum from outside or originating from sources inside the museum, may strongly contribute to the deterioration processes. The results of the dosimeter that was exposed in the storage Depot ''Oost'' of the Rijksmuseum, where light intensity is very low, support the conjecture that light exposure is not the most

important factor and that other factors must play an equally important role. One of these factors is NO_x/SO_2, which also contributes to the dosimeter's DTMS signature in almost the same way as the light ageing effects.

3.6. Considerations for further work on paint-based dosimeters

The tempera dosimetric test systems are now ready for further development and validation to make paint-based dosimetry a viable method for the evaluation of museum environments on the large scale.

In the present survey, the degree of chemical change was calibrated against the light ageing series. If larger training sets, including a great variety of (combinations of) environmental factors, are employed a better calibration can be obtained and chemical differences, expressed as the position in the multivariate space, can be used to indicate which of the environmental factors is causing the chemical change. The results of DA on a set of light aged, thermally aged and pollutant-exposed samples presented in this chapter indicate that this is a valid approach. Alternatively, the difference in relative sensitivity of the various paint systems for specific environmental factors can be used as an indicator of important detrimental environmental factor(s). There is a third approach that focuses less on the calibration of the changes in the dosimeters as a result of laboratory exposure. This involves correlation of the results obtained on field-exposed dosimeters with other, conventional, data such as records on temperature, relative humidity, concentrations of air pollutants, numbers of visitors, light intensity, etc. Correlation with conventional data can give valuable insight into the effects of (combinations of) different factors. When a larger database of results is generated, the assembled data can be used as input (training material) for an expert system, which classifies the tested environments based on the dosimetric results obtained on exposed dosimeters.

Comparison of the results obtained on the field-exposed dosimeters with the artificially light aged systems strongly questions the validity of the reciprocity principle for light ageing. Testing of the reciprocity principle for light ageing under ceteris paribus conditions is strongly recommended. The results of such a survey can contribute to the understanding of light-induced deterioration processes of paint systems.

4. Conclusions

The validity of the principle of paint-based dosimetry has been demonstrated. The degree of chemical change in the light-exposed tempera dosimetric test systems can be correlated with the duration of light exposure. The results of field exposure show that the chemical composition of the paints is changed by exposure in museums: significant differences are observed among dosimeters exposed in different field sites. The effect observed upon exposure of the dosimeters to museum environments is more drastic than anticipated. This suggests that either the reciprocity principle of light ageing is not valid, or that the chemical composition of the museum atmosphere plays an even more important role than the exposure to light alone.

DTMS is a rapid and adequate method to determine the chemical composition (of primarily the lipid fraction) of tempera paint systems and changes therein. DA was successfully applied to quantify the difference between DTMS data obtained on dosimeters exposed under different environmental conditions. Moreover, DA can be used to distinguish and identify different processes that take place in the temperas as a result of exposure. The chemical changes observed upon exposure of the unpigmented dosimeters to NO_x/SO_2 in the dark follow to a great extent the changes induced upon exposure to light. However, small chemical differences are observed. On the one hand, cholesterol is less severely oxidised upon NO_x/SO_2 exposure. On the other hand, hydrolysis of glycerolipids plays a more important role. Thermal ageing has a very small effect on the composition of the lipid fraction of the unpigmented tempera dosimeters.

Comparison of the chemical changes in the field-exposed dosimeters with those in the laboratory-exposed (light, temperature and NO_x/SO_2) dosimeters indicates that the processes taking place during field exposure resemble most those taking place during light ageing. The light ageing series of the dosimeters was used successfully for calibration the degree of chemical change in the field-exposed unpigmented tempera dosimeters. The degree of chemical

change is expressed as numbers that indicate the ''environmental stress'' detected by the dosimeters. Some pigmented temperas show enhanced sensitivity towards specific environmental factors (e.g. sienna for air pollutants) that can be used as indicators of specific factors. The controlled environments have less affected the original paint composition of the unpigmented tempera dosimeters compared to the uncontrolled environments. A particular result obtained for the dosimeter exposed in the almost dark Rijksmuseum Depot ''Oost'' indicates that other factors than light alone play an important role in the chemical processes induced by the museum environment.

Acknowledgements

This research is part of the approved Program No. 28 of FOM, a subsidiary of the Dutch National Science Foundation (NWO). The ERA project is supported by the commission of the EC's environment programme phase II (Grant No. EV5V-CT-94-0538). MOLART, a multidisciplinary NWO Priority Project on Molecular Aspects of Ageing in painted art, is supported by NWO. The authors express their thanks to Mr. R. Belucci (Opificio delle Pietre Dure, Firenze, Italy), Dott. I. Van der Werf (FOM–AMOLF) and Dott. M. Picollo (IROE) for the preparation of the tempera paints, to Dr. J. Townsend and Mr. S. Hackney (Tate Gallery, London) for the light ageing and exposure at the Tate Gallery, to Dr. J. Havermans (TNO, the Netherlands) for air pollutant exposure, to Ing. J. Pureveen, Ing. J. van der Horst and Ing. A.E. Kerkhoff for technical assistance at FOM–AMOLF, and to A. Ruiz Hernando (el Alcázar, Segovia, Spain), Mrs. V. Smith (Segovia, Spain), Dr. O. Casazza and A Petrioli (Uffizi Gallery, Italy), Dr. A. Wallert (Rijksmuseum, the Netherlands), and Mrs. C. Sitwell and Dr. L. Bullock (National Trust, UK) for exposure at the field sites.

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