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Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (azurite tempera) by thermal and spectroscopic analysis

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Abstract

This paper describes the effects of accelerated artificial and natural ageing on samples of azurite paint tempera prepared according to traditional early Italian recipes. The pigment used was basic copper carbonate in the form known as azurite and this was mixed using whole egg tempera medium. Artificial and natural ageing of the dosimeters was performed using controlled ageing chambers and selected sites of varying environmental conditions. The effects of ageing were quantified using a number of analytical techniques, which include the following: thermal analysis (DSC and TGA), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The data were then compared with those obtained from samples which were naturally aged by exposure in selected European art galleries and historic castles for a period of 9 months. It was found that the changes observed on artificial light ageing alone were minimal. Mass spectrometry (DTMS) showed that samples had already undergone oxidation during the curing stage of 3 months [O.F. van den Brink, G.B. Eijkel, J.J. Boon, Thermochim. Acta 360 (2) (2000), this proceedings]. There were, however, measurable differences in the samples that had been subjected to thermal and pollutant ageing, and this was used to rank the sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Azurite tempera; Paint dosimeter; Accelerated ageing; Natural ageing; DSC; DMTA; XPS

1. Introduction

In the previous two papers the effects of ageing have been explored in smalt tempera and basic lead carbonate tempera dosimeters [2,3]. Quantification by DSC of changes on ageing was possible in smalt tempera both for artificially aged and naturally aged samples. With basic lead carbonate tempera chemical processes between the reactive pigment and the binder made it more difficult to quantify changes in the same manner due to the additional shift in the DSC curves to higher temperatures which occurred in the naturally aged samples. In particular, the pollutant exposed basic lead carbonate tempera sample was found to be strongly affected in that part of the DSC curve in which pigment contribution occurred, and where there was poor pigment coverage by the tempera medium. In this paper thermal (DSC, TGA, and DMTA) and spectroscopic (XPS) techniques are used to describe and quantify the changes in azurite tempera dosimeters on both artificial and natural ageing.

The azurite pigment, basic copper carbonate, has the chemical formula $2CuCO_3{\cdot}Cu(OH)_2$. It is a

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mineral that is found in copper ore deposits, and it varies from a deep greenish blue to a pale blue [4]. There is also evidence that it may become green in tempera paint as a result of conversion (on hydration) to the less stable thermally stable form malachite, $CuCO_3{\cdot}Cu(OH)_2$ [5]. Azurite was one of the most frequently used pigments in tempera painting. Mixed with lead white (basic lead carbonate) it was used in the skies of paintings and in draperies of figures [4]. Therefore, there is an interest in studying the alteration of azurite paint tempera with ageing.

The thermal properties of basic copper carbonate have been previously studied [6]. Additionally, the kinetics of its thermal decomposition was examined by both conventional rising temperature thermogravimetry and also by constant rate thermal analysis, where the reaction is driven by sample response. It was found that the H_2O and CO_2 were evolved at different rates throughout the decomposition, with more H_2O evolved at the start of the reaction and more CO_2 at the end [7].

A pilot study into the effects of solvents on artificially aged egg tempera films was performed at the Technology Department of the Courtauld Institute of Art, London, and this involved the preparation of medium rich azurite tempera samples using egg yolk only as the medium [8]. The yolk itself was used as in classical tempera painting technique and the technique of preparation follows the recommendations of Cennini [9] and Thompson [10]. Traditionally, pigments were ground first in water before grinding into the egg yolk binder. In the pilot study, a higher proportion of egg yolk was used than would otherwise be found in a typical tempera painting on gesso ground [8]. The yolk consists of an emulsion of lipids in an aqueous phase containing globular proteins. The lipid fraction contains the following classes of compounds: triglycerides (ca. 65%), glycerophospholipid including mainly phosphatidycholines lecithins (ca. 29%), and cholesterol (ca. 5.2%). Thermoanalytical studies (DSC and TGA) were performed both on these azurite tempera samples and on lead white temperas, and the DSC curves of the azurite tempera (egg yolk only) samples were reported [11]. These samples showed a two peak exotherm. It was also found that extensive changes occurred in the intensity of the two peak exotherm on ageing. The first exothermic peak was reduced in intensity with light ageing only, and then it was further reduced in intensity with both light and heat ageing. Given the scale of the observed changes in these samples it was considered that azurite tempera would serve as a useful dosimeter in the ERA project (Environmental Research for Art Conservation) [12].

In this paper whole egg tempera preparation was used, as described in preceding papers in this issue [1–3]. For additional evaluation of the surface of the paint film, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) studies were performed. The upper layer of the paint film is both the most vulnerable, because it is in contact with the atmosphere, and the most important since it is the surface that is seen. Previous studies have been made using SEM to examine the effects of various cleaning agents on painted surfaces [13].

SEM will provide a description of changes in the surface appearance of azurite temperas on ageing, whilst XPS will be used to study the accompanying chemical changes which occur at the surface on ageing. As only those photoelectrons generated from the top 1–3 nm of the sample surface are detected, the XPS spectrum is surface specific. Elemental surface concentrations are obtained, which give the percentages of metal, carbon, oxygen and the other elements which are present. Calculated O/C ratios provide a measure of the degree of surface oxidation. This has been used in studies of wood and the effect of additives to retard its deterioration [14]. In addition to elemental concentrations, information on the C 1s profiles of the surfaces will be obtained. Differences in the shape of these profiles indicate that changes have occurred in the type of functional groups which are present.

The aim of this paper is to study the physicochemical changes in azurite paint tempera in response to ageing with a view to assessing its suitability as a paint dosimeter for indoor environments in museums and galleries.

2. Experimental

2.1. Sample preparation

The azurite pigment used in this study was natural dark azurite obtained from Kremer (supplier of artists' materials) Aichstetter (D). X-ray diffraction data confirmed its chemical composition as copper carbonate hydroxide, ICDD reference 11-682. The tempera samples were prepared as described in the previous papers, using whole egg as a binding medium and following one of the recipes reported by Cennini [9]. The yolk was separated from the white of an egg. The egg white was whipped so that a layer of foam was formed on the liquid. After the egg white was left to stand for one night, 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 (half the volume of the mixed egg). The pigment was then mixed with the binding medium to form the paint. The samples were painted onto a Melinex (PET) substrate and left for 3 months to cure before being subjected to artificial ageing.

2.2. Artificial and natural ageing

Light, thermal and pollutant ageing was performed as described in preceding papers in this issue [1,2]. Exposure to pollutants was carried out in the laboratories of TNO[1] (Delft, The Netherlands). The experimental set-up was used previously for the exposure of paper to air pollutants, and a detailed description is given elsewhere [15]. During exposure the climate chamber maintained the temperature at 23°C and relative humidity at 55%. No light was admitted. Flows of SO_2, NO_x, and air were tuned continuously and the overall concentrations during exposure were 10.2 ppm SO_2, 11.4 ppm NO and 5.2 ppm NO_2. The samples were exposed to NO_x/SO_2 for a single fixed period of 4 days at a level higher than would normally be experienced in the atmosphere (where outdoor values for urban sites can be of the order of 30–50 ppb NO_2, and indoor 2–30 ppb depending on whether atmospheric filtration using charcoal filters are in use) [12].

Six locations were selected for field site exposure of the paint dosimeters for a period of 9 months, as discussed in more detail in the preceding papers [2,3]. The sites will be referred to by the acronyms given in parentheses. Locations comprised major art galleries where the indoor environment was controlled, such as the Rijksmuseum in Amsterdam (RNW), the Tate Gallery in London (TAT), and the Uffizi Gallery in Florence (UFF), and two additional sites where the environment was uncontrolled, viz. Sandham Memorial Chapel (SAC) at Burghclere (National Trust, England) (SAC) and El Alcázar in Segovia (Spain) (ALC). A dosimeter was also placed in the storage facility "Depot Oost" in the Rijksmuseum (RDO), where light levels are very low. The location of the exposed dosimeter was in the Clore Gallery (adjacent to the Tate Gallery (now Tate Britain)). This represents the least polluted environment (> 2 ppb NO_2 and SO_2) due to the use of particle and carbon filtration of the incoming air. Other sites in urban locations (e.g. RNW + UFF), where the air is not as well filtered, have higher indoor values, particularly for NO_2.

2.3. Instrumentation

DSC measurements were made using a Shimadzu DSC-50 analyser from ambient to 500°C at a heating rate of 10°C/min and a flow rate of O_2 purge gas of 20 cm^3/min. Samples (1–1.5 mg) were measured in triplicate. TGA measurements were made using a Shimadzu TGA-50 analyser at a heating rate of 10°C/min and with an O_2 flow rate of 60 cm^3/min.

DMTA measurements were made using a Rheometric Scientific DMTA (Mk3) in single cantilever bending mode at a frequency of 1 Hz and strain level 4 (approximately 64 μm peak-to-peak displacement) from −130 to 150°C at a heating rate of 3°C/min.

For SEM measurements, rectangular samples, approximately 0.5 cm×0.5 cm, were cut from the paint strips, and mounted on double-sided tape. They were gold coated for about 2 min using a Nanotech sputter-coating unit to improve surface conductivity and reduce charge build-up. The upper surface of the paint was examined using a Jeol Superprobe 733 and magnifications ranging from ×150 to ×3000.

Small spot XPS measurements were made using an M Probe XPS instrument (Surface Science Instruments) operating with a base pressure of 10^{-9} mbar. This instrument uses monochromatic Al Kα (1486.7 eV) as the source radiation which is focused into preselected spot sizes from 1000 μm×400 μm

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(elliptical) down to 150 μm^2 (circular) at constant flux. Samples were cut in the form of small square pieces (4 mm×4 mm) for the analysis.

3. Results

3.1. DSC and TGA analysis of pigment and unaged tempera

The DSC curve of the pure azurite pigment (Fig. 1) shows a single endothermic peak at 420°C due to the decomposition of the basic copper carbonate to copper oxide according to the equation

$$2CuCO_3 \cdot Cu(OH)_2 \rightarrow 3CuO + 2CO_2 + H_2O \qquad (1)$$

This can also be seen in the TGA curve of the sample (Fig. 2), where there is a 30% weight loss with an onset temperature of 400°C. It corresponds to the expected value for the loss of both the CO_2 and H_2O. Individual steps within the decomposition process were not resolved in this experiment, but previous studies in nitrogen and dynamic air of basic copper carbonate have suggested a more complex pathway [6]. The decomposition of malachite (Aldrich basic copper carbonate) Aldrich was also measured, and it was found to be less thermally stable than the azurite pigment, with an onset temperature for decomposition of 290°C.

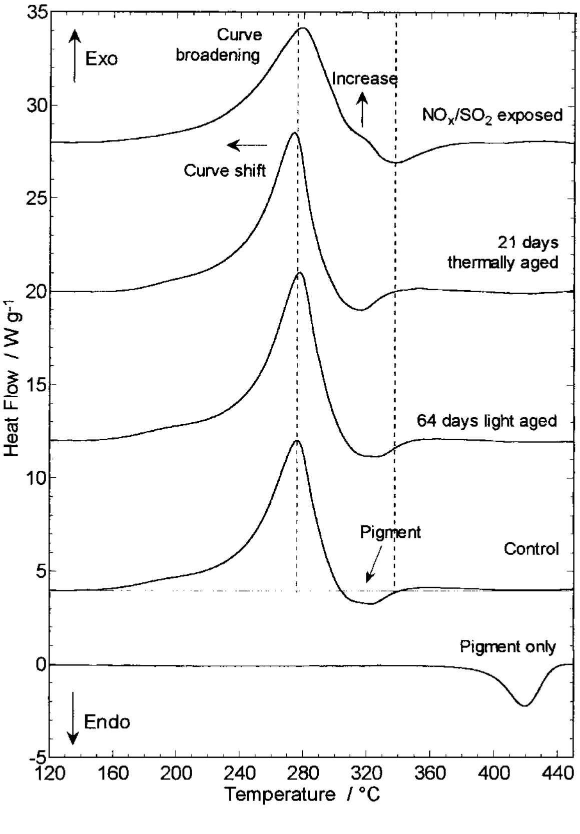


Fig. 1. DSC curves of azurite tempera and pigment. Curves have been vertically offset for clarity.

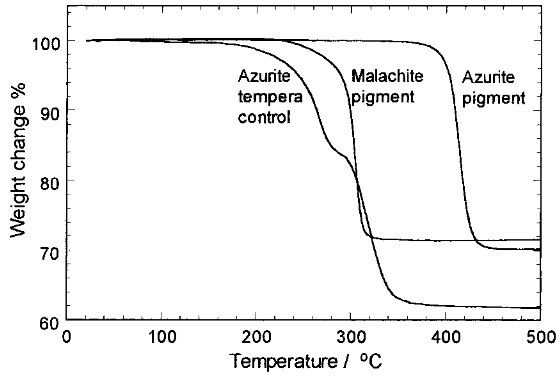


Fig. 2. TGA curves of azurite tempera and pigment, and malachite pigment.

The DSC curve of the azurite tempera control (Fig. 1) shows a main exothermic degradation peak in the region of 280°C due to the degradation of the egg tempera medium. Preceding this is a low temperature shoulder (160–220°C) as was observed in the smalt and lead white tempera particularly on light ageing. The fact it already exists in the azurite tempera control sample confirms DTMS observations that the control sample is more oxidised than the lead white tempera control sample [1].

Following the main exothermic peak is the endothermic peak from the pigment decomposition, which now occurs at 320°C. The change in temperature and lowering of thermal stability of the pigment (from 420°C in the pigment itself to 320°C in the paint tempera) implies a pigment–binder interaction. Unlike the samples in the pilot study, where a two peak exotherm was observed [11], these current samples are lipid lean and so the second exothermic peak is barely discernible, though it is present in some of the samples (e.g. control) and follows immediately on from the endothermic decomposition of the pigment itself. The medium content was determined by thermogravimetry (TGA), where the weight losses of (1) pigment and medium, (2) pigment alone and (3) medium alone were recorded. The medium concentration C_m was calculated from the following formula:

$$C_m = \frac{R_p - R_t}{R_p - R_m}$$

where R_p is the residual mass (percentage mass remaining after heating to 500°C in O_2) for the pigment, R_t is the residual mass of the paint tempera sample, and R_m is the residual mass of the binder. In the sample of binding medium, the decomposition was not complete until 700°C, although in the paint tempera it was complete by 500°C. Thus the residual mass of the binder was found from the heating to 700°C, and gave a value (ash content) of 3%. From the above calculation, it was found that the paint contained 13 wt.% medium.

3.2. DSC and TGA analysis of aged azurite tempera samples

Contrary to what had been observed in earlier work on egg yolk tempera samples [8,11], artificial light ageing of azurite tempera (Fig. 1) resulted in barely measurable differences in the thermo-oxidative degradation process. The previous work involved medium rich samples (ca. 40–50%) containing egg yolk only, rich in lipid content. The present samples, in comparison, are medium lean and also higher in protein content as they contain egg white as well as the egg yolk. In addition, mass spectrometric data showed that the presence of copper catalyses oxidation processes [1]. The oxidation had therefore occurred during the 3 months curing of the control sample, and thus little further reaction was possible on light ageing. The ability of transition metals to act as catalysts of autoxidation reactions has been previously discussed [16]. In future this could be tested by measuring samples during the curing period, or by shortening the curing times. Also the actual preparation method could be altered to use medium rich binder and egg yolk instead of whole egg to optimise the response.

Although there was little change on light ageing, the effects of artificial thermal ageing at 60°C and exposure to pollutants was measurable. In the case of thermal ageing there was a shift in peak maximum position of the DSC curve to lower temperatures, indicating a lowering of the thermal stability of the paint tempera. Storage of the control sample in an atmosphere of 90% relative humidity resulted in a similar lowering of thermal stability. The azurite pigment itself is known to undergo conversion to the green pigment malachite at high humidity [17], and as shown in Fig. 2 malachite has a lower thermal stability than azurite. The effect on the pigment may therefore contribute to the overall lowering of peak temperature.

To quantify this effect for thermal ageing (shown in Fig. 1), the shift in peak temperature was measured and the results are given in Fig. 3. This shows the plot of the artificially aged and naturally aged samples. The strong response to thermal ageing and RH exposure can be seen compared to light ageing, and can in turn

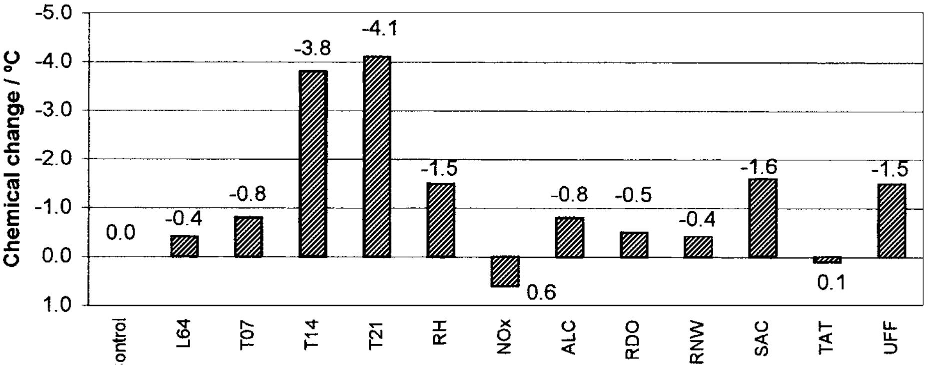


Fig. 3. Chemical change for artificially and naturally aged azurite tempera samples, defined as the shift in position, compared to the control sample of the main DSC peak.

be used to assess the environment at the sites. Of the naturally aged dosimeters, the largest response came from the samples exposed at Sandham Memorial Chapel (SAC) and the Uffizi Gallery (UFF), although the shift in each case was only of the order 1.5°C. The higher average temperature and high visitor numbers at the Uffizi Gallery, compared to the other sites, and the higher average values for relative humidity at Sandham Memorial Chapel could account for these observations.

In the case of pollutant exposure there was little peak shift as shown in Fig. 3. However, the overall shape of the DSC curve, particularly where the pigment contribution occurred, was visibly affected (Fig. 4). Exposure resulted in the growth of an exothermic feature at 315°C, as also reported in the smalt tempera samples, and a pronounced shift in temperature of the endothermic decomposition of the pigment from 320 to 335°C (Fig. 4). This shift in the endothermic decomposition could also be seen to a lesser extent in some of the site exposed samples, as shown in Fig. 4 for the Uffizi samples. Overall, this also serves to visibly broaden the exothermic DSC peak resulting from the binding medium decomposition. Additionally, in the pollutant exposed sample there was a reduction in intensity of the broad low temperature exothermic shoulder between 160 and 220°C, and the main peak itself. This may be explained by DTMS where it was found in unpigmented tempera that oxidation of sterols was less severe but hydrolytic processes affecting the ester bond were more prominent [1].

3.3. DMTA of azurite tempera

The shape of the DMTA curves is altered by thermal ageing and pollutant exposure but is less changed for light ageing (Fig. 5a), as observed in the DSC measurements. However, field site exposure (particularly in uncontrolled environments) resulted in much more significant changes than those seen on artificial ageing. In Fig. 5b the curves for ALC and SAC are shown alongside that of the control. A distinct sharpening of the peak and shift in peak position can be seen for these samples along with an evolution of structure on the higher temperature side of the transition. These changes were quantified by measurement of the ratio of the intensity of the tan δ transition at two fixed points, −10 and 6°C. This calculation is biased towards the effects of site exposure rather than thermal ageing where changes occurred at lower temperatures. It can be seen from the bar plot in Fig. 6 that ALC, UFF and SAC show the greatest degree of change.

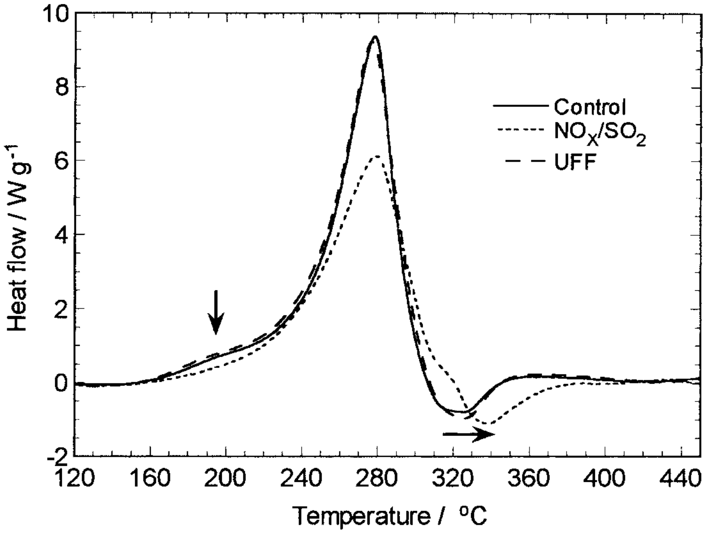


Fig. 4. DSC curves of azurite tempera control, NO_x/SO_2 exposed, and Uffizi Gallery samples.

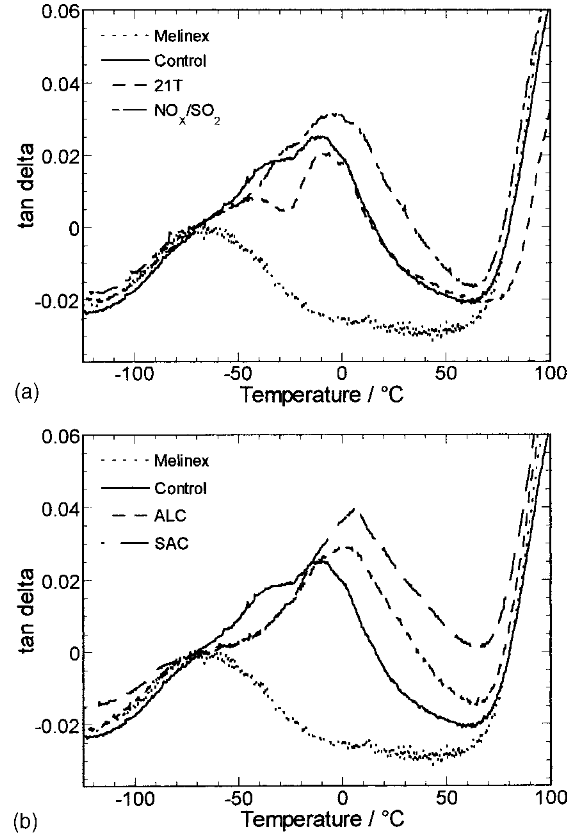


Fig. 5. Tan δ peaks for (a) artifically and (b) naturally aged azurite tempera samples.

3.4. XPS of azurite tempera

XPS survey spectra (in the range 0–1100 eV) were recorded (Fig. 7) to determine the surface elemental composition of the samples. The concentration of each element was determined from the relative area of its peak. Data are given in Table 1, together with the known elemental binding energies [18]. From Fig. 7 and Table 1 it can be seen that carbon, oxygen and nitrogen were the main elements detected, with carbon comprising approximately 80 at.% and oxygen between 10 and 15 at.% of the total. The main signal in azurite tempera came from the medium rather than the Cu pigment indicating that the pigment particles had been fully coated during preparation and were not exposed at the surface.

From the values obtained for oxygen and carbon concentrations O/C ratios were calculated (Table 2). A higher ratio indicates the presence of more oxygenated species, and therefore increased oxidation levels. It can be seen that the pigmented tempera control sample is significantly more oxidised than the unpigmented tempera control, which indicates that autoxidation processes have been occurring, catalysed by the azurite pigment. There is therefore less subsequent change on artificial light ageing in the azurite tempera than in the unpigmented tempera, and this is consistent with the lack of measurable change in the DSC curves on light ageing.

The calculated O/C ratios (Table 2) show that in azurite tempera a small amount of oxidation occurs with increased exposure to light ageing, but a greater amount occurs in the NO$_x$/SO$_2$ exposed sample. In the data for the naturally aged dosimeters (Table 3), O/C values for ALC and SAC are lower than for the TAT (Tate Gallery) dosimeter which appears to have a value that is higher than for the 64 days light aged sample. Lower values for ALC (El Alcázar) and SAC

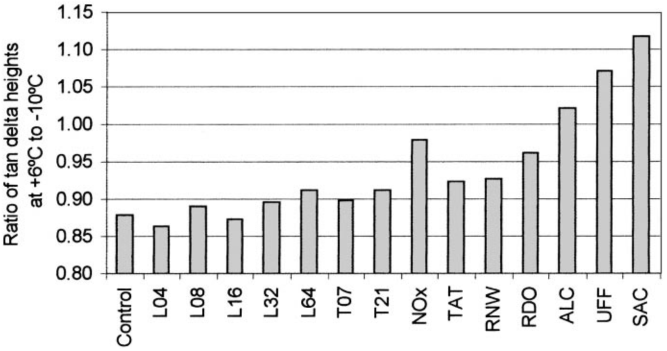


Fig. 6. The ratio of the tan δ values heights at (6°C−10°C) of naturally and artificially aged azurite tempera samples.

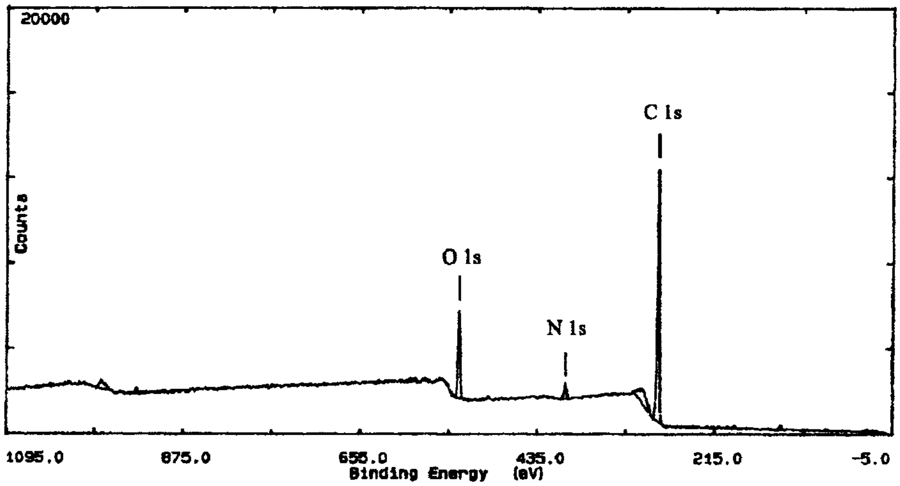


Fig. 7. XPS survey spectrum of azurite tempera control sample.

Table 1
Elemental concentrations (at.%) for azurite tempera samples from survey spectrum (0–1100 eV)

	Sample					
	C 1s	O 1s	N 1s	Cu $2p_{3/2}$	P 2p	S 2p
Binding energy (eV)	286.3	533.6	401.3	934.7	134.6	169.2
Azurite control (L00)	81.0	14.0	3.5	0.2	1.1	–
Azurite 16 days light aged	80.3	13.7	4.3	0.2	1.1	0.4
Azurite 64 days light aged	79.3	15.5	2.8	0.3	0.8	0.3
Azurite NO_xSO_2 exposed	76.9	16.4	3.8	0.6	0.9	1.0
Azurite ALC	76.6	17.9	2.4	0.6	0.9	0.6
Azurite SAC	83.3	14.9	1.5	0.2	Trace	–
Azurite TAT	77.2	16.4	3.4	0.2	1.0	0.7

(Sandham Chapel) samples can be explained in terms of the physical weathering of the surfaces. Evidence for this weathering can be seen in Fig. 9 and the increased levels of Cu for the ALC dosimeter (Table 1).

A high resolution scan (275–295 eV) of the C 1s peak of the azurite control tempera is shown in Fig. 8, with the different carbon species present being marked. This is evaluated on the basis that a chemical shift in binding energy occurs for carbon that is bonded to a functional group, because the binding energy of the core C 1s electron is influenced by its chemical environment. Curve fitting procedures are used to identify the individual components and to determine the amount of each component present, using known values of binding energies (e.g. for polymeric samples the C 1s peak for C–H occurs at 285.0 eV, and serves as a useful internal standard in polymer science [18]). Examples of C 1s binding energy shifts are shown in Table 4 [19].

Table 2
O/C ratios for tempera samples

Sample	L00	L16	L64	NO_x/SO_2
Azurite	0.174	0.171	0.195	0.213
Unpigmented	0.122	0.167	0.194	0.179

Table 3
O/C for Azurite tempera samples

Sample	TAT	ALC	SAC
Azurite	0.212	0.178	0.179

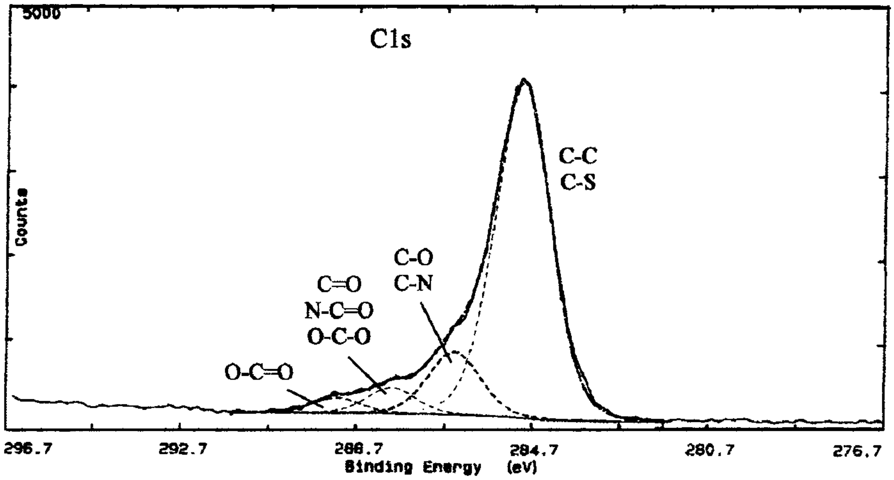


Fig. 8. High resolution XPS spectrum of C 1s peak for azurite tempera control.

Table 4
Some binding energy shifts for C 1s [19]

Compound	Binding energy (eV)
$(CH_2)_n$	283.3–285.3
RCH_2OH	285.5–287.5
RCH_2OR	285.8–287.8
RCOOR	288.0–290.0
RCOOH	288.1–290.1

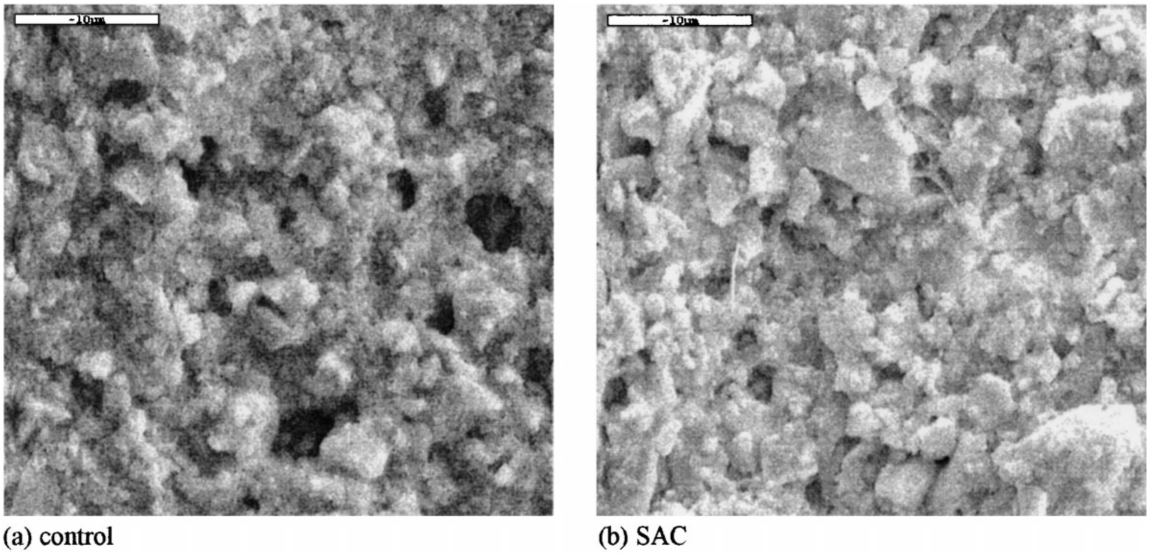
The data obtained from the C 1s spectrum, summarised in Table 5, quantify the change in composition in terms of the functional groups present. The SAC sample shows a decrease in C–O and C–N type bonds; ALC shows a decrease in C–C and C–S type bonds. Most significantly, in both ALC and SAC there is a noticeable increase in O–C=O type bonds (i.e. signifies increased presence of carboxylate groups), which can be linked to results obtained by FT-IR, where growth of new features in the carbonyl region of the spectrum was seen on ageing. DTMS also confirms the formation of long chain fatty acids [1].

Therefore, increased acidification of surfaces could be another parameter for estimating amount of chemical change or damage. SAC and ALC are uncontrolled sites (in northern and southern Europe, respectively), which have been shown by most of the other experimental techniques to be highly changed relative to the control. By contrast, TAT, which is a controlled environment that has been shown to exhibit little change, shows no measurable increase in carboxylate O–C=O bonds relative to the control.

A similar high resolution scan of the N 1s profile (390–410 eV) showed from the chemical shift that in the NO_x/SO_2 sample 34 at.% of the nitrogen was present as nitrate/nitrite with copper as a possible cation, whereas no nitrate/nitrite was detected in the other samples. The formation of inorganic salts (e.g

Table 5
Identity of C 1s functional groups for azurite tempera dosimeters (figures are in percentage of total carbon concentration)

	C 1s profiles of sample			
	C–C, C–S	C–O, C–N	C=O, N–C=O, O–C–O	O–C=O
Binding energy (eV)	285.0	286.5	288.0	289.0
Azurite L00	77	14	5	3
Azurite TAT	79	14	5	3
Azurite ALC	76	13	6	5
Azurite SAC	80	10	4	7



(a) control (b) SAC

Fig. 9. SEM micrographs (×3000) of azurite tempera (a) control and (b) Sandham Memorial Chapel (SAC) samples.

nitrates) can be linked to the appearance of the new exothermic feature at 315°C in the DSC curve of the NO_x/SO_2 exposed sample. The N 1s spectrum also provided a marker for nitrogen as protein and nitrogen as phospholipid on the sample surface. It was found that they were present in the approximate ratio of between 3.2:1 and 4.0:1 in all azurite tempera samples compared to 2.7:1 in the unpigmented tempera control sample. This difference may be attributed to some additional bonding which is known generally to occur between copper and proteinaceous species. High resolution scans of the S 2p showed that the sulphur was present entirely as Sulphoxide moieties in the aged samples, with some S–S species detected in the unaged or slightly aged samples. The SO_x type species is consistent with the presence of sulphate, sulphite or sulphonate, whereas the S–S type bonding would occur in proteinaceous species. Copper was present entirely in the cupric Cu^{2+} state, except in the unaged control sample where some Cu^{+} was also found.

3.5. SEM of azurite tempera

SEM images of azurite control and Sandham Memorial Chapel dosimeter are given in Fig. 9 (magnification ×3000). The rougher surface texture of the azurite tempera SAC sample compared with the control sample together with sharper definition of pigment particles shows that physical weathering effects have occurred, and the surface medium layer has been worn away, which is expected given the uncontrolled environment at this site.

4. Conclusions

Data from DSC and XPS confirm that artificial light ageing has only a small effect on azurite tempera compared with that seen in smalt and lead white temperas. Since copper catalysed autoxidation of the azurite tempera had already occurred during the curing stage as show by mass spectrometry. For future dosimeter design, it is clear that to obtain optimum response from DSC, a lipid rich medium (e.g. egg yolk only) and a paint tempera higher in medium content (than 13%) should be used. This may, however, weaken the DMTA response since a stronger response is generally observed with higher pigment loading [2].

DSC data reveal, however, show that azurite tempera is sensitive to thermal ageing, exposure to enhance humidity conditions, and to pollutant exposure. XPS confirms the impact of pollutant (NO_x/SO_2) exposure, with the formation of oxidation products and new inorganic compounds (nitrates/nitrites, sulphates) being detected on the surface. Thus azurite tempera paint acts as a useful chemical dosimeter. It discriminates between sites where environmental conditions are not well controlled (e.g. ALC + SAC), and those where there is better control (e.g. TAT + RNW). In this way it acts as an early warning device and damage assessment tool.

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