of deposition exceeds the rate of absorption, the water will begin to migrate down the wall (Fig. 19) (Robinson and Baker, 1975). The porosity of materials making up the building surfaces and elements will influence the wetting by concentrated rain deposit and runoff water, either as a film or as a concentrated stream. Highly porous surfaces and elements will become wetter than less porous materials and will stay wet longer (Amoroso & Fassina, 1983). The texture of the materials will affect the distribution of the flow, with irregular and concentrated streams tending to form on smooth or lightly textured materials, and in uniformly distributed broken flow more likely to form over heavily textured materials (Robinson and Baker, 1975).

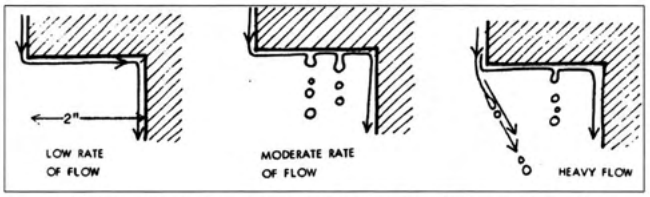


Fig. 19 - Observation of flow over a polished granite return (Courtesy of Robinson and Baker, 1975).

OCCULT PRECIPITATION: SOFT DRIZZLE, FOG AND DEW

The interaction between gaseous and particulate pollutants and the stone surface is strongly influenced by the presence of a liquid phase, which speed up any reaction. *Occult precipitation* occurs in particular circumstances such as soft drizzle, fog and dew, and it is providing sufficient moisture to chemically activate dry deposits without removing them thus turning out to be far more damaging than acid rain. The increased time of wetness also allow more time for the capture of airborne gaseous and particulate pollutants. Occult precipitation was investigated in some areas with special climatic conditions such as Venice and California. The deposition of moisture droplets on stone surfaces follows the same mechanisms discussed for particles. However, aerosol deposition is less affected by stone nature than SO_2 deposition (Furlan, 1991).

Fog is formed by smaller droplets than rain, consequently since the acid is less diluted, ion concentrations in fog are substantially higher than those found in rain samples and fogs are up to twenty times more acidic than rain. In order to explain these differences we must remember that (Brewer et al., 1983):

i) fog occurs closer to the ground level and therefore is exposed to greater concentrations of pollutants,

ii) fog droplets have smaller diameters thereby having a far greater combined surface area, permitting enhanced diffusion of ions or gases and therefore a higher final concentration,

iii) rainstorms are generally accompanied by the addition of fresh air masses. Hence, raindrops fall through an increasingly clean environment as opposed to fog droplets, which experience a more uniformly polluted environment.

8. Stone-atmosphere interaction for sulphur dioxide and the formation of black crusts

Both wet and dry deposition of pollutants can cause significant deterioration of exposed stonework. When atmospheric concentrations of pollutants are high, dry and wet fluxes will be greatest. This is especially valid for dry mechanisms which are intimately related to air quality in the immediate vicinity of the receptor surfaces. Dry deposition is a slower but more continuous process than wet deposition. The latter process imposes sudden but infrequent doses of pollutants, most of which will be in dilute solution. It is always possible that incident precipitation will wash off material previously deposited by dry processes and in highly polluted areas rainfall can promote the subsequent deposition of soluble gases and small particles to those areas (such as crevices) which remain moist.

There is no doubt that the largest contribution to the deterioration of stone are sulphur pollutants, especially SO_2. One of the fundamental questions is how SO_2 interacts with the stone, that is whether sulphites are formed first and subsequently oxidized or whether sulphates are the only reaction products (Charola, 2002).

Stone deterioration is a complex interactive phenomenon and cannot be understood simply in terms of the reaction:

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 + CO_2 \qquad (46)$$

The initial and the end products are well known but little is known about the intermediate steps. For conservation purposes it is very important to describe the different mechanisms through which the reactions take place. For this reason we have considered the different pollutants involved and their atmospheric chemistry. The crucial point is the oxidation of sulphur dioxide which can take place according to a number of mechanisms depending on different atmospheric conditions.

$$CaCO3 + \boxed{\begin{array}{l}\text{Oxidation of } SO_2\\ \text{-in the atmosphere}\\ \text{-on the surface}\end{array}} \longrightarrow CaSO_4 + CO_2 + H_2O$$

For instance in rural atmospheres uncatalyzed oxidation of SO_2 by ozone may domnate over the oxygen reaction in clouds with a pH 5 at a typical ozone concentration of 50 ppb. For urban fog, mixed-salt (manganese and ion chloride) catalyzed SO_2 oxidation is 1000 times faster than the uncatalyzed oxidation or the iron-catalyzed oxidation. Carbonaceous particles are also efficient catalysts in the sulphur dioxide oxidation. The various mechanisms have been described according to the present state of knowledge.

(i) Heterogeneous oxidation of sulphur dioxide in the aqueous phase

This is probably the most important process in sulphate formation and stone deterioration. Sulphuric acid formed according to this mechanism can reach the stone surface as droplets or can be formed on the surface in the presence of a liquid film.

(a) Oxidation in the atmosphere

In the first stage gaseous sulphur dioxide in air is dissolved in water droplets in clouds or fog. In the pH range of atmospheric droplets, between pH 3 and 6, SO_2 is 90% dissolved. The dissolution of SO_2 is a very rapid process, while the subsequent oxidation of SO_2 to H_2SO_4 is slower (second stage). Therefore, the rate-determining step in the overall heterogeneous SO_2 transformation is the oxidation. The latter takes place through catalysts, especially iron and manganese compounds. The sulphuric acid formation increases the acidity of the droplets and stops at pH values below 2, since SO_2 cannot dissolve further. Basic substances such as NH_3 increase the pH of the droplet, permitting further dissolution of SO_2, which is oxidized successively by catalysts into sulphuric acid. When

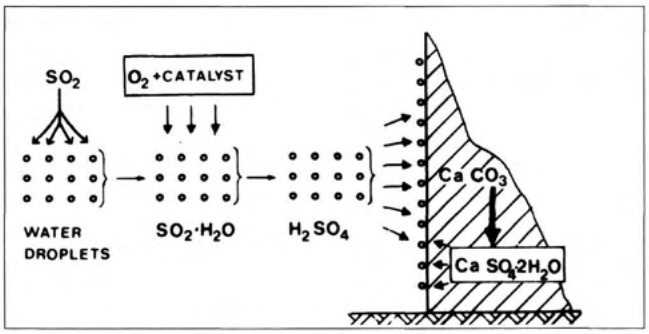


Fig. 20 - Heterogeneous sulphur dioxide oxidation in the atmosphere and subsequent attack by sulphuric acid on stone surface (From Amoroso & Fassina, 1983).

these acid droplets are deposited on the stone surface they transform calcium carbonate into gypsum (Fig. 20). The main stages in this process may be outlined as follows:

$$\underset{\text{dissolution}}{} \quad \underset{\text{oxidation}}{} \quad \underset{\text{attack}}{}$$
$$SO_2 \rightarrow SO_2 \bullet H_2O \rightarrow H_2SO_4 \text{ (droplets)} \rightarrow CaSO_4 \qquad (47)$$

(b) Oxidation on the surface

When there are temperature and humidity gradients near the stone surface, the surrounding air containing gaseous SO_2 is swept onto the surface and passes into the water deposited on the stone. If the amount of water is small, the SO_2 concentration will be very high. This highly concentrated pollutant solution can penetrate inside the stone at a depth which depends on the porosity of the stone and on the amount of solution available.

The transfer of SO_2 into solution is very rapid and is followed by the oxidation to sulphuric acid in the presence of a considerable amount of carbonaceous particles, which act as catalysts. In this case the pH of the solution cannot fall below 2, because it is continuously neutralized by the calcium carbonate of the stone. As a consequence, the basic nature of the stone allows the dissolution and oxidation of SO_2 to continue indefinitely, depending on the amount of SO_2 and water available (Fig. 21). The most active of the mechanisms involved in the formation of thick gypsum crusts appears to be the surface oxidation process.

ii) Homogeneous oxidation of SO2 to sulphate aerosol in the troposphere

This mechanism results from reaction with hydroxyl and other peroxy radicals. Simulations of SO_2 oxidation in polluted urban atmospheres suggest that these reactions can lead to removal rates of as high as 5% h^{-1}. Airborne sulphate thus formed can dissolve in atmospheric water droplets which are subsequently deposited on stone surfaces. Part of the sulphate in the droplets can be present as sulphuric acid, which is very aggressive on limestone. The main stages in this process may be outlined as follows:

$$\underset{\text{oxidation}}{} \quad \underset{\text{dissolution}}{} \quad \underset{\text{attack}}{}$$
$$SO_2 \text{ (gas)} \rightarrow SO_3 \text{ (aerosol)} \rightarrow H_2SO_4 \text{ (droplets)} \rightarrow CaSO_4 \qquad (48)$$

The probable overestimation of the maximum removal rate for SO_2 of close to 5% h^{-1} indicates that the rate of photoxidation of SO_2 is significantly below this value and is probably less important under atmospheric conditions.

iii) Dry deposition

When sulphur dioxide reaches the stone surface in gaseous form, its rate of adsorption depends on the nature of the surface. The rate of SO_2 uptake is a function of pH; therefore in the presence of calcium carbonate and a low amount of water (low relative humidity) calcium sulphite is formed.

This mechanism was confirmed by Gauri et al (1973) in laboratory experiments using marble specimens which were made to react with 3000 ppm SO_2. Other evidence for this mechanism was obtained by scrubbing sulphur oxides from power-plant stack gases with wet powder limestone. According to Mc Clellan and Mills (1973), when partially reacting in the slurry mixture, the calcite developed a very porous appearance.

$$CaCO_3 + SO_2 \xrightarrow{H_2O} \left\{ \begin{array}{l} CaSO_3 \bullet H_2O \\ \\ CaSO_3 \bullet 2H_2O \end{array} \right\} + CO_2 \qquad (49)$$

9. Principal decay patterns on Venetian monuments

During recent decades many authors have studied the forms of decay of building materials on different Venetian monuments (Fassina et al. 1976, Fassina 1978, Fassina 1988a, Fassina 1994c, Fassina 1999, Fassina et al. 2000, Lazzarini 1972, Lazzarini 1979, Marchesini 1970, Torraca 1969). The attempt to correlate the decay forms observed on buildings with atmospheric agents was systematically carried out since the UNESCO Venice campaign launched in 1971 for the safeguard of Venetian monuments which were decaying at an increasing rate during that period.

The rapid increase in industrialization and urbanization, which took place in the district of Mestre and Marghera at the beginning of fifties, sharply increased air pollutant concentration

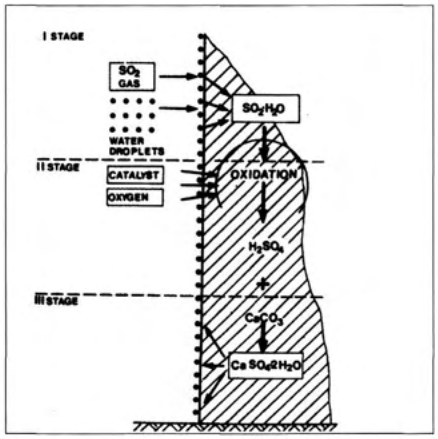


Fig. 21 - Heterogeneous suplhur dioxide on stone surface and subsequent attack by sulphuric acid (From Amoroso & Fassina).

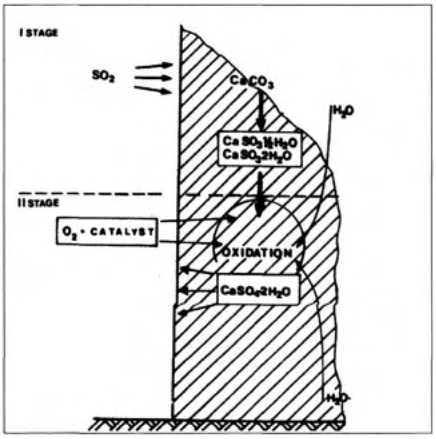


Fig. 22 - Adsorption of sulphur dioxide on stone surface by dry deposition (From Amoroso & Fassina, 1983).

in the atmosphere. Contemporaneously stonework built several centuries ago started to deteriorate very quickly as a consequence of increased air pollution.

In most Venetian monuments studied, stone decay was mainly ascribed to the transformation of calcium carbonate into calcium sulphate. To explain the mechanism of stone decay and black crust formation it is important to focus attention on the stone-atmosphere interface in order to estimate qualitatively and quantitatively the new-formation products and try to correlate them with the different decay features commonly observed on the facade of monuments. Characteristic marking patterns, defined in terms of *black and white areas*, are frequently observed and are generally correlated to different degree of decay due to the diverse mechanism of deterioration involved (Amoroso & Fassina 1983, Fassina 1994, Fassina et al. 2000).

The investigation was mainly focused on:

i) the new-formation products present in areas characterized by different morphologies of decay, ii) the mechanism of decay taking place on the most common lithotypes present on Venetian monuments, iii) the composition of rain and fog in Venice in relation to the building materials decay.

To assess the diverse processes of decay, surface samples of decayed stone were taken from several monuments according to the following criteria:

i) the degree of decay through a macroscopic observation, ii) the orientation of the individual architectural elements, iii) the exposure to direct rainfall (white areas), iv) the degree of shelter from rainwater (black areas).

The collection of fog water was carried out by using active collectors with a fan attachment, which draws the air laden with fog droplets into the collector.

To assess the different alteration products the following analytical methods were used:

i) cross-section to identify the different layers on the surface, ii) Scanning Electron Microscopy (SEM) providing morphological information on crystals, iii) X-ray distribution by Energy Dispersive Spectrometry (EDS) of chemical elements which allows determination of their origin in relation to conservation treatments carried out in the past or atmospheric pollution decay, iv) ion chromatography (IC) to determine qualitatively and quantitatively the water-soluble anions most harmful for stone decay.

Fog water composition

During a 5 year measurements campaign carried out in Venice from 1990 to 1995 it was assessed that fog formation occurred primarily during the late autumn and early winter months of November, December and January. Fog during these months, occurs almost twice as often during the night as it does during the daytime hours. Conversely, summer fog, occurs three times as often during the daytime hours as it does during the nighttime.

A comparison of the fog and rain sample data found in this study finds average concentrations of chlorides and sulphates to be 7-16 times higher in fog samples while concentrations of nitrates were discovered to be slightly higher than the rain samples (Fig. 23). This finding could be due to the fact that fog samples show the chemistry of the local air while rain tends to be more general in that it can represent air quality due to either long or short range transport (Fassina 1992, Fassina et 2002).

As regards the pH of fog samples collected only 13% of the events have a pH above 6, while the remaining ones showed a pH lower and in particular 65% have a pH between 3 and 5. In Fig. 23 the average pH values are reported.

The data show a predominant concentration of sulphates

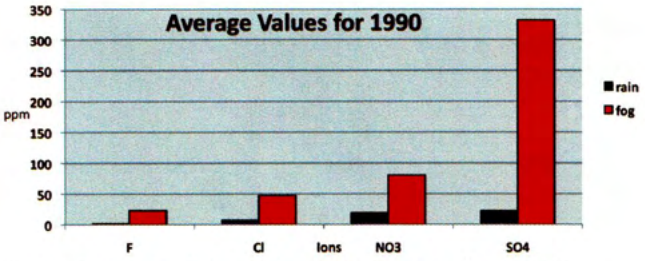


Fig. 23 - Comparison of rain and fog samples. Average values for 1990.

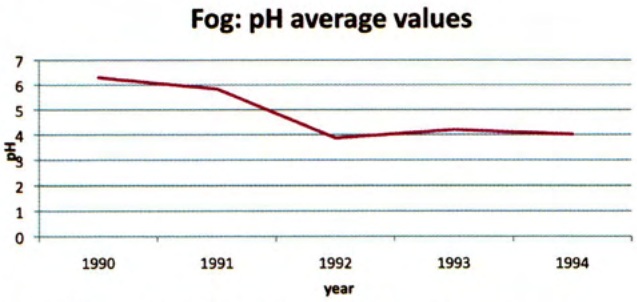


Fig. 24 - Average values of pH for fog during a five year period.

with respect to the other ions. In urban conditions generally nitrate concentrations are similar to the sulphate ones and as it is well known automobiles are the primary source of nitrates. In Venice the low amount of nitrates is ascribed to the lack of automobiles, while chlorides become predominant during fog events which are accompanied by wind blowing from the sea. In this condition fog incorporates sea salt aerosols dominated primarily by chlorides (Fassina & Stevan, 1992).

10. Mechanisms of decay in relation to exposure to rainwater: white washing, dirt accumulation, dirt wetting

On limestone building surfaces different situations creates a marked contrast between washed and unwashed areas. On the top and sides of an exposed face of a building deposition of rain is usually several times greater than over the remainder of the walls due to deflection of air and rain. This causes a *white washing* area. Sometimes on vertical surfaces a fairly even accumulation of dirt is observed except where some feature causes a concentration, tending to produce a lighter cleaner streak across the general pattern.

In ***white washing areas*** the formation of a surface skin is prevented because the stone is exposed to the washing action of the rain, which has the effect of removing both the soluble compounds and the deposited soot.

In places sheltered from the rain, dirt can accumulate as incoherent stratification, as an incoherent powder adhering to the stone, or as incrustations strongly bound to the surface. These surfaces are black due to the collection of black carbonaceous particles and other atmospheric particles and represent a growth zone in which the transformation of calcium carbonate into gypsum takes place. A close observation of sheltered areas shows two different morphologies of deterioration which are defined as *dirt accumulation and dirt wetting.*

Dirt accumulation takes place far from rain washing areas and is characterized by black superficial deposits that grow on the surface due to the collection of atmospheric particles and to the transformation of calcium carbonate into gypsum (Robinson & Baker, 1975).

Dirt wetting takes place at the interface between running water and sheltered areas. The thick and hard crust has a

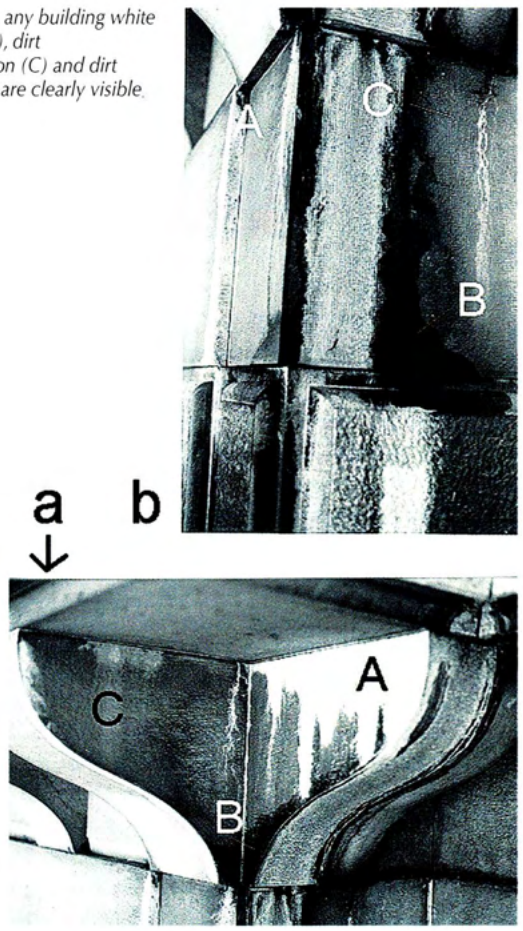


Fig. 25 - On any building white washing (A), dirt accumulation (C) and dirt wetting (B) are clearly visible.

Fig. 26 - The main Portal of Saint Mark's Basilica showing the blackening of surface in sheltered areas.

Fig. 27 - The main Portal after restoration carried out in 1983-85.

rough and spongy appearance and grows upon the original surface. According to our observation *dirt accumulation, dirt wetting and white washing* are generally present together on any buildings as it is schematically represented in Fig. 25.

In order to assess if there is a relationship among the marking patterns above described and the composition of deterioration layers occurring in the different areas, many samples were taken from some monuments in correspondence to the observed features. The quantitative analytical data collected has allowed to build a simple model to explain in a general way the decay phenomena.

This simplified model was then tested on several Venetian monuments in correspondence to the features visible on stone surfaces. The quantitative analyses carried out on stone samples, taken from diverse areas, stressed that sulphates are present in different amounts according to the degree of sheltering irrespective of differences in stone texture-structure.

As example of application two important studies are now considered:

a) the main portal of the St. Mark's Basilica (Fassina, 1988b),

b) the Portal of the SS. Giovanni and Paolo Church (Fassina, 1992),

a) Main portal of the St. Mark's Basilica (Figs. 26, 27)

- The extent of sulphation in protected areas was found to be depending on the distance from the rain washing areas.

- *dirt accumulation* takes place far from running water and shows a thin deposition of black carbonaceous particles and the extent of sulphation is generally less than 40%,

- *dirt wetting* is located at the interface between washed and unwashed areas and shows a very thick and rough black dendrite-shaped crust and the extent of sulphation is larger than 40%.

Table 6. *Percentages of soluble sulphates from samples taken from the third arch, representing the Arts and Crafts, from the main Portal of Saint Mark's Basilica.*

Arts and Crafts	Sample	Sulphates (%) Black crust dirt wetting	Sulphates (%) black deposit dirt accumulation
Bakers	SM1	67.3	
Bakers	SM2		40.3
Bakers	SM3	56.4	
Bakers	SM15	60.9	
Butchers	SM4	56.8	
Butchers	SM5		29.6
Butchers	SM16		32.5
Milkmen	SM6	59.5	
Milkmen	SM7	60.8	
Bricklayers	SM8	62.4	
Shoemaker	SM9	52.7	
Shoemaker	SM14	60.7	
Barbers	SM11	69.7	
Joiners	SM12		37.3
Joiners	SM13		40.5
Sawyers	SM18	69.9	
Blacksmiths	SM19		43.7
Blacksmiths	SM20	52.4	
Fishermen	SM21		32.6
Fishermen	SM22		41.5

In the panel of Bakers the different decay areas, white washing, dirt accumulation and dirt wetting are clearly visible (Figs. 28 e 29 a, b, c):

b) Portal of SS. Giovanni and Paolo church

The macroscopic observations on the Portal of SS. Giovanni and Paolo Church show different types of deterioration depending on the geometry of the Portal, that is due to the degree of shelter from rainwater (Figs. 30 a, b, c).

From quantitative data it can be seen that there are a low concentrations of sulphate on the external arch of Istrian Stone (Table 7) where running water washes pollutants from the surface and prevents the accumulation of significant amounts of sulphate. The second and third arches, respectively of Verona red stone and saccharoidal marble (fine grained), show intense sulphation due to their sheltered position.

The fourth and fifth arches, of Istrian stone, show, however, lower degrees of sulphation.

A similar decrease is found in the sixth and seventh arches which are made, respectively, of Saccharoidal marble (large grained) and Verona red stone.

Table 7. *Sulphate percentage in the dirt wetting and dirt accumulation areas.*

Sample lithotype and description	Dirt wetting (%)	Dirt accumulation (%)
I arch-SGP1-Istrian stone-black deposit		12.4
II arch-SGP2-Verona red stone-black crust	45.0	
II arch-SGP3-Verona red stone-black crust	52.0	
III arch-SGP4-White marble, fine grained-black crust	41.3	
III arch-SGP5-White marble, fine grained-black crust		8.6
IV arch-SGP6-Istrian stone-black scales		14.9
IV arch-SGP7- Istrian stone-black deposit		12.7
IV arch-SGP8- Istrian stone-black deposit		9.5
VI arch-SGP9-White marble, large grained-black scales		11.2
VII arch-SGP10-Verona red stone-black deposit		21.9
VII arch-SGP11-Verona red stoneblack deposit		6.9

The quantitative data offer a clear picture of increasing sulphation, with increasing degree of sheltering until a certain point (second and third arches). From this point onwards, moving towards areas more sheltered decreasing sulphation is observed. This apparent contradiction is explained by taking into account that in black areas two different morphologies of decay are distinguishable which are dependent on the distance from the rain washed areas (Fassina, 1992):

-the dirt-wetting area takes place at the interface (second and third arches) (Fig. 30 a e b) between running water (first arch) and the more sheltered areas (fourth and subsequent arches). The thick and hard black crust has a rough and spongy appearance and grows with respect to the original surfaces.

Fig. 28 - In the panel of Bakers the dirt accumulation area (C) is grey-black in colour and deposition of carbonaceous particles occurs, whereas the dirt wetting area (B) shows the formation of a thick, rough, black debdrite-shaped crust which grows upon the original surface.

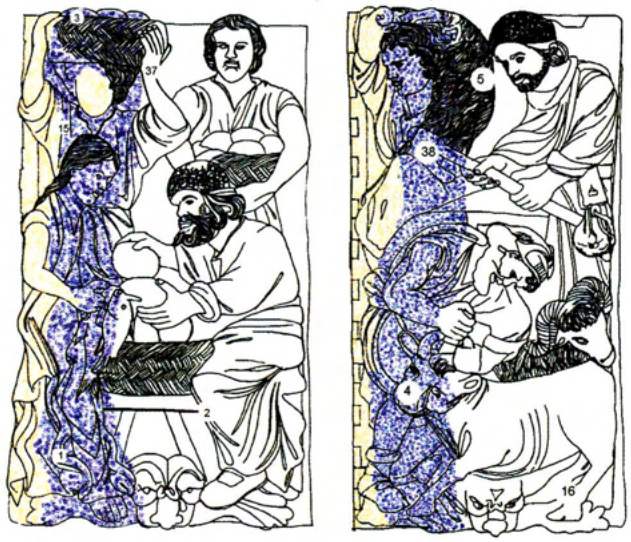


Fig. 29 a, b - Bakers' and Butchers' panels showing the three different decay areas: dirt wetting area is in blue, while dirt accumulation is in white.

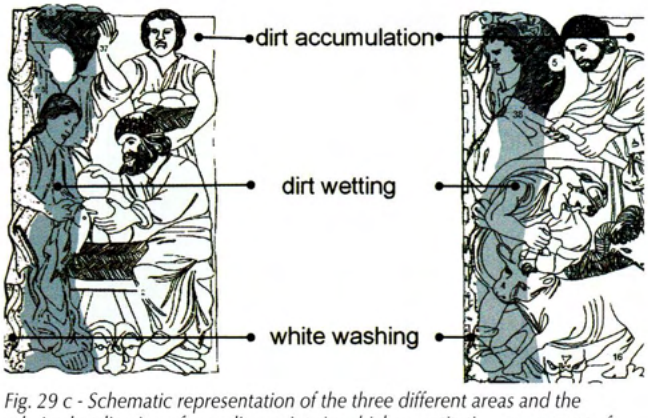


Fig. 29 c - Schematic representation of the three different areas and the relative localization of sampling points in which quantitative assessment of sulphation was carried out.

Fig. 30 a - Portal of the main facade of SS. Giovanni and Paolo church. Sulphation is dependent on the degree of shelter from rainwater.

Fig. 30 b - Detail of the portal with the localization of sampling points.

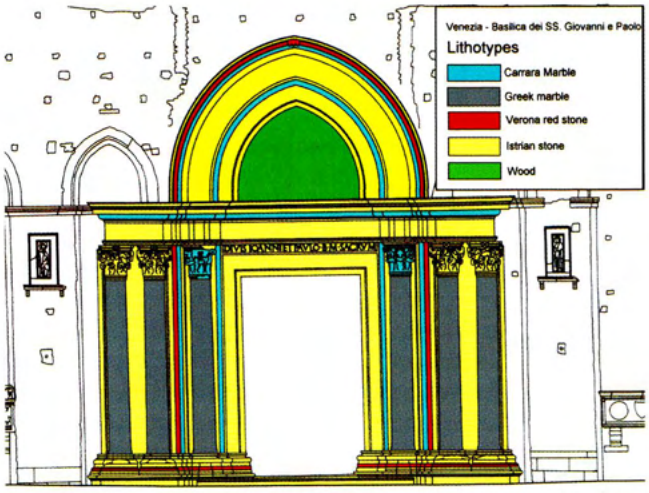


Fig. 30 c - Schematic representation of stone materials: Istrian stone in yellow, Carrara marble in blu, Verona red stone in red, Greek marble in grey, wood panel in green.

-dirt accumulation takes place far from rain washing areas in well-sheltered areas (fourth and subsequent arches) and is characterized by black superficial deposits that accumulate on the surface due to the deposition of atmospheric particles

11. Forms of decay in relation to different rock texture and structure properties: e.g. Istrian limestone and marble

Observations carried out on many Venetian monuments have shown that each lithotype decays differently according to its textural and structural properties. A typical example is represented by Istrian stone and marble, which are the materials most commonly used in built monument.

Istrian stone is very compact limestone characterized by a very low porosity (0.25-0.33 $cm^3/100g$), which presents three types of weathering: white superficial deposits, black superficial deposits, and dendrite-shaped black crusts.

-*White superficial deposits* were classified as *white washing*. A careful observation of the white areas indicates that these are always associated with running water and airborne particles which are deposited among rain episodes are washed out by the next ones and any gypsum cement which has started to precipitate is dissolved: in this case, the surface may show evidence of loss of material together with erosion features. Furthermore the formation of a white thin layer tightly adhering to the stone is due to the continuous reaction between acidic water and the stone surface.

According to many authors the whiteness of limestone surfaces was ascribed for a long time to sulphation processes. In order to ascertain the mechanism of whitening formation many samples were taken from white areas and were observed at the optical microscope and analyzed by X-ray diffraction and ion chromatography.

An optical microscope observation show that a thin re-crystallization white layer is present above the limestone. As the ion chromatography data showed the presence of low amounts of sulphates, less than 1%, and X-ray diffraction analysis showed the absence of gypsum and the presence of calcium carbonate it can be concluded that this white layer is due to re-crystallization of calcite previously dissolved by acidic water according to the well known reaction:

Gas-phase carbon dioxide dissolution

$$CO_2+H_2O \rightleftharpoons H_2CO_3 \qquad (50)$$

Leaching action of acidic water in run-off areas

$$CaCO_3+CO_2+H_2O \rightarrow Ca(HCO_3)_2 \qquad (51)$$

re-precipitation of bicarbonate and whitish new calcite layer formation

$$Ca(HCO_3)_2 \rightarrow CaCO_3+CO_2+H_2O \qquad (52)$$

In this case the high solubility of calcium sulphate does not allow the formation of a thick gypsum layer.

Charola (1988) provides a general discussion of the various factors affecting the acid dissolution rate of calcareous materials: below pH 4, the dissolution is transport-controlled, while between pH 4 and 6 the reaction appears to be controlled by surface kinetics and influenced by other factors such as hydrodynamic flow and the pressure of CO_2.

ii) *Black areas characterized by superficial deposits* were classified as *dirt accumulation*. Black deposits show the presence of carbonaceous particles mixed together with gypsum crystals (Fig. 31a). If the surface is very compact then gypsum formation affects the stone only in the superficial layer without penetrating in depth, as it is clearly visible in Figs. 31 b, c.

The presence and growth of gypsum black crusts above the surface of materials consists both in the continuous supply of atmospheric particles and in their cementation by gypsum crystals originating from the reaction between atmospheric SO_2 and calcium ions present in the fog droplets or in calcium-rich particles present in the air (calcite and gypsum). A supply of calcium from the substrate, even if present in mobilized form, is not indispensable as demonstrated by the presence of gypsum crusts on bronze outdoor artifact.

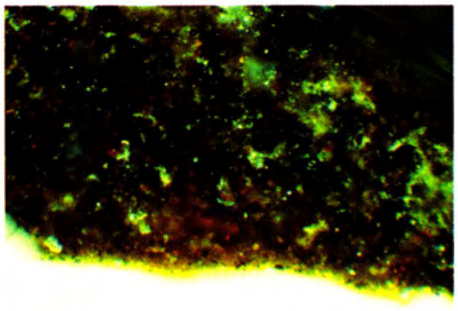


Fig. 31 a - At the optical microscope numerous black spherical carbonaceous particles are with few red oxide aggregates are visible on the white stone.

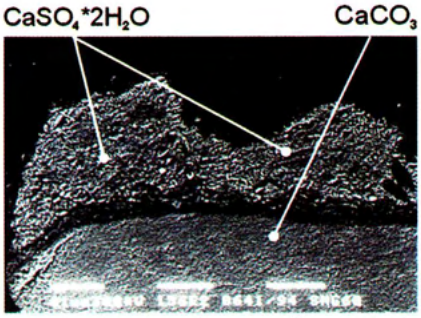


Fig. 31 b - Black areas characterized by superficial deposits were classified as dirt accumulation areas: at SEM observations gypsum formation on compact limestone is forming on the surface without damaging the stone surface beneath.

Fig. 31 c - X-ray map of sulphur distribution shows the localization of gypsum on the surface.

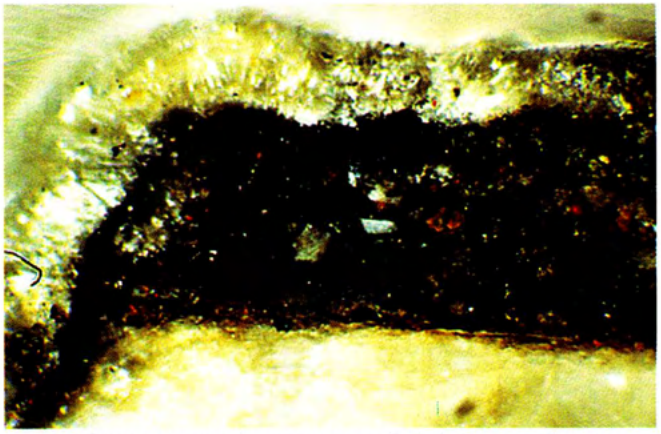


Fig. 32 - White gypsum crystals growing perpendicularly to stone surface are clearly visible. A thick and black layer of carbonaceous particles is also observed.

iii) *Black areas characterized by dendrite-shaped crust* were classified as *dirt wetting*. These are generally present on sheltered areas and have a rough and spongy appearance and a thickness of 3-5 mm. Under the optical microscope, a close observation of the crust shows the formation of many gypsum crystals growing perpendicularly to the stone surface. The black crust is forming without any damage of the beneath stone surface, which was originally exposed to the atmosphere (Figs. 32 and 33). The very low porosity of the stone does not allow any penetration of pollutants, such as sulphuric acid, but only a superficial interaction, which causes the transformation of the calcium carbonate into gypsum. The increase in roughness of the surface is ascribed to the higher molecular volume of the gypsum, which is double that of the calcium carbonate. When the stone surface presents microcracks or contains abundant clay impurities along the sedimentation beds a penetration of sulphuric acid solution can occur causing the formation of a white gypsum powder in the interstices between scales provoking the exfoliation of the stone.

Saccharoidal marbles are very pure metamorphic limestones, characterized by a crystalloblastic structure and calcite crystals with a density between 0.85 and 1.25 $cm^3/100g$.

According to Kessler (1919), thermal changes can cause a permanent expansion of marble very probably due to a slipping of the individual calcite crystals one on another. According to Marchesini et al. (1972) the weathering of marble is at first purely physical, due to the increase in the porosity caused by thermal changes. For instance, in experiments carried out on different types of saccharoidal marbles the porosity increased by up to 40-50% of the original material, when they are subjected to fluctuations of temperature of 50°C. The increase of porosity is

Fig. 33 a - Sampling areas.

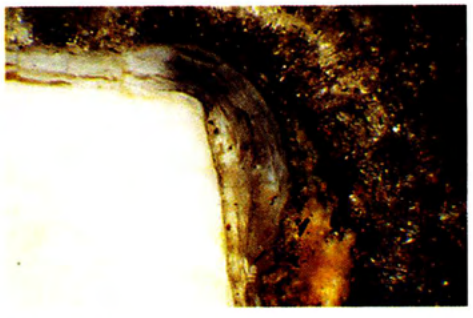


Fig. 33 b - Gypsum crystals and black crust formed compact limestone surface without penetrating inside it.

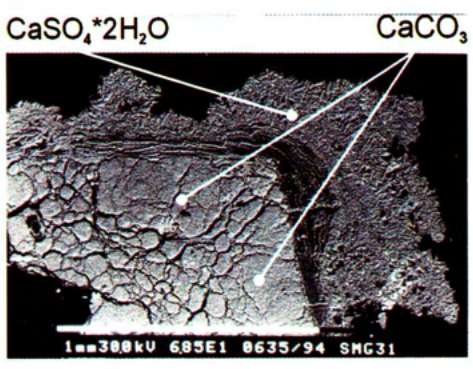


Fig. 33 c - At SEM the formation of a massive crust is observed favoured by re-crystallization of gypsum due to wetting and drying cycles. The thickness of the crust is proportional to the period of exposure and the frequency of wetting and drying cycles.

Fig. 34 a - Marble exposed to weathering agents. Dechoesion of calcite crystals due to thermal changes is visible.

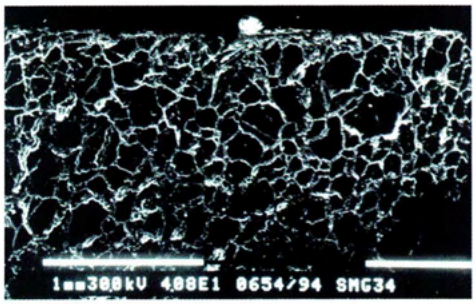
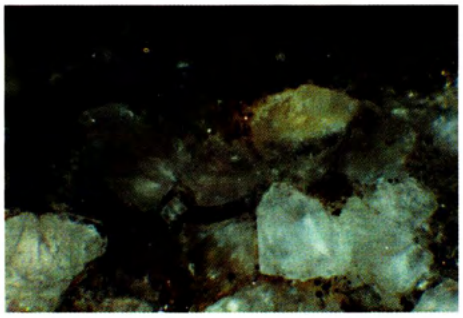
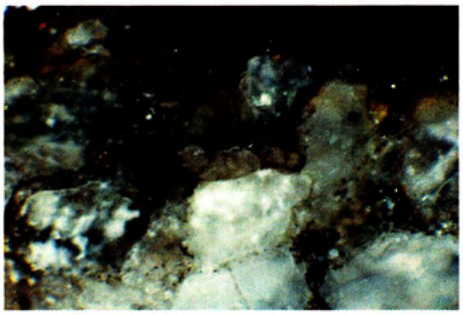


Fig. 34 b - At SEM observation marble calcite crystals are clearly visible.

Fig. 37 - Portal of SS Giovanni and Paolo church. Carrara marble is strongly decayed due to marble sulphation process. At the latest stage crumbling of black crusts of different size show white areas of the underlying white marble which is now exposed to air acidc pollutants.





Figs. 35 & 36 - At optical microscope detachment of calcite crystals is clearly visible. In the intergranualr spaces carbonaceous particles and other particulate pollutants can penetrate causing further decay as a result of chemical reactions of sulphuric acfid solution anf the edges of the calcite crystals.

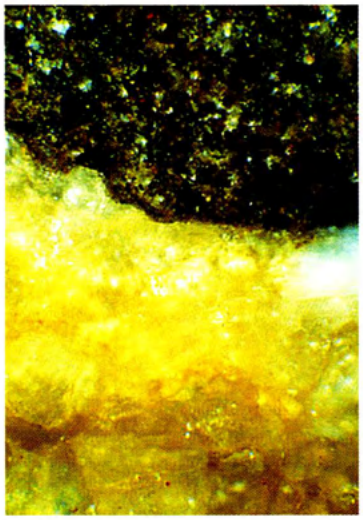


Fig. 38 a - Optical microscope observation of black carbonaceous particles.

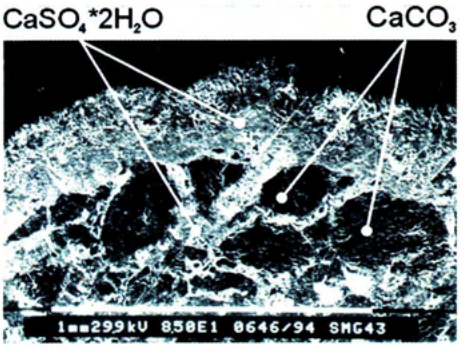


Fig. 38 b - At SEM observation gypsum crystals are located on the surface as well as in the inner part of the stone .

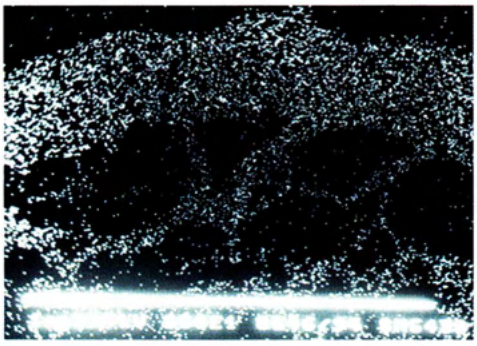


Fig. 38 c - X-ray map of sulphur distribution shows the presence of gypsum on the surface and between marble grains.

caused by the marked anisotropy of calcite crystals, it means that when an increase of temperature takes place the crystal expands in one direction and contracts in the transverse direction. Such movements cause an internal cleavage of crystals and detachment of one crystal from another.

Other agents easily attack saccharoidal marbles, which have suffered an increase in porosity; in particular the circulation of water containing soluble salts is favoured by the increase in porosity.

Among the disaggregated crystals the penetration of water containing pollutants from the atmosphere cause a reaction between calcite crystals and the solution (Marchesini et al. 1972, Fassina 1993).

A careful examination of Carrara marble from the Basilica of St. Mark (Fassina, 1988 a,b, Fassina 1999), the Portal of SS. Giovanni and Paolo church (Fassina 1992 a), Pilastri Acritani (Fassina et al., 1993 a), Madonna dell'Orto church (Fassina et al., 1994 a), Ca' d'Oro facade (Fassina & Rossetti 1994 b, Fassina 2001) indicates the presence of three different morphologies of deterioration.

i) Superficial granular disaggregation on the surfaces directly exposed to rainwater (white washing) is mainly ascribed to natural agents, such as thermal changes, and is strongly accelerated by the decreasing pH of acid rain of urban polluted environment (Figs. 34 a,b).

ii) Black superficial deposits (dirt accumulation). Under the optical microscope thin layers of black deposits appear to be formed by a very dark external layer which progressively becomes less dark moving towards the inner part of the marble.

iii) Dendrite shaped-crust mainly located in sheltered areas (dirt wetting) is caused by the transformation of calcium carbonate into gypsum which is more active than in other areas (Fassina 1994c). The microcracks generated by thermal changes are easily penetrated by sulphuric acid solutions, which attack the edges of calcite crystals to form calcium sulphate. The final result is a disaggregation of calcite crystals (Figs. 35, 36) and the crumbling of large pieces of marble exposing the underlying surface to the aggressive action of atmospheric pollutants. The emerging surface is white and lacks cohesion (Fig. 37).

The mechanism above described was found on numerous samples taken from sheltered positions and is easily recognizable under optical microscope and SEM. Cross sections of altered layers generally show the presence of:

-an external layer which was in contact with the atmosphere

which contain a generous deposition of carbonaceous particles (which are easily recognizable under the optical microscope) (Fig. 38 a) and gypsum crystals (which can be recognized by X-ray map of sulphur).

-under the dark external layer calcite crystals appears detached (Fig. 38 b) SEM observations and X-ray maps show the presence of gypsum crystals, which are formed by reaction of calcite crystals and sulphuric acid penetrated in microcracks.

In Fig. 38 c it is possible to observe the penetration of pollutants from the atmosphere, black carbonaceous particles and gypsum crystals. Under SEM the microcracks appear filled with microcrystals with no easily recognizable habit and their sizes are very small in relation to calcite crystals (Figs. 38 b, c).

Many X-ray maps of sulphur were carried out to test the hypothesis that intergranular spaces are filled with crystals resulting from the chemical transformation of calcite due to sulphuric acid attack (Fig. 38 c).

The primary gypsum forms on calcite crystal surfaces along the intergranular spaces; it is found at progressively deeper locations below the surface with increasing duration of exposure to the polluted atmosphere. In sheltered areas gypsum formed on marble surface builds a massive crust, the thickness of which is proportional to the period of exposure and the frequency of wet-to-dry cycles (Figs. 39 a, b, d).

A schematic representation of the mechanism of black crust formation is reported in fig. 40. In dirt wetting areas calcium carbonate is transformed into gypsum which is growing upon the original surface (I stage). Subsequently gypsum penetrating inside the pores causes de-cohesion of calcium grains and detachment of large pieces of marble. Within the marble the edges of calcite crystals show an erosion due to then aggressive attack of sulphuric acid (II stage). In white washing areas running water causes erosion of the surface due to the transformation of calcium carbonate into calcium bicarbonate (II stage).

BLACK SLABS OR CRUSTS DETACHMENT

White grey and black jigsaw-like patterns has been observed due to the process of continuous detachment of small black slabs from a façade leading to the exposure of white stone parts that again darken progressively with time, being subjected to airborne particulate deposition. Detachment of black slabs occurs through a significant loss of material together with unacceptable surface recession of the building façade (Figs. 41 a, b).

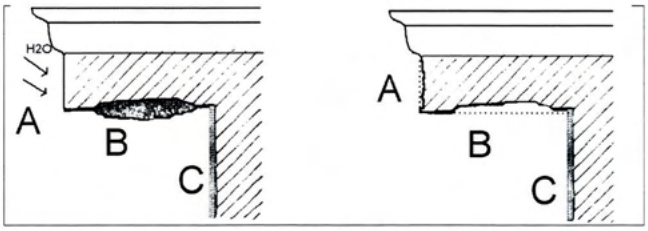


Fig. 40 - Schematic representation of the mechanism of black crust formation in sheltered areas.

I stage
A) white-washing areas
B) black dendrite-shaped crust (dirt wetting).Gypsum formation and accumulation of carbonaceous particles.
C) grey-black deposits due to accumulation of carbonaceous particles (dirt accumulation)

II stage
A) missing material due to run-off (white washing)
B) detachment of black crust together with original material due to the progressive decohesion of calcite grains and to mechanical stresses occurring inside the pores during cyclical crystallization of gypsum (dirt wetting)
C) grey-black deposits continue to accumulate carbonaceous particles (dirt accumulation)

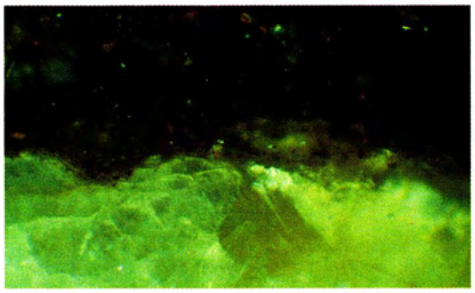


Fig. 39 a - Optical microscope observation shows black carbonaceous particles.

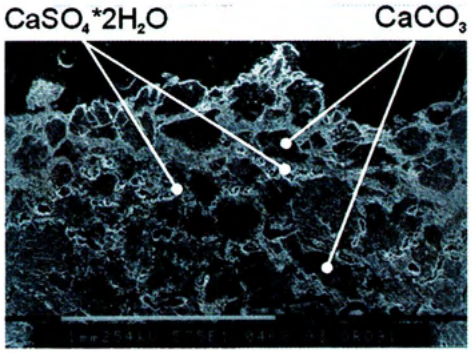


Fig. 39 b - Beneath the external surface calcite crystals appear detached.

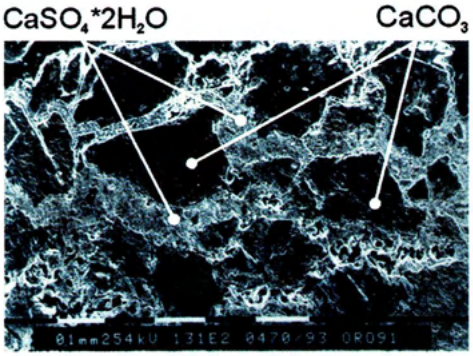


Fig. 39 c - Small crystals inside the intergranular space left by dechoesion of calcite crystals.

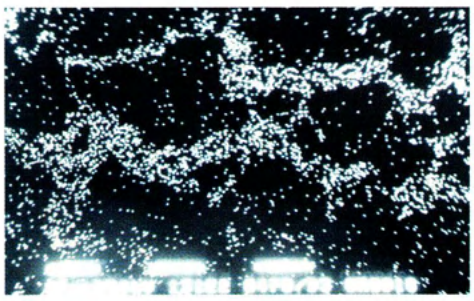


Fig. 39 d - X ray map distribution of sulphur shows the presence of gypsum in the intergranular space.

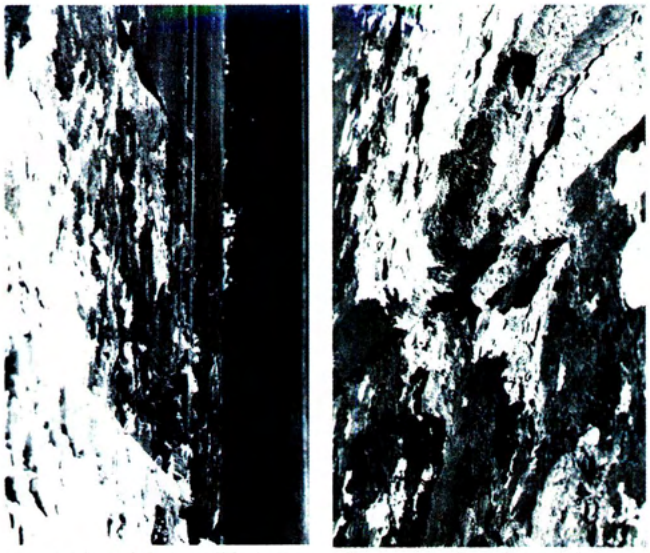


Fig. 41 a, b - Exfoliation of black crusts and subsequent loss of material.

Fig. 42 - Gypsum nucleation on carbon particles

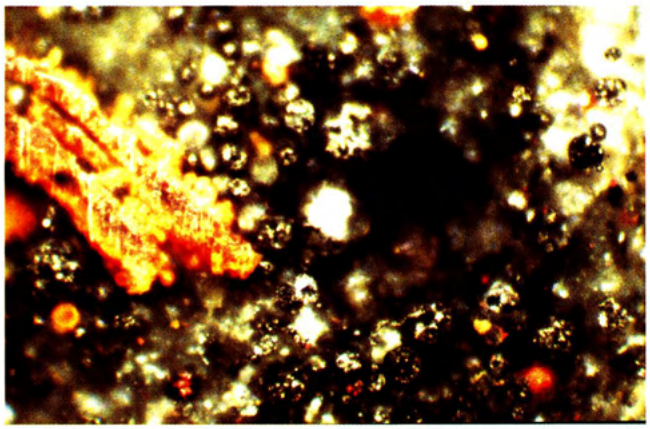


Fig. 43 a - At the optical microscope black carbonaceous and red iron oxides particles are clearly visible.

Fig. 44 a - Black crust on Carrara marble in the Portal of SS. Giovanni and Paolo Church.

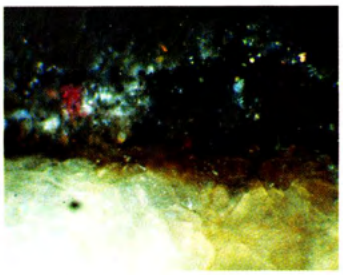


Fig. 44 b - Gypsum crystals and black carbonaceous particles at the optical microscope.

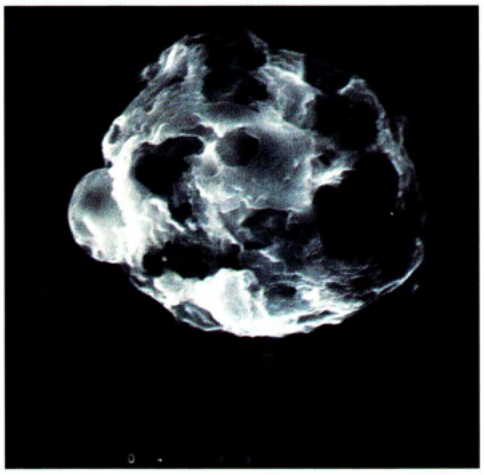


Fig. 43 b - At SEM porous carbonaceous particles detected by air filtration on cellolose acetate filters.

12. Airborne particles in the atmosphere and in the black crusts-Smooth and spongy particles

According to many authors (Camuffo et al., 1982; Camufo et al., 1983; Camuffo 1994, Camuffo 1990; Fassina et al. 1976; Fassina 1978; Fassina 1993; Fassina 1994) carbonaceous particles are very active in forming black crusts when they are wet, because they contain both sulphurous compounds and catalysts. They can also absorb SO_2 from the atmosphere and can serve to nucleate gypsum crystals. Thus the gypsum in the crust is partly due to the transformation of calcareous surface and partly contributed from particle deposition and nucleation (Fig. 42).

Pollutant particles present in the Venetian area were studied by means of optical microscope and SEM examinations of filter papers. Carbonaceous particles having a spherical and globular shape, a sparkling appearance and a variable diameter between 7 to 40 microns were the most prevalent. Less abundant particles, with a earthy yellow or brown appearance and iron-based compounds were also detected (Figs. 43 a, b)

As regards the black carbonaceous particles the smallest particles often formed aggregates, while the larger uniform, opaque ones, which in some cases surpass one millimetre, are less numerous. Rarer yet are the small spheres not identified at the optical microscope, having the following characteristics: metallic in appearance, bronze coloured, highly reflective, with a diameter from 30 to 80 microns. By means of chemical attack some of the particles were isolated and examined by using a SEM-EDAX. Alongside the EDAX spectrum shows , as well as clearly prevalent quantities of silicon and aluminum indicating an alluminosilicate composition.

On the black crusts (Fig. 44a) the optical microscope observations show that the most abundant component are carbonaceous particles, which are mainly spherical with a glass-like transparent or opaque appearance and their dimensions correspond well with the ones already observed in the filters. Carbonaceous particles are sometimes rounded and sometimes linked together to form large, irregular aggregates (Fig. 44b).

For more precise identification, the same samples were analyzed by a SEM interfaced with an X-ray dispersive energy analyzer (EDAX). At high magnification of spherical particles of different size and appearance can be distinguished. The particles are typical in shape (SEM), size (SEM), colour (optical microscope) and chemical composition (EDAX)) of incomplete combustion of coal- or oil-fired power plants.

Two different types of spherical particles can be distinguished: the smooth ones (typical of coal combustion) and the porous ones (comes from the combustion of oil-fired fuel) (Cheng et al., 1976).

i) During combustion minerals containing alluminosilicate and iron compounds melt and form liquid drops, which during emission in the chimney are rapidly cooled, and form glass spheres. Those with a smooth surface have a metallic composition: the prevailing components are silicon and aluminum (Fig. 45) with minor components of iron always present (Fig. 46), together with other metals such as titanium or copper.

Among the non-metallic components are significant amounts of calcium and sulphur. The composition of these smooth particles is typical of allumino-silicate compounds which come from clayey impurities in original fuels.

Sometimes smooth spherical particles entirely formed of

iron can be found. Pure iron particles are less frequent than the silicon/aluminum spheres.

Non-metallic contributions of calcium and sulphur are always present, and indicate the potential of these particles for the formation of gypsum crystals on their surfaces.

This process is clearly visible on the stone surface, but it does not appear to be very important as a nucleating process as was emphasized by some authors.

Fig. 45 - Smooth alluminosilicate-based particle.

Fig. 46 - Spherical iron-based particle.

ii)The second type of particles, the porous ones are characterized by a rough surface completely different to the smooth one previously described. The surface cavities have different size and different depth and the specific surface of the particles is very high with respect to a smooth spherical particle having the same radius (Figs. 47 a, b, c).

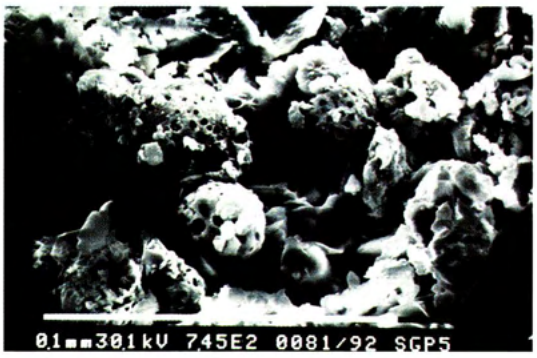
This property is very important and from an industrial point of view it is very well known that the use of carbonaceous particles favours oxidation processes.

A logical consequence of this behaviour is to ascribe to carbonaceous particles a fundamental role in the formation of sulphuric acid which in turn causes the gypsum formation (Fig. 48).

The porous carbonaceous and the smooth spherical particles of aluminum and silicon are very active as catalysts in the transformation of calcium carbonate into gypsum. In this case the degree of sulphation is higher than in the superficial deposit and reaches in some cases the value of 60%. The analyses carried out on white areas confirm the inhibition of skin formation in exposed positions.

Black fly-ash emitted by coal and heavy oil combustion processes: contain significant amount of sulphur together with elements such as V, Ni and Fe which act as catalyst in the sulphation reaction (Lefevre, 2002).

The embryonic stage of black crust formation can be observed: fly-ash particles are anchored to the surface of the stone through precipitation of gypsum crystals. These crystals are present on the surface of the fly-ash and on the surface of the surrounding stone (Ausset et al., 1999).



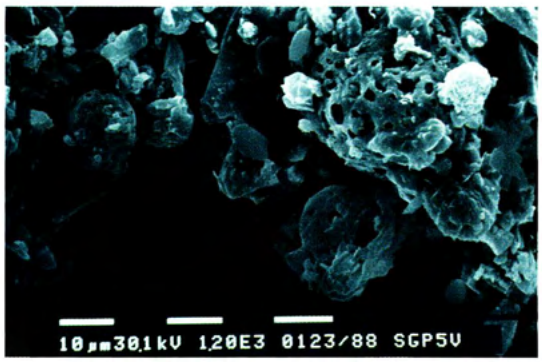


Fig. 47 a, b, c - Carbonaceous particles at SEM.

Memory effect

In the Basilica of Saint Mark the amount of sulphates found at the beginning of seventies with the ones analysed 15 years later has been compared. The increasing amount of sulphates, from 40% to 60%, showed that the sulphation process was still active, notwithstanding that in the same period the sulphur dioxide concentration in the Venetian environment was drastically reduced, due to reduced emission of industrial pollutants and the substitution of oil by methane in domestic heating systems.

This is only an apparent contradiction because the building materials are affected by the so-called *memory effect,* which means that the decay processes are strongly influenced by the cumulative exposure of materials to the environment. Certainly the decrease in environmental pollution represents a positive step in slowing down the decay processes, but there is not a proportional change between the decrease in pollution and the decrease in deterioration processes because the new-formation products are always active in an environment which is characterized by thermal and moisture fluctuations.

Typically gypsum is very unstable and according to wet and dry cycles it can be cyclically dissolved and crystallized so exerting mechanical stresses.

Fig. 48 - Gypsum crystals at SEM.

13. Summarizing considerations on decay patterns and related mechanisms of deterioration

From macroscopic observations three types of decay are generally distinguishable on monument's surfaces: *white washing, dirt accumulation and dirt wetting.*

Quantitative data obtained by sampling in different areas according to the degree of blackness and the degree of shelter from rain water has allowed to develop a simplified model of the deterioration morphologies.

In white washing areas the formation of a surface skin is prevented because the stone is exposed to the washing action of the rain, which has the effect of removing both the soluble compounds and the deposited soot. As a consequence skin formation does not occur in rain-washed areas.

The whiteness of the stone surface was wrongly ascribed for a long time by many authors to the sulphation process. Our analyses showed that the white washing areas are due to the re-crystallisation of calcite.

Dirt accumulation and dirt wetting are confined to black areas and represent two different morphologies of decay, which are dependent on the distance from the rain washed areas.

Dirt accumulation takes place in well-sheltered locations away from rain washing areas and it is characterized by black superficial deposits that accumulate on the surface due to the precipitation of atmospheric particles. In addition to carbonaceous particles a moderate sulphation process is also present.

Dirt wetting area is found at the interface between running water and the more sheltered areas. The thick and hard black crust has a rough and spongy appearance and grows upon the original surface. Observations show that the sulphate formation is greater in the black dendrite-shaped crusts, which are generally formed at the interface between the white-washing areas and the sheltered ones. The reason why dirt wetting areas show greater concentration of sulphate is that, after every rain event, they remain moist for a longer time with respect to dirt accumulation areas. Wetness time play an important role favouring the dissolution of gaseous sulphur dioxide and the deposition of carbonaceous particles which, as it is well known, speed up the oxidation to sulphuric acid and the subsequent gypsum formation.

In the dirt wetting area the thick and hard black crust has a rough and spongy appearance and grows with respect to the original surface. The gypsum formation is taking place according the following steps:

a) dissolution of SO_2 in water droplets and subsequent oxidation in the presence of catalysts

$$SO_2 + H_2O \underset{\text{catalysts*}}{\rightleftharpoons} SO_2 \bullet H_2O \qquad (53)$$

$$SO_2 \bullet H_2O + \tfrac{1}{2}\, O_2 \rightleftharpoons H_2SO_4 \qquad (54)$$

*(Carbonaceous particles, oxides of Fe, Cr, Mn ect.)

b) reaction of sulphuric acid with calcium carbonate

$$CaCO_3 + H_2SO_4 + 2H_2O \Rightarrow CaSO_4 \bullet 2H_2O \text{ gypsum} + H_2O + CO_2 \qquad (55)$$

As regards the morphology of deterioration of marble and Istrian stone the macroscopic observations show that they exhibit different types of decay, notwithstanding they have the same chemical composition and are exposed to the same environment. The factors responsible for this different behaviour are, on the one hand the intrinsic properties of the stone, that is their texture and structure, and on the other hand the geometry of the monument, that is the degree of shelter from rainwater.

Istrian stone, after the removal of the black crusts, appears to be in a good state of conservation and indicates that decay is only superficial, probably due to the low porosity of the stone that does not allow the penetration of water and consequently limits any deterioration process.

White marble is severely damaged due to the different texture of calcite grains which, after a certain time, allows water to penetrate into intergranular spaces, and favours the reaction of acid sulphur-bearing solutions which form gypsum around the grains. This is the starting point from which a progressive attack of calcite marble takes place. In contrast to the Istrian stone, there is penetration of gypsum crystals inside the marble, which causes an intimate mixture of original calcite, gypsum, carbonaceous particles, and natural or man-made atmospheric dust. Gypsum crystals found in the intergranular space can be ascribed to different mechanisms:

i) primary formation due to the penetration of sulphuric acid solution coming from the atmosphere and the subsequent reaction with calcite crystals.

ii) secondary formation due to the penetration of gypsum previously formed in the atmosphere,

iii) gypsum, firstly formed on the surface, can penetrate inside the marble during the wetting phase;

The presence of gypsum crystals inside the marble can cause mechanical stresses inside the pores during the drying phase because crystallization causes expansion.

Summarizing the mechanism of marble decay takes place in different steps:

i) exposure to natural atmospheric thermal changes shows a long-term effect of crystal de-cohesion (*physical alteration*);

ii) penetration of sulphur-bearing solution into intergranular spaces (previously formed by thermal changes) and subsequent transformation of calcium carbonate into gypsum (*chemical alteration*);

iii) gypsum crystallization inside the pores due to drying phase causes expansion and consequently mechanical stresses (*mechanical alteration*).

The first step is very slow and the time-scale to occur is hundred years. The second and third steps became important starting from the middle of last century according to an exponential relationship between time and damage effects. The time-scale of damage function is strongly reduced to a few decades.

References

Abeles, F.B., Craker, L.E., Forrence, L.E. & Leather, G.R., 1971. Science, 173-914.

Amoroso, G.G. & Fassina, V., 1983. Stone Decay and Conservation. Elsevier Science Publishers, Amsterdam, 1-453.

Ausset, P. Crovisier, J.L., Del Monte, M., 1996. Experimental study of limestone and sandstone sulphation in polluted realistic conditions: the Lausanne Atmospheric Simulation Chamber (LASC). Atmospheric Environment, 30, 3197-3207.

Barbaray, B., Contour, J.P. & Mouvier, G., 1977. Sulphur dioxide oxidation over atmospheric aerosol-X ray photoelectron spectra of sulphur dioxide adsorbed on V_2O_5 and Carbon. Atmospheric Environment, 11, 351-356.

Barrie, L.A., & Georgii, H.W., 1976. An experimental investigation of the absorption of sulphur dioxide by water drops containing heavy metal ions. Atmospheric Environment, 10, 743-749.

Beilke, S., 1985. Acid deposition. Commission of the European Communities, Directorate General for Science Research and Development Environmental Research Programme.

Beilke, S., & Gravenhorst, G. , 1978. Heterogeneous SO_2 oxidation in the droplet phase. Atmospheric Environment, 12, 231-239.

Beilke, S., & Gravenhorst, G. , 1979. Cycles of pollutants in the atmosphere. In B. Versino and H. Ott (eds.) Proc. 1st European Symposium Physico-Chemical Behaviour of Atmospheric Pollutants, Ispra, October 16-18, 1979. Commission of the European Communities, 1980, pp. 331-353.

Beilke, S., Lamb D. & Muller, J., 1975. On the uncatalyzed oxidation of atmospheric SO_2 by oxygen acqueous systems. Atmospheric Environment, 9, 1083-1090.

Blokker, P.C., 1978. Atmospheric sulphates: occurrence, formation, fate and measurement-A critical review. Conservation Clean Air Water Europe (CONCAWE) Report n.7.

Brimblecombe, P., 1987. The big smoke. Metuhen, London.

Brimblecombe, P. & Spedding, D.J., 1974. The catalytic oxidation of micromolar acqueous sulphur dioxide (oxidation in dilute solutions of iron III). Atmospheric Environment, 8, 937-945.

Brewer, R.L., Gordon, R.J., Shepard, L.S. & Ellis, E.C., 1983. Chemistry of mist and fog from the Los Angeles urban area. Atmospheric Environment 17, 2267-2270.

Butlin, R.N., Coote, A.T., Devenish, M., 1992. Preliminary results from the analysis of stone tablets from National Materials Exposure Programme (NMEP). Atmospheric Environment, 26B, 189-198.

Cadle, R.O. & Allen, E.R., 1970. Science, 167-243.

Calvert, J.G. & Stockwell W.G., 1983. Acid generation. Environmental Science Technology, 17 (9), 428A-443 A.

Calvert, J.G., Fu Su, Bottenheim, J.W & Strausz, O.P., 1978. Mechanism of the homogeneous oxidation of sulphur dioxide in the troposphere. Atmospheric Environment, 12, 117-126.

Camuffo, D., 1984. The influence of run-off on weathering on monuments. Atmospheric Environment, 18, 2273-2275.

Camuffo, D., Del Monte, M., Sabbioni C., 1982.Wetting deterioration and visual features of stone surfaces in urban area. Atmospheric Environment, 16, 2253-2259.

Camuffo, D., Del Monte, M., Sabbioni C., 1983. Origin and growth mechanisms of the sulphate crusts on urban limestone. Water, Air and Soil Pollution, 19, 351-359.

Camuffo, D.,1990. Acidic precipitation research in Italy. In: Bresser, A.H.M. & Salomons W. (eds) Acidic precipitation. Vol. 5. International Overview and Assessment. Springer Verlag, New York, 229-265.

Chameides, W., Stedman, D., Dickerson, R., Rush, D.& Cicerone, R., 1977. NOx production in lightening. J. Atmosph. Sci., 34: 143-149.

Chang, S.G., Brodzinski, R., Toosi, R., Markowitz, S.S. & Novakov, T., 1978. Catalytic oxidation of SO_2 on carbon in acqueous suspensions. In Conference on Carbonaceous particles in the Atmosphere. Laurence Berkeley Laboratory, Berkeley, CA, LBL-9037, CONF 7803101, pp. 122-130.

Cheng, R.J., Mohen V.A., Shen T.T., Current M. & Hudson J.B., 1976. Characterization of particulates from power plants. Journal of Air pollution Control Association, 210, 787-790.

Charola, A.E. & Ware, R., 2002. Acid deposition and the deterioration of stone: a brief review of a broad topic. In S. Siegesmund, T. Weiss & A. Vollbrecht (eds.): Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies, Geological Society Special publication No. 205, 393-406.

Cofer, W.R., Schryer, D.R. & Rogowski R.S., 1980. The enhanced oxidation of SO_2 by NO_2 on carbon particulates. Atmospheric Environment 14: 571-575.

Coughanour D. R. & Krause, F. E., 1965. The reaction of SO_2 and O_3 in acqueous solutions of $MnSO_4$. Ind. Eng. Chem., Fundam., 4, 61-67.

Cox, R.A., 1974. Particle formation from homogeneous reactions of sulphur dioxide and nitrogen dioxide. Tellus, XXVI: 235-240.

Cox, R.A. & Penkett, S.A., 1972. Aerosol formation from sulphur dioxide in the presence of ozone and olefinic hydrocarbons. J. Chem. Soc. Faraday Trans. 1, 68: 1735-1753.

Cox, R.A. & Penkett, S.A., 1983. Formation of atmospheric acidity. In S. Beilke & A. Elshout (eds), Proc. CEC Workshop on Acid Deposition, Berlin, 9 September 1982. Reidl, Dordrecht, The Netherlands, pp. 56-81.

Crutzen, P. J., 1979. The role of NO and NO_2 in the chemistry of the troposphere and stratosphere. Ann. Rev. Earth Planet Sci., 7: 443-472.

Cullis, C.F. & Hirshler, M.M., 1979. Emissions of sulphur into the atmosphere. In: Proc. Int. Symp. Sulfur Emissions and the Environment, London, 8-10 May 1979. The Chemical Society, London, pp. 1-24.

Daum, P.H. Schartz, S.E., & Newman, L., 1983. Studies of the gas and acqueos phase composition of stratiform clouds. In: H. Pruppacher, R.G. Semonin and W.G.N. Slinn (eds), Proc. 4th Int. Symp. on Precipitation Scavenging, Dry deposition and Resuspension, Santa Monica, CA, 29 November-3 December 1982. Elsevier.

Eggleton, A.E.J. & Cox, R.A., 1978. Homogeneous oxidation of sulphur compounds in the atmosphere. Atmospheric Environment, 12, 227-230.

EPA, 1971. Air quality criteria for nitrogen dioxides. U.S. Environmental Protection Agency, Report No AP84- Research Triangle Park, NC.

Fassina, V., Lazzarini, L. & Biscontin, G., 1976. Effects of atmospheric pollutants on the composition of black crusts deposited on Venetian marbles and stones, in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 201-211.

Fassina, V., 1978. A survey on air pollution and deterioration of stonework in Venice, Atmospheric Environment, 12, 2205- 2211.

Fassina, V., 1988 a. Stone decay of Venetian monuments in relation to air pollution, Proc. of Int. Symp. on the Engineering Geology of Ancient Work, Monuments and Historical Sites. Ed. P.G. Marinos and G. Koukis, A.A. Balkema, Rotterdam, 787-796.

Fassina, V., 1988 b. The stone decay of the main Portal of Saint Mark's Basilica in relation to natural weathering agents and to air pollution, VI th Int. Congress on Deteterioration and Conservation of Stone, Torun 12-14 Sept., 276-286.

Fassina V., 1988 c. Environmental pollution in relation to stone decay. Durability of Building Materials, Special issue, Air Pollution and Conservation, vol. 5, 317-368.

Fassina, V., 1992 a. The stone decay of the Portal of the Basilica of SS. Giovanni e Paolo in Venice, Proc. of the 7th Int. Congress on Deterioration and Conservation of Stone, Lisbon, June 15-18 , 119-128.

Fassina, V. & Stevan A.1992 b. Fogwater composition in Venice in relation to stone decay, Proc. of the 7th Int. Congress on Deterioration and Conservation of Stone, Lisbon, June 15-18, 365-373.

Fassina, V., Fumo, G., Rossetti, M., Zezza, F., Macrì, F. 1993 a. The marble decay of Pilastri Acritani and problems of conservation. Proc. of the Int. RILEM/UNESCO Congress on the Conservation of Stone and other materials, Paris 29 June - 1 July, 75-82.

Fassina, V., 1993 b. The weathering mechanisms of marble and stone of Venetian monuments in relation to the environment. Proc. of the 10th Triennial Meeting of ICOM, Committee for Conservation, Washington, August 22-28, 345-351.

Fassina, V., Basso, A. & Rossetti, M., 1994 a. Studies of patinas on the stone surface of Madonna dell'Orto church, Proc. of the III International Symposium on the Conservation of Monuments in the Mediterranean Basin, Venice, June 22-25, 835-842.

Fassina, V. & Rossetti, M., 1994 b. Weathering of marble in relation to natural and anthropogenic agents on the Ca' d'Oro facade (Venice), Proc. of the III International Symposium on the Conservation of Monuments in the Mediterranean Basin, Venice, June 22-25, 825-834.

Fassina, V., 1994 c. The influence of atmospheric pollution and past treatments on stone weathering mechanisms of Venetian monuments, European Cultural Heritage newsletter, vol. 8, n°. 2, 23-35.

Fassina, V., 1999. Il degrado delle formelle dell'arcone centrale della Basilica di S. Marco in relazione all'inquinamento atmosferico, in E. Vio e A. Lepschy (eds.), Scienza e tecnica del restauro della Basilica di S. Marco, Istituto Veneto di Scienze Lettere e Arti, Venezia, 611-650.

Fassina V., Favaro, M., Crivellari, F., Naccari, A., 2000. The stone decay of monuments in relation to atmospheric environment. Annali di Chimica, 91, 2001, 767-774.

Fassina, V., 2001. Studio dello stato di conservazione dei materiali della facciata di Ca' d'Oro in relazione al degrado di origine naturale e antropica. Quaderno 22, Soprintendenza BAS Venezia, Venezia 2001.

Fassina, V., Favaro, M. & Naccari, A., 2002. Principal decay patterns on Venetian monuments, in S. Siegesmund, T. Weiss & A. Vollbrecht (eds.): Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies, Geological Society Special publication No. 205, 381-391.

Furlan, V. & Girardet, F., 1991. Pollution atmospherique et durabilite des pierres de construction. Colloque International sur la Deterioration des Materiaux de Construction. La Rochelle, 79-91.

Furlan, V. & Girardet, F., 1992. Pollution atmospherique et reactivite des pierres. In Delgado J. (ed.) 7th International Congress on Deterioration and Conservation of Stone, Lisbon, 156-161.

Girardet, F., Ausset, P., Del Monte, M., Furlan, V., Jeanette, D. & Lefevre, R. A., 1996. Etude experimentale de prise en soufre de deux pierres calcaires dans la chambre de simulation atmospherique de Lausanne. 8th International Congress on Deterioration and Conservation of Stone, Berlin, vol. I, 349-358.

Galbally, I.E. & Roy, C.R., 1978. Loss of fixed nitrogen from solis by nitric oxide exhalation. Nature, 275: 734-735.

Gauri, K.L., Doderer, G.C., Thornton Lipscomband, N. & Sarma, A.C., 1973. Reactivity of treated and untreated marble specimens in an SO2 atmosphere. Studies in Conservation, 18: 25-35.

Hegg, D.A. and Hobbs, P.V., 1978. Oxidation of sulphur dioxide in aqueous systems with particular reference to the atmosphere. Atmospheric Environment 12, 241-253.

Glover, G.M., Kallend, A.S. & Marsh, A.R.W., 1980. The role of sulphur in acid rain, in B. Versino and H. Ott (Eds.), Proc. 1st European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Ispra, October 16-18, 1979, Commission of the European Communities, pp. 419-430.

Hales, J.M., 1978. Wet removal of sulphur compounds from the atmosphere. Atmospheric Environment, 12, 389-400.

Hicks, B.B., 1981. Wet and dry surface deposition of air pollutants and their modeling. In: S.M. Barkin (ed) Conservation of histotic Stone Buildings and Monuments, Washington, February 2-4. 1981. National Academy of Sciences, Washington, DC.

Hirschler, M.M., 1981. Man's emission of carbon dioxide into the atmosphere. Atmospheric Environment 15: 719-728.

Hudec, P., 1989. Durability of rock as function of grain size, pore size and rate of capillary absorption of waters, Journal of Materials in Civil Engineering 1, No 1, 3-9.

Johansson, L.G., Lindquist, O. & Mangio, R.E ,1988. Corrosion of calcareous stones in humid air containing SO_2 and NO_2. Durability of Building materials, 5: 439-449.

Johnstone, H.F. & Coughanour, D.R., 1958. Absorption of sulphur dioxide from air. Ind. Eng. Chem., 50; 972-976.

Junge, C.E., 1963. Air Chemistry and Radioactivity. Academic Press, New York, NY.

Kessler, D. W., 1919. Physical and Chemical tests on the commercial marbles of the United States U.S.B. Stand., Techn. Paper No. 123, Washington, Government Printing Office.

Kessler, C. & Platt, 1984. Nitrous acid in polluted air masses-sources and formation path ways. In Proc. 3rd European Symposium, Varese, Italy, 10-12 April, 1984. Project COST 61a bis, pp. 412-422.

Krumbein, W.E., 1988. Biotransformations in monuments. A sociobiological study. Durability of Building Materials, Special issue, Air Pollution and Conservation, vol. 5, 359-382.

Lazzarini, L., 1972. Forme e cause di alterazione di alcuni marmi e pietre a Venezia, Centro di Studio Cause di Deperimento e metodi di Conservazione delle Opere d'arte, CNR, Roma.

Lazzarini, L., 1979. Morfologia del degrado dei materiali lapidei a Venezia, Atti del Convegno Associazione Civica Venezia Serenissima, 47-57.

Marchesini, L., 1970. Effetti dell'inquinamento atmosferico sui materiali lapidei a Venezia, Aria e Acqua, III, 22.

Larson, T.V., Horike, N.R. & Harrison, H., 1978. Oxidation of sulphur dioxide by oxygen and ozone in acqueous solution: a kinetic study with significance to atmospheric rate processes. Atmospheric Environment, 12: 1597-1611.

Lenelle, Y.,1975. Contribution a l'etude de l'oxidation des sulfites dans la pluie. European Suplphur Symposium, Ispra, Italy, October 1975.

Lewin, S.Z., 1983. Preface of the book, Stone Decay and Conservation, Amoroso & Fassina (eds.), Elsevier Science Publishers, Amsterdam, 1-453.

Lewin, S.Z. & Rock, E.J., 1979. Chemical considerations in the cleaning of stone and masonry. In B. Badan (ed), Proc. 3rd Int. Congr. On the Deterioration and Preservation of Stones, Venice, October 24-27, 1979, Libreria Progetto, Padova, pp. 343-368.

Liberti, A., Brocco, D. & Possanzini, M., 1978. Adsorption and oxidation of sulphur dioxide on particles. Atmospheric Environment, 12: 255-262.

Lofvendhal, R., 1992. Weathering of stone. In: J. Gullman (Ed.) Air Pollution and the Swedish Heritage, Progress 1988-1991, Rapport RIK6, Conservation Institute of Central Board of National Antiquities & National Historical Museums, pp. 15-20.

Lofvendhal, R., 1996. Weathering of stone materials. In: E: Osterlund (Ed.) Degradation of Materials and the Swedish Heritage 1992-1995, Rapport RIK11, Conservation Institute of Central Board of National Antiquities & National Historical Museums, pp. 12-17.

Marchesini, L., Biscontin, G. & Frascati, S., 1972. Relazione tra porosità ed invecchiamento di marmi saccaroidi, Centro di Studio Cause di Deperimento e metodi di Conservazione delle Opere d'arte, CNR, Roma.

Martin, L.R. & Damschen, D.E., 1981. Atmospheric Environment, 15, 1615-1621.

Mc Clellan, G.H. & Mills, M.E., 1973. Solids from wet limestone scrubbing of power plant stack gases, Journal of Air Pollution Control association, 23, 122-127.

Noxon, J.F., 1978. Tropospheric NO_2, Journal Geophysical Research, 83, 3051-3057.

Penkett, S.A., Jones, B.M.R. & Eggleton, A.E.J. 1979a. A study of SO_2 oxidation in stored rainwater samples. Atmospheric Environment, 13, 139-147.

Penkett, S.A., Jones, B.M.R., Brice, K.A. & Eggleton, A.E.J., 1979b. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rainwater. Atmospheric Environment, 13, 123-137.

Pierotti, D. & Rasmussen, R., 1976. Combustion as a source of nitrous oxide in the atmosphere. Geophysical Research Letter, 3, 265-267.

Platt, U. & Perner, D., 1985. The atmospheric lifetime of nitrate radicals (NO3). Paper presented at Joint meeting of WP's 4 and %, COST 611, Bilthoven, The Netherlands, 23-25 September 1985.

Pratt, P.F., Barber, J.C., Cornin, M.L., Goering, J., Hauck, R.D., Johnston, H.S., Klute, A., Knowles, R., Nelson, D.N. Pickett, R.C. & Stephens, E.R., 1997. Climatic Change, 1. 109-135.

Price, C.A., 1996. Stone Conservation, An Overview of Current Research. Research in Conservation, The Getty Conservation Institute, Santa Monica, CA.

Robinson, G. & Baker, M.C., 1975. Wind-driven rain and buildings. Technical Paper n. 445, Division of Building Research. National Research Council of Canada, Ottawa.

Robinson, G. & Robbins, R.C., 1972. Emissions, concentrations, and fate of gaseous atmospheric pollutants. In: W. Strauss (ed), Air Pollution Control, Part II. Wiley Interscience, New York, NY, pp1-93.

Roswall, J., 1988. Air Pollution and Conservation. Durability of Building Materials, Special issue, Air Pollution and Conservation, vol. 5, 209-278.

Schaffer, R.J., 1932. The weathering of natural building stone. Building Research Special report. No 18, London.

Sidebottom, H.W., Badcock, C.C., Jackson, G.E., Calvert, J.G., Reinhardt, G.W. & Damon, E.W., 1972. Photo-oxidation of sulphur dioxide. Enviromental Science Tecnology, 6, 72-79.

Stumm, W. & and Morgan, J.J., 1981. Aquatic chemistry, 2nd ed. John Wiley and Sons, New York.

Torraca, G., 1969. L'attuale stato delle conoscenze sulle alterazioni delle pietre, cause e metodi di trattamento, in C. Gnudi (ed.), Sculture all'Aperto, Degradazione dei Materiali e Problemi Conservativi, Rapporto della Soprintendenza alle Gallerie di Bologna, No.3, Edizioni Alfa, Bologna.

Torraca, G., 1988. Air pollution and the conservation of building materials. Durability of Building Materials, Special issue, Air Pollution and Conservation, vol. 5, 383-392.

Tuazon, E.C., Atkinson, R., Plum, C.N. Winer, A.M. & Pitts, N., 1983. The reaction of gas phase N_2O_5 with water vapour, Geophysical Research Letter, 10 (10): 953-956.

Urone, P., 1976. The primary air pollutants –gaseous, their occurrence, sources, and effects. In A.C. Stern (Ed.), Air Pollution, Vol I, Academic Press, New York, NY, 3rd edn. Chap 2, pp 23-75.

Weiss, R.F., & Craig, H., 1976. Production of atmospheric NO_2 by combustion. Geophysical Research Letter, 3: 751-753.

Wilson, M.J., 1995. Interactions between lichens and rocks: a review. Cryptogamic Botany 5, 299-305.

Winkler, E. M., 1970. Decay of Stone, Conservation of Stone. Vol I, IIC, New York, NY, pp 1-14.

Winkler, E.M., 1973, Stone: Properties, durability in Man's environment. Springer Verlag, New York.

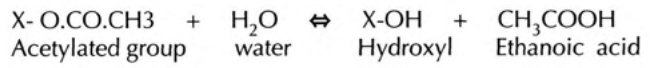
Chapter 8

Volatile organic compounds (VOCs) released by wood

Marianne Odlyha, Carl Johan Bergsten, David Thickett

Introduction

Wood is commonly used in the interior of museums either in furnishings or in showcases of museums or it may be in direct contact with the objects. This chapter describes the damaging effect of volatile organic compounds (VOCs) released from wood onto heritage objects, in particular lead based objects. The issue with VOCs was first voiced in conservation by Oddy (Oddy,1973) at the British Museum where condition of metal objects stored in showcases was then studied (Thickett & Bradley,1998). This has been followed by studies in display cases in historical houses (Thickett, Stanley & Booth, 2008). Based on studies of metal objects and behaviour of metal coupons acceptable levels of organic acids, in particular ethanoic (acetic) acid have been recommended (Tétreault, 2003). Generally wood is known to have a corrosive action on metals due to the presence of ethanoic (acetic) acid which is volatile. The National Physical Laboratories (UK) in their online corrosion guides have a section on specific applications which includes corrosion of metals by wood (http:// www.npl.co.uk, accessed 07/02/10) and in this introduction some of the basic background information which appears in their review is presented. The starting point is the structure of wood. Wood is composed of complex organic molecules cellulose, hemicellulose and lignin. Of these, the principal component of wood is cellulose,a polysaccharide, where some of the units contain hydroxyl groups and some of these are acetylated. In the presence of water these acetyl groups can combine to give ethanoic acid, which is volatile and can escape. The acetyl group is considered to constitute about 1 to 6% by weight of dry wood. The value is higher in hardwoods than in softwoods.



Where X is the D-Glucose unit in the chain.

For a given wood species, the rate of formation of ethanoic acid depends on the temperature and the moisture content of the wood, and its rate of escape depends on the geometry of the wood. The corrosive nature of wood is also affected by methods used in the pre-treatment of wood such as kiln drying, salt seasoning which enhances chloride content, addition of flame retardants and preservatives. In practice, kiln dried wood is much more likely to cause corrosion than air dried wood (Umney,1992). Overall there is a wide range of initial acid contents in different species of wood and the woods vary in the ease with which acetyl is hydrolysed to free ethanoic acid. The corrosiveness of the vapours emitted by woods is considered to be due largely to the presence of initial free ethanoic acid in the wood and also ethanoic acid derived from the hydrolysis of the acetyl groups of the hemicelluloses at high RH (Arni et al., 1965). This was measured using gas chromatography and spectrophotometry which showed that the main acidic constituent of vapours emitted by woods on incubation was ethanoic acid and this was accompanied by significant quantities of methanoic acid. Table 1 shows the levels of ethanoic and methanoic acids from a range of wood species (Arni et al., 1965).

Table 1. *Levels of ethanoic and methanoic acids from a range of wood species (Arni et al, 1965).*

Wood	ethanoic acid (ppb)	methanoic acid(ppb)
Sweet chestnut heartwood	151	59
Oak heartwood	146	21
Douglas fir sapwood	62	18
Wych elm heartwood	58	13
Norway spruce heartwood	52	-
Douglas fir sapwood		49
Wych elm sapwood	47	6
Norway spruce heartwood	32	-
Beech sapwood	14	2
Beech heartwood	12	-

More recent studies on different species of untreated wood also measured the emissions of ethanoic acid and other volatile organic compounds (Risholm-Sundman et al., 1998). It was found that the main emissions from softwood were terpenes and from hardwood was ethanoic acid. Highest emission rate of ethanoic acid was found in cherry and oak, and was measured as 2000 and 2800 $\mu g.m^{-2}.h$ respectively.

Acids within wood can cause corrosion by contact and the evaporation of acids from wood can cause vapour corrosion within enclosed spaces. A study of the susceptibility of various

metals to vapour corrosion inside wooden containers gave the following list in terms of degree of susceptibility to attack (http:// www.npl.co.uk). In Table 2 zinc and zinc alloys are listed together with lead and lead alloys as being most susceptible to attack. Studies made by Tétrealt (Tétreault, 2003) using metal coupons have shown a differential response of metals within Group 1; lead shows a higher vulnerability to acetic acid than does zinc and respective NOAELs (no observed adverse effect) of 400 and 22,000µg/m3 were obtained.

Table 2. *Susceptibility of various metals to vapour corrosion inside wooden containers.*

Group 1	**Group 2**	**Group 3**	**Group 4**
Severe attack	*Moderate attack*	*Very slight attack*	*Insignificant attack*
Lead and lead alloys	Copper and its alloys *	Aluminium and its low strength alloys ; slightly greater for Al-Cu and Al-Zn	Gold
Zinc and Zinc alloys		Nickel	Silver
Low alloy steels			Tin
Magnesium and its alloys	* note vapour corrosion can occur in presence of ammonium salts		Titanium and its alloys Stainless steel

The effect of relative humidity was also tested . Metals were enclosed in a vessel at various RH levels containing 1% ethanoic solution. Values show the influence that an increase in RH has on corrosion suspectibility (http:// www.npl.co.uk). Table 3 gives values for extent of corrosion which occurs at various values of relative humidity. Studies have also been performed on lead (Tétreault,Sirois and Stamatopoulou,1998).

Table 3. *Corrosion (g/dm^2 in 40 days) of metals by ethanoic acid at various humidities at 30C.*

Metal	**RH(72%)**	**RH(85%)**	**RH(96%)**	**RH(100%)**
Zinc	0.12	1.4	1.6	Very large
Steel	0.12	0.75	1.05	Large
Copper	Trace	Trace	0.65	1.0

Recent work has also explored the effect of low levels of ethanoic acid (475-2,275µg/m^3) and RH values (50-95%) on lead coupons, and a tentative mechanism of the corrosivity of ethanoic acid is proposed (Niklasson et al 2005). The rate of corrosion is directly proportional to the ethanoic acid vapour concentration. It is suggested that the corrosivity of gaseous ethanoic acid towards lead is explained by the acidity of ethanoic acid and its high solubility in water. This dissolves the native PbO films and triggers an electrochemical corrosion process that generates lead ions and OH-ions producing fresh PbO. Corrosion products formed in the presence of ethanoic acid vapour are a mixture of litharge (α-PbO), massicot (β-PbO), plumbonacrite ($Pb_{10}O(OH)_6(CO_3)6$, and lead acetate oxide hydrate ($Pb(CH_3COO)_2.2PbO.H_2O$. This study in flowing air showed limited susceptibility of lead coupons to RH so mechanism may be different in static air.

Wood can act as a source of water for corrosion processes. There is the situation where an object can be contained in a sealed wooden box and the sealed wooden box is warmed. At 20°C and 55%RH both a cubic metre of air and a 6 cm cube of wood contain about 10 cm^3 of water (Umney,1992). Increasing the temperature causes a reduction in the moisture content of the timber and an increase in the relative humidity of the surrounding air. Moisture will be released from the wood so that the relative humidity actually increases. In this case the moisture content of the wood will contribute to the corrosive conditions. For example if an object is contained within a sealed wooden box and the temperature is increased then a value of 80%RH, at which acid corrosion proceeds rapidly, can be readily achieved within the container. Table 4 shows the approximate moisture content of wood required to give RH of 80% inside the wooden box for different temperatures. The figures show that even with well dried wood which has a moisture content of 16-18% a level of RH, at which corrosion can occur, can be achieved readily in a temperate climate and all the time in warm tropical climates. Temperatures of 40-50°C can be reached in wooden boxes exposed to the sun in the UK, while air inside boxes in a tropical climate may reach 70°C. Table 4 shows how the moisture content changes with temperature

Table 4. *Shows the approximate moisture content of wood required to give 80% relative humidity (RH) inside a wooden box.*

Temperature, C	Moisture content of wood required to give 80%RH in container
15	20%
25	18%
40	16%
70	12-14%

In addition to corrosion caused by exposure to acidic environments corrosion of metals can also be caused by contact with wood. In an article on corrosion of metals by wood Umney (Umney,1992) mentions that the acidity of wood can be measured by preparing a suspension of wood particles in distilled water in the proportion of five parts of water to one of wood and then measuring the pH of the suspension with a glass electrode pH meter. Though this does not provide an accurate measure of the true pH of the moisture in the wood because of the large dilution effect involved in preparing the sample for measurement, it does provide useful information on the relative degrees of acidity of different woods. He indicates that for practical purposes, a pH of 4.0-4.3 represents the limit below which the rate of corrosion of steel increases rapidly in the presence of moisture. He also gives values of the measured pH values for some common timbers (Table 5). It is important to note that pH values do not necessarily correlate with ethanoic acid emission rates.

Table 5. Measured pH values for some common timbers (Umney,1992).

Sofwoods	pH	Hardwoods	pH
Western Hemlock	4.8-5.4	Elm	6.0-7.2
European Spruce	4.8-5.0	Balsa	5.4-7.2
Sitka spruce	4.0-5.5	Beech	4.5-5.9
Scots pine	4.3-4.6	Obeche	4.4-5.5
European Larch	4.0	Mahogany (African)	4.5-5.1
Maritime pine	3.8	Afrormosia	4.3-4.8
African pencil cedar	3.5	Sapele	4.3-4.6
Western red cedar (American)	2.9-4.0	Teak	4.5
Western red cedar (English)	4.0-4.7	Idigbo	3.5-4.1
		Chestnut	3.6
		Jarrah	3.0-3.7
		Oak (European &US)	3.3-3.9
		Oak (Japanese)	4.0-4.7

Oak, sweet chestnut, Western red cedar and Douglas fir are the woods most commonly associated with corrosion of metals when in contact with them under damp conditions. With regard to the metals, iron and steel are much more susceptible to the corrosive influence of wood than aluminium, copper or brass. In this article Umney also quotes an example of cadmium plated radio sets that had corroded in storage. This had been caused by the birch wood in their cabinets rather than by other materials present. He also makes the point that sometimes, corrosion of metals occurs in contact with woods that are not unduly acidic and this may be promoted by the presence of common salt. For example, salt can promote bi-metallic corrosion of nickel plated steel and coppered iron. Cases have been observed where alkali produced by the corrosion of coppered iron nails holding canvas to a wooden frame has caused rotting of the canvas. Salt is not a normal constituent of wood but it can be introduced into wood by logs being floated to the sea or being exposed to sea spray. Also, in North America, a salt seasoning process is used for drying certain hardwoods including maple (Umney,1992).

As mentioned at the start of the chapter, wood is commonly used in the interior of museums and its effect on heritage objects has become an area of great concern. Detailed studies have been made of the tendency of lead to corrode in ethanoic (acetic) acid environments as frequently observed in display and storage settings (Tetreault, 2003; Costa and Urban, 2005). From the studies using lead coupons, it was found that over a period of 12 months no damage was detected in lead coupons at ethanoic acid concentrations below 0.43mgm^{-3} and RH below 75% . Unpublished data from the British Museum shows no corrosion after 10 years of exposure to ethanoic acid levels of up to 0.43mg/m3 (Thickett, private communication). Measurements were made of mass gain and colour change. Composition of the corrosion products was performed using X-ray diffraction.

In recent times attention has been directed to the situation of lead-based organ pipes in historical organs (Niklasson et al, 2008) and in microclimate frames for paintings (Grøntoft et al, 2010). The latter two were studied within the framework of two European projects COLLAPSE "Corrosion of lead and lead-tin alloys of organ pipes in Europe" (EVK4-CT-2002-00088,http://www.goart.gu.se/collapse and PROPAINT "Improved Protection of Paintings during Exhibition, Storage and Transit" (FP6 SSPI no 044254, http://propaint.nilu.no), and in both cases it was demonstrated that the VOCs, in particular ethanoic (acetic) and methanoic (formic) acids were released either from the wood in organ windchests or within microclimate frames. This was considered to be the cause of corrosion of historical organ pipes studied in the COLLAPSE project, and of lead coupons that were exposed in the vicinity of the pipes. Lead coupons were also exposed in the PROPAINT project and differing levels of corrosion were measured based on the conditions assessed within the frames. These results will be discussed in the framework of existing information on corrosion of metals by wood, and particularly on heritage objects.

Lead coupon testing performed in the COLLAPSE project showed differences between coupons exposed at selected sites. A comparison of coupons exposed in the slightly corroded and heavily corroded organs in Italy (Figure 1) and Netherlands showed that the amount of accumulated acetate and formate was consistently greater in the more corroded organs. In summary, the high concentration of organic acid vapours present in the wind systems of the corroded organs and the tendency for acetate and formate to accumulate on the lead coupons indicated that the two organic acids ethanoic (acetic) and methanoic (formic) acids play an important role in the corrosion of the organ pipes (Chiavari et al,2008).

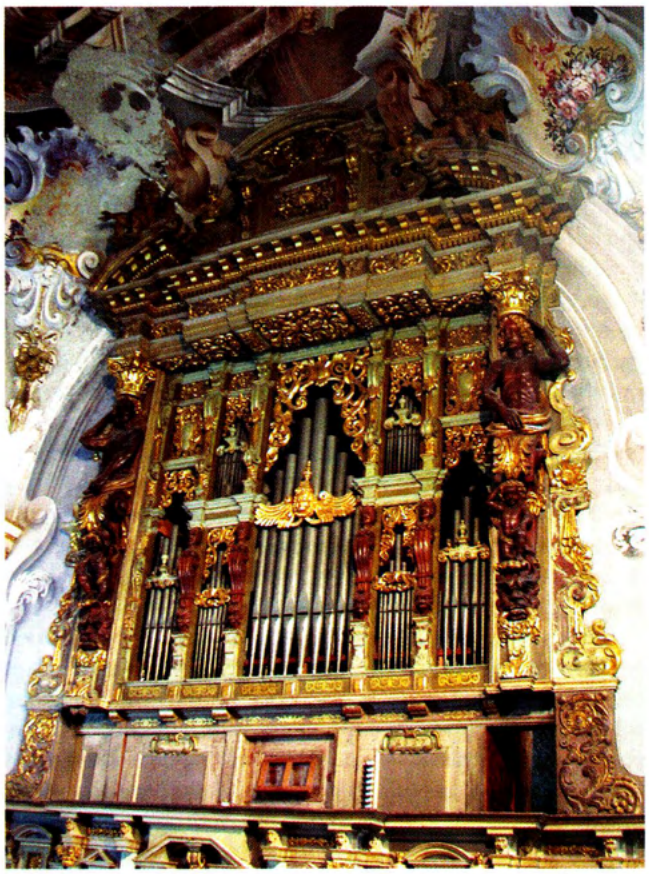


Fig. 1 - The non-corroded organ in the Church of Madonna di Campagna, Ponte in Valtellina, Italy with oldest parts from 1518.

In the European project SENSORGAN "Sensor system for Detection of Harmful Environments for Pipe Organs" (project no. 022695,http://www.goart.gu.se/sensorgan) lead coupons were also exposed in oak and pine containing environments generated in glass vessels in the laboratory. It was found that the corrosion products obtained in pine differed from that in oak generated environments. In the latter predominantly acetate and carbonate salts formed whereas in pine generated environments formates and carbonates formed. This was observed by ATR/FTIR and confirmed by Raman spectroscopy (de la Faria, 2007). Recent studies have also used Raman spectroscopy and electrochemical reduction to study the corrosion products (Bernard et al., 2009) and the authors have advocated their use as dosimeters.

The effect of VOCs from four species of wood (western red cedar, spruce, kiri, and sugi) has also recently been measured on two different metals (iron and copper) and eight different pigments (litharge, white lead, malachite, calcium carbonate, red lead, vermilion, red iron oxide) (Oikawa et al. 2005). Previous studies of corrosion of copper by methanoic and ethanoic acids had shown that at levels of 0.4ppm (based on volume) 75%RH copper had reacted mainly with methanoic acid, and at levels above this value it reacted also at 54%RH. The main product was cuprite (copper I oxide) (Tetreault et al., 2003).

Recommendations for lead conservation were also made in this paper (Tétreault,1998) which include examination of lead artefacts to distinguish between uniform and local corrosion. The former covers the complete surface with a compact film and the latter is responsible for deeper damage and significantly alters the surface morphology, resulting in pitting and efflorescence. The surface of the artefact can become covered by white, voluminous corrosion products, and eventually disintegrate completely A damaged artefact when removed should be cleaned to stop active corrosion, and then maintained in environments where the ethanoic acid concentration is below 0.1mgm^{-3}. This figure may need treating with caution as it is derived from linear extrapolation of much shorter term experiments. Many lead objects have survived for decades in atmospheres with ethanoic acid levels above this value. In setting up theses guidelines it is also important to keep in mind that the effects of patination on objects also play a role. Corroded lead generally shows a different response and is usually less reactive. This relationship means it is extremely difficult to set 'limits' based on ethanoic acid concentration alone. Practically if this approach is taken then the limits need to be extremely low, which means they essentially exclude wood products which has very major cost implications. In terms of testing the environment a useful guide is given in the paper (Tétreault,1998), that odours of acetic acid and formaldehyde (methanal) are detectable by humans when the concentrations of these volatile compounds exceed 2.5mgm-3 . Recently, in the SENSORGAN project acid-indicator (A-D) strips were found to be very useful for testing environments containing blocks of wood used for ageing lead-based dosimeters (http://www.cwaller.de/ accessed 6/02/2010).

Studies of concentrations of ethanoic acid emitted from wood coatings in enclosures have also been made (Tétreault & Stamatopoulou,1997). The rationale for this study is the fact that wood products and commercial coatings are frequently used in museums for display, storage or packing, and at the time of the study, little was known about the emission of VOCs from paints and varnishes. Twenty-two commercial coatings were chosen and it was found that almost all coatings released ethanoic acid, but at different rates (Tétreault & Stamatopoulou, 1997). Conclusions were that consideration should be given to sufficient drying periods (3 to 4 weeks) for the coatings before their use in coated enclosures, in order to reduce the VOC concentrations within the enclosures. Some studies on museum showcase materials, show that where an internal covering of PVC-coated plywood was used, significant levels of ethanoic acid were still detectable (Mapelli, 2003).

Case Studies

Historical Organs

The next part of this chapter will describe in more detail case studies where corrosion of objects has been observed. The particular case of the atmospheric corrosion of lead-rich organ pipes in European churches has attracted the attention of organ builders in many countries. This prompted the study of the influence of low concentrations of acetic acid vapour (425-2750 µg/m3) on the atmospheric corrosion of lead (Niklasson et al., 2005). Mass gain results were reported and the corrosion products were analysed by ion chromatography and X-ray diffraction. Results showed that low concentrations of acetic acid vapour are very corrosive towards lead. Mass gain was linear with exposure time and depending directly on the acetic acid concentration. It also prompted further work within the SENSORGAN project which was responsible for development of new instrumentation for monitoring volatile organic acids in pipes (PQC-lead dosimeters) acoustic emission sensors for detecting cracks in wood, and monitoring of dew point within pipes to determine whether condensation is occurring (Bergsten, 2010). The lead-PQC dosimeters will be described in chapter 9 in this book.

In historical organs, organ builders and organ restorers have observed an increasing frequency of corrosion attack inside organ metal pipes (lead and lead-tin alloys). An especially heavy corrosion attack was observed inside the Principal 16' prospect pipes from 1467 in the Stellwagen (Small) organ in St Jakobi church in Lübeck, Germany (Figure 2), and this was the point of departure for the COLLAPSE project. The project objectives were to better understand the factors causing pipe corrosion and to recommend conservation strategies regarding the pipe corrosion (Chiavari et al., 2004).

Fig. 2 - The Stellwagen organ,St Jacobi, Lübeck,where the prospect pipes were found to be corroded.

The corrosion in the Stellwagen organ pipes had started inside the lower part of the foot and then moved gradually upwards in the pipe foot towards the mouth area. In many of the pipes there were cracks and holes in the pipe foot wall (Figure 3). If the corrosion would reach the mouth, the sound properties will gradually change and finally the pipe will be silent. This is of course very serious because the historical sound quality would be lost and the sounding cultural heritage would be lost forever.

Fig. 3 - Cracks in the pipe foot wall caused by corrosion (Photo:Ibo Ortgies).

The results from the COLLAPSE project showed that an important factor contributing to the corrosive environment inside the pipe foot was the concentration of organic acids emitted by the wood of the windchest. The windchest is a wooden box containing channels and valves distributing the organ wind to the pipes when the corresponding keys are pressed by the organist. The pipes stand on the windchest and the airborne organic acids slowly enter the pipe foot through the foot hole when the organ is not played (Figure 4). Because the pipe foot constitutes an almost closed space (only a very narrow opening where the organ wind enters the pipe body) the organic acid concentration is slowly built up in the (almost) not ventilated foot and a corrosive environment is created. When the pipe is played the foot is of course very well ventilated (but initially with wind from the wind system containing accumulated organic acids). However, a pipe spends most of its time not being played. The described situation is very similar to the problem of corrosion of metal objects in showcases: emission of organic acids from wood into a closed or almost closed space.

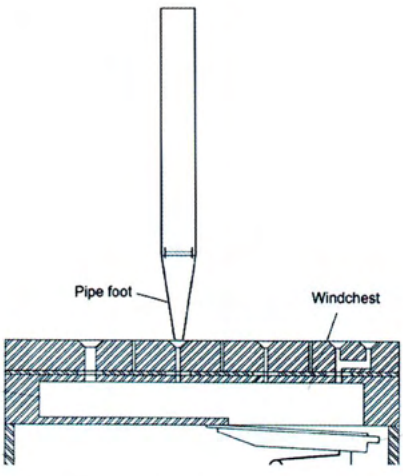


Fig. 4 - Diagram of a pipe standing on the windchest.

As mentioned previously different types of wood emit different amounts of organic acids and there is no "perfect" wood without any emissions. However, oak wood is known for its high emission of organic acids, especially of ethanoic acid. Ethanoic acid is known to be very corrosive to lead and from the corrosion aspect it is unfortunate that oak wood has been frequently used for making windchests, especially in the older tradition of organ building.

For a corrosive environment to create conditions of corrosion in the pipes this will mainly be dependent on the pipe metal alloy, the temperature, and the relative humidity in the organ.

The pipe metal is normally a lead-tin alloy. The composition of the pipe metal is a very important factor having an influence on the corrosion situation. In a corrosive environment, it was found in the COLLAPSE project that metal containing less than about 1% tin is very sensitive to corrosion, like the corroded pipes in St. Jakobi church, but a few percents of tin in the alloy makes the metal more corrosion-resistant (Figure 5). Tin, however, will have a protecting effect at lower humidity but at higher humidity the protecting effect gradually disappears.

Fig. 5 - Two reed pipes standing side by side in the same environment in an organ. The corroded metal part, the block,contains 0,2% tin and the non corroded block contains 3.9% tin.

The temperature and the humidity will influence the emission rate of organic acids from the wood. Especially the higher humidity will increase the emissions of organic acids, and consequently higher humidity will also speed up the corrosion process in the pipe.

The question remains how old organs could survive several hundreds of years without any corrosion problems when oak has always been used for making windchests. However, there are historic documents from the 17th and 18th centuries describing frequent corrosion problems and also that the pipes in a new organ could be completely destroyed by corrosion in less than 30 years, especially if the pipes were made of high lead content alloy.This means that the corrosion problem is not new but today there can be a problem if new wood is introduced into an old organ during restoration or repair work. The recommendations when restoring or repairing an historical organ could be summarized in the following way:

- If possible, try to avoid to introduce new wood in the windchests, especially the toeboards constituting the top layer of the windchest.
- It is important not to create a corrosive environment if intro-

ducing new wood when repairing or restoring an old organ, especially if the instrument contains high lead alloy pipes.

- The wood should not be fresh but it should be stored for a long time.

- Avoid using oak wood (even if it is historically correct), especially for the toeboards, but use wood with lower emissions of organic acids.

Results from field studies within SENSORGAN following the COLLAPSE project, showed that from the corrosion point of view it is desirable to keep the relative humidity no higher than ca. 60%. On the other hand very low humidity (less than 40% RH) will increase the risk for crack damages in the wooden parts of the organ.

Showcases

The other examples are drawn from case studies involving showcases where wood and wood products such as plywood and more latterly medium density fibreboard (MDF have been extensively used in their construction. Wood emits small amounts of methanal and some ethanal, whilst some plywoods and MDFs emit much greater amounts of methanal. A great deal of concern arose around methanal from the early 1980s when relatively cheap detection methods developed in the health field were used in museums and deterioration to lead often wrongly ascribed to methanal. Series of corrosion tests with lead used plywood or MDF as a methanal source. These materials also emitted the much more damaging ethanoic acid which was responsible for most of the damage observed. Methanal certainly will corrode lead alloys, through its oxidation to methanoic acid at higher RHs and in the presence of oxidising agents (wood and particularly resins in wood products emit a range of oxidising species). There is stong evidence that methanal is a significant risk to paper, dramatically accelerating oxidation (paper chapter) and certain glass and enamel compositions (indoor mechanisms chapter) and concerns about affects on proteinaceous materials. This shows the danger of relying on detection of just one species from a complex atmosphere to assess corrosion. The complex atmospheres generated above wood products have synergistic effects with methanoic acid and methanal mixtures with ethanoic acid causing greater corrosion of lead than the same concentration of ethanoic acid alone. This is where single parameter studies also require complementary information from dosimeters which respond to the synergistic action of different volatile species.

The choice of materials is very important as the use of inappropriate materials in enclosures can rapidly accelerate deterioration. In these case studies examples will be given to illustrate this fact. Metal objects are obviously the most affected, and lead is particularly susceptible to the affects of ethanoic acid. All wood products emit a wide range of VOCs with hard wood species emitting around 200 different volatile components on average and soft woods around 120 different components with ethanoic acid being the most damaging of these gases towards lead alloys. Methanoic acid is also ubiquitous but is less corrosive and generally is emitted at below a quarter of the rate of ethanoic acid. Recent studies in Germany of modern-type museum showcases directly after production identified between 26 and 45 individual VOCs, in modern type showcases in museum use between 10 and 46 and in old-type enclosures in museum use individual VOCs ranges between 4 and 35 Ethanoic acid was found to be still one of the main problems which is still unresolved (Schieweck, 2009).

The choice of materials is frequently restricted where wooden historical showcases are part of the building and so materials which out-gas have to be accepted. In this case measures need to be implemented to improve conditions within the showcases and to make sure that materials used have been properly evaluated. This would include (1) reducing overall RH fluctuations to provide a more suitable stable environment and (2) making modifications to remove internal pollutants produced by materials within the cases. An example where mitigation procedures have been used is in the in the King's Library of the British Museum. The King's Library is the grandest room in the British Museum and it is lined with wood book presses. Before its redevelopment (2000-2001) measurements were made of ethanoic acid which indicated that mitigating measures were required. (Thickett & Short, 2002) Activated carbon cloth was initially considered but since the wood had to be exposed further tests were made to establish that activated carbon granules had the same effect . The conclusions were that a high surface area was required and given the levels of pollutant gases in the Museum should be replaced regularly, probably every two years. Active filtration is a more effective method but is not always possible to use (Bradley et al., 2004).

A particular case study at English Heritage will be described where bookshelf cabinets at the Iveagh Bequest, Kenwood, were converted to display jewellery (Thickett et al., 2008). Despite the fact that great care was taken in selection of materials an untested paint inside the cases caused corrosion to occur on the solder of jet jewellery. Corrosion was identified as lead methanoate with X-ray diffraction and the jewellery was removed from the cases. Concentrations of methanoic acid between 3,000 and 6,000 ug/m3 were measured. Three approaches were tried to mitigate the paint's effect inside the cases. The air exchange rate was increased to reduce the concentration of ethanoic acid in the air. A series of holes were drilled into top and bottom panels of the case doors. Though concentration was reduced to about 2,000µg/m3 this still remained sufficiently high for corrosion to take effect. Finally closefitting MDF boards were constructed to block emissions and levels were lowered to 42 and 70µg/m3. A risk assessment was undertaken for the remaining cases containing portrait miniatures, and the watercolours and supports were not considered to be at risk. In the case of the portrait miniatures some had copper alloy frames in which lead was found to be present. (Figure 6) As a precaution fans are planned to be installed with activated charcoal filters for the two cases containing these portrait miniatures.

Fig. 6 - Converted cabinets at Iveagh Bequest, Kenwood.

The influence of ventilation in showcases and the effect of their measured air exchange values on emissions within showcases has also been studied. This involved a set of showcases at the British Museum which had been built about twelve years ago. They were of a similar design and made of similar materials but measured air exchange rates gave a range of values. Recent availability of relatively inexpensive equipment has made such measurements more available (Thickett,2007). Cases were used without objects that could be themselves sources of carboxylic acids and the surface area of an internal source, Moistop sealed MDF base and back boards, was measured. All other materials in the showcases had undergone and passed accelerated corrosion tests with lead, indicating that they had an extremely low emission rate of carboxylic acids. Values for air exchange rates, and ethanoic acid concentrations are shown in Figure 7.

Measurements made in summer were found to be significantly higher, since both temperature and RH increase the emission rate from wood products (Figure 7) (Thickett,2008). The ethanoic acid concentrations were found to increase dramatically when the AER fell below 0.5. This result has important ramifications for showcase design. However, the geometry of a showcase needs to be taken into account. All the showcases investigated in this case were approximately 2m high, 0.5 to 1m deep and 2 to 4 m wide, with 'pull and slide' doors as the front face.

If the tolerance to RH range is known then a much more targetted risk assessment can be made. In many instances this can reveal that the risk from wood products in certain situations is negligible and indeed large numbers of lead alloy objects have survived in showcases and storage enclosures made of wood for centuries without observable damage. However,it should be noted that changes in RH conditions can occur in buildings through a number of causes. In buildings without HVAC systems the temperature and RH often undergoes a strong seasonal cycle. Both temperature and RH have an important affect on ethanoic acid emission rate from wood products.

The temperature and RH ranges for these experiments were targeted towards conditions in showcases in the UK. The annual temperature range translates to 15°C (with winter heating) and 35°C with lighting generating up to 5°C increases in temperature above room ambient inside showcases. The winter heating often causes RH to fall below 30% inside showrooms, but the wood has a buffering affect on RH. This effect and the effect of RH on the corrosion rate of lead alloys at a given ethanoic acid concentration means that lead corrosion is often dramatically faster during summer in the UK.

Microclimate frames (mc-frames) for paintings can also be considered as an example of a modified showcase where the overall volume is significantly reduced. Due to an increase in the use of mc-frames there is growing concern about the quality of the environment within the frames. Recent studies of mc-frames which included those that had been adapted and those that were purpose built and with a range in air exchange values, showed that in all cases measured levels of ethanoic and methanoic acids using pollutant passive samplers were found to be higher than those in the rooms. Exposed lead coupons also showed that the values within the frame gave higher values for mass gain per unit area. Lead-PQC dosimeters which will be described in detail elsewhere (this book chapter 9) were also used to monitor several commercial frames with different exchange rates. Some commercial frames were also tested. They were of similar size and materials and were sealed to give different air exchange rates. Where values of AER were lower then the values for measured changes were higher; and where the values of AER were higher then measured changes were lower.

Conclusions

In conclusion, it appears that any enclosures which use wood and wood products need to be monitored for emissions of volatile organic acids, and that evaluation of conditions within enclosures also need to take into account the air exchange rate and the environmental conditions (RH,T). For wood and wood products, the types of wood and their methods of treatment determine the nature and amount of volatile emissions of organic compounds, in particular the organic acids. Methods of mitigation of emissions within enclosures need to be further investigated, especially in locations such as microclimate frames for paintings.

Acknowledgements

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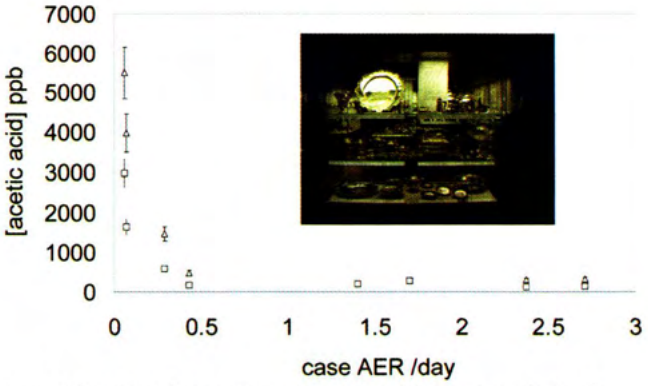

Fig. 7 - Ethanoic acid concentrations in a series of showcases at the British Museum. Concentration increases sharply when air exchange rate drops below 0.5/day. Summer concentrations (indicated by open triangles) are higher than winter concentrations (indicated by open squares) because temperature and RH increase emission rate of medium density fibreboard (Thickett, 2008).

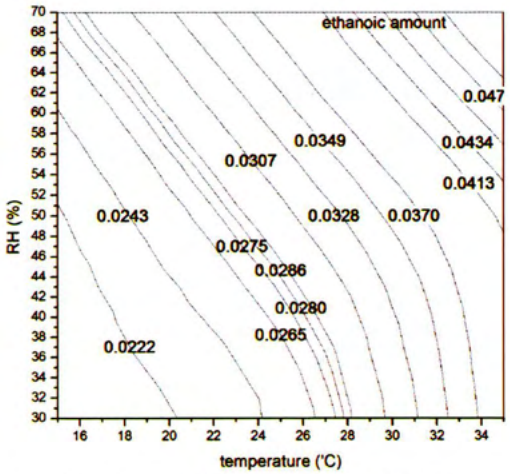

Fig. 8 - Graph of ethanoic acid concentrations at different values of temperature and RH.

References

Arni, P.C., Cochrane, G.C., and Gray, J.D., 1965, The emission of Corrosive Vapours by Wood.II The Analysis of the Vapours emitted by certain freshly felled Hardwoods and Softwoods by Gas Chromatography and Spectrophotometry, J. Appl. Chem., 15, 463-468.

Bergsten, C.J., Odlyha, M., Jakiela, S., Slater, J.M., Cavicchioli A., de Faria, D.L.A. Niklasson, A., Svensson, J-E., Bratasz, L., Camuffo, D., della Valle, A., Baldini, F., Falciai, R., Mencaglia, A., Senesi, F., "Sensor system for detection of harmful environments for pipe organs (SENSORGAN)", e-Preservation Science (in press).

Bradley, S., Parker, J., Fletcher, P., and Lee, L., "Mitigation of the effects of Pollutant gases on susceptible objects" (http://www.isac.cnr.it/iaq 2004/abstract/ (accessed 12.02.10).

Bernard, M.C., Costa, V., and Joiret, S., 2009, Assessing Indoor Lead Corrosion using Raman Spectroscopy during Electrochemical Reduction, e-Preservation Science, 6, 101-106.

Chiavari, C., Martini, C., Prandstraller, D., Niklasson, A., Svensson, J.-E., Åslund, A., and Bergsten, C.J., 2008, 'Atmospheric corrosion of historical organ pipes: The influence of environment and materials', Corrosion Science 50, 2444-2455.

Chiavari, C., Martini, C., Poli, G., and Prandstraller,D., 2004, "Conservation of organ pipes: protective treatments of lead exposed to acetic acid vapours", METAL04, Proceedings of the International ICOM-CC Metal WG conference, Canberra, Australia, 4-8 October, 2004, Ashton J. and Hallam D. (ed.) National Museums of Australia (publishers), 281-293.

Costa, V., and Urban, F., 2005, Lead and its alloys: metallurgy, deterioration and conservation" Reviews in Conservation, 48-62.

de Faria, D.L.A., 2007, SENSORGAN 1st year project report.

Grøntoft, T., Odlyha, M., Mottner, P. , Dahlin, E. , Lopez-Aparicio, S., Jakiela, S., Scharff, M.,Andrade, G., Obarzanowski, M., Ryhl-Svendsen, M., Thickett, D., Hackney, S., Wadum, J "Dosimetry for evaluation of environmental conditions for paintings in microclimate frames"Journal of Cultural Heritage (in press).

Mapelli, E., Pedrocchi-Fantoni G., Strini A., 2003, Volatile Organic Compound Emissions from Museum Showcase Materials (http://iaq.dk/iap/iaq2003/2003_07.htm,accessed 12.02.10).

Nikklasson, A., Johansson, L.G. and Svensson, J.E., 2005, Influence of Acetic Acid vapour on the atmospheric corrosion of Lead, Journal of the Electrochemical Society 152 B519-B525.

Niklasson, A., Langer, S., Arrhenius, K., Rosell, L., Bergsten, C.J., Johansson, L.-G., and Svensson, J.-E., 2008, "Air pollutant concentrations and atmospheric corrosion of organ pipes in European church environments" Studies in Conservation 53: 24-40.

Oddy, 1973, "An unsuspected danger in display" Museum Journal 73, 27-28.

Oikawa, T., Matsui, T., Matsuda, Y., Takayama, T., Niinuma, H., Nishida, Y., Hoshi, K., Yatagai, M., 2005, Volatile Organic Compounds from wood and their influences on museum artefact materials 1. Differences in wood species and analyses of causal substances of deterioration J Wood Science 51: 363-369.

Ryhl-Svendsen, M., 2007, Air Quality in Museum Storage Buildings, PhD Thesis, The Royal Academy of Fine Arts School of Conservation, 99-114.

Risholm-Sundman, M., Lundgren, M., Vestin, E., and Herder, P., 1998, Emissions of acetic acid and other volatile organic compounds from different species of solid wood, Holz als Roh-und Werkstoff, 56 No. 2,125-129.

Schieweck, A., 2009, "Airborne Pollutants in Museum Showcases-material emissions, influences, impact on artworks", Ph.D thesis, Dresden.

Tétreault, J., Sirois, J., and Stamatopoulou, E., 1998, "Studies of Lead Corrosion in Acetic Acid Environments" Studies in Conservation , 43, 17-32.

Tétreault, J., and Stamatopoulou, E., 1997, "Determination of Concentrations of Acetic Acid emitted from Wood Coatings in Enclosures" Studies in Conservation 42, 141-156.

Tétreault, J., Cano, E., van Bommel, M., Scott, D., Dennis, M., Labrousse-Barthes, M.G., Minel, L., and Robbiola, L., 2003, Corrosion of Copper and lead by Formaldehyde, formic and acetic acid vapours, Studies in Conservation 48, 237-250.

Tétreault, J., 2003, "Airborne Pollutants in Museums,Galleries and archives: Risk Assessment,Control Strategies, and Preservation Management ", Canadian Conservation Institute.

Thickett, D., Bradley, S.M. and Lee, L.R., 1998, "Assessment of the Risks to Metal Artefacts Posed by Volatile Carbonyl Pollutants", METAL 98, Proceedings of the International Conference on Metals Conservation, ed: W. Mourey and L. Robbiola, James and James Ltd, London, 260-264.

Thickett, D., Stanley, B., and Booth, K., 2008, "Retrofitting old display cases" in ICOM Committee for Conservation 15th Triennial Meeting, New Delhi, September 2008, Preprints ed J. Bridglad, Vol. II, 775-782.

Thickett, D., Fletcher, P., Calver, A., and Lambarth, S., 2007, "The Effects of Air Tightness on RH Buffering and Control", Museum Microclimates, The National Museum of Denmark, Copenhagen, 245-251.

Thickett, D. and Short, K., 2002, Assessment of risk posed by acetic acid in wall presses of the Kings Library and its mitigation with activated carbon, British Museum, Department of Conservation, Conservation Research Group, Internal Report 9.

Umney, N., 1992, "Corrosion of Metals Associated with Wood" V&A Conservation Journal on-line Issue 4 (www.vam.ac.uk, accessed 15/05/10).

Chapter 9

Measuring gaseous and particulate pollutants Instruments and instrumental problems

Erwin Rosenberg, Franco De Santis, Velichka Kontozova-Deutsch, Marianne Odlyha, René van Grieken, Francesca Vichi

9.1 Introduction

The measurement of gaseous and particulate pollutants in museums, galleries and archives is important to ensure acceptable conditions for the protection of artwork during storage and exhibition (Grzywacz, 2006). The identification of potential pollutants and their concentrations in indoor atmospheres is relevant to decide whether any particular means of precaution have to be taken, e.g. installation of chemical air filtration systems, protective housings, adsorbents etc. While it is normally assumed that air pollutants are infiltrated from the outside to the indoor environment and may consequently affect the cultural heritage objects, it must also be taken into consideration that some of the materials used in the design of exhibitions or the construction of showcases can be emission sources of air pollutants. Moreover, the objects themselves can also, as an effect of ageing, emit substances that may have adverse effects to the object, or even catalyze further decomposition (Figure 1). The auto-catalytic decomposition of cellulose acetate films is a well studied example for this (Dupont & Tétreault, 2000).

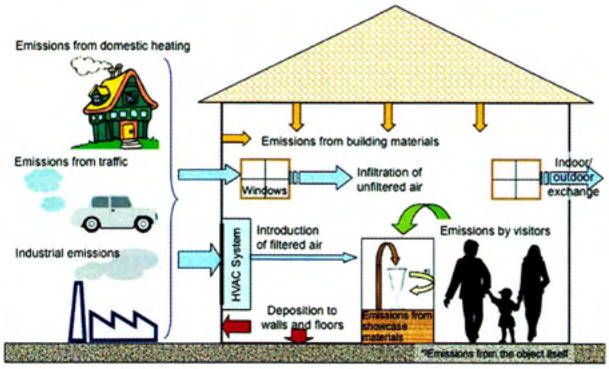

Fig. 1 - Outdoor and indoor sources of air pollution in museums, galleries and archives.

There are many methods and approaches for analysing gaseous and particulate pollutants in the indoor atmosphere of museums and galleries (Brimblecombe, 1990; Camuffo, 1998, Hatchfield, 2002; Tétreault, 2003). This section intends to give an introduction to the various common approaches for indoor air pollutant measurements before these are discussed in more detail in the three following sections.

Many of the methods that are in use in indoor air monitoring have initially been developed for either environmental or occupational health monitoring, and have been adopted to fulfil the particular requirements of monitoring air pollutants in a museum or archive environment. Of paramount importance for the proper choice of analytical technique are the questions what is the purpose of the particular monitoring campaign, what analytes are to be monitored, and at which concentration levels these are expected to be present. The need to determine the average concentration to which an object is exposed over a longer period of time will require a different analytical approach than the monitoring of short time maximum exposure levels, or daily trends of pollutant concentration, e.g. as a function of the number of visitors being present at a given time (Figure 2).

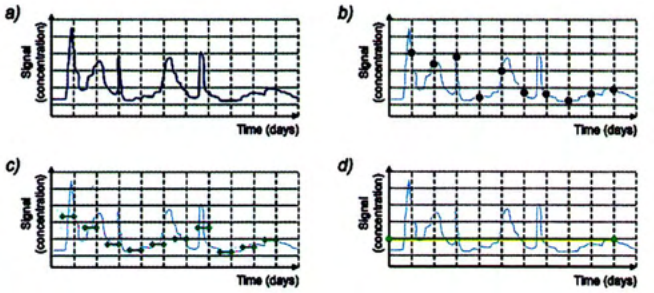

Fig. 2 - Concentration profile of a relevant indoor air pollutant when measured with a) a continuously monitoring device, b) with a discrete short-time sampling technique (e.g. by grab sampling), c) with sample collection over a short period (e.g. by active sampling), and d) with sample collection over a long period (e.g. by diffusive sampling).

When planning to perform a single measurement or a measurement campaign for indoor air pollutants, the following criteria should be taken into consideration:

Time of measurement. Even when analysing the emissions from a source of constant emission strength, the time of measurement can have a massive impact on the result. As most analytical techniques do not determine the emission strength of a source, but the airborne concentrations during the sampling or measurement period, the actual concentration of indoor air pollutants will depend on whether the air has been stagnant in the room, or the room has been aired shortly before the measurement. In such case, concentrations observed at different times may deviate by more than order of magnitude. The time of measurement is even more important for an emission source that is no longer active. Assuming that the concentration of air pollutants will decrease in an exponential manner after the stop of the emission, the time of measurement will have a great effect on the result. This example also demonstrates that it should be defined whether the measurement is to reflect the highest observed concentrations (as a 'worst case

scenario') or a representative, time weighted average (TWA).

When deciding about the time of measurement, it should also be taken into account that very often there are seasonal variations, which also will have an effect on indoor air pollutant concentrations and profiles: Assuming that the largest fraction of air pollutants observed indoors is infiltrated from the outdoor atmosphere, it will be important whether the outdoor atmosphere has high levels of trace gases and particulate matter, as typically observed in wintertime due to domestic heating or from seasonal traffic. In turn, outdoor air pollutant concentrations can be expected to be lower in summertime, perhaps with the exception of ozone levels.

Duration of measurement. In many cases, indoor air measurements rely on sampling and laboratory analysis of samples. In this case, sampling conditions can be chosen as to accomplish short term measurements, typically lasting up to one hour, or intermediate to long term measurements with duration from one hour up to weeks and months. The actual duration of measurement will depend on the purpose of the measurement and on the characteristics of the method and the analyte. If peak concentrations of air pollutants are to be monitored, then either continuous monitors or short term sampling methods are to be used. The problem with sampling durations that are very short or instantaneous is that they have a higher probability of obtaining an unrepresentative sample. An instantaneous concentration could potentially represent a peak or trough in the concentration profile which might not reflect the true time-integrated average concentration to which an object may be exposed over the longer term. If the general level of indoor air pollution is to be monitored, then long term sampling is adequate. It will also depend on the concentration levels of the air pollutants whether short term sampling is sensitive enough, or long term sampling has to be used in which the detection limits typically improve with the duration of sampling or exposure.

Location of measurement. The selection of a suitable location for an indoor air quality measurement is also a non-trivial issue. Different situations in a building may arise from the presence or absence of a HVAC (heating/ventilation/air conditioning) system, greatly different air exchange rates due to doors, windows or ventilation shafts, or differences in temperature or relative humidity. As a general recommendation, it should be attempted to perform the sampling close to the object of interest, if possible. If, for example an object is exposed in the centre of a showroom, then the most relevant information on the potential threat to this object by indoor air pollutants will be obtained if the measurement or sampling is performed close to this object. If it is not possible to perform the measurement at this place, e.g. for aesthetic reasons or to not interfere with the display of the object, then one or several other sampling locations are to be chosen that resemble the location of the object under study as closely as possible in its aerodynamic and climatic situation.

Expected concentration levels. It is very important to establish from the start the minimum amount of a compound that must be identified or quantified in the study. If, for example, the concentration data will be used to conduct risk assessments, the routine detection limits of the sampling/analysis methods to be used to conduct the sampling/analysis should be at least as low, if possible, as the lowest threshold level that will be used to conduct the evaluation. If it is not feasible to achieve these detection limits, then the utility of conducting such a study may be questioned. Two types of detection limits are defined and used in this context. These include a method detection limit (MDL) for a specific methodology as well as a practical quantitation limit (PQL) or Reporting Limit (RL). The MDL is a statistically derived number that represents the minimum amount of an analyte that can be identified with 99% confidence above background instrument noise. The PQL or RL is the lowest level that can be reliably achieved within specified limits of precision and accuracy. A PQL is approximately three to five times the MDL. For sorbent media samples (e.g., Tenax), there may be a blank background level for some target compounds and parameters which may need to be accounted for when determining the MDL. Thus the MDL is influenced by the overall efficiency of its components, including the sampler as well as the analytical instrument. Factors that may influence the efficiency of the sampler include sampling rate, sample size, etc. An important parameter that can affect sampling efficiency is the breakthrough volume of an analyte that can be collected using a particular collection sorbent. The breakthrough volume is depending on both, the volume of air sample and the pollutant concentration in this air sample that is passed through the sorbent medium, as well as on the environmental conditions during sampling (temperature, RH). Breakthrough occurs when the absorptive capacity of the sampling media is exceeded. Thus, further sorption of contaminants in the air being passed through the media does not occur and/or some of the contaminants already sorbed onto the media may desorb. Sorbent-specific breakthrough volumes can be estimated given the approximate concentration of contaminant in the air and the volume of air to be passed through the media. Finally, every method used is characterized by a particular degree of accuracy, or ability to quantify what is actually there, and precision, the ability to obtain reproducible results.

It should be noted that the occupational health field offers many standardized sampling and analysis procedures for monitoring compliance with occupational air standards. Many of these methods are not suitable for environmental level sampling because of insufficiently sensitive detection capabilities. The major inherent difference with regard to detection levels between occupational health samples and environmental samples is that occupational samples are mostly solvent (CS_2) extracted and only a small amount of the extract is injected for analysis. In environmental level samples, typically the whole sample is thermally desorbed for analysis. Occupational samples are collected using tubes which are usually smaller and contain less adsorbent material, resulting in less collected volume. Because of lower cost and easier access to services, indoor air monitoring may incorrectly be performed with such an occupational method which however often does not meet the stipulated performance criteria.

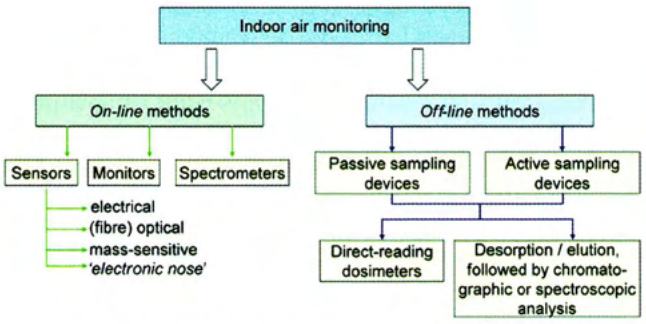

Fig. 3 - Classification of sampling and analysis techniques for the assessment of indoor air quality.

In the following, we will give a classification of measurement methods that can be used in indoor environments of museums and archives (Figure 3), and discuss their characteristics.

On-line (continuous) measurement

Where air pollutant concentrations exhibit large temporal variations, and where it is relevant to record these variations, an *on line* measurement instrument that can provide real time measurement is required (Zhang & Mo, 2009). The two principles that lend themselves best to *on line* monitoring are optical and electrical/electrochemical detection. Optical detection, in the form of absorption measurement, is particularly useful in the mid-infrared (IR) spectral region (2.5 – 25 μm) where both inorganic and organic trace gases have their vibrational and rotational absorption bands. While Fourier transformation-IR-(FTIR-) spectrometers can in principle be used for the monitoring of air pollutants, it is typically non-dispersive IR (NDIR) instruments that are used for continuous monitoring. In contrast to the spectrometers that record the specific absorption of trace gases in a gas cell, NDIR instruments are only able to monitor one analyte at one time due to their non dispersive principle of operation. They are typically designed as two-beam instruments in which quantitation is accomplished by recording the temperature or pressure increase caused by absorption of IR radiation by the sample in the measurement cell in comparison to the reference cell. As instrument dimensions are typically rather small (most NDIR instruments fit into industry standard 19" racks, or even have smaller footprint), and as the sensitivity of optical absorption detection is proportional to the optical pathlength, detection limits in the low ppm range can be reached for most trace gases. Analytes that are typically monitored by NDIR are CO, CO_2, NO, NO_2 and SO_2. N_2O and SF_6, which are often used in tracer experiments for the determination of the air exchange rate, can also easily be monitored (ASTM, 2006).

A further possibility to make use of IR absorption for the detection of indoor air pollutants is in the form of photoacoustic spectroscopy (PAS). In this technique, the analyte is irradiated by a modulated IR beam in the measurement cell. Due to the modulation of the IR radiation, the sample is periodically heated and expands with the periodicity of the modulation. This induces a pressure or acoustic wave which is detected by a very sensitive microphone. The characteristics of this technique with respect to the detection of gaseous indoor air pollutants are similar to those of the NDIR technique. With more intensive light sources, such as semiconductor lasers even low- and sub-ppb detection limits can be reached.

Optical absorption measurement can be used also in the UV range for the monitoring of ozone levels. Due to the strong absorption of ozone in the 200-280 nm range it can easily be determined with a simple optical set-up with a mercury vapour lamp as light source. This principle of measurement is relatively robust and hardly affected by interferences. Instrument drift can be eliminated by incorporating a switching valve and additional flow path in the instrument that alternates measurement between the sample stream and a sample that has been scrubbed of ozone. This results in a more accurate and stable ozone measurement. Detection limits in the low ppb range can be reached in this way.

A very versatile technique for the monitoring of total hydrocarbons is the flame ionisation detector (FID). In this instrument, a small portion of the sample gas is delivered to a hydrogen/air detector flame. During the combustion process, volatile organic compounds in the sample are ionized and are detected subsequently by the instrument and reported as a concentration. The detector's response must be calibrated and is checked regularly for this purpose which also compensates for any long-term drift. Detection limits of less than 10 ppb (for the sum of total volatile organic compounds, TVOC) can be attained by this technique. The TVOC value obtained by this technique, often denoted $TVOC_{FID}$, does not necessarily correlate completely with the results from other measurement methods.

Of similar usefulness is the continuous monitoring of VOCs by a photoionization detector (PID). In a such instrument, organic compounds are ionized by an intensive UV light source with excitation energy in the range of 8 – 14 eV, see Figure 4. The excitation wavelength of 10.6 eV is commonly used at which aromatic compounds respond particularly sensitive. The selectivity of detection can be tailored to a certain extent, although only UV absorbing compounds can be detected (these are mainly aromatic compounds and non-aromatic compounds that have functional groups with double bonds, such as aldehydes, ketones, acids etc.).

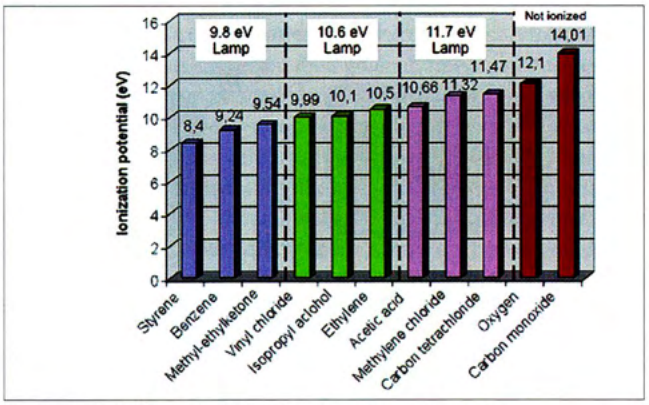

Fig. 4 - Ionisation potential of various (organic) compounds in photoionization detection and resulting selectivity with different PID lamps. (data from: RAE Systems, San Jose, CA, http://www.raesystems.com/).

For the continuous monitoring of nitrogen oxide(s), determination by chemiluminescence is very useful. In this technique, NO which is a relatively unstable molecule, will oxidize to NO_2 in the presence of O_3 supplied by an ozone generator. This reaction produces a quantity of light (hν) for each NO molecule which is reacted:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

This light can be measured using a photomultiplier tube or solid state device. Assuming that the volumes of sample gas and excess ozone are carefully controlled, and that the amount of ozone present is sufficient to react all of the nitric oxide, the light level in the reaction chamber is proportional to the concentration of NO in the gas sample.

The chemiluminescence technique may be also used to measure total oxides of nitrogen (NO_x) by passing the sample first over a heated catalyst to reduce all oxides of nitrogen to NO. This is done within the instrument, just prior to the reaction chamber. If the instrument is capable of automatically switching the catalyst in and out of the sample path, then the resulting signals may be compared to determine NO_2 levels from the difference of the two signals (NO_x – NO).

In response to the need of monitoring the effects of indoor air pollution on cultural heritage objects, rather than the con-

centrations of individual air pollutants, a real time monitoring device has been developed by the Purafil company (Purafil, Doraville, GA). The OnGuard® 3000 instrument measures in real-time the overall reactivity level of Airborne Molecular Contaminants (AMC) present in the local environment as well as temperature and relative humidity. A Quartz Crystal Microbalance sensor (QCM, see the section on Dosimetry for Cultural Heriatage for more details on the operating principle) is plated with copper or silver and used to measure the mass accumulation of the corrosive film that results from the reaction of the contaminants with the metals. The mass increase is described in terms of the corrosion film thickness in Angstroms (Å). This method provides adequate sensitivity to detect environments with reactivity corresponding to atmospheric contaminant concentrations at the level of or less than 1 ppb. These data can either be logged by an internal data logger or can be transmitted directly to the facility monitoring system via a 4-20 mA output signal. Reactivity monitoring is an accurate and reliable method of evaluating the quality of makeup and recirculation air characterizing the museum or archive environment, and evaluating the effectiveness of chemical filters (Figure 5).

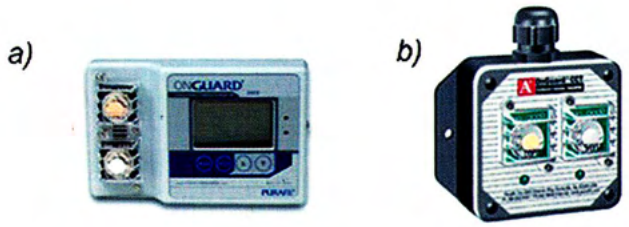

Fig. 5 - Photographs of Purafil®'s instruments to measure the reactivity of Airborne Molecular Contaminants (AMCs). a) Purafil® OnGuard 3000 instrument with internal data logger; b) Purafil® CCT (Continuous Corrosion Transmitter) instrument that measures in real-time the amount of corrosion forming on copper and silver surfaces, and transmits this information to the control system via a 4-20 mA output signal. The two piezo crystals which are coated with copper (red-brown) and silver (white) can clearly be seen on the instruments' front. (Photographs courtesy of Purafil Inc., Doraville, GA).

Discontinuous (discrete) sampling and measurement techniques

Discontinuous measurement is based on either active or passive (diffusive) sampling of the analytes by suitable techniques or devices. From these, the response can either be read out directly, or requires subsequent analysis in the laboratory. The choice of the sampling technique, and the decision whether direct-indicating samplers or samplers requiring laboratory analysis are to be used, depend on the analyte, on the expected concentration level, and on the duration of monitoring. Not all options are possible or feasible, and the rationale for their selection shall be given in the following (Dettmer & Engewald, 2003).

Active sampling

In active sampling, a defined volume of air is drawn through a container holding an adsorbent bed or an absorbing liquid. A single analyte or a class of analytes are thus adsorbed to or absorbed by the collection medium, and can also undergo further chemical reaction which lead to their immobilization, stabilization, or better detectability, e.g. by forming a coloured reaction product. The advantage of active sampling is that the sample volume and also the sampling conditions are well defined. Active sampling requires the use of a sampling pump by which the air is drawn through the collecting medium. At the end of a sampling event, samples are taken to the laboratory for thermal or solvent desorption and chromatographic analysis. For the collection of volatile organic compounds, glass or stainless steel tubes are normally used that are filled with various kinds of sorbents. Their formats are compatible with commercial thermal desorption instruments, such as 3 ½" length × ¼" OD for the Markes and Perkin Elmer thermal desorption units, or 7" length × ¼" OD (4 mm ID) for the Teledyne/Tekmar and Gerstel thermal desorption instruments. The choice of adsorbent depends on the analyte(s) that are to be monitored. The more volatile the analyte, the stronger an adsorbent is required. However, it is not recommended to generally use the strongest adsorbent available, because incomplete desorption of less volatile analytes may result. For this reason, there exists a wide range of adsorbent materials that are suitable for collecting VOCs of different volatility and polarity. These include inorganic materials (silica gel, aluminium oxide, inorganic molecular sieves), carbon-based materials (active charcoal, carbon-based molecular sieves) and porous organic polymers (polyphenylene oxide (=Tenax®), polystyrene-divinylbenzene copolymers, polyurethane foams). Where a wide volatility and/or polarity range of analytes has to be covered, a set-up with two or even three different adsorbent materials in series is used. During collection, the sample flow is from the weakest to the strongest adsorbent (with the sampling pump being placed downstream of the adsorbent tube(s) in order to avoid potential contamination), while the desorption is done in the reverse direction, from the strongest to the weakest adsorbent (Figure 6).

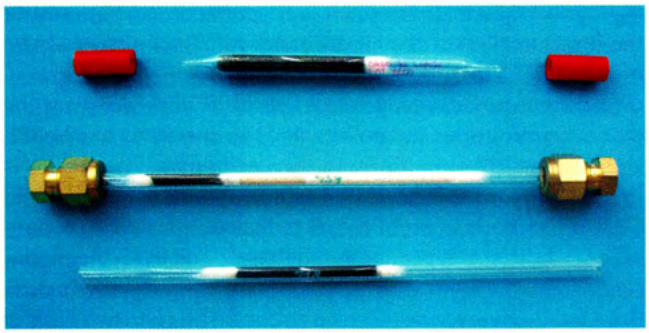

Fig. 6 - Photographs of adsorbent tubes for active sampling and solvent desorption (top, filled with active charcoal) and for active sampling and thermal desorption (middle, multi-layer tube, filled with Carbosieve/Molsieve 5A/Tenax; and bottom, single adsorbent tube filled with Carbosieve).

Sensitivity is maximized when the largest volume of air is sampled without that breakthrough of the analytes occurs. "Breakthrough" is defined as the sample volume at which the analyte is no longer trapped completely in the adsorbent bed and appears in the tube effluent (Matisová & Krabáková, 1995; Dettmer & Engewald, 2002). Breakthrough is dependant on the adsorbent used, the target pollutant, mass of adsorbent contained in the trap, flow rate, temperature of sampling and the presence of other analytes or interferents, such as water.

Solvent desorption of VOC samples (e.g. using carbon disulfide) is commonly practiced in industrial hygiene applications, but is usually insufficiently sensitive for indoor air quality measurements. Thermal desorption involves the preconcentration of a sample by desorbing the VOCs from the media by passing inert carrier gas (while heated) through the

trap and concentrating them on a smaller downstream trap (cold trap) which is usually cryogenically cooled. The concentrated sample is then flash-heated to a GC or GC/MS system for analysis. Thermal desorption offers the analysis of the whole sample, rather than an aliquot as is the case for solvent desorption. A disadvantage of thermal desorption is the commitment of the whole sample for one analysis without the possibility of replicate analyses.

Key aspects of adsorbent sampling include:

1. Breakthrough is always a concern and must be accounted for in determining sampling duration and flow rate (i.e., *via* the Safe Sampling Volume).

2. Back-up traps for detecting breakthrough are necessary.

3. Quality control should be extensive. Many quality control measures (such as duplicates, field blanks, lab blanks) demonstrate the ease of adsorbent media to be contaminated by non-sampling related passive adsorption of VOCs. Storage life of exposed samples and unexposed sampling traps is limited.

It is possible to achieve a method detection limit of 0.1 ppb, although high confidence is only held for identifications made for compounds detected at and over 0.5 ppb.

While organic trace gases can only be collected by adsorbent sampling, inorganic trace gases can be collected by both ad- and absorptive sampling. In the latter case, so-called impingers are used, small vessels filled with a defined volume of absorbent solution through which the air sample is drawn in finely dispersed form to improve collection efficiency (Figure 7). After sampling, the solution can be analysed directly, or after further preconcentration. As this method is particularly suitable for the analysis of acidic trace gases (formic and acetic acid, NO_x, SO_2), ion chromatography is commonly used for analysis.

Fig. 7 - Photographs of an impinger sampling train with glass impinger and glass in-line holder mounted on a Universal mod. PCXR8 air sampling pump. (Photograph courtesy of SKC Inc., Eighty Four, PA).

Direct reading devices

Particularly for industrial hygiene application, a wide range of direct reading devices based on active sampling have been developed, so called 'indicator tubes'. They are based on the colour formation or change occurring when a defined air volume with a reactive analyte is drawn over the solid bed impregnated with a selective reagent. The glass tube is already calibrated and allows thus to directly read the concentration of this particular analyte for a defined sample volume. An example of an indicator tube for acetic acid and a manual bellows pump is given in Figure 8. With detection limits in the low ppm range, in most cases, they are not sensitive enough for indoor air monitoring at relevant concentration levels for museums, galleries and archives.

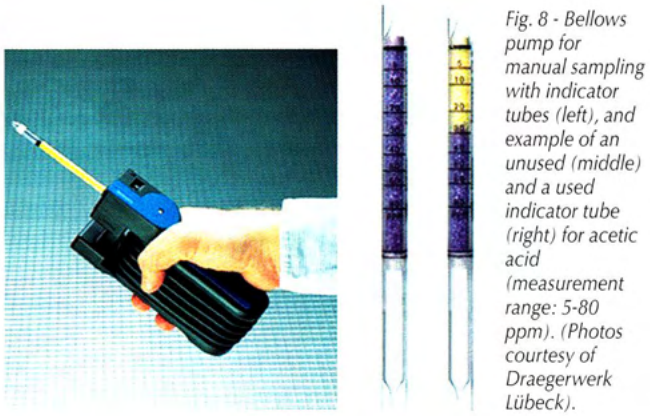

Fig. 8 - Bellows pump for manual sampling with indicator tubes (left), and example of an unused (middle) and a used indicator tube (right) for acetic acid (measurement range: 5-80 ppm). (Photos courtesy of Draegerwerk Lübeck).

Passive (diffusive) sampling

In contrast to active sampling, passive (= diffusive) sampling relies on the transport of analytes to a collection layer driven only by diffusion (Brown, 1993, and Brown, 2000). While the various types of diffusive samplers with their advantages and disadvantages are discussed in the subsequent chapter, it shall be pointed out here that passive sampling is the method of choice for long-term monitoring for which it provides a time-weighted average (TWA) concentration value for the analyte(s). As the amount of analyte collected for a given concentration is depending on the sampler geometry and the exposure time, the detection limits of a passive sampler can be improved by a suitable sampler design (so called radial or high-uptake rate diffusive samplers) and by extending the exposure time. Combined with thermal desorption, detection limits can be reached that come close to the ones obtained by active sampling, however, using an experimentally much simpler approach that essentially does not require any sampling infrastructure. Simultaneous sampling of indoor air quality at different sites is thus much easier to perform by diffusive, rather than by active sampling.

Grab (whole air) sampling

A sampling method more frequently applied in environmental rather than in indoor air monitoring is grab sampling whereby whole air samples are collected in a short time interval. This is typically done by allowing a previously evacuated, ultra-clean stainless steel canister to be filled with the air sample, or by drawing the air into a sealed Tedlar (PVDF) bag (Figure 9). Typical volumes are 3.2 - 15 L (for Summa® canisters) and 1 - 25 L (for Tedlar bags). The whole air samples are brought into the laboratory and analysed by suitable methods, depending on the concentration levels (e.g. direct injection of small volumes of sample into the GC, or after cryogenic preconcentration of a defined sample volume). While the use of highly inert container materials (electropolished stainless steel, or PVDF, polyvinylidenfluoride) ensures that no losses of reac-

Fig. 9 - Tedlar bag (left), and Summa® electropolished stainless steel canisters of various sizes (right) for the collection of whole air samples. (Photos courtesy of the manufacturers and suppliers, CEL Scientific Corporation, Santa Fe Springs, CA, and RM Environmental Systems Incorporated, Camarillo, CA).

tive sample components occur, whole air sampling has the disadvantage that an appropriate transport and storage infrastructure must be available due to the fact that relatively large air volumes are collected and must be transported to the lab in contrast to the methods where the air pollutants are preconcentrated already in the sampling step. This has prevented this method from finding wider acceptance for indoor air measurements in museums and archives.

In summary, it can be concluded that there are many choices for measuring indoor air pollutants in the atmospheres of museums, archives, and galleries. There cannot be a general recommendation for the best suitable technique. The proper choice of sampling and/or analytical method will rather depend on the individual situation, where the particular analyte(s) to be monitored, their expected concentration levels and variability and the particularities of the sampling location will have to be considered.

The principles, as well as the benefits and pitfalls of the more important sampling techniques for particulate and gaseous air pollutants, are discussed in the three following sections.

Acknowledgment

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Erwin Rosenberg

References

American Society for Testing and Materials, (ASTM) 2000. Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution (ASTM E 741-00(2006)e1). West Conshohocken, PA.

Brimblecombe, P., 1990. The composition of museum atmospheres. Atmospheric Environment. Part B, Urban Atmosphere 24: 1-8.

Brown, R. H., 1993. The use of diffusive samplers for monitoring of ambient air, Pure and Applied Chemistry, 65, 1859-1874.

Brown, R.H., 2000. Monitoring the ambient environment with diffusive samplers: theory and practical considerations, Journal of Environmental Monitoring, 2: 1-9.

Camuffo, D., 1998. Microclimate for Cultural Heritage. Elsevier, Amsterdam.

Dettmer, K. & Engewald, W., 2002. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. Analytical and Bioanalytical Chemistry 373: 490-500.

Dettmer, K. & Engewald, W., 2003. Ambient air analysis of volatile organic compounds using adsorptive enrichment. Chromatographia 57 (Suppl.): S339-S347.

Dupont, A.-L., Tétreault, J., 2000. Cellulose degradation in an acidic environment, Studies in Conservation, 45: 201-210.

Grzywacz, C.M., 2006. Monitoring for gaseous pollutants in museum environments. The Getty Conservation Institute, Los Angeles.

Hatchfield, P.B., 2002. Pollutants in the museum environment: practical strategies for problem solving, exhibition and storage. Archetype Publications, London.

Matisová, E. & Krabáková, S., 1995. Carbon sorbents and their utilization for the preconcentration of organic pollutants in environmental samples. Journal of Chromatography A, 707: 145-179.

Stranger, M., Potgieter-Vermaak, S., Sacco, P., Quaglio, F., Pagani, D., Cocheo, C., Godoi, A.F.L., Van Grieken, R., 2009. Analysis of indoor gaseous formic and acetic acid, using radial diffusive samplers. Environmental Monitoring and Assessment 149: 411-417.

Tétreault, J., 2003. Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies, and preservation management. Canadian Conservation Institute, Ottawa.

Zhang, Y. & Mo, J., 2009. Real-Time Monitoring of Indoor Organic Compounds. In: T. Salthammer, E. Uhde (eds.), Organic Indoor Air Pollutants: Occurrence, Measurement, Evaluation, Weinheim, Wiley-VCH, 65-100.

9.2 THE USE OF DIFFUSIVE SAMPLERS

Introduction

During the past few years, diffusive sampling has been increasingly used for the assessment of environmental exposure to air pollutants both in outdoor and indoor air. The two main factors responsible for the increasing popularity of this method are its simplicity and low cost. Following the definition of the European standard EN 13528-1 (2002), a diffusive sampler is defined as a "*device which is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static layer or a porous material and/or permeation through a membrane, but which does not involve the active movement of air through the device*". The same source recommends the use of the expression "diffusive sampler" instead of "passive sampler" even if the latter expression came into everyday use long time ago and is still largely used. The availability of traditional monitoring devices to assess the air quality in relation to the conservation of cultural heritage can be a problem considering that many institutions are often underfunded. Therefore, the acquisition of expensive instruments to carry out occasional measurements of air pollutants might not be justified. The cheap and easy to use diffusive monitoring technique can be a viable tool to overcome this difficulty. Diffusive sampling devices allow measurements of an average exposure over a long period of time, on the order of days to several weeks, according to the intrinsic characteristics of the various samplers which can be more or less suitable for an extended use (ideally one month) particularly useful for monitoring cultural heritage objects. The low cost and easy operation of the diffusive sampling technique make it an ideal tool for large scale air pollution surveys with a high spatial resolution (De Saeger et al. 1995; De Saeger & Payrissat 1996). The technique is particularly suited to determine the pollutant distribution over a large area near a monument, or to assess air quality indoors simultaneously in many different rooms of museums, galleries and archives. Speaking in broad terms, which lie outside the specific goal of cultural heritage protection, the class of diffusive samplers is wide and comprises different types of devices having various features such as geometry, adsorbing media etc. These devices can generally be classified as *adsorption samplers* and *reaction samplers*. In adsorption samplers, the substance to be determined is enriched on the sampling phase only as a result of physical adsorption and remains unchanged whereas in reaction samplers the substance is immobilised and enriched by chemical transformation. In the case of absorption/adsorption samplers substance-specific properties, such as molecule size of the adsorbent, its polarity and volatility determine the adsorbed weight of substance per weight of adsorbent. Obviously, if several substances are present simultaneously, competition can occur during adsorption. In the case of reaction samplers, these can either display the results directly, or after analysis. For the former type of reactive samplers, the reaction product causes a change in the colour of an indicator, whose colour intensity (for badge-type samplers) or length of the coloured zone (for tube-type samplers) is evaluated after sampling. Reaction samplers which do not display the result directly must be analysed in the laboratory after sampling as it is done with the adsorption samplers. Overall, the diffusive technique is basically used for the determination of time-weighted average concentrations of analytes over a long period of time. Diffusive sampling is particularly suitable for long-term exposure because a single device and a single determination are sufficient to yield information on the time-weighted average concentrations of analytes during the entire exposure period. In contrast to this, with real-time automatic instrumentation or "quick" diffusive samplers (i.e. samplers that cannot be used for long time due to their limited collection capacity for the analyte) it is necessary to collect a number of subsequent samples to cover the entire period of interest. It is clear that "slow" diffusive samplers (that is, samplers with low analyte uptake rate, and consequently lower sensitivity) cannot be used for short sampling time and therefore it is fundamental to choose the proper device for a given measurement goal. Maps of the pollutant concentrations over the area surrounding a monument can be obtained by interpolation of the diffusive sampler measurements. More than a room of a museum can be monitored at the same time giving a representative picture of air pollution integrated over a given period. A guide for general principles, requirements, selection and application of the diffusive sampling technique was prepared by CEN - Technical Committee 264 - Working Group 11 (EN 13528-1,2,3:2002).

Principles of diffusive sampling

All diffusive samplers operate on the principle of diffusion of gases from the atmosphere along a sampler onto an absorbing medium according to Fick's law (Figure 1).

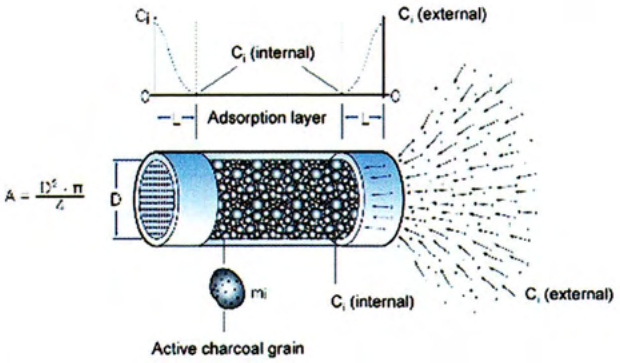

Fig. 1 - Schematic drawing of a diffusive sampler of diffusion path length, L, *and active area* A *and resulting analyte concentration profile.*

The theoretical uptake rate of the sampler is a function of the length L (cm) and the cross-sectional area, A (cm^2), of the stationary air layer within the sampler, and can be calculated provided that the diffusion coefficient D (cm^2 s^{-1}) of the gas of interest is known. The uptake rate U_r (cm^3 s^{-1}) is defined as:

$$U_r = \frac{DA}{L}$$

U_r has the physical dimension of a flow rate even though in diffusive samplers no movement of air is present. Such sampling rate is, theoretically, a constant for a given analyte, but this is based on the assumption that the concentration at the entrance of the sampler is equal to the ambient concentration. In order for this to occur, it is necessary that the concentration gradient at this point be negligible. This means that the concentration change of the measured atmosphere due to the uptake of analyte by the sampler must be negligible. This is the case either at relatively low uptake rates (and hence sensitivity of the diffusive sampler), or when the convection of the atmosphere around the sampler is sufficiently strong to provide effective supply of the analyte. For the above reason, all diffusive

samplers work in steady state conditions only when the air velocity exceeds a given limit, and are unreliable when the air velocity is below such limit. Constant sampling rate should be expected for air velocities above 10 cm s^{-1}, this value corresponding to the average velocity of air in an indoor environment due to natural convection. Therefore, the sampler should work in optimal conditions even with a minimum velocity of the ambient air. The diffusion path length is nominally the distance from the mouth of the sampler to the reaction surface at the other end of the sampler. Disturbance of the stationary air layer, such as the effect of wind turbulence, can shorten the nominal path length (Brown, 1993). Conversely, the use of a turbulence-damping membrane at the inlet can increase the effective path length due to a quasi-laminar layer of air forming adjacent to the outside of the membrane. In a similar manner, under conditions of low external air velocity, the effective diffusion path is also increased. The value of the extra length of static air depends on the external geometry of the sampler, being roughly proportional to the linear cross-section of the sampler surface, and depending also on its nominal path length. Thus a sampler with a small cross-section and a long internal air gap will be relatively less affected by air velocity in comparison to a short and large-diameter sampler.

Choice of a proper diffusive sampler

Diffusive samplers have been developed for various gaseous pollutants. The Palmes diffusion tube for the measurement of NO_2 is certainly the best known (Figure 2). This diffusive sampler, which can be called the "ancestor" of the diffusive sampler family, was developed in the United States of America as an on-person air sampler (Palmes & Gunnisson, 1973; Palmes et al. 1976), for field studies on NO_2 related to occupational health. Palmes samplers were first introduced for monitoring ambient NO_2 by Atkins (1986) and since then they have been widely used for studies in urban and rural areas (Campbell et al. 1994 and references therein).

One end of the sampler contains a sorbent that fixes the pollutant at a rate controlled by molecular diffusion. The absorption medium is triethanolamine (TEA) on a stainless steel mesh for NO_2. After the period of deployment (ideally 2 weeks) the sampler is sent to the laboratory for chemical analysis using either colorimetry or ion chromatography. It is important to note that the reliability of TEA as a coating material for NO_2 has not yet definitively been assessed. As a matter of fact, there is now a wealth of studies which have reported conflicting results for NO_2 in comparison to the reference technique for NO_2 (i.e. chemiluminescence). For instance, overestimation of NO_2 has been reported by Campbell et al. (1994) and by Gair & Penkett (1995). They have found overestimation of up to 40% that they attributed to a shortening of the diffusion path due to air velocity across the face of the tube. However, in contrast to these results, Campbell (1988) and Atkins & Lee (1995) reported an accuracy within 7% and 3%, respectively, in comparison to active monitoring. In a study of Heal and Cape (1997) a numerical model of coupled chemistry and diffusion within the tube was used to investigate the possibility that chemical reactions within the tube can alter the concentration of NO_2 leading to the overestimation noticed in the other studies mentioned above. In another study, Heal et al. (1999) have shown that the extent of overestimation depends on the relative concentration of NO_2, NO and O_3. Overestimation is likely to be the greatest in urban locations (i.e. at high NO levels) whereas in rural areas, where [NO] < NO_2], the overestimation is within the measurement uncertainty. It is also interesting to mention that many field intercomparison exercises were organised as part of the quality assurance and control procedures of the UK Department of Environment Transport and Regions NO_2 network. In one of them (AEA 1999), thirty eight laboratories took part in the exercise. As a result of the study, there was a substantial range in the average bias from –39% to + 58% relative to the chemiluminescence technique when the samplers were analysed in the laboratory of the single participants. In addition, reanalysis of samples performed by a single central independent laboratory for all participants showed a general increase in the concentrations (explained on the basis of incomplete extraction of absorbed NO_2 on TEA) and a difficult to explain decrease for many of them. The key aspect for TEA is that the TEA adduct that during the analysis gives nitrite can be sensitive to temperature, to light and perhaps also to bacterial degradation as it was suggested by Heal et al. (2000). In summary, it seems likely that a mixture of positive and negative biases can occur when the Palmes sampler is used. As a consequence the final result will depend on a series of confounding processes. It goes without saying that if this type of diffusion sampler is to be used with confidence by a curator, then it is important that its performance with regard to the reference method is understood. Other samplers have also been developed, among them the Passam sampler, produced in Switzerland, directly derived from the Palmes design and still based on the use of TEA. Devices based on other collecting surfaces such as treated carbon (i.e. the Analyst® sampler represented in Figure 3) are much more reliable. A slightly different design was adopted to

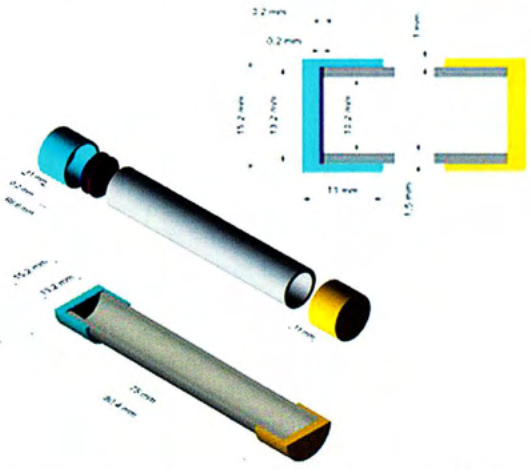

Fig. 2 - Tube type sampler: light blue = cap; purple = mesh grid; grey = polyacrylic body; yellow = cap.

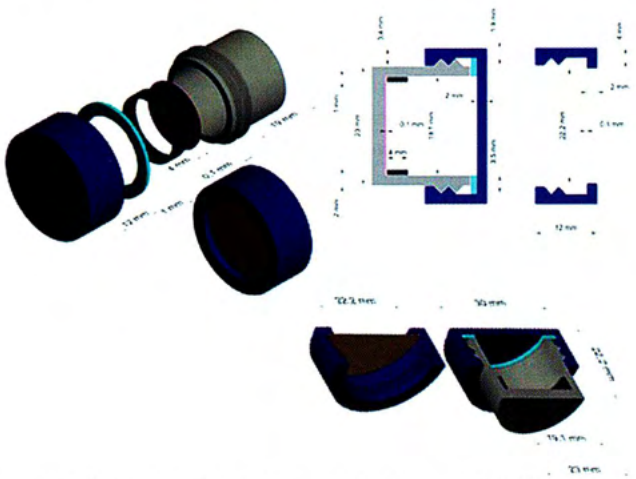

Fig. 3 - Exploded view of the Analyst® sampler: Blue = cap; light blue = gasket; black = spacer ring ; purple = carbon treated filter; grey = body.

monitor NO_x. For this sampler the absorbing pad is placed in front of an oxidant surface, placed at the bottom of the vial, which is able to convert NO to NO_2. These samplers have been used for several successful campaigns and intercomparisons both for NO_2 and for NO_x (e.g. De Santis et al 2002) and for monitoring air quality in connection with the protection of cultural heritage (De Santis et al. 2000; De Santis et al. 2001).

While the Palmes sampler which can be classified as a "tube sampler" needs a relatively long time of exposure, it should be recognised that sampling often has to be performed with better time resolution (e.g. in a workplace to determine shift worker exposure). In order to have maximum sensitivity a sampler design should have a high *A/L* ratio where *A* is the active area and *L* is the diffusion length of the sampler. This type of sampler is called "badge sampler". Figure 4 shows an example of a badge type sampler.

Tube type samplers are therefore less sensitive compared to badge type samplers and hence the former should be privileged for the use in the field of cultural heritage and for longer exposure periods. The same line of reasoning applies to radial devices (i.e. Radiello®; Figure 5) which, due to their high uptake rate, are intended for short term monitoring.

While it is true that high sensitivity provided by radial or badge-type samplers is of interest for occupational and environmental monitoring, in the case of delicate surfaces the determination of a long-time weighted average is clearly much more important. In Table 1 a list of commercially available diffusive samplers is shown.

Table 1. *Summary of the most widespread commercially available diffusive samplers.*

Passive sampler	Species determined	Reference
Tube type		
Gradko	NO_x, NO_2, NH_3, VOC, SO_2, H_2S, O_3, HCHO, Acid Gases	http://www.gradko.co.uk
Passam	NO_x, NO_2, NH_3, SO_2, H_2S, O_3, C_6H_6	http://www.passam.ch
Analyst™	NO_x, NO_2, NH_3, VOC, SO_2, H_2S, O_3, HCHO, HCl, HF, HNO_3, HONO, BTEX	http://www.marbaglass.net/
ORSA	VOC	http://www.draeger.de
Badge type		
Passam	NO_2	http://www.passam.ch
Ogawa	NO_x, NO_2, NH_3, SO_2, O_3	http://www.ogawausa.com
IVL	NO_2, NH_3, VOC, SO_2, O_3, HNO_3, Organic Acids, Hg, VOC	http://www.diffusivesampling.ivl.se
Maxxam	SO_2, H_2S, NO_2, O_3, NO_x, NH_3, VOC, BTEX	http://www.maxxam.ca
SKC	Organic Vapours	http://www.skcinc.com
Radial type		
Radiello® sampler	SO_2, NO_2, O_3, HF, HCl VOC, BTEX, Aldehydes	http://www.sigmaaldrich.com
DSD-DNPH Passive Sampling Device	Aldehydes	http://www.sigmaaldrich.com

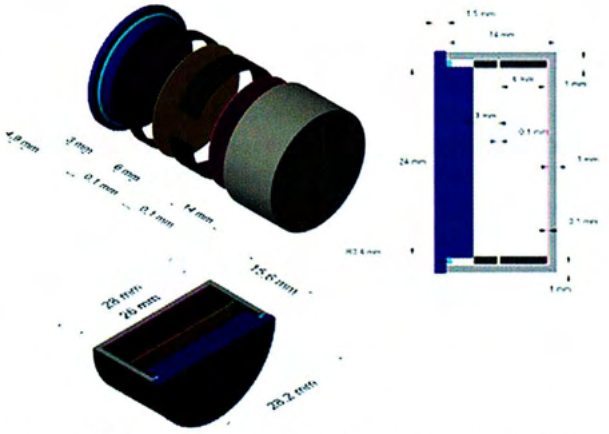

Fig. 4 - Exploded view of a badge type sampler: Blue = cap; black = spacer ring; brown = teflon membrane; purple = glass fibre filter; grey = body.

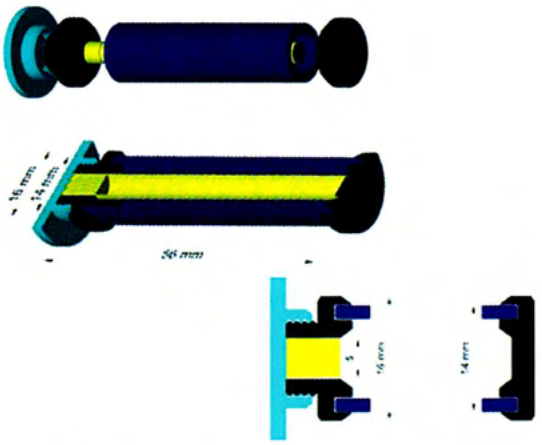

Fig. 5 - Radial symmetry sampler: light blue = cartridge holder; yellow = cartridge; blue = diffusion membrane.

Diffusive sampling of other analytes relevant for the protection of cultural heritage

The determination of NO_x is certainly the best studied application of diffusive sampling. Due to its environmental relevance, many studies have been performed for the development and validation of diffusive samplers for NO_x, and some inherent weaknesses of the common practice of sampling NO_2 by TEA-based samplers have been demonstrated. The principle of diffusive sampling, however, is a general one and lends itself ideally to the sampling and analytical determination of airborne gaseous contaminants with environmental relevance or relevance for cultural heritage protection. Most of these samplers have not been developed particularly for the purpose of air quality monitoring in museums, archives and galleries (see Table 1), but they can easily be used for this purpose, provided their sensitivity is sufficient. This is depending on the individual analyte, the duration of exposure, and the principle of detection or analytical method applied. As was discussed in the previous section, a diffusive sampler is a device that collects a time-weighted average (TWA) concentration of an analyte. The longer the period of exposure, or the higher the concentration, the larger is the amount of analyte collected (= the dose) on the diffusive sampler. This allows to roughly estimate what concentration levels can still be monitored by a given sampler. Clearly, this is a certain simplification. It assumes that there is no back-diffusion of the analytes collected on the adsorbent, and, further, that there is no degradation of the analyte by e.g. light,

ozone, or other airborne contaminants. Moreover, it is assumed that the diffusive sampler has a sufficiently large capacity, so that high concentrations of a concomitant airborne pollutant do not lead to the competition for binding sites with the analyte.

With few exceptions, diffusive samplers require laboratory analysis by chromatographic or spectroscopic methods. The analytical method depends on the actual analyte to be determined.

Volatile organic compounds (VOCs) can be sampled and analysed by adsorption onto active charcoal, polymeric adsorbents or molecular sieves. As discussed above for the analysis of NO_2, there are three common designs for diffusive samplers for VOCs: *i)* tube type samplers (Figure 6), *ii)* badge type samplers (Figure 7) and *iii)* radial samplers (Figure 5). Due to their different designs, they differ significantly in their uptake rate which is a critical factor in the design of a sampling campaign (see Table 2). It is evident that the uptake rate is governed by the physical dimensions of the diffusion path of the sampler; however, for a more accurate quantitation the exact uptake rates for individual analytes must be determined experimentally. Uptake rates for the various common sampler designs such as the Radiello® sampler (Supelco, 2004), badge-type samplers (HSE, 2001) and the Perkin Elmer diffusive sampler (HSE, 2001b) have been published.

Table 2. *Typical uptake rates of diffusive samplers for VOCs.*

Sampler	Supplier	Type of sampler	Dimensions	Uptake rate
Ultra Passive Samplers	SKC Inc., Eighty Four, PA, USA	Badge	3.5 [dia.] x 6.3 x 1.5 cm	11 – 17 ml min^{-1} @ 10-200 cm s^{-1} linear velocity; 5 – 10 ml min^{-1} @ <5 cm s^{-1} linear velocity
Radiello diffusive samplers	Supelco, Bellefonte, PA, USA	Radial diffusion tube	60 mm length x 4.8 (5.8) mm dia (sampler); 60 mm length x 16 mm dia (diffusive body)	40 – 125 ml min^{-1} @ 25°C
Perkin Elmer thermal desorption tubes equipped with diffusive sampling cap	Perkin Elmer Inc., Wellesley, MA, USA	Tube type	Desorption tube: 90 mm x 6.3 mm O.D. x 5.0 mm I.D. Sampling distance: 14 mm	0.3 – 0.7 ml min^{-1}
Dräger ORSA diffusive sampler	Drägerwerk AG & Co. KG, Lübeck, Germany	Short tube with both ends open	Sampler: 35 mm x 10 mm ID, diffusion length 5 mm (on both sides)	3.5 – 9.5 ml min^{-1}
3M Organic vapour monitor (Type 3500)	3M, St. Paul, MN, USA	Badge type sampler	Active area 30 mm diam., 10 mm diffusion length	20 – 40 ml min^{-1}

When selecting the best-suited sampler for a particular task, the choice of adsorbent material is of paramount importance. Strong adsorbents, such as active charcoal, are preferred as they provide quantitative trapping of the analytes. However, this can become a disadvantage as thermal desorption is applied. In this case, a compromise must be made, and a weaker sorbent be applied that also ensures quantitative desorption of the analyte prior to GC analysis. Polymeric adsorbents, such as Tenax are a good choice then. However, Tenax is

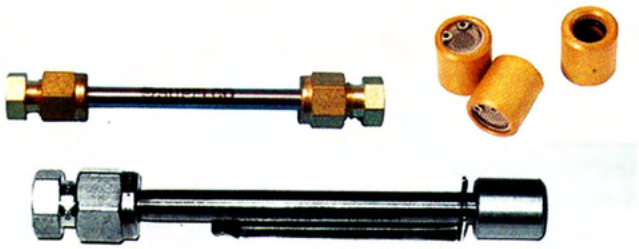

Fig. 6 - Top left: Thermal desorption tubes for Perkin-Elmer ATD 400 or Turbo Matrix thermal desorbers with fitting diffusion caps (top right). Below a photograph of a stainless steel thermal desorption tube with attached diffusion cap. (Photos courtesy of Supelco, Bellefonte, PA).

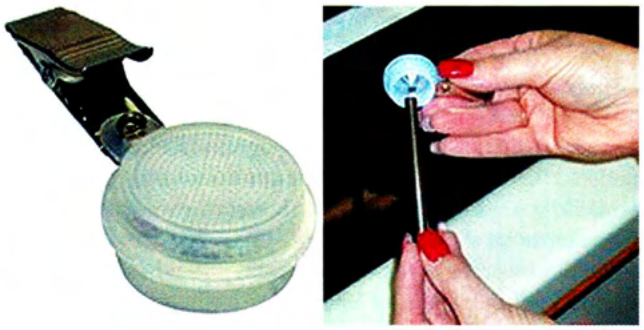

Fig. 7 - Left: A badge-type sampler for the collection of Volatile organic compounds by diffusive sampling. Right: The adsorbent material can easily and directly be transferred from the badge-type sampler to a thermal desorption tube for subsequent analysis in the laboratory. (Photos courtesy of SKC Inc., Eighty Four, PA, USA).

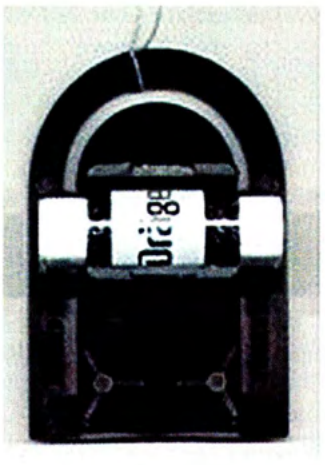

Fig. 8 - ORSA sampling tube for volatile organic compounds with holder. Photo courtesy of Draegerwerk, Lübeck, D.

only suitable for moderately to non-polar compounds ≥ C6. Solvent desorption (typically by CS_2) provides good recoveries even from strong adsorbents such as active charcoal. The general disadvantage of solvent desorption versus thermal desorption is the significantly lower sensitivity, resulting from the ability of transferring only a small sample fraction to the chromatographic system while in thermal desorption the entire sample trapped onto the adsorbent tube or cartridge is analysed.

While the principles of diffusive sampling do not allow for strong deviations from the three general sampler designs that have been presented before (tube type, badge type and radial sampling), there are frequent variations of the main types. One of the well-known types is the ORSA ('organic sampler') marketed by e.g. the Dräger company (Figure 8). It consists of a diffusion tube of short length and large diameter (ca. 35 x 10 mm)

which is open at both ends. Analytes can thus diffuse from both sides to the active charcoal trapping zone. Due to the low uptake rate, extended periods of sampling (7 to 14 days) are usually required. Gas chromatographic analysis is performed after elution with CS_2. The 'TOPAS' sampler, produced by Gerstel (Mülheim, Germany) provides a diffusive sampler that, due to its badge format has a large collecting surface and thus uptake rate. On the other hand, this sampler can be thermally desorbed due to its particular design (Figure 9): the adsorbent material (Tenax) is contained in an aluminum body that has a spiral grove. When the sample is to be desorbed, the badge is placed in a particularly adapted autosampler that seals the sampler body hermetically. Then the carrier gas is directed over the adsorbent from the central to the outer hole, thereby thermally desorbing the analytes and transferring them to the GC.

The fact that the sampler requires a dedicated thermal desorption unit which is hardly compatible with other types of active or passive sampling, explains why this interesting realisation of passive sampling has not found widespread acceptance on the market.

*Fig. 9 - TOPAS badge: basic aluminium body with cut groove (*left*), badge fitted for measuring, filled with Tenax and encapsulated with the microporous Teflon membrane (*middle*) and reverse view of badge fitted for storage and GC analysis; view of desorption gas inlet and outlet (*right*). (Photos courtesy of Gerstel GmbH, Mülheim/Ruhr, Germany).*

Generally speaking, VOC monitoring in museums, archives and galleries has a different importance than in the monitoring of environmental or occupational exposure: in the latter case, VOCs are monitored because they are toxic or may even be classified as carcinogenic. In contrast to this, VOC monitoring in museums, archives or galleries is considered of lower importance as long as there are no carbonyl or otherwise (re-)active analytes. This calls for a different evaluation of VOC levels encountered: while elevated benzene levels may be considered very critical in indoor environments (due to the classification as proven carcinogenic substance), it does not raise any particular concern from the conservation point of view since it is essentially non-reactive under normal environmental conditions.

In contrast to simple hydrocarbons (aliphatic or aromatic), *aldehydes* represent a class of analytes that raises far bigger concern due to their reactivity. Particularly the two lowest members of the group of aliphatic aldehydes, formaldehyde (methanal) and acetaldehyde (ethanal) are important to be monitored, since they can be emitted from various indoor sources, and they can be further transformed by photochemical reactions to the corresponding acids (formic acid (methanoic acid) and acetic acid (ethanoic acid)) which poses an even higher risk to the objects of collections and archives. For the higher (and thus less reactive) aldehydes, collection is possible onto organic polymer- and carbon based adsorbents, such as Carboxen 569, Carbopack B or Tenax TA (Hallama et al., 1998), followed by thermal desorption and gas chromatographic analysis. The lower aldehydes, however, do not possess a sufficiently high collection efficiency in passive sampling of the unmodified compounds. For this purpose, diffusive samplers have been developed which combine the adsorption with a simultaneous derivatization step. The reaction used most commonly for this purpose is the one of aldehydes of aldehydes with dinitrophenylhydrazine (DNPH, typically in the form of impregnated particles or pads as collecting surface) to form the corresponding dinitrophenylhydrazones. These dinitrophenylhydrazones are relatively stable compounds that immobilize the analyte by reaction onto the solid support. After exposure, the DNPH derivatives of the carbonyl compounds are eluted from their solid support with acetonitrile and subjected to high-performace liquid chromatographic (HPLC) analysis. Due to their strong UV absorption, they can be detected with good sensitivity. The reaction is nearly quantitative only for formaldehyde, but reaction yields decrease for higher homologues (Liu et al., 2001). This may be an issue when total carbonyl compounds concentrations are to be reported by this method. For formaldehyde and acetaldehyde, however, the quantitative results will not be affected significantly.

Samplers for aldehydes exist in all formats previously discussed, i.e., tube type (Gibson et al., 1997), badge type (Druzik, 1991) and radial diffusion devices (Levin and Lindahl, 1994). In the case of badge type samplers, the format of a flat, square diffusive sampler has become particularly popular, such as the one marketed now by SKC and initially developed at Umea University (Figure 10). The advantage of this design is that it integrates already a reference which can serve as a field blank for the measurement. Due to the ubiquitous occurrence of carbonyl compounds, it is mandatory for aldehyde analysis to assess field and laboratory blanks. In the case of the SKC badge type sampler, the reference section of the DNPH-impregnated tape is contained within the same housing as the active section, but is not exposed. It is therefore assumed that this section reflects the background level of contamination that arises from the transport, handling and storage of this analyte prior to analysis. Although a highly versatile approach, the DNPH sampling of aldehydes remains problematic for longer sampling times: quantitative evaluation can be interfered by other atmospheric pollutants (ozone, NO_x) that also produce coloured products and may co-elute with the reaction prod-

*Fig. 10 - Photograph of a badge-type diffusion sampler for aldehydes based on collection onto a DNPH-impregnated filter pad (*left*) and a tube-type diffusion sampler for formaldehyde, based on the adduct formation with sodium bisulfite (*middle*) as well as a badge-type sampler (*right*) of the same principle for 15 min – 8 h exposure and subsequent laboratory analysis in both cases. The DNPH derivatives of the carbonyl compounds are analysed by HPLC, whereas the aldehyde-bisulfite complex is analysed in the laboratory by the chromotropic acid method and photometric determination (all photos courtesy of SKC Int., Eighty Four, PA, USA).*

ucts of aldehydes and ketones even after chromatographic separation (Pötter & Karst, 1996). Moreover, the trapped DNPH-aldehydes can react with other atmospheric pollutants which reduces the possibility of extending a collection period for more than 7 days to improve detection limits. In contrast to this, the collection of formaldehyde on a sodium sulfite-impregnated sampler (by the formation of an adduct that can be analysed colorimetrically) is practically unaffected by other indoor air pollutants, and also produces more stable derivatives. The procedure is (due to the use of the chromotropic acid method for the photometric determination) however only applicable to formaldehyde. Higher aldehydes or carbonyl compounds do not react.

A further method is available for the determination of formaldehyde in indoor atmospheres by diffusive sampling, developed and marketed by Draeger (Luebeck, Germany) under the name BioCheck F (Figure 11). This method is based on the enzymatic conversion of formaldehyde in the course of which a coloured product is formed in a coupled reaction. The enzyme is immobilized and all required reagents are contained in the test kit in solution in a sealed ampoule which is opened and whose content is brought into contact with the enzyme to start the exposure and measurement period. After two hours, the colour formation is evaluated in comparison to a comparator strip. This assay is not only very sensitive, but gives a relatively fast response and

Table 3. *Overview of commercially available diffusive samplers for formaldehyde and other aldehydes.*

	SKC Indoor Air Formaldehyde Sampler	**UMEx 100 Passive Sampler for Formaldehyde**	**SKC Personal Formaldehyde Samplers**	**Dräger BioCheck F**	**Radiello 165 aldehyde sampler**	**DSD-DNPH Passive Sampling Tubes**
Measurement Principle	Formation of formaldehyde-bisulfite adduct; laboratory analysis by chromotropic acid assay	Formation of dinitrophenylhydrazin derivatives of carbonyl compounds, and subsequent HPLC-UV analysis	A permeable plastic membrane allows for controlled diffusion of air onto a chemically impregnated paper; no liquid reagents are necessary for sampling. Formaldehyde combines with the reactive media (sodium hydrogen sulfite) on the paper and forms the stable compound formaldehyde bisulfite. The sampler is then sent to an accredited laboratory for chromotropic acid analysis.	Enzyme-based badge measurement system for conducting guideline measurements of formaldehyde which can be used without any additional accessories	Stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. Aldehydes react with 2,4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones are then extracted with acetronitrile and analyzed by reverse phase HPLC and UV detection.	Silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) acts as the adsorbent. Aldehydes and ketones diffuse through the porous PE membrane reacting with DNPH to form stable derivatives. The DNPH-derivatives are then eluted with acetonitrile and analyzed by high performance liquid chromatography (HPLC).
Sampling Time	5-7 days	24 hours or 7 days	PEL: 8 Hours STEL: 15 Minutes	2 hours	15 min-7 days (uptake rate: 99 ml min^{-1} (formaldehyde); acetaldehyde: 84 ml min^{-1}; other aldehydes: 11-90 ml min^{-1} (at 25°C and 1013 hPa)	24 h to 7 days (uptake rate: 71.9 ml min^{-1} for formaldehyde; 53.6 ml min^{-1} for acetaldehyde and 24-46 ml min^{-1} for other aldehydes)
Detection Limit	0.01 ppm ± 30% 0.02 ± 15%	24-hrs: 2 ppb (0.002 mg m^{-3}) 7 days: 0.2 ppb (0.0002 mg/m^3)	PEL: 0.2 to 2 ppm STEL: 0.5 to 6 ppm	0.05 – 0.3 ppm	0.1 (formaldehyde, acetaldehyde) to 0.9 µg m^{-3} (quantitation limit)	1-2 ppb (est.)
Interferences	None known	Ozone at levels > 0.5 ppm. Large amounts of carbonyl compounds may reduce the uptake of formaldehyde.	None known	None known	Ozone at levels >100 ppb (only for acetaldehyde); acetone at very high concentrations (50,000 µg m^{-3}) partially suppresses the formation of acrolein-DNPH derivative.	
Shelf life	1 year	1 year when stored at ≤ 39.2 F (4°C)	1 year		6 months before analysis, 60 days after sampling (at 4°C in the dark)	
Size	3.8 inches (9.7 cm) long	8.6 x 2.8 x 0.89 cm				
Accuracy	0.025 - 1.0 ppm ± 15%	± 25%, exceeds OSHA requirements	Better than 1%		14-23% total expanded uncertainty (2σ)	5.5 and 8.6% for formaldehyde and acetaldehyde, respectively
Precision			PEL: 6.1% STEL: 6.3%		Ca. 5%	2-3% for formaldehyde and acetaldehyde

PEL: personal exposure level; STEL: short-term exposure level

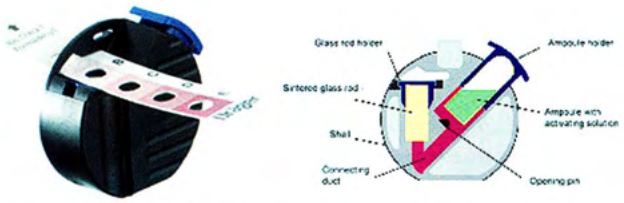

Figure 11 - a) Dräger BioCheck F formaldehyde sampling device and b) schematic drawing of the working principle (Anon., 2001).

again is specific for formaldehyde while other aldehydes and other atmospheric pollutants do not interfere.

Organic acids. Being able to determine formic and acetic acid concentrations in the indoor atmosphere of museums, galleries and archives is most relevant for conservators and restorers (Gibson and Watt, 2010). Several sampling and analysis techniques exist for these analytes (and are often suitable to determine as well higher organic acids, or hydrofluoric acid). One of the earliest passive sampling devices designed for the collection of organic acids was the Palmes tube that was optimised by Gibson et al. (1997b) for the collection of acetic acid (HAc) and hydrofluoric acid (HF). This consists of a polyethylene tube which holds inside a polyethylene cap two stainless steel mesh discs that are impregnated with a small volume (typically 40 µl) of a solution containing 1 M potassium hydroxide and 10% (v/v) ethylene glycol dimethyl ether (Figure 2). The samplers are typically freshly prepared before use, or must be stored at 4°C before use. After exposure, the acids, collected in the form of their potassium salts, are eluted with deionised water and the eluate is subjected to ion chromatographic analysis. The chromatographic separation and thus uninterfered determination of concurrent acetate and fluoride is a particularly difficult task and requires careful optimisation of the chromatographic conditions (Kontozova-Deutsch et al., 2008).

Although generally feasible and frequently used, the tube-type design of the Palmes diffusion sampler leads to only low sampling rates, this implying the necessity of sampling for extended exposure times (Gibson et al., 1997a). Alternatively, Radiello® radial diffusive samplers have been developed and validated for the simultaneous sampling of formic, acetic and hydrofluoric acid (Stranger et al., 2009). Sampling rates range from 80-110 ml/min^{-1} for formic acid, and from 90-100 ml/min^{-1} for acetic acid for exposure times between 24 h and 7 days (Stranger et al., 2009).

Alternatively, Dremetsika et al. (2005) reported the determination of acetic and formic acid using activated charcoal personal passive samplers in 15 display cases and 5 cabinets of the National Archaeological Museum and the Numismatic Museum of Athens.

Although not passive samplers in the typical sense, two further techniques for the determination of atmospheric concentrations of formic and acetic acid shall be mentioned due to their importance in the assessment of indoor atmospheres in museums, galleries and archives: A-D strips and metal targets for the Oddy test.

A-D Strips, developed by the Image Permanence Institute of the Rochester Institute of Technology (Rochester, NY, USA), are dye-coated paper strips that detect and measure the severity of acetate film deterioration. Initially developed to monitor the state of degradation of cellulose acetate films in film archives, the A-D strips have been used also in other museum or archive environments to assess concentrations of organic acids in a semi-quantitative way. Acetic acid (and other acids as well) lead to a clearly detectable colour change of the paper strip impregnated with an acid/base indicator (bromocresol green) that is sensitive in the relevant concentration range. When placed inside a closed can, bag, box, or cabinet, A-D Strips change colour in the presence of the acidic vapour given off by degrading film (Figure 12). As the level of acidity increases, they change from their original blue colour through blue-green, green, and yellow-green, and finally to bright yellow. The reference pencil included in the kit is printed with four bands of colour, numbered from 0 to 3; these correspond to strip colours at four levels of acidity. After exposure to film in a sealed enclosure for the required length of time, the strip colour is compared to the colour bands on the pencil. The number of the band most closely matching the colour of the strip is recorded. The exposure time of A-D-strips is depending on the environmental temperature and increases with decreasing temperature. A-D-strips are not suitable for monitoring during extended periods of time since the colour of the indicator may shift, or bleach under the influence of daylight (Image Permanence Institute, 2001). If materials are to be tested for their emissions of acetic acid, it is recommended to perform the tests with A-D strips in small, opaque containers.

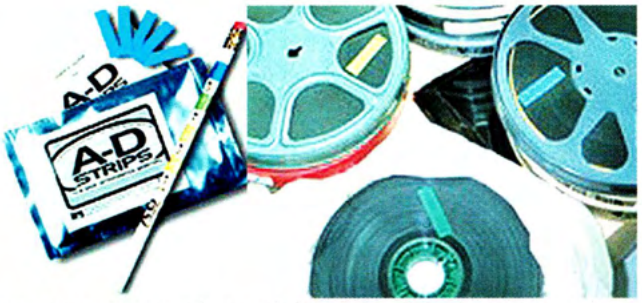

Figure 12 - A-D strips with pen with the colour scale for the assessment of cellulose acetate film condition, based on the concentration of acetate in a closed container (left), and A-D strips attached to cellulose acetate film roll exposed for the corresponding period of time. (Courtesy of the Image Permanence Institute, Rochester, NY).

Similar to the A-D strips, the Oddy test also is more functioning as a dosimeter, rather than a diffusive sampler. The test has been introduced by Andrew Oddy, conservator at the British Museum in London, into the field of cultural heritage and conservation in 1973 (Oddy, 1973).

The Oddy test determines the corrosivity of emissions of materials to be tested (e.g. for their suitability to be used in display cases) on metal coupons in a closed container at controlled temperature and relative humidity. In most cases, copper, silver or lead coupons are used, but other metals, such as aluminium, manganese or zinc have also proven useful (Green and Thickett, 1993)

The Oddy test has to be performed under very well controlled conditions, since otherwise its results become hardly interpretable (Green and Thickett, 1993). For this reason, and also to accelerate the formation of observable changes on the surface of the metal coupons, these are exposed in a closed exposure chamber at 60°C and close to 100% RH to the materials to be tested for 28 days. After this period, the deterioration of the surface of the metal coupon in comparison to a coupon that has been exposed to the same environmental conditions, however, without the material to be tested, is evaluated.

While the simplicity of this test makes it to be commonly used in many museum and conservation laboratories, its drawback is the lack of selectivity when effects (deterioration of the surface of metal coupons) are evaluated. These may be caused by different pollutants (e.g., acids, carbonyl compounds), and their effects may even be enhanced in a synergistic way. It is thus often difficult to conclude from a positive response in the Oddy test the source of

the gaseous pollutant. Also, the 28 days exposure period may be considered too long in many instances.

Among the inorganic trace gases, diffusive sampling of the two acidic gases H_2S and SO_2 shall be discussed due to their great importance for the conservation of cultural heritage. For SO_2 monitoring, similar formats of diffusive samplers are used as for NO_2 monitoring: the Palmes diffusion tube, as improved and marketed by Gradko International Ltd. (Winchester, UK) is frequently used for SO_2 monitoring in indoor environments. It consists of a FEP (fluorinated ethylene polymer) tube that holds on one of its ends a stainless steel mesh impregnated with potassium hydroxide. A porous polyethylene frit is attached to the other end of the tube to avoid turbulence inside the tube and to define the diffusion pathlength (see Figure 2). The SO_2 collected is eluted with deionised water and oxidised with H_2O_2 to form sulphate which is determined by ion chromatography. Given the requirement of monitoring airborne SO_2 and NO_2 concentrations often simultaneously, a simultaneous NO_2/SO_2 diffusive sampler is also existing.

The determination of hydrogen sulphide (H_2S) is more complicated than that of the other acidic trace gases NO_2 and SO_2 because of its lower acidity, and the lower concentration levels that are typically to be monitored. There are commercially available passive samplers for H_2S, based on the diffusion tube (Analyst®, Gradko), badge (Passam) and the radial diffusion type (Radiello®) design (Table 5).

The general principle of the Radiello is the collection and immobilisation of airborne H_2S onto a solid support impregnated with zinc acetate. H_2S reacts and forms the relatively stable, insoluble ZnS from which sulphide can be eluted after the exposure period in strongly acidic medium. In contact with an oxidizing agent such as ferric chloride in a strongly acid solution it reacts with N,N-dimethyl-p-phenylendiammonium ion to yield methylene blue. This coloured reaction product is determined by spectrophotomety at 665 nm.

Table 4. *Comparison of various commercially available diffusive samplers for SO_2 (also in combination with NO_2).*

	Analyst ® – Sulphur dioxide	**Gradko DIF-600 RTU – Sulphur dioxide sampler**	**Passam SO_2 passive sampler**	**Gradko DIF-500 RTU-RA – combined SO_2/NO_2 sampler**	**SKC UMEx 200 Passive Sampler for Sulfur Dioxide and Nitrogen Dioxide**	**Radiello® combined NO_2 / SO_2 sampler**
Measurement Principle	Absorption of SO_2 on a sodium carbonate impregnated filter. Extraction with a solution containing H_2O_2 and ion chromatographic determination	Absorption of SO_2 in KOH solution, oxidation by H_2O_2, elution and ion chromatographic determination	The diffusive sampler for sulphur dioxide is based on the principle of the diffusion of sulphur dioxide molecules onto an absorbant medium, in this case a mixture of potassium carbonate and glycerine. The total amount of sulphur dioxide is extracted and ion-chromatographically determined.	Absorption of SO_2 (and NO_2) in TEA solution, oxidation by H_2O_2, elution and ion chromatographic determination	Absorption of SO_2 (and NO_2) on a TEA impregnated tape, elution, oxidation by H_2O_2 and ion chromatographic determination	The sampler is made of microporous polyethylene coated with triethanolamine (TEA). NO_2 and SO_2 are chemisorbed onto TEA respectively as nitrite and sulphite or sulphate ions. Nitrite is quantified by visible spectrophotometry while sulphite and sulphate are analysed by ion chromatography (NO_2 and SO_2 can be analysed together by ion chromatography).
Uptake rate	13 ml min^{-1}	0.95 ml h^{-1}	11.9 ml min^{-1} (at 20°C)	55 ml h^{-1}	15.1 ml min^{-1}	119 ml·min^{-1} (at 25°C abd 1 atm)
Sampling Time	From 1 week to 2 months. Shorter exposure times for high concentrations	1-4 weeks	2-4 weeks	1-4 weeks	15 min to 8 h	Up to 15 days (only up to 7 days recommended at RH > 70%)
Detection Limit	2 ppb for a week-long exposure, 0.5 ppb for a month (3 on 12 blanks for an exposure time of one week)	0.5 ppb over a 2 weeks exposure period	0.2 µg/m^3 for sampling periods of four weeks	2.4 ppb over a 2 weeks exposure period	15 minutes: 2 ppm 8 hours: 0.1 ppm	1 ppb after 7 days of exposure
Working range		4-200 µg m^{-3}	1 - 240 µg m^{-3}	4-200 µg m^{-3}	0.4 to 8 ppm	10,000 to 5,000,000 ppb·min SO_2
Interferences	None known	By sulphate particles		By sulphate particles	None identified	
Shelf life	Before use: 6 months, after exposure: 2 months	12 weeks	12 months before use; 4 months after exposure	12 weeks	18 months	12 months before and 4 months after sampling if stored at 4°C in the dark
Size	25.4 mm x 20 mm	71 mm x 11 mm ID	20 mm ID active surface	71 mm x 11 mm ID	8.6 x 2.8 x 0.89 cm	
Accuracy	At 20 ppb 25%				±30%	
Precision	Relative standard deviation better than 7% (triplicate measurements)	±7% expanded measurement uncertainty	23.4% expanded uncertainty at levels of 20-40 µg	±7% expanded measurement uncertainty		9% expanded uncertainty (2σ)

Table 5. *Comparison of commercially available diffusive samplers for H_2S.*

	Analyst® H_2S sampler	**Gradko DIF-200 RTU – Hydrogen sulphide sampler**	**Radiello® H_2S sampler**	**Passam H_2S Diffusive sampler**
Measurement Principle	H_2S is chemisorbed by silver nitrate. Final quantitation by densitometry.	H_2S is chemisorbed by zinc acetate and transformed into stable zinc sulphide which is then quantitatively determined by visible spectrophotometry	Reaction with zinc acetate to form ZnS. This is eluted in a strongly acidic solution and forms in the presence of an oxidizing agent and an organic compound a blue organic dye (methylene blue)	Collection of H_2S onto an adsorbent medium (cadmium sulphate). To reduce wind disturbance a glass fibre membrane is attached, supported by a wire net.
Uptake rate	7.5 ± 1.2 ml min^{-1}	not reported	69 ml min^{-1}	10.9 ml min^{-1} (at 20°C)
Sampling Time	1 – 4 weeks	2 – 4 weeks	1 h to 15 days	2 – 4 weeks
Detection Limit	400 µg m^{-3} h	0.16 ppb (0.23 µg m^{-3}) for 2 weeks of exposure	30 ppb for 1 h exposure; 1 ppb for 24 h exposure	0.2 µg m^{-3} for a sampling time of 14 days
Working range	400 to 250,000 µgm^{-3} h	not reported	2,000-50,000,000 ppb·min of H_2S	1 — 50 µg m^{-3}
Interferences	None known.	Ozone may reduce the recovery of H_2S. Some reducing agents such as SO_2 may inhibit colour development.		None
Shelf life	12 months before and 6 months after sampling if stored at 4°C in the dark	4 weeks (when stored at 4°C)	12 months before and 6 months after sampling if stored at 4°C in the dark	12 months before use; 3 months after exposure
Size	25 mm x 20 mm	71 mm x 11 mm ID		
Accuracy / Uncertainty	Expanded measurement uncertainty: 15%	Expanded measurement uncertainty: 10%	Total expanded uncertainty (2σ): 9%	Expanded uncertainty: 25.2% at concentration levels of 1 - 30 µg m^{-3}
Precision	4 – 6 %			

Several other concepts and forms of diffusive samplers for H_2S have been presented, but not commercialised or used on a wider basis. Shooter et al. (1995) have reported on the adaption of a fluorimetric method for the determination of sulphide after diffusive sampling. To this purpose, hydrogen sulphide is collected onto a solid support impregnated with silver nitrate. The silver sulphide quenches the fluorescence of fluorescein mercuric acetate which can be detected in a very sensitive way. With a one week exposure period, a detection limit of 50 pptv could be reached.

More recently, De Santis et al. (2006) have investigated the possibility the possibility of using a colorimetric reaction for the detection of hydrogen sulphide by diffusive sampling. A cylindrical black polyethylene housing of 2.54 cm length and 2.04 cm ID serves as the body of the sampler and is closed by caps on both ends. H_2S is collected on a disc of $AgNO_3$-impregnated paper filter placed at the bottom of the housing, facing one of the two end caps which is held in place by a stainless steel ring. During the collection period, when the cap opposite of the collecting pad is replaced by a windscreen, air diffuses to the collecting surface via three open sectors. At the end of the measurement, optical density of the filter paper (caused by the formation of dark Ag_2S) is recorded after opening the cap on the reverse side, and converted to dose or concentration, respectively, via a calibration curve. The working range of this dosimeter is reported as 400 to 250,000 µgm^{-3} h^{-1} where the detection limit is determined by the blank value. Uptake rate is given as 7.5 ml min^{-1} and the precision ranges form 4-6%. No interferences by other trace gases at relevant concentration levels are observed.

An amazingly simple approach for airborne sulphide monitoring was proposed by Horwell et al. (2004). They used black-and-white photographic paper that was cut into small pieces and exposed in opaque film roll boxes to protect from daylight. After washing and fixation, the tarnishing of the silver nitrate gelatine layer is measured by densitometry, or evaluated by comparison with a scale. The method is reported to respond to H_2S concentrations in the range <30 ppb to ~1000 ppb.

Anghelone et al. (2010) recently studied the usability of various heavy metal salts for the colorimetric assay of airborne hydrogen sulphide. In addition to silver nitrate, also lead, cadmium, antimony and mercury salts were studied as they yield dark or coloured reaction products upon exposure to H_2S. Whatman filter paper was soaked in aqueous solutions of the metal salts (acidified and with glycerol added) and cut into rectangular pieces. A polyethylene gasket allowed the exposure of a well-defined area on the filter paper strip to a controlled atmosphere while the covered area was unaffected by the H_2S concentration and served to determine the background value (caused by blank values during storage or handling). Although $AgNO_3$ was again proven to show the most sensitive reaction with H_2S, preference was given to the only slightly less sensitive lead acetate since this is more stable and does not give rise to as high blank values or tanning as does $AgNO_3$. All other metal salts investigated produced a significantly less sensitive response. The dosimeters were evaluated for short term exposure (1-24 h) and showed a working range from 500 ppb.h to >> 12,000 ppb.h. The detection limit is around 100 ppb.h, but this is largely determined by the blank value of the sampler. Further work is required to construct a routinely usable diffusive sampler according to this approach.

Some practical applications

The attention of museum curators to indoor environment was focused in the past mainly to microclimatic parameters rather than to air quality. In the mid 1980s maybe one of the first environmental research programmes on air quality was undertaken by the Getty Conservation Institute (Grzywacz, 1993): the measurement of indoor generated carbonyl compounds in museum environments was performed throughout the USA. The measurements were made in museums, galleries, storage areas, display cases and storage cabinets. The concentrations ranged from less than 2 ppb to nearly 1600 ppb. The highest concentrations were found in areas with little air circulation such as display cases. The use of a diffusive device for the collection of formaldehyde and other carbonyl compounds based on 2,4-dinitrophenylhydrazine was evaluated. The sensitivity was less than one ppb for 24 hours exposure. The agreement with conventional active sampling technique was within 13%. A later work on air pollution assessment inside museums is reported by Hisham and Grosjean (1991), again for the USA (California). Nine southern California museums were chosen for the survey, among them: George C. Page Museum, Natural History Museum, J. Paul Getty Museum, Huntington's Virginia Steele Scott Gallery, LACMA Pavilion for Japanese Art and Southwest Museum. The selection of the institution involved followed three criteria: diversity of the collections, outdoor/indoor air exchange characteristics and geographical locations within Los Angeles area. The air pollutants measured (both by continuous and discontinuous methods) were nitrogen dioxide, nitric acid, peroxyacetylnitrate (PAN) and two chlorinated hydrocarbons (1,1,1-trichloroethane and 1,1,2,2- tetrachloroethene). Nitrogen dioxide and nitric acid were measured by discontinuous active methods. The former was sampled onto small C18 cartridges coated with an alkaline solution of TEA. The cartridges were then extracted with deionized water and analyzed by liquid chromatography. Nitric acid was collected on nylon filters. The filters were extracted with deionized water and analyzed by liquid chromatography. This survey was not really performed by diffusive sampling, a technique which was at the beginning at the time, but TEA coatings and nylon filters employed for pollutant collection were subsequently used in the diffusive sampling development.

In the framework of a European project (ENV4-CT95-088 AER) aimed to identify the main causes of environmental risk to cultural heritage due to unsound use of technology and mass tourism, measurements of gaseous pollutants (SO_2 and NO_2) were performed inside several European museums (Koninklijk Museum voor Schone Kunsten, Antwerp, Correr Museum, Venice, Kunsthistorisches Museum, Vienna, KMSK and Sainsbury Centre for Visual Arts, Norwich) using diffusion tubes based on TEA (Gradko). The results of the monitoring activity carried out inside Koninklijk Museum voor Schone Kunsten are reported by Gysels et al. (2004). Twenty sites were monitored with three replicates for either pollutant. Measurements of aerosol were carried out as well. The results show little differences between different seasons and a homogeneous distribution throughout the museum. An average concentration of 12 ppb was found for NO_2 and of 5-6 ppb for SO_2. The indoor concentration of a given pollutant is a function of its outdoor level and the indoor/outdoor ratio (sometimes called the infiltration factor) which is basically a function of three parameters: the air exchange rate (which can be measured), the deposition rate and the penetration efficiency which are extremely difficult to measure directly.

Little differences were found for the different seasons apart from an indoor/outdoor (I/O) ratio higher in summer than in winter (1.3 times). This indicates a better air exchange in summer. Furthermore the I/O ratio for NO_2 was about twice the one for SO_2 reflecting the higher deposition velocity for the sulfur compound. The results regarding the Correr Museum are reported in a previous work by Camuffo et al. (1999). The diffusive samplers employed are also in this case long term exposure Gradko-type sampler (2-4 weeks average exposure) using TEA as coating agent for trapping NO_2 and potassium hydroxide for the collection of SO_2 subsequently determined by ion chromatography as sulphate. The precision of the method (not the accuracy, however) was estimated by employing three diffusion tubes at each site (the rooms examined were "The Bellini room", "Lorenzo Lotto and the late Renaissance Period" and other six nearby rooms). After a more extensive study during the winter period fewer sampling sites were used in the summer campaign because of the homogeneity of the concentrations found. The levels of pollution outside were higher during the winter than in summer due to reduced atmospheric mixing properties and/or to increased emission, whereas nitrogen dioxide level indoors were similar in the two seasons. The I/O NO_2 concentration ratio was 0.43 during the winter and it increases to 0.75 during the summer period; the I/O SO_2 ratio during the winter was 0.17. The average NO_2 indoor values were around 10 $\mu g/m^{-3}$ whereas the average outdoor value was around 19 $\mu g/m^{-3}$, the values found indoors for SO_2 were approximately 5$\mu g/m^{-3}$ whereas the average outdoor value was around 26 $\mu g/m^{-3}$. A comparison with other European museums (in London, UK, and in Würzburg, Germany, as reported by Leissner et al. 1996) is made by the authors and it was found that significantly higher outdoor levels of SO_2 were found in Venice compared to the other two locations. Another European project concerning the prevention of effects of air pollution and microclimate on artworks was the MIMIC project, *Microclimate indoor monitoring in cultural heritage preservation* (EVK4-CT-2000-00040). In the framework of this project several museums and historical residences were monitored in the period 2001-2004. The monitoring activity was extended to as much as six pollutants (NO_2, NO_x, SO_2, O_3, HNO_3 and HONO) on a monthly basis. The monitoring sites were: Uffizi Gallery, Florence (Italy), National Museum of Denmark (NMD), Copenhagen, Sandham Memorial Chapel, London (UK), El Alcazar, Segovia (Spain). The measurements were performed using the Analyst® sampler. Environmental monitoring of atmospheric pollutants was carried out in selected locations having different climate and pollution conditions chosen both in the Southern and Northern Europe. Upon request from some curators who showed a particular interest in the project, other sites became available for monitoring with time. The most relevant was the Accademia Gallery (Florence, Italy) where the David by Michelangelo is housed. Other sites were the photo archives of NMD, the British Library and some selected locations belonging to the National Heritage Trust (Chiswick and Ranger's House). Following previous research activity in this field regarding in particular HNO_3, it was possible to verify how this pollutant can be formed also indoors through a chain of reactions that involves O_3, NO_2 and radical species. The objective was to understand the factors that govern the indoor concentrations

of the monitored pollutants and their relationship with the concentrations outdoors. The extended duration of the study has revealed seasonal variations as well as different properties of the various locations. Ozone concentrations also tend to increase with the outdoor temperature. Hence, in places without air conditioning (e.g the Cord room at the Alcazar) the ventilation rate is at its highest value when the ozone concentrations are also at their highest value. A regression of the linear fit between outdoor and indoor concentrations has been used to calculate the slope which can be interpreted as a penetration factor of the outdoor pollutant. The I/O value, i.e. the ratio of the indoor (I) to the outdoor (O) air concentration of a certain pollutant, reveals the relationship between outdoor and indoor sources, which is even more informative than the absolute concentrations. If I/O > 1, there must be indoor pollution sources. Typical I/O values of various pollutants in indoor environments and correlation between indoor and outdoor air measured using the Analyst® diffusive sampler (De Santis et al., 2003) for three different rooms of the Uffizi Gallery (Florence, Italy) are summarized in Table 6. In all the rooms investigated, the I/O values for NO_2, SO_2, HNO_3 and NOx are < 1.

Table 6. *Slope of the regression line (I/O ratio) for five pollutants in the three rooms studied in the period from 18/02/2002 to 23/06/2003 at the Uffizi Gallery (Florence, Italy).*

Pollutant	Room 9	Room 15	Room20
NO_2	0.55	0.55	0.51
O_3	0.11	0.11	0.08
SO_2	0.14	0.16	0.12
HNO_3	0.20	0.21	0.06
NO_x	0.86	0.84	0.89

It is apparent that very reactive species such as SO_2 and HNO_3 tend to have the lowest I/O ratios. The surface/volume (S/V) ratio for the single room is also important: note the very low I/O level (0.06) found for HNO_3, a very reactive species, in room 20 which is the smallest room studied. High I/O levels were found for less reactive species such as NO_x. As a matter of fact the I/O level found for NO_x can be seen as a tracer of penetration of air from outdoors. The high I/O values found for HONO clearly imply that indoor sources of this compound must be present. Clearly, indoor HONO levels were found to largely exceed those outdoors. This concentration-time behaviour is supportive of a formation of nitrous acid indoors via reaction of NO_2 with water on surfaces. Since indoor environments are characterised by high surface-to-volume ratios in comparison to those outdoor, the formation of HONO is highly favoured in these conditions. In addition, given the absence of sunlight, photolysis is less important indoors. Obviously, the precursors of HONO (i.e. NO_2 and NO_x) come exclusively

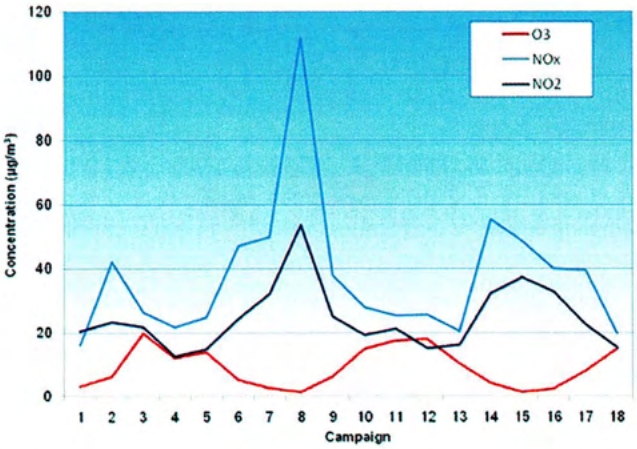

Fig. 13 - O_3, NOx and NO_2 measured by diffusive sampling in Room 9 at the Uffizi Gallery (Florence) in the period from 18/02/2002 to 23/06/2003.

from outdoor-to-indoor transport. As a further example of the type of information which one can expect from the application of a diffusive monitoring in a museum it could be useful to consider Figure 13. Figure 13 shows the relation that exists among the three pollutants O_3, NO_x and NO_2 in one of the rooms monitored. Similar results were observed in the other rooms. A clear anticorrelation between NO_x and O_3 is evident whereas, typically, NO_2 is the product of the reaction: $NO + O_3 \rightarrow NO_2 + O_2$.

Conclusions

Diffusive samplers provide a simple and economical alternative to traditional sampling methods for gases and vapours. It is thus well understandable that interest in the use and development of diffusive samplers for monitoring air quality in relation with cultural heritage protection is increasing. This review shows that it is important that the concentrations determined using diffusive sampling devices reflect the true picture of the air quality. This can only be achieved by a comprehensive validation of the passive sampling method, and by critically assessing operating principle, sampler design and performance under field conditions. Quality control procedures, which, up to now, have been only applied to the diffusive sampling of NO_2 and VOCs, should address issues such as contamination (use of blanks and controls) and loss of trapped analytes, accuracy and precision of the results.

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References

AEA Technology Environment See at: http://www.aeat.co.uk/netcen/airqual/reports/home.html. Issued (3), 3 August, 1999.

Anghelone, M., Hilfrich, U., Kleber, C., Vetter, W., Schreiner, M., Rosenberg, E., 2010. Development of a direct-reading passive sampling device for the measurement of hydrogen sulphide based on colorimetric detection. e-Preservation Science, 7, in press.

Anon, 2001. Vorort-Bestimmung der Raumluftbelastung mit Formaldehyd.

Atkins, D.H.F., Sandalls, J., Law, D.V., Hough, A.M. & Stevenson, K., 1986. The measurement of nitrogen dioxide in the outdoor environment using passive diffusion tube samplers. U.K.A.E.A., Harwell, Report AERE R 12133.

Atkins, D.H.F. & Lee, D.S., 1995. Spatial and temporal variation of rural nitrogen dioxide concentrations across the United Kingdom. Atmospheric Environment, 29: 223-239.

Brown, R.H., 1993. The use of diffusive samplers for monitoring of ambient air. Pure and Applied Chemistry, 65: 1859-1874.

Campbell, G.W., 1988. Measurements of nitrogen dioxide concentration at rural sites in the United Kingdom using diffusion tubes. Environmental Pollution, 55: 251-270.

Campbell, G.W., Stedman, J.R. & Stevenson K., 1994. A survey of nitrogen dioxide concentrations in the UK using diffusion tubes, July-December 1991. Atmospheric Environment, 28: 477-486.

Camuffo, D., Brimblecombe, P., Van Grieken, R., Busse, H. J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D., De Bock, L., Gysels, K., Wieser, M. & Kim, O., 1999. Indoor air quality at the Correr Museum, Venice, Italy. Science of the Total Environment 236: 135-152.

Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Official Journal of the European Communities, L163/41 (1999).

De Saeger, E., Gerboles, M., Perez Ballesta, P., Amantini, L. & Payrissat, M., 1995. Air Quality Measurements in Brussels (1993-1994) - NO_2 and BTX Monitoring Campaigns by Diffusive Samplers, EUR Report 16310 EN.

De Saeger, E. & Payrissat, M., 1996. Quality of air pollution measurements in the EU monitoring networks. In proceedings of the workshop "Quality assurance and accreditation of air pollution laboratories", Belgirate, 15-16 October 1996. EUR Report 17698 EN. Brussels: European Commission.

De Santis, F., Fino, A., Tiwari, S., Vazzana, C. & Allegrini, I., 2000. A Performance Evaluation of the Open Tube Diffusion Sampler (Palmes Sampler) for Monitoring Nitrogen Dioxide. In: Air Pollution VIII. Longhurst, J.W.S., Brebbia, C.A., Power H., Eds., Southampton: WIT Press, 421-429.

De Santis, F., Fino, A., Vazzana, C. & Allegrini, I., 2001. Monitoring of Atmospheric Pollutants by Passive Sampling for the Protection of Historic Buildings and Monuments. Annali di Chimica, 91 (11-12): 759-765.

De Santis, F., Dogeroglu, T., Fino, A., Menichelli, S., Vazzana, C. & Allegrini, I., 2002. Laboratory development and field evaluation of a new diffusive sampler to collect nitrogen oxides in the ambient air. Analytical and Bioanalytical Chemistry, 373: 901-907.

De Santis, F., Vazzana, C., Menichelli, S. & Allegrini, I., 2003. The measurement of atmospheric pollutants by diffusive sampling at the Uffizi Gallery, Florence. Annali di Chimica, 93: 45-53.

De Santis F., Allegrini I., Bellagotti R., Vichi F., Zona, D., 2006. Development and field evaluation of a new diffusive sampler for hydrogen sulfide in the ambient air, Analytical and Bioanalytical Chemistry 384: 897–901.

Dremetsika, A.V., Siskos, P.A., Bakeas, E.B., 2005. Determination of formic and acetic acid in the interior atmosphere of display cases and cabinets in Athens museums by reverse phase high performance liquid chromatography, Indoor and Built Environment, 14: 51-58.

Druzik C.M.G., 1991. Formaldehyde: Detection and Mitigation. WAAC Newsletter, 13(2) May 1991. Western Association of Art Conservators, 13-16. Also available on the WWW: http://palimpsest.stanford.edu/waac/wn/wn13/wn13-2/wn13-208.html

EN 13528-1,2,3:2002, Ambient air quality - Diffusive samplers for the determination of gases and vapours - Require. ments and test methods - Part 1: General requirements. Part 2: Specific requirements and test methods. Part 3: Guide to selection, use and maintenance.

Gair, A.J. & Penkett, S.A., 1995. The effects of wind speed and turbulence on the performance of diffusion tube samplers. Atmospheric Environment, 29: 2529-2533.

Gibson, L.T., Cooksey, B.G., Littlejohn, D., Tennent, N.H., 1997a. Determination of experimental diffusion coefficients of acetic acid and formic acid vapours in air using a passive sampler. Analytica Chimica Acta, 341: 1-10.

Gibson, L.T., Cooksey, B.G., Littlejohn D. and Tennent N.H., 1997b. A diffusion tube sampler for the determination of acetic acid and formic acid vapours in museum cabinets. Analytica Chimica Acta, 341: 11-19.

Gibson, L.T., Watt C.M., 2010. Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments, Corrosion Science, 52(1), 172-178.

Green, L.R. and Thickett, D., 1993. Interlaboratory comparison of the Oddy test, in: Conservation science in the UK: preprints of the meeting held in Glasgow, May 1993, N.H. Tennent (ed.), 111-116.

Green, L.R., and Thickett, D., 1995. Testing Materials for Use in the Storage and Display of Antiquities: A Revised Methodology. Studies in Conservation, Vol. 40, No. 3 (Aug., 1995), pp. 145-152.

Grzywacz, C.M., 1993. Using passive sampling devices to detect pollutants in Museum Environments. Paper presented at the 1993 ICOM Meeting, Washington D.C., August 1993.

Gysels, K., Delalieux, F., Deutsch, F., Van Grieken, R., Camuffo, D., Bernardi, A., Sturaro, G., Busse, H. J. & Wieser, M., 2004. Indoor environments and conservation in the Royal Museum of fine arts, Antwerp, Belgium. Journal of Cultural Heritage, 5: 221-230.

Hallama, R., Rosenberg, E., Grasserbauer, M., 1998. Development and application of a thermal desorption method for the analysis of polar volatile organic compounds in workplace air. Journal of Chromatography A, 809: 47-63.

Heal, M.R. & Cape, J.N., 1997. A numerical evaluation of chemical interferences in the measurement of ambient nitro-

gen dioxide by passive diffusion samplers. Atmospheric Environment, 31: 1911-1923.

Heal, M.R., O'Donoghue, M.A. & Cape, J.N., 1999. Overestimation of urban nitrogen dioxide by passive diffusion tubes: a comparative exposure and model study. Atmospheric Environment, 33: 513-524.

Heal, M.R., Kirby, C.& Cape, J.N., 2000. Systematic biases in measurement of urban nitrogen dioxide using passive diffusion samplers. Environmental Monitoring and Assessment, 62: 39-54.

Hisham, W.M. & Grosjean, D., 1991. Air pollution in Southern California Museums: Indoor and Outdoor levels of nitrogen dioxide, peroxyacetylnitrate, nitric acdi and chlorinated hydrocarbons. Environmental Science and Technology 25 (5): 857-862.

Horwell, C.J., Allen, A.G., Mather, T.A. and Patterson, J.E., 2004. Evaluation of a novel passive sampling technique for monitoring volcanogenic hydrogen sulphide. Journal of Environmental Monitoring, 6: 630 – 635.

HSE, 2001. Health and Safety Executive Committee on Analytical Requirements, Working Group 5, The Diffusive Monitor, Issue 12, July 2001, Diffusive Uptake Rates – Draeger, 3M, SKC and Radiello, 9-14.

HSE, 2001b. Health and Safety Executive Committee on Analytical Requirements, Working Group 5, The Diffusive Monitor, Issue 12, July 2001, Diffusive Uptake Rates on PerkinElmer Sorbent Tubes, 6-9.

Image Permanence Institute, 2001. User's Guide for A-D Strips. Rochester, NY.

Kontozova-Deutsch, V., Krata, A., Deutsch, F., Bencs, L., Van Grieken, R., 2008. Efficient separation of acetate and formate by ion chromatography: Application to air samples in a cultural heritage environment. Talanta 75(2): 418-423.

Leissner, J., Beuschlein, S., Pilz, M., Martin, G., Blades, N. & Redol, P., 1996. Final report to European Commission DG XII.

Levin, J.O. & Lindahl, R., 1994. Diffusive Air Sampling of Reactive Compounds - A Review. Analyst, 119: 79-83.

Liu, L.J.S., Dills, R.S., Paulsen, M., Kalman, D. A., 2001. Evaluation of media and derivatization chemistry for six aldehydes in a passive sampler, Environmental Science and Technology, 35: 2301-2308.

Oddy, A.W., 1973. An unsuspected danger in display, Museums Journal (London) 73, 27-28.

Palmes, E.D & Gunnisson, A.F., 1973. Personal monitoring device for gaseous contaminants. American Industrial Hygiene Association Journal, 34: 78-81.

Palmes, E.D., Gunnisson, A.F., Dimattio, J. & Tomczyck, C., 1976. Personal samplers for nitrogen dioxide, American Industrial Hygiene Association Journal, 37: 570-577.

Plaisance, H., Gerboles, M., Piechocki, A., Detimmerman, F., de Saeger, E., 2007. Radial diffusive sampler for the determination of 8-h ambient ozone concentrations. Environmental Pollution 148: 1-9.

Shooter, D., Watts, S.F., Hayes, A.J., 1995. A passive sampler for hydrogen sulphide, Environmental Monitoring and Assessment, 38: 11-23.

Stranger, M., Potgieter-Vermaak, S., Sacco, P., Quaglio, F., Pagani, D., Cocheo, C., Locateli Godoi, A.F., Van Grieken, R., 2009. Analysis of indoor gaseous formic and acetic acid, using radial diffusive samplers, Environmental Monitoring and Assessment 149: 411-417.

Supelco, 2004. Radiello® manual, Supelco Edition; Fondazione Salvatore Maugeri – IRCCS, Padova and Supelco, Bellefonte, PA, USA.

Van Reeuwijk, H., Fischer, P.H., Harssema, H., Briggs, D.J., Smallbone, K. and Lebret, E., 1998. Field Comparison of Two NO_2 Samplers to Assess Spatial Variation. Environmental Monitoring and Assessment 50: 37-51.

9.3 Dosimetry

Introduction

Assessment of damage to indoor cultural heritage is a major and growing concern for curators and conservators-restorers, in particular, the synergistic effects of pollutants with other environmental factors. Studies of lead-based objects have provided evidence of the enhanced corrosive effects of ethanoic acid (acetic acid) and relative humidity (this book, chapter 8), and accelerated aged studies of parchment have shown the synergistic effects of light and NO2, and light heat and NO2 (Larsen, 2007). These observations have demonstrated the need for dosimeters, and this was recently highlighted in a study of air quality in museum storage buildings (Ryhl-Svendsen, 2007). The basic idea of a dosimeter is to provide an early warning signal of the degree of corrosivity of the microclimate surrounding heritage objects. Ideally the dosimeter should consist of a material which is similar to that used in particular objects but which will react faster than the objects in the collection being monitored and which will show correlation between the damage received and the synergistic effect of environmental parameters. This will then provide an early warning signal for the conservation scientist. In a recent Ph.D thesis (Ryhl-Svendsen, 2007) "Air Quality in Museum Storage Buildings: the effect of ventilation, filtration and passive sorption on indoor air pollution in archives and storage rooms" attention is drawn to the fact that the idea is not new to environmental monitoring in museums. An example is given of the fading of dyed textile strips ('Blue Wool Standard', ISO 105) used to assess damage rates for art on paper (Colby, 1992). For this type of dosimeter the dominant response was the effect of light. Recently further developments for monitoring light damage have been made in the framework of the EC project LIDO (EVK4-CT-2000-00016). LightCheck® was introduced as a new early warning system which allowed the evaluation of the quantity of light received by an object during exhibition. A strip of LightCheck® is placed close to the object so that it receives the same light exposure conditions as the object. LightCheck® is made of a light sensitive coating on a substrate, whose colour changes during exposure to light. After calibration, it can give an indication of the potential damage of the lighting conditions on site (Römich et al., 2004).

Some of the other dosimeters that have been developed in EC funded projects in the last fifteen years will also be described in this chapter. These include ERA (*Environmental Research for Art Conservation*, EV5V-CT94-0548), MIMIC (*Microclimate Indoor Monitoring for Cultural Heritage Preservation* EVKV-CT-2000-00040), SENSORGAN (*Sensor system for detection of harmful environments for pipe organs*, contract no 022695), MASTER (*Preventive Conservation Strategies for Protection of Organic Objects in Museums, Historic Buildings and Archives* EVK4-CT-2002-00093), AMECP (*Assessment and Monitoring of the Environment of Cultural Property*, EV5V-CT-92-0144), and PROPAINT (*Improved Protection of Paintings during Exhibition, Storage and Transit* FP6 SSPI no 044254). The chapter will also include some case studies where metal coupons have been used in museums and historic houses.

The use of metal coupons is widespread as a monitoring method in indoor environments in museums (Leygraf and Graedel, 2000; Ryhl-Svendsen, 2007) and both inside and outside showcases (Thickett et al., 2006; Costa and Dubus, 2007). Corrosion products of the metal coupons have been characterised using a range of analytical techniques. The manner of exposure of metal coupons has also varied. Recent studies used metal coupons inclined and supported on a stand to study additional effects of dust deposition (Costa and Dubus, 2007). In addition to showcases lead coupons have also been used to monitor environments in pipe organs (Niklasson et al., 2008) and in microclimate (mc)-frames of paintings (Grøntoft et al., 2010).

Examples of some dosimeters developed in EC funded projects

The next section will present information on the different dosimeters developed in the EC projects mentioned above.

In the ERA project mock paintings were prepared and used as dosimeters in which the physico-chemical changes could be related to the quality of the environment surrounding the artwork. Differently pigmented tempera strips were prepared and tested (Odlyha et al., 1999; van den Brink, 2001). Accelerated ageing studies were made using different light levels, thermal ageing and pollutant gases (NO_x, SO_2). Exposure was also made at selected sites for a period of nine months. Detailed studies were performed using advanced analytical techniques (Bacci et al., 2000; Odlyha et al., 2000; van den Brink, 2001) which provided valuable information on the ageing of paint tempera. It also showed that differing extent of alteration to the medium was already caused by the various pigments. Despite these differences it was possible to demonstrate that differently pigmented tempera paint showed different sensitivities to the effect of environmental parameters. Some ranking of damage and differences between sites was made. In general measured damage at sites exceeded measured changes in the accelerated aged samples which illustrated the synergistic effects of environmental parameters acting on the dosimeters. As expected, changes in uncontrolled environments occurred to a greater extent than in controlled environments. It also showed that light was not the only factor but that pollutants contributed to the damage. This led to further testing in the MIMIC project where the effect of different levels of pollutant gas (NO_2) was tested on varnish (resin mastic) and this study was continued within the recent PROPAINT project.

The MIMIC project introduced the first use of organic coatings (artists' media e.g. egg tempera and resin mastic) on piezoelectric quartz crystals (PQC) and used them as dosimeters by exposing them to environments where relative humidity, temperature, light, and pollutant levels were measured (Odlyha et al., 2005). Artists' varnish (resin mastic) was used as the coating on the PQC crystals as this is sensitive both to the presence of light and oxidising agents. The advantage of PQC crystals acting as dosimeters is that they can be used as passive samplers or as continuous recording devices. Metallic lead was the alternative coating that was used in the SENSORGAN project for monitoring the damaging effects of ethanoic acid and RH on the organ pipes. This was followed by the PROPAINT project where both coatings were used in conjunction with other dosimeters (EWO, MASTER project) and glass (AMECP project) to test environments within microclimate frames for paintings (Grøntoft et al., 2010).

The principle of operation of the PQC crystals is that their

oscillation frequency depends on the mass of the coating as related by the Sauerbrey equation and their preparation and exposure in seven different sites in museums, historic houses, and castles is discussed (Odlyha et al., 2005). The rationale for the selection of the artists' coatings was based on previous mass spectrometric studies which showed that systematic changes in chemical composition occurred with accelerated light ageing (van den Brink et al., 2001). Further studies continued with resin mastic alone, since it was found that egg tempera was unsuitable due to its response to RH as well as the other environmental parameters. Resin mastic (RM) coated crystals, on the other hand, showed a small and reversible change with fluctuations with RH which could be subtracted from the overall response. Furthermore controlled accelerated light-induced deterioration of the coatings on the PQC crystals was accompanied by systematic changes in the crystal frequency (van den Brink, 1996; Cavicchioli, 1996). The study was extended to test the effect of increased dose levels of NO_2 alone under controlled laboratory conditions, and this showed that the crystal response measured as ratio of the frequency shift to that of the original coating frequency *[Δf(Hz)/F (kHz)]* could be correlated with the dose of NO_2 received. So the coating was sensitive to photooxidising effects (light and NO_2), and this has recently been demonstrated once again in the PROPAINT project (Grøntoft et al., 2010). Testing at sites, as in the ERA project, showed that in uncontrolled environments there were higher levels of change. In addition seasonal variation was observed, in particular where an increase in measured levels of oxidising agents occurred (Odlyha, 2007). Data from site exposures were collected using RM-PQC dosimeters either as passive samplers or as continuously recording devices. The results were summarised with a graphical plot of dosimeter change *[Δf(Hz)/F (kHz)]* against days of exposure. These data were then used as a basis for ranking damage measured at sites. Resin mastic coated steel strips were also exposed with the RM-PQC crystals and evaluated using reflectance FTIR. The combined PQC, climate, and chemical data from accelerated ageing and site exposure were then used for damage assessment. The clear advantage of using the RM-PQC dosimeter was the fact that a frequency signal could be measured and correlated with damage to the coating (resin mastic) which was sensitive to photooxidsing effects.

The RM-PQC dosimeter has recently been used together with the EWO (Early Warning Organic) dosimeter for combined testing within microclimate frames in the PROPAINT project. The EWO dosimeter was developed in the EU project MASTER (2003-2006; http://tarantula.nilu.no/master/) as a tool for the measurement and evaluation of air quality for organic cultural heritage objects located indoors. The sensitive part of the dosimeter is a polymer film that becomes slightly more opaque due to the synergistic effect of air pollutants and climate. The EWO is sensitive to the photo-oxidizing factors in the atmosphere: NO_2, O_3, UV light and temperature. It has also been found sensitive to SO_2 at high concentration and humidity. The calibration of the dosimeter response was performed by statistical correlation with values for the environment (NO_2, O_3, UV-light and temperature) in 30 locations in 11 European museums. The PROPAINT project gave the opportunity to test the performance of the dosimeters since both are sensitive to photooxidising effects. The EWO (Early Warning Organic) dosimeter is shown in Figure 1 exposed in a showcase in the Trøndelag Folk Museum in Trondheim, Norway for a period of three months in the MASTER project The EWO was indirectly calibrated for RH using RH-T isoperm values (Sebera, 1994). The resulting correlation equation (between environmental dose and EWO response) for the dosimeter was used to determine tolerable impact levels on the dosimeter for indoor cultural heritage locations with different degree of protection against the outdoors, ranging from archives to outside stores with no control Table 1. Suggested environmental standards for indoor cultural heritage locations as reported in the literature were used as input to the calculation of the tolerable impact levels (Tétreault, 2003). The dosimeter is exposed for three months on location in the cultural heritage institution to obtain a value for the time averaged pollution and climate impact. The resulting reading is presently performed by UV spectrophotometry after return to the laboratory. The result is reported to the user in a tolerability – location diagram (Figure 2) that can also include tolerability of the measured concentration of ethanoic acid or mea-

Fig. 1 - The EWO dosimeters mounted for 3 months exposure in a showcase in the Trøndelag Folk Museum, Trondheim, Norway, during the measurement campaign in the EU project MASTER. The EWO results reading for this location was a category 2 (Table 1 and arrow in Figure 2).

Table 1. *Results evaluation diagram for EWO (Developed by Centre for Sustainable Heritage, UCL, London).*

Determined expectation	**EWO-G dosimeter response level after exposure.**				
	1	**2**	**3**	**4**	**5**
Archive store	**Expected environment (acceptable)**	Environment could be better	Environment is poor	Something is wrong with control	Serious problem with building or control
Purpose built museum	Environment is very good	**Expected environment (acceptable)**	Environment could be better	Environment is poor	Something is wrong with control
House museum	Excellent environment	Environment is very good	**Expected environment (acceptable)**	Environment could be better	Environment is poor
Open structure	Dosimeter is not responding	Excellent environment	Environment is very good	**Expected environment (acceptable)**	Environment could be better
External store with no control	Dosimeter is not responding	Dosimeter is not responding	Excellent environment	Environment is very good	**Expected environment (acceptable)**

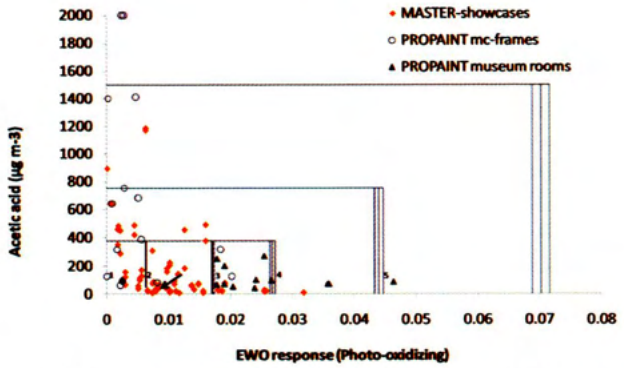

Fig. 2 - Results reporting tolerability – location diagram for EWO (and acetic acid if available). Interpretation of the reported results (impact) level is performed using Table 1. Results from EWO and acetic acid measurements performed in the EU projects MASTER (showcases) and PROPAINT (microclimate frames and museum rooms) are shown. The arrow points at the result reading for the location shown in Figure 1.

sured impact of organic acids on a complementary dosimeter. The methodology for combined dosimetry and reporting of results was developed in the PROPAINT project.

The dosimeters used in the PROPAINT project in combination with EWO and RM-PQC dosimeters were the glass dosimeters and the lead coated PQC (L-PQC dosimeter). The overall aim of the PROPAINT project was to test the levels of corrosivity within microclimate frames for paintings (http://propaint.nilu.no/)

The Fraunhofer Glass Slide dosimeter (GSD) developed in the EU project AMECP (EV5V-CT-92-0144) is a thin wafer of calcium and potassium rich glass highly susceptible to corrosion (Mottner, 2006). The dosimeter is very sensitive towards pH changes and thus acidic species and monitors the corrosivity of the atmosphere on site, quantified by FTIR-absorption measurements at 3300 cm^{-1} in the OH-band. Microscope and ATR-FTIR analysis can be performed of the corrosion products including surface crystal salts, leaching, cracking and intrusion of water into the corroded glass surface, allowing correlation with main impact factors like RH, T, or pollutant gases. Environmental impact levels, from acceptable to dangerous, for cultural heritage objects have been determined for the dosimeter. The GSDs have been used for the last 15 years as environmental impact sensors for cultural heritage in a broad range of applications indoors in museums and showcases, and outdoors. Figure 3 shows the exposure of a glass dosimeter in a showcase in the Romano-Germanic Museum Cologne, Germany. For the PROPAINT sampling reported in this work the M1.0 GSD with fire polishing finish was used.

The lead coated (L-PQC) dosimeter was developed within the SENSORGAN project and underwent miniaturisation, as did the RM-PQC dosimeter, for use in the microclimate frames tested in the PROPAINT project. It was used for monitoring levels of organic acids within frames. Levels of ethanoic acid measured using passive samplers within frames were found to be higher than in rooms (Grøntoft et al., 2010). The frequency response of crystal dosimeters (L-PQC) could be correlated with measured levels of ethanoic acid and varied with air exchange rate of the frames (Odlyha and Thickett, 2010). Since the lead coating is thin, the response is fast in environments where ethanoic acid levels are high (c >1000 µg/m^3). Also it is possible to characterise corrosion products on the crystal films using Raman microscopy (de Faria, 2007). Correlation was also found with values obtained with measurements using the glass dosimeter (Grøntoft et al., 2010).

There is interest in monitoring within frames as there are more paintings which are now enclosed within microclimate frames for their protection, in particular in uncontrolled environments. An example is given of a panel painting (oil) of William the Conquerer (c.1580) in a microclimate frame at Battle Abbey, English Heritage, UK (Figure 4). The surrounding environment often experiences daily RH fluctuations of around 20%. A microclimate frame was constructed by glazing the front of the frame and building up the back to allow incorporation of a backboard (Thickett, 2010). Though the materials had passed the accelerated corrosion tests for metals, it would be useful to know if there is a build-up of gases within the frames. Daily RH fluctuations have been attenuated to below 1.5% and the RH in the frame has held steady between 50 and 65% over almost two years. The frame also limits the moisture exchange between the panel and the room environment, hence reducing changes in the moisture content of the panel itself. So additional monitoring using dosimeters would be useful to assess the conditions within the frame. Recent measurements which were made in a painting in a microclimate frame in Cracow National Museum have shown that using L-PQC dosimeters it was possible to measure a difference in dosimeter response of the lead coated PQC dosimeter in front and behind the framed painting (Odlyha and Jakiela, 2010).

The L-PQC has also been used in the SENSORGAN project

Fig. 3 - Set-up for the exposure of a glass dosimeter in a showcase in the Romano-Germanic Museum Cologne, Germany.

Fig. 4 - Painting of William the Conquerer in microclimate frame at Battle Abbey, UK (Courtesy of D. Thickett, English Heritage).

(contract no. 022695: *Sensor System for Detection of Harmful Environments for Pipe Organs*). The aim in this project was to monitor the emission of volatile organic acids, which is mentioned in Chapter 8 in this book. A continuously recording lead-PQC system was developed and especially adapted for use with organ pipes. Figure 5a shows the installation of the dosimeter in Örgryte New Church, Gothenburg, Sweden. Measurements of concentrations of volatile organic compounds had been made in the previous COLLAPSE project (Niklasson et al., 2008). Figure 5b shows the detail of the coated crystals within the holder. The dosimeter was initially calibrated in the laboratory using controlled levels of ethanoic acid and RH and then exposed in different locations. This includes exposure within the organ at St Botolph Aldgate, London, which has been described elsewhere (Bergsten et al., 2010). Differences were observed between exposure in three locations; in the windchest, in a Haut boy pipe, and in a trumpet pipe. The response in the windchest was higher than in either of the two locations tested within the organ pipes. Differences due to seasonal variations were also observed between organs in Olkusz (Poland) and St Botolph, Aldgate, London. Changes were of a smaller magnitude where levels of ethanoic acid and RH were lower than in Örgryte, Sweden, where levels of ethanoic acid and RH were higher (Bergsten et al., 2010).

Prior to the SENSORGAN project lead coupons were used for monitoring within the pallet-box (windchest) of historical organs in the COLLAPSE project. (Niklasson et al., 2008). Lead and lead-2%Sn coupons were exposed and then analysed using ion chromatography and grazing angle X-ray diffraction. Figure 6 shows the exposure of lead coupons in the pallet-box of an organ. High concentrations of organic acid vapours were measured using passive samplers in the wind systems of the corroded organs. Polished samples of pure lead (99.95%) and Pb-2%Sn alloy were exposed in the pallet-box of selected organs for periods of 4, 10, and up to 22 months. Site exposures demonstrated that corrosion of lead coupons occurred and significant amounts of ethanoate (acetate) and methanoate (formate) formed on the lead only coupons, while amounts detected on Pb-2%Sn were much smaller. The tendency for ethanoate and methanoate to accumulate on the lead coupons was taken as an indication that the two organic acids which play an important role in the corrosion of the organ pipes were ethanoic and methanoic acids.

The case study with organ pipes provides a special example of a challenging microclimate due to the restricted space for monitoring, as does the example with monitoring of microclimate frames. PQC-dosimeters have shown that it is possible to provide continuous recording of damage. The next section will look at case studies involving metal coupons in display cases and in rooms in museums.

A case study is described for display cases built for English Heritage which house the Werner collection of small and precious objects at Ranger's House, London (Figure 7a). The display cases contained MDF (medium density fiberboard) and MDF coated with Dacrylate which emit significant amounts of acetic acid (Thickett, 1998). Exposed coupons (Figure 7b) were

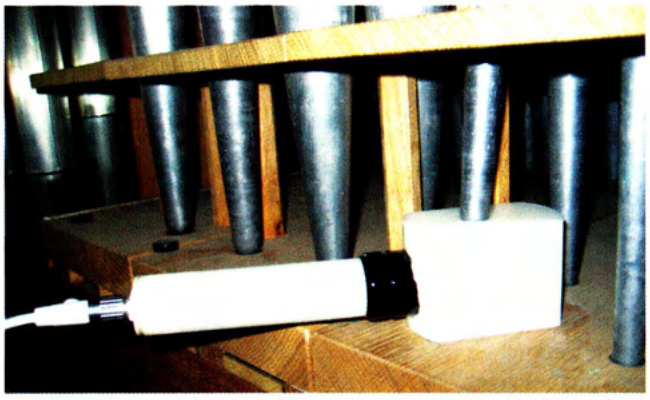

Fig.5a - Installation of the L-PQC dosimeter in Oegryte New Church, Sweden, in the frame of the SENSORGAN project.

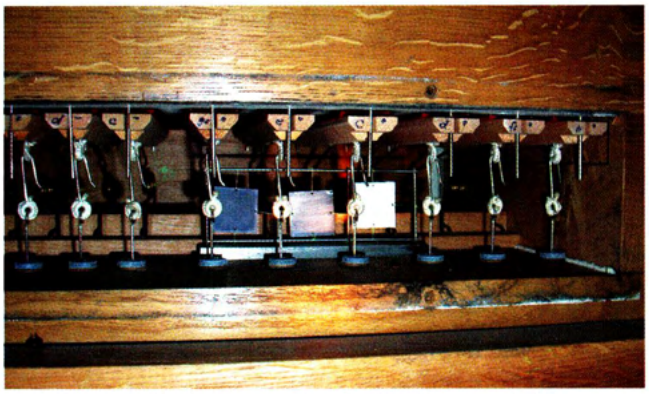

Fig.6 - Exposure of lead coupons in the pallet-box of an organ in the COLLAPSE project.

Fig.5b - Detail of the L-PQC coated PQC crystals in the holder.

Fig.7a - Showcase with gilded silver, Werner Collection, Rangers House, London.

Fig. 7b - Detail of showcase with gilded silver, Werner Collection, Rangers House, London, with metal coupon dosimeters in stand.

examined by eye and colour measurements of the surface were made with a Minolta 2500D spectrometer. Lead coupon analysis of the darkening of the lead could be followed by the decrease in L^* values for the lead coupons. Previous investigations have shown that there is a correlation between L^* and the amount of corrosion of lead in an acetic acid environment (Tétreault et al, 1998). The increase in darkening occurred with reduction in air exchange rates of the showcases (AER) (<0.5/day). After exposure the lead coupons were analysed using ATR/FTIR (Thickett et al., 2006). Analysis detected only plumbonacrite. Since no lead acetate hydrate or hydrocerrusite were detected, there was no evidence of ethanoic acid initiated corrosion (Tétreault et al., 1998) for the period of testing. Where activated charcoal felt was incorporated this showed a significant decrease in the darkening of lead coupons.

Lead coupons have also been recently used in a study of the corrosivity of nineteen different indoor environments and their characterisation was based on an adapted methodology from ISO 1184 involving weight measurements (Ryhl-Svendsen, 2007). The coupons were exposed in storage areas in museums and archive buildings. Concurrently with the coupon exposure climate (RH, T) and pollutant gas data (H_2S, SO_2 and organic acids) were measured. It was found that lead is a usable material for corrosion dosimetry in indoor environments. Exposure after three month periods allowed the possibility of ranking in terms of corrosivity of the environments tested. A relationship was found between RH, organic acids, H_2S and the corrosion mass. For longer exposure periods attention is drawn to the possible formation of a passivation or patina layer on the surface which would cause deviations from observed linear relationship found in this study.

Metallic coupons (sterling silver, copper and lead) were also used to evaluate the environmental conditions in fifteen French cultural institutions (Costa and Dubus, 2007). Surfaces were prepared by gently abrading both sides with a glass fibre brush to obtain a homogeneous surface finish. To evaluate the effect of particulate matter on the tarnishing reactions, a support structure was designed for the three metals tested, silver, copper and lead, so that the coupons were inclined at 45°, as shown in Figure 7b. This meant that one side was facing up and the other faced down Coupons were exhibited in storage and exhibition rooms, inside and outside showcases. After exposure they were evaluated using electrochemical techniques. The tarnish layers were extremely thin and barely perceptible by eye but could be readily detected by electrochemical reduction. Differences were observed, in particular for lead, between coupons exposed in showcases and in rooms.

Detailed surface analysis of metallic coupons can also provide valuable information about the corrosion products and the environmental conditions. An example of this is the study of the exposure of silver coupons in showcases in the British Museum (Hallett et al., 2003). Levels of pollutant gases (hydrogen sulphide and carbonyl sulphide) were measured concurrent with the exposure of the coupons. Prior to surface analysis colour measurements were made after coupon exposure. Indication of tarnishing was taken from the increase in b using the CIELAB system. The b value has been found to correlate well with human perception of tarnishing as the silver acquires a brown tint and an increase in b value. X-ray Photon Spectroscopy (XPS) and SIMS (Secondary Ion Mass Spectrometry) were then performed on the tarnish layers. The analysis indicated that a much more complex mixture of compounds than just silver sulphide formed on the surface. XPS showed the presence of sulphate, chloride, oxide, organic carbon, an oxygenated organic carbon species. Several other species such as sodium, potassium, and silicon were also detected which probably originate from particulate deposition. SIMS detected a large range of ions (e.g. SO_3^{2-}, Cl^-, S^{2-}) and organic species up to C6, including some oxygenated ions. Control coupons stored in a metal container had very much reduced levels of organic species. This demonstrated that the tarnish layers have a complex nature and are not composed solely of silver sulphide.

In addition to the use of metal coupons, rubber dosimetry has been proposed for detection of damage due to ozone (Ryhl-Svendsen, 2007). Two types of rubber dosimeters were used: "postoffice" rubber bands were stretched on an aluminium holder to double the length of their relaxed state, and then rubber strips were cut from a large sheet and mounted on a cylinder. Visual analysis, appearance of edge cracks, and spectroscopic analysis (Fourier transform infra-red spectroscopy, FTIR) were used to evaluate the scale of the damage. In FTIR the increase in values of the absorbance of the peak in the carbonyl region was recorded. The rubber strip dosimeter performed better at low ozone concentrations <500 ppb.days than the rubber band dosimeter and allowed a much higher degree of resolution in quantification of ozone exposures in the interval 0-1000 ppb.days (Ryhl-Svendsen, 2007).

Conclusion

This section on dosimetry has attempted to demonstrate the most recent advances in this area. A wide range of dosimeters are available and the advanced analytical methodology which can be used has made it possible to obtain detailed information on the damage incurred. Two main types can be distinguished: those that are sensitive to photooxidising effects and the measured change correlates with the dose received, and those that are sensitive to damage due to organic acids where the dosimeter response also correlates with the dose received. In addition there is now the added advantage of continuously recording devices which can be integrated with current climate monitoring systems.

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References

Bacci, M., Picollo, M., Porcinai, S., and Radicati, B., 2000, Evaluation of the museum environmental risk by tempera-painted dosimeters. Thermochimica Acta 365: 25-34.

Bergsten, C.J., Odlyha, M., Jakiela, S., Slater, J.M., Cavicchioli. A., de Faria, D.L.A., Niklasson, A., Svensson, J.-E., Bratasz, L, Camuffo, D., della Valle, A., Baldini, F., Falciai, R., Mencaglia, A., Senesi, F., 2010, Sensor system for detection of harmful environments for pipe organs (SENSORGAN)", e-Preservation Science (in press).

Cavicchioli, A., 1996, MSc Analytical Chemistry Thesis, Birkbeck College, University of London.

Colby, K.M., 1992, A suggested exhibition policy for works of art on paper, Journal of the International Institute of Conservation-Canadian Group 17: 3-11.

Costa, V., and Dubus, M., 2007, Evaluation of the Environmental Impact on Metal Artefacts by Electrochemistry and Grazing Incidence X-ray Diffraction, IAQ 2006 Indoor Air Quality (http:iaq.dk/iaq2006/Costs IAQ2006.pdf, accessed 28.02.10).

de Faria, D.L.A., 2007, private communication, SENSORGAN 1st year project report.

Grøntoft, T., Odlyha, M., Mottner, P. , Dahlin, E. , Lopez-Aparicio, S., Jakiela, S., Scharff, M., Andrade, G., Obarzanowski, M., Ryhl-Svendsen, M., Thickett, D., Hackney, S., Wadum, J., 2010, Dosimetry for evaluation of environmental conditions for paintings in microclimate frames, Journal of Cultural Heritage (in press).

Hallett, K., Thickett, D., McPhail, D.S., Chater, R.J., 2003, Application of SIMS to silver tarnish at the British Museum. Applied Surface Science 203-204: 789-792.

Larsen, R., 2007, Improved Damage Assessment of Parchment (IDAP) Assessment, data collection and sharing of knowledge, European Communities, ISBN 978-92-79-05378-8.

Leygraf, C., and Graedel, T., 2000, Atmospheric Corrosion, Electrochemical Society Series, Chichester: John Wiley & Sons.

Mottner, P., 2006, Early warning dosimeters for monitoring indoor museum climate: Environmental Impact Sensors and LightCheck™. 7th Indoor Air Quality 2006 Meeting (IAQ 2006). http://iaq.dk/iap/iaq2006/Mottner_IAQ2006.pdf

Niklasson, A., Langer, S., Arrhenius, K., Rosell, L., Bergsten, C.J., Johansson, L.-G., and Svensson, J.-E., 2008, Air pollutant concentrations and atmospheric corrosion of organ pipes in European church environments" Studies in Conservation 53: 24-40.

Odlyha, M., Wade,N., Wang, Q., Campana, R., and Slater, J.M., 2005, Microclimate Indoor Monitoring : Damage Assessment for Cultural Heritage Preservation, Preprints ICOM-CC 14th Triennial Meeting Hague , 670-676.

Odlyha, M., Cohen, N. S., Campana, R. Foster, G.M., 1999, Environmental Research for Art Conservation and Assessment of Indoor Conditions Surrounding Cultural Objects, Journal of Thermal Analysis and Calorimetry, 56, 1219-1232.

Odlyha, M., Cohen, N.S., Foster, G.M., West, R.H., 2000, Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (azurite tempera) by thermal and spectroscopic analysis, Thermochimica Acta 365 (1): 53-63.

Odlyha, M., Theodorakopoulos, C.,Thickett, D., Ryhl-Svendsen, Slater, J.M. and Campana, R., 2007, Dosimeters for Indoor Microclimate Monitoring for Cultural Heritage" Proceedings of Museum Microclimates p. 73-79, ed. T. Padfield and K. Borcherson, Copenhagen.

Odlyha, M., and Jakiela, S., 2010, private communication.

Römich, H., Martin, G., Lavedrine, B., Bacci, M., 2004 "LightCheck®: A New Tool in Preventive Conservation" V&A Conservation Journal On-line Issue 47.

Ryhl-Svendsen, M., 2007, Air Quality in Museum Storage Buildings, PhD Thesis, The Royal Academy of Fine Arts School of Conservation, Copenhagen, 99-114.

Sebera, D.K., 1994, Isoperms: An environmental Management Tool Commission of Preservation and Access, Washington, DC.

Tétreault, J., 2003, Airborne Pollutants in Museums, Galleries and Archives: Risk Assessment, Control Strategies, and Preservation Management, Ottawa: Canadian Conservation Institute.

Tétreault, J., Sirois, J., and Stamatopoulou, E., 1998, Studies of Lead Corrosion in Acetic Acid Environments, Studies in Conservation, 43: 17-32.

Thickett, D., David, F., and Luxford, N., 2005/6, Air Exchange Rate-the Dominant Parameter for Preventive Conservation ?, The Conservator 29: 19-33.

Thickett, D., 1998, Sealing MDF to Prevent Corrosive Emissions, The Conservator 22: 49-56.

Thickett, D., 2010 (private communication)

van den Brink, O.F, 2001, Molecular Changes in Egg Tempera Paint Dosimeters as tools to Monitor the Museum Environment, PhD Thesis, Amsterdam: AMOLF, ISBN 90-801704-6-1.

van den Brink, O.F., Boon, J.J., O'Connor, P.O., Duursma, M.C., Heeren, R.M.A., 2001, Matrix –assisted laser desorption/ionisation Fourier transform mass spectrometric analysis of oxygenated triglycerides and phosphatidylcholines in egg tempera paint dosimeters used for environmental monitoring of museum display conditions, Journal of Mass Spectrometry, 36(5): 479-492.

van den Brink, O.F., 1996, private communication.

9.4 Atmospheric particulate pollutants

1. Introduction to Atmospheric Particulate Pollutants

Besides adverse health effects (e.g. Pope et al. 1995; Dockery et al. 1993) and the influence on earth's climate (e.g. Andreae, 2001, Andreae et al. 2005), aerosol particles have adverse effects on Cultural Heritage (CH) objects. Calculations of the economical costs of material damage in the EU due to air pollution have been carried out. The estimated cost of material damage amounted to 1.1 billion € per year in the year 2000 (IIASA, 2005).

Cultural heritage plays an important role in our modern-day society and its conservation and preservation have become a main concern in Europe during the last decades. As a result, research on objects of cultural heritage importance has grown exponentially, as scientific support and verification became imperative in the quest for preventative conservation.

1.1 Properties of aerosol particles

Atmospheric (aerosol) particles can be a predominant factor in material degradation of CH objects (e.g. Boubel et al. 1994, Bridgman, 1990, Owen et al. 1992, Sabbioni et al. 2003). The particulate matter (PM) can imply a wide variety of particle sizes, chemical compositions and physical properties. Besides the direct emissions of primary particles, airborne PM is also produced by chemical reactions of precursor compounds in the atmosphere. The most important examples of these secondary aerosols in the atmosphere are particles consisting of ammonium nitrate or ammonium sulphate and the Secondary Organic Aerosols (SOA).

The size distribution of atmospheric aerosols is mainly influenced by three processes: nucleation, condensation and coagulation (e. g. Seinfeld and Pandis, 1998). Condensable gases can form new particles in the atmosphere with very small diameters, especially when the atmosphere is rather clean. If there are already a considerable number of particles present, the condensable gases will rather condensate on the surface of the existing particles instead of nucleating new particles. Thirdly, particles have the tendency to coagulate to form agglomerates of particles with larger diameters. Especially for very small particles such as freshly emitted soot particles from a diesel engine, coagulation is a fast process.

The size distribution ranges from the small nucleated particles with typical diameters of around 1 nm up to dust particles with diameters of around 50 to 100 µm. The maximum of the distribution of the particle mass as a function of the particle diameter is often found at diameters between 0.5 and 1 µm in urban environments. The number distribution of the particles as a function of the particle diameter in contrast shows the highest values for the smallest particle diameters.

Often a particle diameter of 2.5 µm is used to distinguish between "fine" and "coarse" atmospheric particles. $PM_{2.5}$ (all particles with an aerodynamic diameter below 2.5 µm) is referred to as the fine fraction of the particle size spectrum, and the fraction $PM_{10\text{-}2.5}$ with aerodynamic diameters between 2.5 and 10 µm is referred to as the coarse fraction.

1.2 Sources of aerosol particles

On a global scale the natural sources of PM dominate in comparison to all anthropogenic sources due to their emission from extended source areas such as the oceans, which cover 70 % of the globe. On a local scale, however, in urban and industrial areas, the important anthropogenic (point) sources are likely to exceed the natural ones.

Primary natural aerosols are mainly derived from sea salt spray, soil erosion and biological sources such as e.g. pollen. It has been described several times in literature that e.g. sea salt particles cannot be regarded as unreactive particles. The emitted sea salt particles, consisting mainly of NaCl, are "ageing" during their transport over the continents, especially when they come into contact with polluted air masses. During this reaction the chloride is replaced by nitrate and/or sulphate leading to particles with variable compositions between NaCl and $NaNO_3$ or Na_2SO_4 (e.g. Ro et al. 2001, Ebert et al. 2004). Hence, often mixtures of these salts are found in atmospheric aerosols.

Soil dust particles are mainly composed of aluminosilicates. This particle type is often found in the size ranges with diameters above 1 µm and the particles have typically a non-spherical morphology.

Primary anthropogenic aerosols are derived from e.g. industrial combustion sources (fly ash), traffic (soot particles, abrasion of tires, brakes and the road surface), domestic heating (soot and organic particles) and agricultural activities (enhanced dispersal of soil dust). Fly ash particles have often a similar chemical composition as soil dust particles, but they are predominant in the size classes with diameters below 1 µm, have often a spherical morphology and may contain more sulfur. Soot particles are often an important particle type in the smaller size classes with diameters below 1 µm, especially in polluted air masses (e.g. Ebert et al. 2004). Secondary anthropogenic aerosols, especially nitrates and sulphates, make up large parts of PM_{10} in most urban areas.

Electron Probe Microanalysis (EPMA) is an especially suitable method to characterize PM, as it combines imaging techniques with a chemical characterization of the particles based on the analysis of characteristic X-rays. Hence, shape and composition of the particles can be investigated simultaneously (see e.g. Van Grieken et al. 2000, de Hoog et al. 2005 and references therein).

Generally, the anthropogenic contribution to the size fraction $PM_{2.5}$ is significantly higher than the anthropogenic contribution to $PM_{10\text{-}2.5}$. Components such as non-sea salt sulphate, nitrate, ammonium and elementary carbon, all of them predominant in $PM_{2.5}$, are mainly derived from anthropogenic sources. In contrast, sea salt and soil dust can be regarded as predominantly natural. These components are mainly present in the size fraction $PM_{10\text{-}2.5}$. The organic aerosols can either be derived from natural sources such as from biogenic terpene emissions or from forest fires, or they can be derived from anthropogenic combustion processes. Following this approach, an anthropogenic contribution of around 60 % can be calculated for $PM_{2.5}$. For $PM_{10\text{-}2.5}$, the anthropogenic contribution amounts only to around 30 %.

1.3 Indoor aerosol particles

In many cases, indoor aerosol particles inside a certain CH monument originate from the outdoor air and are transported indoors with indoor/outdoor (I/O) air exchange, just like many gaseous pollutants. Hence, the same particle types are found indoors and outdoors to a certain extent, but often with different abundances. Higher indoor abundances can be due to accumulation and resuspension of particles, lower abundances due to filtration processes or deposition to indoor surfaces.

However, certain particle types are typically formed indoors and can hence be more abundant in the indoor air. To these

particle types belong e.g. particles originating from the debris of building materials (e.g. calcium carbonate, calcium sulphate and aluminosilicates) and particles from indoor combustion processes such as soot particles from the burning of candles. Some particle types may also be the product of chemical reactions indoors, such as the formation of nitrates and sulphates. One of the main differences between the ambient air and the indoor environment is the higher surface-to-volume ratio of indoor environments. Because of this, the interaction of gaseous and particulate pollutants with indoor surfaces via deposition is of higher importance in the indoor environment than it is the case for outdoor air (e.g. Nazaroff et al. 1993).

Abadie et al. (2001) carried out experiments to investigate the deposition of particles of various size ranges to indoor surfaces with different textures and different orientations. They observed that larger particles (with diameters of around 5 µm) deposit mainly to the floor and to a much lesser extent to walls or to the ceiling of a room. This is of course due to the gravitational settling of these rather large particles. The result was also independent of the roughness of the investigated surface. However, small particles with diameters between 0.5 and 1 µm deposit almost to the same extent to the ceiling or to the walls as they deposit to the floor, if the surface is rather rough, such as e.g. a carpet. In contrast, if the surface was covered with a very smooth material such as glass, wood or very smooth wallpaper, also the small particles deposited predominantly to the floor, and only to a very small extent to the ceiling and to the walls. This result shows that, although the deposition of small particles is governed by Brownian motion and not by gravitational settling, the sticking of a particle to a surface is very dependent on its texture. The probability to remain stuck is much larger on rough surfaces than it is on smooth surfaces.

When atmospheric particles have been deposited to a certain indoor surface their possible adverse effects to the surface depend mainly on their chemical composition and, related with the latter, to their hygroscopic characteristics. Major aerosol components such as ammonium sulphate ($(NH_4)_2SO_4$) are hygroscopic and at a certain relative humidity, deliquescence of these compounds occurs. For ammonium sulphate a deliquescence relative humidity of around 80 % was reported by Cheng et al. (2003) and Ebert et al. (2002). For NH_4HSO_4 which is possibly also present in atmospheric aerosol particles, deliquescence occurs already at a relative humidity of 39 %. For NaCl, a value of 78 % is reported and for NH_4NO_3, a value of 74 % at 5 °C and of 68 % at 15 °C (Ebert et al. 2002). These results show that at the relative humidity often encountered in indoor environments, deliquescence of certain aerosol compounds can occur.

Deliquescence of a hygroscopic compound deposited to a certain surface would, however, have dramatic consequences for that surface. The compound dissolves in the moisture attracted due to its own hygroscopicity. The created liquid phase can have very high concentrations of dissolved ions and possibly a pH-value far away from neutral conditions. Hence, this liquid can attack the surface e.g. of a work of art and can cause serious damage.

2. Sampling Techniques

The choice of the sampling technique depends on the type of analytical techniques that will be applied. The chemical and physical properties of the aerosol particles should be altered as little as possible during sampling and sample preparation should be avoided if possible.

PM sampling techniques can generally be divided into two groups: sampling for bulk elemental analysis and sampling for the analysis of individual particles (single particle analysis or SPA) for its chemical composition. A detailed overview of the various samplers is given by Cahill (1990), Akselsson (1994), Annegarn et al. (1988) and Van Grieken & Markowicz (2002).

2.1 Sampling for bulk particle analysis

Aerosol particles can be sampled by high- or low-volume filtration on filter membranes as total or size segregated with a stacked filter unit (Otten, 1991), with a dichotomous sampler or a virtual impactor (Van Grieken & Markowicz, 2002). For bulk elemental, mass and ionic concentration analyses, the most convenient method of sample collection is via impaction or filtration.

Filter holder unit

For the sampling of bulk particles in the size fraction PM_{10}, air is sucked through filter membranes, e.g. Nuclepore® polycarbonate membranes, which are mounted on a filter holder made of e.g. Plexiglas® (Fig. 1). Sampling times typically range from 12 to 24 hours.

Fig. 1 - Sampling of bulk particles by means of a filter holder unit (Kontozova-Deutsch, 2007).

Stacked filter unit

For the collection of size segregated PM, a stacked filter unit (SFU) can be used in order to collect the coarse (2.5-10 µm) and fine (<2.5 µm) aerosol particles (Otten, 1991). The SFU also collects particles on Nuclepore® filters. Coarse particles are collected on an 8.0 µm pore-size filter while fine particle collection is carried out on a 0.4 µm pore-size filter. Filters are mounted in a Plexiglas® cylinder which does not influence the size and the mass distribution of the aerosol samples.

Harvard-type impactor

According to current and anticipated future air quality standards (mainly for human health), the most relevant size fractions of atmospheric aerosols are PM10, PM2.5 and PM1. An impactor that allows the collection of particles in these size ranges is the Harvard-type impactor (MS&T Area Samplers, Air Diagnostics and Engineering, Inc., Harrison, ME, USA). Inside the impactor the air stream is drawn through an inlet and a nozzle. After the nozzle, particles larger than 1 or 2.5 or 10 µm (depending on the impactor type) impact on a sintered metal impactor plate and particles smaller than 1,

2.5 or 10 µm are collected on a Teflon membrane filter, placed onto a support ring.

A homogeneous layer of PM allows X-ray fluorescence (XRF) analysis for bulk elemental analysis, mass concentration determination by gravimetry, water-soluble ionic content after desorption by means of Ion Chromatography (IC) and molecular analysis by means of micro-Raman spectrometry (MRS). The collection time depends on the research aims and the analytical limits and requirements. In general a 24 h sampling period is applied to investigate the daily changes in the composition of PM. Sufficient loading (thin layer) enables the detection of elements by means of XRF. SPA could also be performed on these filters by means of EPMA provided that particle collection takes place in such a manner that PM is collected as spatially separated particles. It should be noted that low-Z elemental analyses are compromised due to the chemical composition of the filter.

2.2 Sampling for Single particle analysis

Cascade impactors

In impactors, separation of particulate matter from the gas phase is based on the much higher inertia that particles have compared to gases. In a conventional flat plate impactor, particle loaded air passes through a nozzle where the particles are accelerated. At the nozzle exit, the air streamlines are deflected sharply over an impaction plate, the impaction surface of the impactor stage, so that particles larger than a certain size (cut-off size) impinge on the collection surface, whereas smaller particles follow the air stream. By using more than one impaction stage, the aerosol sample can be fractionated into several size intervals. This type of impactors is called cascade impactor (see Fig. 2).

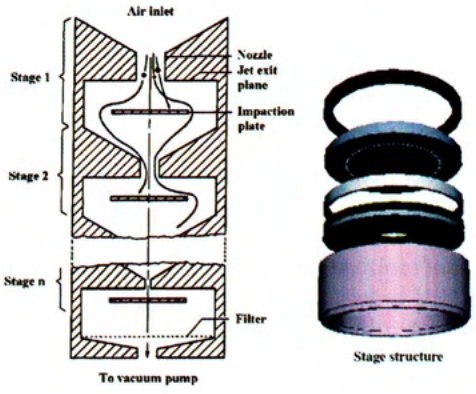

Fig. 2 - Scheme of a single orifice impactor (left) and exploded view of a single stage of a multi-orifice impactor (right) (Harrison & Van Grieken, 1998).

Among the various types of cascade impactors, some shall be presented in this chapter. The Berner impactor (de Hoog, 2005) has up to 9 different impaction stages with cut-off diameters of 16, 8, 4, 2, 1, 0.5, 0.25, 0.12 and 0.06 µm, respectively (Fig. 3). For an optimal size fractionation, the air flow through the impactor has to be adjusted to 26 L/min. Another type of impactor is the small-sized Battelle impactor (Gysels & Van Grieken, 1999) with cut-off diameters of 20, 8, 4, 2, 1, 0.5 and 0.25 µm. The air flow through the Battelle impactor has to be adjusted to 1.2 L/min. Finally, the Dekati PM10-PM2.5-PM1 impactor (Dekati, Finland) shall be mentioned in which sampling is carried out on impactor stages covered by a filter membrane which enables e.g. the analysis of soluble ions in the aerosol particles by IC.

Fig. 3 - Nine-stage Berner impactor, structure and exposure for sampling.

2.3 Sampling of deposited aerosol particles

For the sampling of dry deposition of aerosol particles substrates are usually exposed for a certain time to let particles deposit onto them. As substrates, filter membranes can be used for the subsequent analysis of the particles' mass, elemental composition and soluble ion content. For single particle analysis, silicon can be used as a substrate.

3. Analysis of Aerosol Particles

3.1 Energy Dispersive X-ray fluorescence spectrometry (EDXRF)

Principles

The theory of EDXRF is explained in detail in e.g. Bertin (1969), Jenkins et al. (1981), Van Grieken & Markowicz (2002). Generally, XRF is commonly applied for the characterization of the bulk elemental composition of samples in the context of CH and environmental studies (e.g. Van Grieken et al. 1998).

XRF is based on the interaction processes between electromagnetic radiation and the sample. The energy or the wavelength of the emitted X-rays is characteristic for the chemical elements, and thus can be used for the identification of elements present in the sample. The intensities of the characteristic X-rays can be related to the concentration of the elements present in the sample. Hence, XRF can be used for qualitative as well as for quantitative analysis.

For elemental analysis, XRF has the advantage of not needing a sample preparation, fast analyses at low cost, simultaneous detection of a wide range of concentrations (from some ppm to several percent) with high precision, the indifference to the chemical state of the analyte and the preservation of the sample during analysis. The technique can be applied to all elements with $Z > 12$, in bulk, liquid or thin layer samples. On the other hand, EDXRF has also some disadvantages: low-Z elements cannot be determined accurately, due to the presence of a detector window, which prevents the penetration of low-energy X-rays and spectral interferences can occur because the energy resolution of the detector is limited.

3.2 Electron Probe Micro Analysis (EPMA)

Principles

EPMA is an ideal technique for the characterization of samples from environmental and CH studies. The combination of

EPMA and X-ray spectrometric analysis enables the simultaneous investigation of the morphology and the elemental composition of individual aerosol particles. Automation of computer controlled EPMA enables the analysis of some hundreds of particles in a few hours. An overview of the most relevant techniques used in environmental single particle analyses and their application can be taken from e.g. Jambers et al. (1995), Jambers & Van Grieken (1996), Rodriguez-Navarro & Doehne (1999), Rodriguez-Navarro & Doehne (2000), Ro et al. (2004), Osán et al. (2000) and de Hoog (2005).

Energetic electrons interact with the atoms and electrons of a material in many ways. In EPMA a nm-sized electron beam with an energy typically in the range of 5-25 keV and a diameter of 0.1 μm is used. Different kinds of information can be obtained from the large variety of specimen-beam interactions. The detection of characteristic X-ray lines provides information about the elemental composition of the sample. Morphological information about the sample can be obtained from secondary electron (SE) and backscattered electron (BSE) images.

Instrumentation and experimental

Although the thin-window detectors, allowing low-Z element determinations, have been used for nearly a decade in X-ray spectrometry, they had not been applied systematically in single particle analysis (SPA) of aerosols until a couple of years ago. Detection of the low-Z elements in particulate matter allows enlarging the scope of SPA, firstly because the low-Z elements are abundantly present in environmental particles and secondly because quantitative information is necessary for the speciation of individual microscopic particles. Indeed, many environmental particles are present in the form of nitrates, sulphates, oxides, or mixtures including a carbon matrix (Ro et al. 2003).

To avoid evaporation problems with volatile components of the investigated particles, a stage with the possibility for cryo-cooling is used during the analyses, allowing the analysis of particulate samples at liquid nitrogen temperature, about -193 °C. For the same reason, the accelerating voltage is usually set to 10 kV, because a large energy dissipation in the sample material can cause similar effects. The low electron energy improves the analytical sensitivity, because of the low X-ray background originating from the Bremsstrahlung radiation of the decelerated electrons. The beam current is chosen at 1 nA, excitation is carried out in the point analysis mode and the measuring time is set at 20 s. Measurements are carried out in the manual mode using Si wafers as a substrate for the particles and in the automatic mode using Ag substrates.

This technique offers the possibility of studying more volatile species, like ammonium sulphate and ammonium nitrate. In environmental analysis, these compounds are very important since their abundance in atmospheric particles is very high (Osán et al. 2000, Szaloki et al. 2001).

Cluster analysis

On a large data set, multivariate statistical techniques have to be applied. Cluster analysis is a method frequently applied. Cluster analysis can be either hierarchical (HCA) or non-hierarchical (NHCA). Hierarchical clustering is most commonly used due to the relative simplicity of the calculations. Clustering in this way means successive agglomeration or division of objects to clusters. The main drawback of the HCA is the imposition of a hierarchical structure of the data by the method, even if such a structure is not present. This problem can be solved by the non-hierarchical method. Non-hierarchical clustering analysis (NHCA) divides the set of data into a number of clusters in such a way that the elements of the same cluster are close to each other and the different clusters are well separated. Since the clusters are generated simultaneously, no hierarchical structure is imposed on the data. The NHCA can be carried out by means of the Forgy algorithm (Massart & Kaufman, 1983) and the DPP software (Van Espen, 1984).

In real environmental samples, the particle compositions are unknown. So, it is clear that the cluster identification also requires some interpretation by the analyst, some expert opinion. In practice, this is done by using identification tables that are built up from experiences in the past. A lot of particle types can usually be identified without any doubt, but certain particle types are difficult to distinguish in single particle analysis, such as the distinction between biogenic, carbon-rich and organic particles. Biogenic particles are identified when the C and O content of the particles is similar, and they also contain some N, P, S, K, and/or Cl, which are characteristic elements for biogenic particles. Carbon-rich particles are identified when the sum of the C and O contents is larger than 90 % in atomic fraction and the C content is 3 times larger than the O content. Organic particles are identified if the sum of the C and O contents is larger than 90 % in atomic fraction, and they are not yet assigned to either biogenic or carbon-rich particles (de Hoog, 2005).

3.3 Raman Spectroscopy

Principles

Raman spectroscopy is named after the Indian physicist C. V. Raman, who observed this kind of spectra for the first time in 1928. Whereas infrared spectra originate from transitions between two vibrational levels of a molecule and are usually observed as absorption spectra, Raman spectra originate from the electronic polarization caused by ultraviolet or visible light. Due to this electronic polarization during irradiance with light of the frequency ν, light with the frequencies ν and $\nu \pm \nu_i$ is emitted, where the first one is referred to as Rayleigh scattering and the second one as Raman scattering. ν_i represents in this case a vibrational frequency, which is observed as Raman shift from the incident frequency ν. Only those molecular vibrations of a molecule are Raman active which are accompanied by a change of its polarizability (Nakamoto, 1986). Both rotational and vibrational Raman spectroscopy is possible.

3.4 Ion Chromatography

Principles

An ion chromatograph consists of several components. The mobile phase is pumped through the chromatographic system by means of a pump which is electronically controlled to ensure an almost pulse-free flow of the eluent. A loop injector is used for the introduction of the sample into the system. Between the injector and the actual separator column, a guard column is placed to protect the analytical column from contamination. The suppressor reduces the background conductivity of the eluent. The ions that exit the column are detected by a conductivity cell. For details see e. g. in Weiss (2004).

Experimental

For the determination of anions such as chloride, nitrite, nitrate, sulphite, sulphate, formate and acetate and cations

such as sodium, ammonium, potassium, magnesium and calcium, e.g. a DX-120 ion chromatograph (Dionex) can be used. For the separation e.g. an AG14-4mm guard column and an AS14-4mm analytical column can be used. Calibration is usually carried out using certified standard multi-ion solutions (e. g. Combined Seven Anion Standard II, Combined Six Cation Standard II, Dionex).

4. Application Examples

XRF, EPMA and Raman spectrometry are applied in CH research for a variety of reasons, among others for the fundamental interest in materials and methods used by artists, the tracing of forgeries and questions in connection with the preventive conservation and restoration of works of art. Some examples of CH related research projects will be given in this section:

Problems concerning preventive conservation of works of art were studied in the Correr Museum (Venice), the Kunsthistorisches Museum (Art History Museum, Vienna), the Museum of Fine Arts (Antwerp) and the Sainsbury Centre for Visual Arts (Norwich) in the framework of the European project *"Assessment of Environmental Risk Related to Unsound Use of Technologies and Mass Tourism"* (e.g. Camuffo et al. 1999, Gysels et al. 2002; Sturaro et al. 2003). E.g. in the Correr Museum problems with the darkening of Bellini paintings had been noticed. XRF analysis of indoor bulk aerosol revealed very high concentrations of Ca and S. Additional SPA by EPMA showed high abundances of $CaSO_4$, Ca-rich and Ca-Si-S-Cl-particles, interestingly especially in samples taken when the windows of the museum were closed and no visitors were present. Hence, no outdoor sources were responsible for the darkening of the paintings but instead the plastered walls of the museum were deteriorating and releasing particles. The solution of this problem was to plastify the walls. In contrast, analyses carried out in the Kunsthistorisches Museum in Vienna showed that the problems with high concentrations of particulate matter encountered there were in fact due to outdoor sources and a poor air filtration system. Particles from road de-icing in winter ($CaCl_2$) and from construction works carried out in the vicinity (Ca-silicates) entered the museum. An improvement of the air filtration system could solve this problem.

In the European project "VIDRIO" *(Determination of conditions to prevent weathering due to condensation, particle deposition and micro-organism growth on ancient stained glass windows with protective glazing)* air pollution inside churches with historic stained glass windows with and without a protective glazing system were studied (e.g. Kontozova et al. 2005, Kontozova-Deutsch et al. 2008a, b, Godoi et al. 2006). For this purpose, the Sainte Chapelle in Paris, the Cathedral of Cologne and the Basilica Saint-Urbain in Troyes were investigated. XRF, EPMA and IC were applied to indoor and outdoor samples and samples collected in the interspace between historic window and protective glazing. The obtained EPMA results showed that e.g. in Cologne and Troyes nitrate and soot particles were more abundant indoors than outdoors due to the burning of candles. Indoor concentrations of NO_2 were in these churches also higher than outdoor ones. On the contrary, in Paris, where the monument is not used as an active church but is visited by thousands of tourists every day, high indoor elemental concentrations of Ca, K, Al, Si, Pb and Zn were detected. The visitors are probably the most important indoor source of fine dust particles which are continuously resuspended. Concerning the glass window interspace, no accumulation of particles was observed in the interspace of the three monuments.

Another European project, "Friendly Heating" (Effects on air quality of new heating systems in churches), had as one of the aims to analyse the air movements connected to the heating system of the church and to determine the influence of the old and the new heating systems on the works of art inside (Spolnik et al. 2005, Bencs et al. 2007). Particle analysis showed that the conventional (hot air blowing) heating system distributed particles throughout large parts of the church leading to a high amount of particle deposition on works of art. The proposed new heating system (electrical heating in the pews) leads to less turbulence of the air, but re-suspends particles carried on the boots of the church-goers.

In a project carried out for the Metropolitan Museum of Art in New York, an assessment of the indoor air quality with respect to particulate and gaseous air pollutants has been carried out (Kontozova-Deutsch, 2007). One of the results obtained by EPMA in combination with Raman spectrometry was a rather high abundance of sodium nitrate and soot particles in indoor (galleries and showcases) as well as outdoor samples of the fine particle fraction. Probably these particles are formed from sea salt and nitric acid (from the oxidation of NO_x from e.g. car traffic). They can pass the filters of the air conditioning system and deposit on works of art.

Another example of the application of particle analysis methods in the framework of a CH study is a project currently carried out at the UNESCO World CH complex of the Alhambra in Granada, Spain (Lyamani et al. 2009). In this project not only environmental particles are analysed but also materials used in the monument, such as authentic pigments. The preliminary results show high amounts of soil dust particles in Granada, due to the geographical location (natural basin surrounded by mountains) and the prevailing dry weather conditions. Also soot particles show high abundances. Hence, soiling of the works of art is probably the main problem at the Alhambra.

The characterisation of particles and the related deposition of particles on old books and manuscripts in display cases is the focus of a project currently carried out for the Plantin-Moretus Museum in Antwerp (Kontozova-Deutsch, 2007), the only museum included into the UNESCO list of World CH sites. In this museum one of the first printing offices in Europe is preserved and a large collection of manuscripts and printing equipment is displayed. Different types of display cases are compared and I/O-ratios of particle concentrations are investigated. An accumulation of fine particles has been observed in the museum, especially of aluminosilicates. In contrast, carbonaceous particles and nitrates were not enriched in comparison to the ambient air. The carbonaceous particles are dangerous from a conservation perspective as they cause blackening of surfaces and constitute a medium for the adsorption and oxidation of gases to acids, partly oxidised by transition metals agglomerated to those particles.

Finally, fundamental research was carried out in the framework of the "Multi-Assess" project (Model for multi-pollutant impact and assessment of threshold levels for cultural heritage) in order to investigate the effects "modern" mixtures of air pollutants (dominated by high concentrations of NO_x, O_3 and fine particles) have on different kinds of materials, in contrast to the "old" type of air pollution, dominated by SO_2. The development of dose-response relations for these pollutant mixtures constitutes a necessary condition for the prediction of damage and the establishment of threshold levels (e.g. Ferm et al. 2006).

5. Conclusions

Atmospheric particulate pollutants play a crucial role in many processes contributing to the deterioration of our Cultural Heritage, e.g. the soiling of surfaces of works of art and the deposition of aggressive components, such as acidic salts. Modern analytical techniques enable us to probe different characteristics of atmospheric particles, such as their chemical composition and morphology. In many cases these analyses can even be carried out in a non-destructive way, which is of vital importance when particles are deposited on works of art. Especially the combination of different analytical techniques provides us with complementary information regarding particulate pollutants such as their bulk elemental composition (XRF), soluble components (IC), abundance patterns of elements in single particles (EPMA) and chemical compounds (Raman).

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References

Abadie, M., Limam, K. & Allard, F., 2001. Indoor particle pollution: effect of wall textures on particle deposition. Building and Environment 36: 821–827.

Akselsson, K.R., 1984. Aerosol sampling and samplers matched to PIXE analysis. Nuclear Instruments and Methods B3: 425-430.

Andreae, M.O. 2001. The dark side of aerosols. Nature 409: 671-672.

Andreae, M.O., Jones, C.D. & Cox, P.M., 2005. Strong present-day aerosol cooling implies a hot future. Nature 435: 1187-1190.

Annegarn, H.J., Cahill, T.A., Sellschop, J.P.F. & Zucchiatti, A., 1988. Time sequence particulate sampling and nuclear analysis. Physica Scripta 37: 282-291.

Bertin, E., 1969. Introduction to X-ray Spectrometric Analysis. New York: Plenum Press.

Bencs, L., Spolnik, Z., Limpens-Neilen, D., Schellen, H.L., Jütte, B.A.H.G. & Van Grieken, R., 2007. Comparison of hot-air and low-radiant pew heating systems on the distribution and transport of gaseous air pollutants in the mountain church of Rocca Pietore from artwork conservation points of view. Journal of Cultural Heritage 8: 264-271.

Boubel, R.W., Fox, D.L., Turner, D.B. & Stern, A.C., 1994. Fundamentals of Air Pollution. San Diego: Academic Press.

Bridgman, H. A., 1990. Global Air Pollution: Problems for the 1990s. London: Bellhaven Press.

Cahill, T.A., 1990. Analysis of air pollutants by PIXE: the second decade. Nuclear Instruments and Methods. B49: 345-350.

Camuffo, D., Brimblecombe, P., Van Grieken, R., Busse, H.-J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D., De Bock, L., Gysels, K., Wieser, M. & Kim, O., 1999. Indoor air quality at the Correr Museum, Venice, Italy. Science of the Total Environment 236: 135-152.

Cheng, L.-Y., Jeng, F.-T., Chen, C.-C. & Hsiao, T.-C., 2003. Hygroscopic behavior of atmospheric aerosol in Taipei. Atmospheric Environment 37: 2069–2075.

de Hoog, J., 2005. Optimization and environmental application of TW-EPMA for single particle analysis. Ph.D. thesis. University of Antwerp, Belgium.

de Hoog, J., Osán, J., Szalóki, I., Eyckmans, K., Worobiec, A., Ro, C.-U. & Van Grieken, R., 2005. Thin-window electron probe X-ray microanalysis of individual atmospheric particles above the North Sea. Atmospheric Environment 39: 3231-3242.

Dockery, D.W., Pope, C.A. III, Xiping, X., Spengler, J.D., Ware, J.H., Fay, M.A., Ferries, B.G. Jr. & Speizer, F.E., 1993. An association between air pollution and mortality in six US cities. New England Journal of Medicine 329: 1753-1759.

Ebert, M., Inerle-Hof, M. & Weinbruch, S., 2002. Environmental scanning electron microscopy as a new technique to determine the hygroscopic behaviour of individual aerosol particles. Atmospheric Environment 36: 5909–5916.

Ebert, M., Weinbruch, S., Hoffmann, P. & Ortner, H.M., 2004. The chemical composition and complex refractive index of rural and urban influenced aerosols determined by individual particle analysis. Atmospheric Environment 38: 6531–6545.

Ferm, M., Watt, J., O'Hanlon, S., De Santis, F. & Varotsos, C., 2006. Deposition measurement of particulate matter in connection with corrosion studies. Analytical and Bioanalytical Chemistry 384: 1320-1330.

Godoi, R.H.M., Kontozova, V. & Van Grieken, R., 2006. The shielding effect of the protective glazing of historical stained glass windows from an atmospheric chemistry perspective: Case study Sainte Chapelle, Paris. Atmospheric Environment 40: 1255-1265.

Gysels, K. & Van Grieken, R., 1999. Field evaluation of a wind tunnel-impactor system for sampling ambient aerosols. Journal of Aerosol Science 30: 639-650.

Gysels, K., Deutsch, F. & Van Grieken, R., 2002. Characterisation of particulate matter in the Royal Museum of Fine Arts, Antwerp, Belgium. Atmospheric Environment 36: 4103-4113.

Harrison, R.M. & Van Grieken, R.E., 1998. Atmospheric Particles. Chichester: John Wiley & Sons.

IIASA, 2005. Commission Staff Working Paper, Annex to: The Communication on Thematic Strategy on Air Pollution and The Directive on "Ambient Air Quality and Cleaner Air for Europe", Impact Assessment of the Thematic Strategy and the CAFE Directive (SEC(2005) 1133); http://ec.europa.eu/environment/air/cafe/pdf/ia_report_en 050921 _final.pdf.

Jambers, W., De Bock, L. & Van Grieken, R., 1995. Recent advances in the analysis of individual environment particles. Analyst 120: 681-692.

Jambers, W. & Van Grieken, R., 1996. Present and future application of beam techniques in environmental microanalyisis. Trends in Analytical Chemistry 15: 114-122.

Jenkins, R., Gould, R. & Gedcke, D., 1981. Quantitative X-ray Spectrometry. New York: Dekker.

Kontozova, V., Godoi, R.H.M., Spolnik, Z., Worobiec, A., Deutsch, F. & Van Grieken, R., 2005. Characterization of air pollutants observed in three European cathedrals. Is the protective glazing really effective? Rivista della Stazione Sperimentale del Vetro 3: 33-40.

Kontozova-Deutsch, V., 2007. Characterisation of indoor gaseous and particulate pollutants for conservation in museums and churches, Ph.D. thesis, University of Antwerp, Belgium.

Kontozova-Deutsch, V., Deutsch, F., Godoi, R.H.M., Spolnik, Z., Wei, W. & Van Grieken, R., 2008a. Application of EPMA and XRF for the investigation of particulate pollutants in the field of cultural heritage. Microchimica Acta 161: 465-469.

Kontozova-Deutsch, V., Godoi, R.H.M., Worobiec, A., Spolnik, Z., Krata, A., Deutsch F. & Van Grieken, R., 2008b. Investigation of gaseous and particulate air pollutants at the Basilica Saint-Urbain in Troyes, related to the preservation of the medieval stained glass windows. Microchimica Acta 162: 425-432.

Lyamani, H., Olmo, F. J. & Alados-Arboledas, L., 2009. Physical and optical properties of aerosols over an urban location in Spain: seasonal and diurnal variability. Atmospheric Chemistry and Physics Discussion 9: 18159-18199.

Massart, D. & Kaufman, L., 1983. The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis. New York: Wiley.

Nakamoto, K. 1986. Infrared and Raman Spectra in Inorganic and Coordination Compounds. New York: Wiley & Sons.

Nazaroff, W.W., Ligocki, M.P., Salmon, L.G., Cass, G.R., Fall, T., Jones, M.C., Liu, H.I.H. & Ma, T., 1993. Airborne Particles in Museums, Research in Conservation, The Getty Conservation Institute.

Osán, J., Szalóki, I., Ro, C.-U. & Van Grieken, R., 2000. Light element analysis of individual microparticles using Thin-Window EPMA. Microchimica Acta 132: 349-355.

Owen, K.M., Ensor, S.D. & Sparks, L.E., 1992. Airborne particle sizes and sources found in indoor air. Atmospheric Environment 26: 2149-2162.

Pope, C.A. III, Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E. & Heath, C.W. Jr., 1995. Particulate air pollution as predictor of mortality in a prospective study of US adults. American Journal Respiratory and Critical Care Medicine 151: 669-674.

Ro, C.-U., Oh, K.-Y., Kim, H., Kim, Y.P., Lee, C.B., Kim, K.-H., Kang, C.H., Osán, J., de Hoog, J., Worobiec, A. & Van Grieken, R., 2001. Single-particle analysis of aerosols at Cheju Island, Korea, using low-Z electron probe X-ray microanalysis: a direct proof of nitrate formation from sea salts. Environmental Science and Technology 35: 4487-4494.

Ro, C.-U., Osán, J., Szaloki, I., de Hoog, J., Worobiec, A. & Van Grieken, R., 2003. A Monte Carlo program for quantitative electron-induced X-ray analysis of individual particles. Analytical Chemistry 75: 851-859.

Ro, C.-U., Kim, H. & Van Grieken, R., 2004. An expert system for chemical speciation of individual particles using low-Z particle electron probe X-ray microanalysis data. Analytical Chemistry 76: 1322-1327.

Rodriguez-Navarro, C. & Doehne, E., 1999. Salt weathering: influence of evaporation rate, supersaturation and crystallisation pattern. Earth Surface Processes and Landforms 24: 191-209.

Rodriguez Navarro, C., Doehne, E. & Sebastian, E., 2000. Influencing crystallization damage in porous materials through the use of surfactants: experimental results using sodium dodecyl sulfate and cetyldimethylbenzylammonium chloride. Langmuir 16: 947-954.

Sabbioni, C., Ghedini, N. & Bonazza, A., 2003. Organic anions in damage layers on monuments and buildings. Atmospheric Environment 37: 1261–1269.

Seinfeld, J.H. & Pandis S.N., 1998. Atmospheric Chemistry and Physics. New York: Wiley.

Spolnik, S., Bencs, L., Worobiec, A., Kontozova, V. & Van Grieken, R., 2005. Application of EDXRF and Thin Window EPMA for the investigation of the influence of hot air heating on the generation and deposition of particulate matter. Microchimica Acta 149: 79-85.

Sturaro, G., Camuffo, D., Brimblecombe, P., Van Grieken, R., Busse, H.-J., Bernardi, A., Valentino, A., Blades, N., Gysels, K., Deutsch, F., Wieser, M. & Buczolits, S., 2003. Multidisciplinary environmental monitoring at the Kunsthistorisches Museum, Vienna. Journal of Trace and Microprobe Techniques 21: 273-294.

Szalóki, I., Osán, J., Worobiec, A., de Hoog, J. & Van Grieken, R., 2001. Optimization of experimental conditions of thin-window EPMA for light element analysis of individual environmental particles. X-Ray Spectrometry 30: 143-155.

Van Espen, P., 1984. A program for the processing of analytical data (DPP). Analytica Chimica Acta 165: 31-49.

Van Grieken, R., Gysels, K., Hoornaert, S., Joos, P., Osán, J., Szalóki, I. & Worobiec, A., 2000. Characterisation of individual aerosol particles for atmospheric and cultural heritage studies. Water, Air and Soil Pollution 123: 215-228.

Van Grieken, R. & Markowicz, A., 2002. Handbook of X-ray Spectrometry, 2nd edition. New York: Dekker.

Van Grieken, R., Delalieux, F. & Gysels, K., 1998. Cultural heritage and the environment. Pure and Applied Chemistry 70: 2327-2331.

Weiss, J., 2004. Handbook of Ion Chromatography. Weinheim: Wiley-VCH.

Chapter 10
Soiling damage and perception

Peter Brimblecombe

1. Introduction

The late 20th century has seen a profound reduction in the aggressive primary air pollutants that had dominated the air of cities of Europe and North America. Reductions are now evident elsewhere. This has meant a concomitant reduction in the level of material damage exerted by aggressive acidic pollutants and the deposition of coal smoke. Although a hundred years of such improvements has led to cleaner buildings, improved appearances have not always been maintained. The increased use of diesel engined vehicles, particularly in European cities, has often been blamed for increased blackening in the 21st century.

The acid rain issue of the 1980's allowed the appearance of buildings to become a *cause célèbre* and resulted in many campaigns to improve the state of urban facades. In the long term the aggressive approaches to cleaning over this period may have caused almost as much public disquiet as the original damage. There were also concerns about the way in which materials were displayed indoors. The dusty perceptions of museums and historic interiors provoke negative response and present many management challenges. Dusty, mouldy interiors and their furnishings have been iconic for many who have visited important historic properties (Lithgow et al., 2005). Libraries and their books have increasingly been perceived as dusty and are perhaps in contrast to the apparent cleanliness and perfection of the materials that are to be found on the internet.

It is arguments like these that emphasise soiling to be as much an issue of perception as one of science. This has frequently created problems in terms of research methodologies straddling as it does the physical world and the aesthetic. This paper tries to link the physical aspects of soiling and its economic impact with perception issues.

2. Soiling definition

The term *soiling* is widely used to describe the process where surfaces become dirty. In scientific writing there are sometimes objections to this term because it should be reserved for descriptions of a light dusting to a surface that is essentially reversible. This has led to other terms such as *blackening* being adopted. This word carries less suggestion of reversibility. This term has a problem in that it implies a loss of reflectance, but suggests no change in chroma. In cases where there is a distinct colour change it might be better to refer to this as say *yellowing* as have been done for the increasingly warm tones found on some buildings or more generally as *colouring* (Grossi and Brimblecombe, 2008). However, such terms remain imperfectly defined, so it is well for authors to think about them carefully within scholarly articles and be clear about how they are to be used.

Soiling and discolouration often arises from atmospheric deposition of combustion products. The orange reddish patinas on some Mediterranean monuments indicate the role played by iron oxides as colouring patina (Garcia-Valles et al., 1998; Valls Del Barrio et al., 2002). However, there are other sources. The patterns of soiling in Oxford suggests the importance of biological activity (Thornbush and Viles, 2004) and black deposits on surfaces of some Iranian monuments were found to be mainly microbial crusts from cyanobacteria (Bonazza et al., 2007b). The presence of coloured artificial patina (Vázquez-Calvo et al., 2007) or surface treatments (Sgobbi et al., 2010) were applied since ancient times to improve the aesthetics and durability of the surfaces. In processes at the surface such as the oxidation of surface organics can cause warmer tones e.g. diesel soot has many organic compounds that can oxidise to brownish-coloured humic-like materials (Grossi et al., 2007).

3. Exponential blackening

The change in colour of surface over time as it is randomly covered with another differently coloured material would be expected to be an exponential process (Mack, 1954). In the case of blackening this has been seen as a monotonic exponential loss of reflectance (Haynie, 1986). Such models are attractive because it is a typical first order rate equation, but there are a wide variety of other suggestions. Other models may simply come about through best fits derived from regression analysis and frequently lack any underlying view of the processes involved. The exponential process has a good theoretical basis and in when expressed with properly defined boundaries in the form:

$$R_t = R_p + (R_o - R_p) \exp(-kt)$$

in many cases works very well. Here R_t is the reflectance of the stone at time t, R_p the reflectance of the depositing particles and R_o the reflectance of the fresh stone. In many cases, authors recognise that $R_p << R_o$, so reduce the equation to $R_t = R_o \cdot exp(-kt)$. This is valid if R_p is close to zero, but can be a problem because when building surfaces are completely blackened they still reflect as much as 30% of the light (Brimblecombe and Grossi, 2004).

Some authors (e.g. Ionescu, 2006) have fitted a range of logistic functions, such as the Hill equation, to the soiling process. This is convenient as a way of describing the situation where the rate of colouration is different at the very beginning

of the process.. The problem of more complex forms of change is also apparent when we consider situations where there different processes of colour change are under way at the same time. Stone exposed to polluted air not only becomes black, but at the same time can take on warmer tones as it yellows. The rate of blackening and yellowing may take place at quite different rates (Grossi et al., 2007).

There have been a number of attempts to define the units to be used to describe the blackening process. The % reflectance has been commonly used. This percentage basis is also found in the *soiling unit* sometimes adopted (e.g. Adams et al., 2002) although it is used in various ways, sometimes as % reflectance and at other times as the change % reflectance per week or month. Such rates could be expressed as reciprocal time and thus simply be s^{-1}, but in the case of soiling the changes are slow in these units, so the reciprocal gigasecond can be used. Although this can be formally expressed in terms of SI units lacks an intuitive sense of meaning.

4. Particle size

The blackening process is frequently the result of the deposition of particles that, in urban air, most often contain elemental carbon. Particles of coal smoke, typical of atmospheres fifty or a hundred years ago were 1 μm to 50 μm in size and primarily as smooth spherical particles. The diesel particles found today are much smaller (Searle and Mitchell, 2006) and may be somewhat more uniform in size with diameters around 25 nm, but tend to form loose agglomerates that can stretch many hundreds of nanometres (Lapuerta et al., 2007). The small size and open structure of diesel particles means that their light scattering properties must be complex and as they are below the wavelength of light so their effect will not necessarily a function of geometric coverage. However, little attention has been paid to the potential for Mie scattering by depositing diesel particles on building surfaces although work is available on the optics of particles and their aggregates (Hull et al., 2004; Zhao and Ma, 2009). The deposits of building facades can be very much coarser than this when they incorporate sandy materials blown by the wind (Sgobbi et al., 2010).

Indoors there are fine particles also that can be found deposited on surfaces, but in terms of visual impairment it is often the coarser particles that are evident as deposits on objects on display. These large particles which settle rapidly are often generated by visitors who shed both dust particles and clothing fibres (Lloyd et al., 2002; Yoon and Brimblecombe, 2001).

There is much debate as to the relative importance of fine and coarse particles to material damage. There is often a preoccupation with the smaller particles and their ability to cause damage, yet it is worth remembering that they are often so small that they contain a very low mass of damaging acids, so attention often focuses on their catalytic ability. The potential for enhancement of the rate of sulfation both in the presence of coal and diesel particles has been the subject of much debate and remains unresolved. Although it should be noted that over year long periods weathering loss from *Portland Limestone* were reduced when coated with diesel particles (Searle and Mitchell, 2006).

5. Adhesion/cementation

The black particles on exterior facades have frequently been bound into gypsum crusts which have been very thick at times and form a deep calcareous layer that totally dominates the building surface and was observed by famous architects, such as Sir Christopher Wren three centuries ago (Wren, 1713). Salts and organic compounds have been seen as important in binding elemental carbon into the crust (Searle and Mitchell, 2006). Crusts in the present day are often different to those found in the past. They can be thinner and have a higher organic content. It may well be that particles become bound through other processes(Bonazza et al., 2007a). The increased use of diesel particles carry with them a range of polycyclic aromatic hydrocarbon compounds and these may exert a novel chemistry on the building surface, particularly as compounds such as anthracene could photosensitize oxidation of the organic compounds. The binding may be more of an organic adhesive than a cement.

Indoors such binding processes are less well known. Nevertheless there are some early observations of the gradual binding of particles to surfaces: Susannah Whatman, who wrote an 18th century guide to housekeeping said that "places where the dust lodges should be attended to. Otherwise, if left too long, it takes a long time and much labour to get it off." (Hardyment, 2000). This can be a severe problem if dust becomes bound to sensitive historic materials such as silk. Here the aggressive removal of the bound particles can damage the substrate. Recent work has shown that in some humid environments microcrystalline cements can form in less than a day and bind particles to underlying surfaces (Brimblecombe et al., 2009). This may be a special worry if climate change leads to warmer and more humid conditions indoors (Brimblecombe et al., 2007).

6. Deposition and removal

Particles and gases are deposited on building surfaces. It is usual to describe the rate of this process in terms of the deposition velocity. However the control on the deposition of particles is very different to that of gases. The deposition of gases can often be idealised in terms of Fickian diffusion with a diffusion coefficient reflecting the diffusion coefficient of the gas in still air within the boundary layer at the surface. The situation with particles is altogether more complex as there is a relationship with particle size. Most notably there is a balance between gravitational settling and diffusion, Brownian motion etc (Camuffo, 1998).

Once particles have been deposited and discolour a surface there is a possibility that they can be removed from the building surfaces and in some senses the building is cleaned. This process is less frequently addressed than the accumulation of material, but there are observations of the removal or redistribution of soot by wind driven rain. This can be more evident on buildings at higher elevations where the impingement of rain leads to greater wash-off rates (Davidson et al., 2000). This is not a really a reverse of the deposition process because it appears as rain streaking and often leads to disfiguring patterns that cause offence to those viewing the building (Grossi and Brimblecombe, 2004). Thus although urban buildings can self-clean in this way it is not always desirable. Additionally changing exposure to rainfall alters the balance between accumulation and redistribution which means that future patterns can readily be different to those we are able to accept or are familiar with.

The creation of such blackening patterns creates an aesthetic problem. Some light soiling can enhance the appearance of architecture (Andrew, 1992) or be seen as a patina that was an intent of the architect or restorer. However, in many cases the patterns are not desired. In some cases deposition can also lead to patterns. Outdoors this may be the result of the air flow over complex elements of the architectural form. Indoors it can be especially characteristic for example where thermophoresis can lead to patterns of particle deposition above warm radiators on the wall (Camuffo, 1998).

7. Aesthetic and blackening patterns

Public perception of the patterns on building facades can be investigated by conducting questionnaires using of real or simulated images, with photographs a frequent choice (Andrew, 1992; Ball et al., 2000; Davidson et al., 2000). Other studies (e.g. Grossi and Brimblecombe, 2004) have chosen more abstract images and have evaluated responses to blackening patterns that form on a single architectural element, such as a pedimented window. A study of responses to patterns of blackening around an idealised window required respondents to arrange the images of blackening patterns from the "most to the least acceptable" pattern to the least. The order hinted that certain blackening pattern were important in influencing the ranking. Patterns would potentially confuse our reading of architectural form appeared most objectionable and interestingly it was possible to relate the dislike of patterns to their fractal dimensions with those furthest from unity creating the greatest offense (Grossi and Brimblecombe, 2004).

Some respondents, when asked about the acceptability of a given amount of soiling, comment on the patterns. They may say that it would be fine for the building to be darker or lighter, but the black rain-washed streaks should not disfigure the facade. Thus our perception of this disfigurement depends on the patterns of discoloration and not just the degree of blackening. Such negative views of blackening patterns are familiar in literature. The playwright Ben Jonson savagely attacked Volpone in his 1606 play of the same name, describing him as "an old smoked wall, on which the rain ran down in streaks!"

8. Amount of blackness

As implied in the section above, patterns are important. However, the regulatory perspective typically wishes to establish the quantity of deposit on surfaces which causes offense. Certainly this is easier than establishing the nature of the offense caused by different patterns. A key objective of the CARAMEL project funded by the European Commission was to determine the pollutant concentrations that would lead to building surfaces requiring treatment or management. The project needed to establish the level of blackening that would demand a response and in this way consider what kind of degree of regulatory response would be appropriate in terms of managing particulate pollution in urban air.

This problem was approached by examining the responses of visitors when standing in front of building facades from a number of architecturally significant buildings where degradation in appearance would be readily accepted to be a cultural loss (Brimblecombe and Grossi, 2005). These buildings were chosen to present very different amounts of blackening. The experimental approach was simplified by choosing light coloured stone buildings as they were easily discoloured. The visitors were asked a range of questions about the building. These focused on the tone or colour of a building and its relation to presentation or the need for cleaning. There were questions which used value-laden words such as "dirty" and "pollution" to evoke strong responses.

Quite naturally respondents saw more need for cleaning building where they were regarded as dirty. Perhaps the most quantifiable result was that obtained when visitors were asked to estimate the tone of a building (*perceived lightness*) by comparison with a gray scale. These responses are generalised in Fig. 1, which compares the visitor estimate of *perceived lightness* as a function of the likelihood that it would be said to be "dirty". This was useful because it suggested that there might be a point or threshold at which the perceived tone became unacceptable, because such a high proportion of people would find the building dirty. A range of ways are available to estimate at what point such thresholds occur (Brimblecombe and Grossi, 2005).With these established it is possible to link perceived lightness to measurable properties of the atmosphere such as the concentration of elemental carbon (EC). Perceived lightness of building facades can be related to EC concentration and thus it becomes possible to establish a kind of aesthetically acceptable concentration of elemental carbon in the atmosphere. In the experiments of Brimblecombe and Grossi (2005) concentrations of EC above 3 $\mu g\ m^{-3}$ tended to lead to light coloured stone buildings with an unacceptable level of blackening. This might suggest that it would be best for the appearance of buildings that EC concentrations were less than 3 $\mu g\ m^{-3}$.

It is also possible to do these kind of estimates indoors. One example where this was done was for a library in a historic house. The library shelves were deliberately left un-cleaned for three years and the house-keeping staff then asked to describe them as clean, a bit dusty, dusty and very dusty. There were also measurements of dust loading for some of the shelves. Fig. 2 compares the ranking of the dustiness of the shelves by housekeeping staff, with the measured surface coverage by dust. The figure also shows the words chosen to describe the shelves. Here we can see that only the shelf with less than 6-7% coverage was described as a "bit dusty". Other shelves with higher dust overage drew undue attention and seemed to demand cleaning by the staff. This set a kind of threshold for dust coverage on historic library shelves. Nonetheless, shelves are not especially visible, so it is likely that more visible and shiny surfaces would demand cleaning at much lower levels of dust coverage.

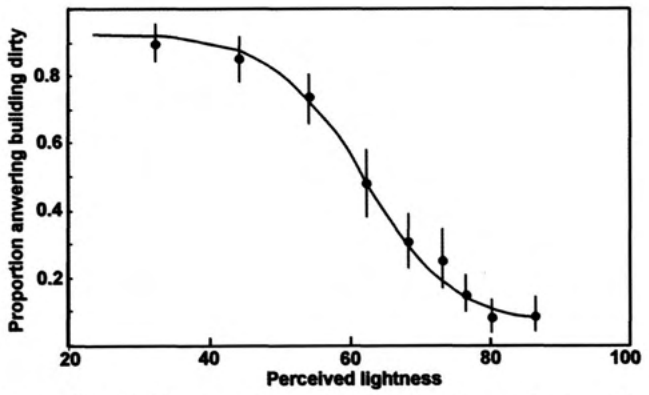


Fig. 1 - The probability of a visitor claiming a facade is dirty as a function of the lightness they perceive by comparison with a greyscale.

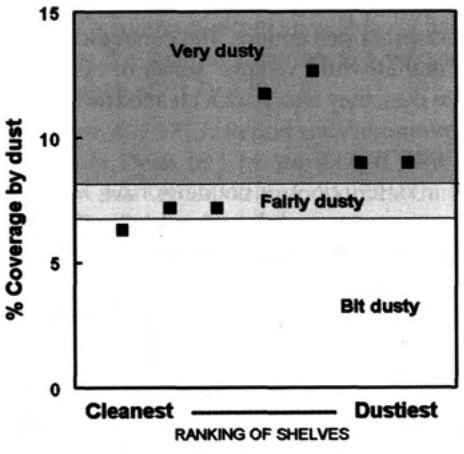


Fig. 2 - The relationship between the percentage coverage by dust on bookshelves and the ranks given to the dustiness of shelves by a booking cleaning team.

9. Visitor and staff perceptions

As we have seen above although measurements of discolouration and dust loading on surfaces are possible, perceptions are an important element of any attempt to manage changes in the appearance of historic surfaces. We have to realise that buildings where they are cleaned do not always evoke a positive reaction. The historic patina can too easily be removed as one respondent said: the building was "not dirty, it merely showed the *patina of time*". The problem for managers is to allow buildings to have an appearance that is a balance between having a patina, yet not appearing neglected.

Indoors a very similar issue arises. There was a sense that dustiness can give a sense of historicity as shown in Fig. 3 where responses regarding the appearance of a room as historic are compared with the responses regarding it as historic. The UK National Trust's Chastleton House in Oxfordshire is deliberately presented in its rather "as found form" and so it is hardly surprising that it is seen as the dustiest of the houses. However, the presentation is also successful as it is regarded as the most historic. Despite this success it was not without problems, because even though visitors recognised its historic presentation they would still ask for more cleaning (Lithgow et al., 2005). Thus there is still a management battle to be won.

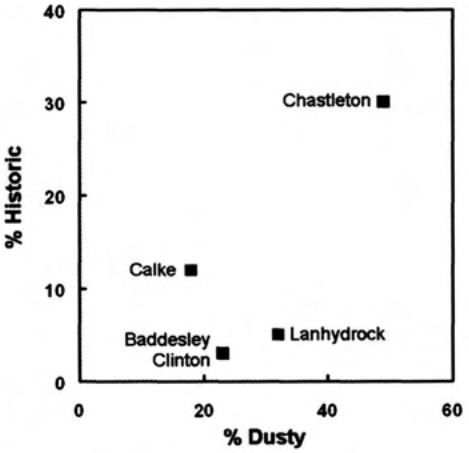


Fig. 3 - The relationship between the percentage of visitors claiming rooms appeared historic and those believing they appeared dusty.

The perceptions of managers and conservation staff of historic properties are also relevant to the way in which cleaning and presentation is approached. When they were questioned about dust the said it suggested ideas such as never ending work and a sense of neglect, but on the other hand could lend a sense of patina and historicity (Lloyd and Brimblecombe, 2003). This was confirmed by visitors who felt oddly enough that "historic houses are nicer when they're dusty" (Lithgow and Brimblecombe, 2003). Again this becomes a problem for the management of historic interiors: - it is clear that dust and cleaning levels affect visitor perceptions. The contradiction for the property staff is that while visitors' sense of history is enhanced with more dust, they also want it cleaned away!

10. Verbal descriptions

The words used in descriptions of buildings have much to tell us of the way monuments and their degradation features are perceived. Approaching a monument even its name can influence perceptions - take for example the *Tower of London*. At its centre we find the *White Tower*, where use of the word "white" raises public expectations and management concerns for those who have to maintain the façade (Grossi and Brimblecombe, 2005).

The Venetian architect Giacomo Boni (1859-1925) and John Ruskin (1819-1900) were against the *scorticamento* (extreme cleaning) of facades. Although promoting restoration Boni said that the palaces were not to be *statue di sale* (i.e. made as white as salt). This led Boni to advocate the use of pigments to imitate the earlier appearance (Sgobbi et al., 2010): "*da poter mettersi cogli anni in armonia di colore colle parti vecchie*" (i.e. to achieve, with passing of time, harmony in colour with old parts). The notion that facades should not appear too dirty or too clean, is also found in modern visitors, when recently restored facades were argued to be too take on too light a tone (Brimblecombe and Grossi, 2005).

Visitors to the Tower of London frequently describe the building by choosing words such as: magnificent, beautiful, old, ancient or historic. Indoors, visitors to National Trust historic properties have somewhat different impressions as reflected in their use of words. They chose not to adopt words that describe a sense of history, but tended to focus words that conveyed ideas such as: comfort, a sense of occupancy, dark-coloured etc (Lithgow et al., 2005).

11. Management issues and conclusion

Maintaining and presenting cultural heritage is expensive. In historic properties cleaning is the most important drain on housekeeping budgets (Lloyd et al., 2007). It remains important to maintain high standards of appearance or complaints arise from visitors concerning the level of care. Conversely there are risks from visitors complaining that the patina has been destroyed scraping away the historic context. Presentation thus remains a delicate balance. One approach is to attempt to minimise the amount of cleaning which is expensive and potentially destructive both physically and aesthetically. This is easiest for historic interiors where a range of relatively simple management tools are available (Lloyd et al., 2002). Outdoors a reduction in air pollution, most relevantly elemental carbon, is important. This is beyond the control of individual building managers, but fortunately a range of legislation related to health impacts of air pollutants means that blackening is likely to decrease in the future. In London there is reason to believe that this is already underway (Brimblecombe and Grossi, 2009).

The potential for dramatic changes in climate and air pollution over the nest century can impose new challenges. Rain washing in less polluted urban environments may readily create new disfiguring patterns. Re-cleaning periods may have to vary, and the approaches account for more contemporary forms of deposits on the facades. Management will also see the need to confront novel perceptions as more subtle, perhaps warmer toned, colorations are revealed. Indoors new warmer and more humid conditions offer the opportunity for cementation of dust to indoor surfaces or biological activity. More than ever there is a need for a link between the aesthetic and the scientific.

References

Adams, S., Kibrya, R. and Brimblecombe, P., 2002. A particle accumulation study during the reconstruction of The Great Court, British Museum. Studies in Conservation, 3: 283-287.

Andrew, C., 1992. Towards an aesthetic theory of building soiling, Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone. Donhead, London, 63-81.

Ball, J., Laing, R. and Young, M., 2000. Stone cleaning: comparing perception with physical and financial implications. Journal of Architectural Conservation, 6: 47-62.

Bonazza, A., Brimblecombe, P., Grossi, C.M. and Sabbioni, C., 2007a. Carbon in black layers at the Tower of London. Environmental Science and Technology, 41: 4199-4204.

Bonazza, A. et al., 2007b. Did smoke from the Kuwait oil well fires affect Iranian archaeological heritage? Environmental Science and Technology, 41: 2378-2386.

Brimblecombe, P. and Grossi, C.M., 2004. The rate of darkening of material surfaces. In: C. Saiz-Jimenez (Editor), Air Pollution and Cultural Heritage. A. A. Balkema, Rotterdam., pp. 193-198.

Brimblecombe, P. and Grossi, C.M., 2005. Aesthetic thresholds and blackening of stone buildings. Science of the Total Environment, 349: 175-189.

Brimblecombe, P. and Grossi, C.M., 2009. Millennium-long damage to building materials in London. Science of the Total Environment, 407: 1354-1361.

Brimblecombe, P., Grossi, C.M. and Harris, I., 2007. Future trends in surface wetness and relative humidity and potential impact on materials. Pollution Atmospherique, Special Issue: 95-100.

Brimblecombe, P., Thickett, D. and Yoon, Y.H., 2009. The cementation of coarse dust to indoor surfaces. Journal of Cultural Heritage, 10: 2009.

Camuffo, D., 1998. Microclimate for Cultural Heritage. Elsevier, Amsterdam.

Davidson, C.I. et al., 2000. Soiling patterns on a tall limestone building: changes over 60 years. Environmental Science and Technology, 34(560-565).

Garcia-Valles, M., Vendrell-Saz, M., Molera, J. and Blazquez, F., 1998. Interaction of rock and atmosphere: Patinas on Mediterranean monuments. Environmental Geology, 36: 137-149.

Grossi, C.M. and Brimblecombe, P., 2004. Aesthetics of simulated soiling patterns on architecture. Environmental Science and Technology, 38: 3971-3976.

Grossi, C.M. and Brimblecombe, P., 2005. The White Tower and the perception of blackening. Journal of Architectural Conservation, 11(34-44).

Grossi, C.M. and Brimblecombe, P., 2008. Past and future colouring patterns of historic stone buildings. Revista Materiales de Construcción, 58: 143-160.

Grossi, C.M., Brimblecombe, P., Esbert, R.M. and Alonso, F.J., 2007. Colour changes in architectural limestones from pollution and cleaning. Color Research and Application, 32: 320-331.

Hardyment, C. (Editor), 2000. The Housekeeping Book of Susanna.

Whatman 1776-1800. National Trust Classics 2000. National Trust Enterprises Limited, London.

Haynie, F.H., 1986. Theoretical model of soiling of surfaces by airborne particles. In: T.S. S.D. Lee, L.D. Grant & P.J. Verkerk (Editor), Aerosols. Lewis Publishers, Boca Raton, pp. 951-959.

Hull, P., Shepherd, I. and Hunt, A., 2004. Applied Optics. 43(3433-3441).

Ionescu, A., Lefèvre, R.-A., Chabas, A., Lombardo, T., Ausset, P., Candau, Y., Rosseman, L., 2006. Modeling of soiling based on silica-soda-lime glass exposure at six European sites. Science of the Total Environment, 369: 246-255.

Lapuerta, M., Martos, F.J. and Herreros, J.M., 2007. Effect of engine operating conditions on the size of primary particles composing diesel soot agglomerates. Journal of Aerosol Science, 38: 455-466.

Lithgow, K. and Brimblecombe, P., 2003. Dust, the visitors' point of view. Views, National Trust, 39: 47-49.

Lithgow, K., Lloyd, H., Brimblecombe, P., T., T. and Yoon, Y.H., 2005. Managing dust in historic houses- a visitor conservator interface. ICOM-CC, 2: 662-669.

Lloyd, H. and Brimblecombe, P., 2003. Focussing on dust. Views, National Trust, 39: 49-52.

Lloyd, H., Brimblecombe, P. and Lithgow, K., 2007. Economics of dust. Studies in Conservation, 52: 135-146.

Lloyd, H. et al., 2002. The effects of visitor activity on dust in historic collections. The Conservator, 26: 72-84.

Mack, C., 1954. The expected number of clumps when convex laminae are placed at random and with random orientation on a plane area. Proceedings of the Cambridge Philosophical Society, 50: 555-558.

Searle, D.E. and Mitchell, D.J., 2006. The effect of coal and diesel particulates on the weathering loss of Portland Limestone in an urban environment. Science of the Total Environment, 370: 207-223.

Sgobbi, M., Brimblecombe, P., Grossi, C.M., Biscontina, G. and Zendri, E., 2010. Surface stratigraphy on limestone of Venetian palaces. International Journal of Heritage Studies.

Thornbush, M. and Viles, H., 2004. Integrated digital photography and image processing for the quantification of colouration on soiled limestone surfaces in Oxford, England. Journal of Cultural Heritage, 5: 285-290.

Valls Del Barrio, S., Garcia-Valles, M., Pradell, T. and Vendrell-Saz, M., 2002. The red-orange patina developed on a monumental dolostone. Engineering Geology, 63: 31-38.

Vázquez-Calvo, C., Álvarez de Buergo, M. and Fort, R., 2007. Overview of recent knowledge of patinas on stone monuments: the Spanish experience. Geological Society Special Publication, 271: 295-307.

Wren, C., 1713. Report on Westminster Abbey to Francis Atterburg, Dean. In: L.M. Soo (Editor), Wren's "tracts" on Architecture and Other Writings (1998). Cambridge University Press, Cambridge, 79-92.

Yoon, Y.H. and Brimblecombe, P., 2001. Clothing as a source of fibres within museums. Journal of Cultural Heritage, 1: 445-454.

Zhao, Y. and Ma, L., 2009. Applicable range of the Rayleigh-Debye-Gans theory for calculating the scattering matrix of soot aggregates. Applied Optics, 48: 591-597.

Chapter 11

Paper deterioration and the role of air pollutants

John Havermans

Introduction

Paper?

Paper is a network of natural fibres, usually forming a web based flexible sheet. Paper had its origin in China. The first sheets of paper found were dated 105 A.D. and dedicated to Tsái Lun. Papermaking was only introduced in Europe at about 1100 A.D. Around the 19th century, at the time of the industrial revolution, the papermaking process became an industrial process. Initially paper was made of cotton or rags. Due to the increasing demand of paper products plant materials were applied resulting finally in the application of wood (Lanting, Logtenberg et al. 1985; Fellers, Iversen et al. 1989).

Paper composition

The main component from paper substrates is cellulose. On the application of unbleached wood pulp, often referred as ground wood, natural polymers as lignin and hemicelluloses are present. Cellulose is a natural (bio) polymer. Chemically it is a linear homopolysaccharide composed of -D-glucopyranoside units linked by (1 4) bonds as shown in Fig. 1. On supramolecular level, the cellulose chains are held together by strong intramolecular bonds. Once this polymer is removed from e.g. wood, it will have for its origin no durability. Simply said, it would easily deteriorate by chemical and biochemical reactions.

Although the end- OH groups look similar, they differ from a chemical point. The C1-OH is an aldehyde-hydrate-group, coming from the ring formation by the intramolecular hemi acetal. This group is also referred to the reducing end-group. This in contrary to the OH-group found at the C4 position at the other end of the cellulose polymer chain, the non-reducing hydroxyl group (Fengel and Wegener 1989; Sjöström 1993).

Due to papermaking from wood pulp, two other natural polymers can be found in paper.

Hemicelluloses are hetero polysaccharides, built from miscellaneous mono saccharides, and have a significant lower degree of polymerisation compared to cellulose. In softwoods the molecular structure of hemicelluloses is based on galactoglucomannan and for hardwood it is xylan. Most hemicelluloses are thought to be unordered. Also for lignin there is a significant difference in lignin from softwoods and hardwoods. In general, lignin is composed of polymers of phenyl propane units (Adler 1977). Further additives as Calcium Carbonate in modern paper, sizing components as the well known Alum-Rosin sizing after Illig (Fellers, Iversen et al. 1989) or the more modern Alkyl Ketene Dimers (AKD) can be found. In recycled fibres deinking components can be present. And of course components from coating the paper, as China clay or starch derivates, can be present.

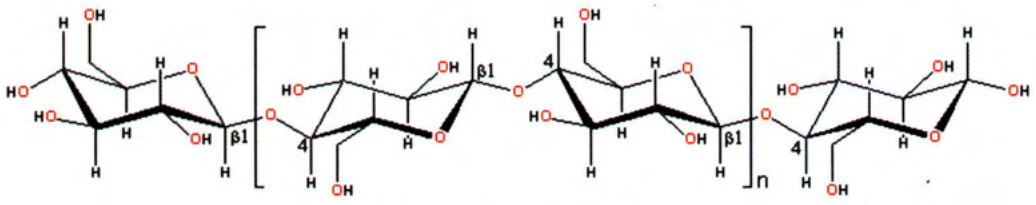


Fig. 1 - shows the structure cellulose (a), an example of lignin (b).
Fig. 1a - The molecular structure of cellulose after Fengel and Wegener (1989).

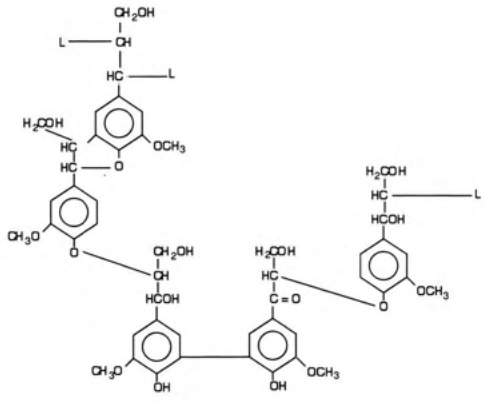


Fig. 1b - A structural segment of softwood lignin. L- means continuation of the polymer. After Adler (1977).

The chemicals used for papermaking and the subsequently following conservation actions will actually take care that the durability and thus the accessibility of objects would be increased in time. Even though, there are quite a lot of factors having a negative effect on the durability of then paper objects. Main causes are light, acid contaminants and moist, summarised as the environment. The following sections will deal mainly with the pollutants being present indoors.

The role of pollutants on paper ageing

Paper ageing, summary

Like all materials, paper is subjected to a change of its physical and chemical properties due time. However, the

ageing of paper is not only a matter of time as it can be accelerated by endogenous and exogenous factors. One of the exogenous factors influencing the permanence and durability of paper objects is air pollution. Initially, outdoor pollution entering the building. This in combination results in a deterioration of the paper as already shown (Havermans and Porck 2002). Here two identical copies of the same book were investigated: one from the New York Public Library which was severely deteriorated and one copy from the Royal Library in The Hague which was still in a reasonable condition. Based on the chemical and physical analyses of the material it was concluded that the role of SO_2 and moist played an evident role in the deterioration of the NYPL book.

Later research showed that collections emit certain gaseous pollution that can be harmful for the collection itself. The three main deterioration types for paper can be summarised as acid catalyzed hydrolyses, oxidation and cross-linking (Lanting 1989; Havermans 1995). These reactions take place naturally and can be enhanced by exogenous factors as air pollution, radiation and inks. A simplified model on paper ageing is shown in Figure 2.

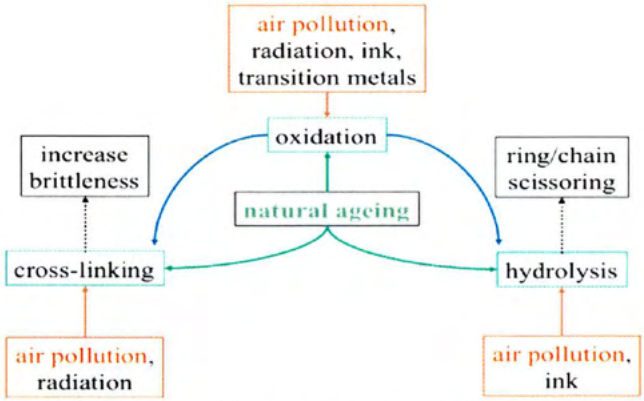


Fig. 2 - Simplified model of the deterioration of paper and the role of air pollutants (after Havermans, 1995).

Although the basics of this model was firstly presented within the Dutch ACBAM research dedicated to paper deterioration by air pollution, the role of air pollution on the accelerated ageing of paper was already announced by Wiessner in 1887 (Wiesner 1887; Lanting 1989). In his work he demonstrated the role of pollution from e.g. gas and candle lighting. These caused serious darkening of paper species, especially those species containing wood fibres. In 1898, the Society of Arts, London, set up a committee on the deterioration of paper. Within this committee it was again concluded that darkening of paper materials spreading from the inwards to the margin could be attributed to external means as air pollution.

Moist is always present

As mentioned before, the papermaking process changed drastically. From cotton/rags to bleached wood pulp. Although paper is still a web of flexible natural fibres, the composition changed not only chemically, but also physically by means of the morphological structure. The result is an important change in the paper composition expressed in crystalline and amorphous fractions. Native cellulose originally consists of both fractions. An example is presented in Figure 3, where a simplified model shows the crystalline and amorphous regions of fibres. Cotton cellulose consists of 70-80% crystalline regions, while cellulose fibres from wood pulp varies from 60-70% (Fengel and Wegener 1989).

In the presence of polyoses, the amorphous fraction in paper increases. In case lignin is present in paper, also hemicellulose is present. The ester type compounds, or lignin-polysaccharide adduct, formed by linking lignin-hemicellulose-cellulose are known to be hydrolysed rapidly. These regions do have also a high degree of amorphous fractions (Havermans 1995).

The amorphous fraction results in a higher accessibility for moisture and therefore the formation of hydrogen ions by acidic pollutants is enhanced. Subsequently, the liquid-phase and acid catalysed hydrolysis of fibres cause a significant decrease in fibre strength and a decrease in the degree of polymerisation.

When deteriorated cellulose is followed by dehydration, for example storage at low relative humidity, bonding and strength properties are generally reduced. The fibres then form larger units and become less accessible to water and the material becomes stiffer. This irreversible process is also known as *hornification* (Laivins and Scallan 1993). Due to the increase in the amorphous fraction, a glassy stage will be reached during the drying of the fibres resulting eventually also to horn-formation" (Akim 1987).

Thus, in case lignin containing paper is stored in a dry environment, the fibres are getting less accessible to moisture and thus air pollution will probably contributes to a lesser extent to the deterioration. However, at that time, the paper is already severely deteriorated.

Fig. 3 - From left to right: a cellulose fibre changing from crystalline to amorphous structure (unknown source).

Outdoor pollutants

In the 19th century many countries used coal combustion for domestic heating and steam engines. This fuel combustion drastically affected the outdoor environment with the generation of a serious industrial outdoor pollutant: sulphur dioxide (SO_2). Acidic rain can be seen as one of the results as the combination of SO_2, oxygen and moisture, generating two acidic components, i.e.: sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4). Another major effect of pollutants was found in archives, libraries and museums: heavily brittle acidic paper. In 1907 Winkler described the effects of mineral acids on the deterioration of paper. Since then, the roles of these acids have been frequently investigated because sulphuric acid is not only derived from the atmospheric pollutant SO_2. Due to the application of alum rosin sizing, acidic deterioration takes place because mineral acids are formed. Edlund described this problem in relation to the use of animal sizing and alum rosin sizing already in 1910. This is often referred to an endogenous factor of acidic paper. Both factors work in synergy causing the acidification and accelerating paper ageing.

Before the 1960s, research on the effects of air pollutants was mainly devoted to the role of SO_2 in paper deterioration. Especially by means of artificial pollution experiments SO_2 was recognized to enhance paper deterioration. Since 1932 Kim-

berley proved the deterioration effects of SO_2 on nine printed and written papers (Kimberly 1932). As mentioned before, SO_2 reacts with moist to form e.g. H_2SO_3. In presence of oxidising agents as oxygen, O_2, ozone, O_3, and moisture, sulphuric acid can be formed. These products will enhance the acid catalyzed hydrolyses of cellulose as shown in Figure 4.

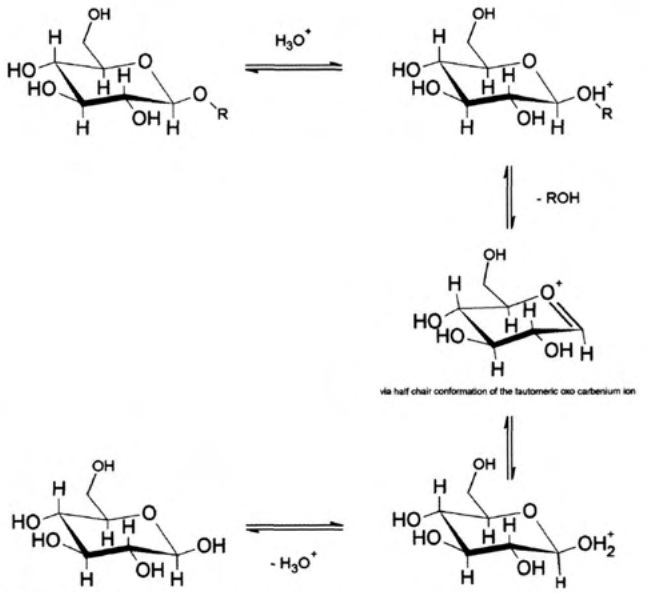


Fig. 4 - A model for the acid-catalysed hydrolysis of cellulose, shown here for a non-reducing end group of cellulose (Havermans 1995).

After 1960, due to a change in outdoor air pollution, more attention was paid to the role of nitrogen dioxide (NO_2) (Fellers, Iversen et al. 1989; Lanting 1989; Havermans 1995; Johansson 2000). NO_2 reacts as a combination of an oxidative agent and an acid hydrolysis catalyst, enhancing deterioration. According to Nevell, oxidation of cellulose by NO_2 results in the oxidation of the primary alcohol group and NO_2 is reduced to NO (Nevell 1963). Later studies included mixtures of pollutants showing for example the synergistic effects of NO_2 on the deposition of SO_2 on paper. Based on the European research in 1994 it was concluded, that the presence of both components should be avoided, especially in the case if the relative humidity is exceeding 60% and in humid environment with large fluctuations (Havermans, Deventer et al. 1994). In the framework of the Swedish R&D Project on Paper Preservation, conclusions were drawn on mechanical and optical properties (Iversen and Kolar 1991). Neutral-sized papers were not affected by NO_2 while for the acid-sized papers a slight fibre modification was observed (relaxation effect). Thus for acid papers, indoor NO_2 will cause poor ageing stability. The mechanical properties of the lignin-containing papers were not affected, but a significant discolouration was observed. One of the latest long term studies, a10 year study on the effect of indoor environment on the changes of paper stored in an archive, arrived to similar conclusions (Havermans and Steemers 2005). At ambient pollution levels of NO_2 (up to 24 ppb on yearly average) and SO_2 (up to 3 ppm on yearly average) severe discoloration was found for lignin containing papers including a fall in pH (measured as the cold water extract).

An example of the oxidation of cellulose is presented in Figure 5, using D-glucose. Oxidation of the primary alcohol group reacts to an aldehyde and subsequently to a carboxylic acid on the C6 site may occur relatively rapidly. Oxidation of secondary alcohol groups at the C2 and C3 sites may also occur, initially leading to the formation of ketones. Further oxidation leads to ring splitting and the formation of carboxylic acids (Sjöström 1993).

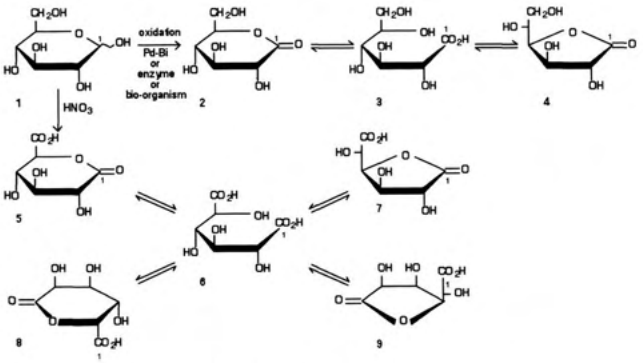


Fig. 5 - Oxidation of D-glucose according to Sjöström (1993)

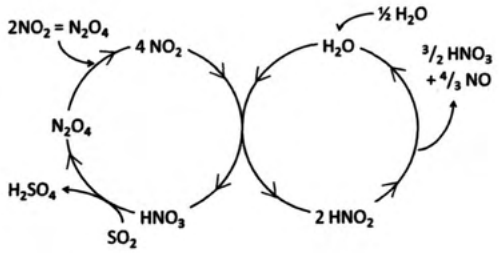


Fig. 6 - The synergism between two specific air pollutants: SO_2 and NO_x.

A scheme showing the synergism of the two above pollutants and the formation of the acidic components is presented in Figure 6 (Havermans 1996). Here it is demonstrated that the presence of both pollutants indeed will result in the formation of sulphuric acid and nitrous and nitric acid. All of these acidic species will negatively influence the natural ageing of paper.

Finally, as papers do have different composition, they may have different reactions in the presence of air pollutants. For example Johansson showed that alkaline papers have a higher uptake of acidic pollutants, but they deteriorate less fast than acidic papers. In this case the alkaline particles in the paper attract the acidic pollutants, they react to form neutral products and the paper fibres are not deteriorated (Johansson 2000).

Indoor Pollutants

The mix of gaseous air pollutants is significantly different for outdoor and indoor environments: previous studies have shown, that in most cases NO_x and SO_2 levels are higher outdoors, whereas organic acids and carbonyl concentrations can be equal or higher indoors (Gustafsson 1992).

The indoor concentration of outdoor pollutants mainly depends on the ventilation rate (the number of air exchanges in a certain room expressed in changes per hour). The higher the ventilation rate, the higher the number of gaseous molecules that will transported from the outdoor to the indoor environment, and the indoor level of external pollutants can rise until it reaches the outdoor level, as a maximum. The fact that the indoor concentration does not reach the external level means that the pollutants will start to react with indoor materials including the ventilation tubes when entering a building. Based on studies of deposition of gaseous pollutants onto indoor material surfaces a new model for the transport of outdoor pollutants was

developed within the European project IMPACT in 2002 (Grøntoft 2004; Anonymous 2008).

The concentration of indoor pollutants is mainly a result of emission of organic volatiles from building materials. Uhde and Salthammer (2007) presented a model on the interactions of outdoor and indoor pollutants. The emission of volatiles present in the materials with direct emission is called "primary emission". In case a reaction takes place followed by emission of volatiles (e.g. curing of lacquers), this is called "secondary emission". The emitted compounds can directly react in a gas-phase reaction with the outdoor pollutants entered indoors.

Recent studies showed that collections too may produce indoor pollutants, known as volatile organic compounds (VOC). An extension of the model of Uhde and Salthammer was proposed at the 9th Indoor Air Quality in Museums and Archives meeting (Havermans 2010). This model is shown in Figure 7. The indoor air can react in our case with paper materials stored e.g. in repositories. This process, often referred as natural ageing, results in the formation of paper deterioration products, i.e. VOC. Most of these products remain in the paper matrix. However, the most volatile and diffusive VOC species will enter the indoor environment (Strlič , Thomas et al. 2010). Thus the archival, library and museum paper collection becomes a new source of indoor pollutants (Fenech, Strlič et al. 2010). For example, studies by Penders on deterioration of paper affected by iron gall ink corrosion showed that paper emits organic acids as e.g. acetic acid (Penders, Havermans et al. 2000). Within a project on mass deacidification with DEZ, over 100 VOC deterioration products were found, and there was a significant difference in the emission before and after treatment (Havermans, Genuit et al. 2001). In 1995 Buchbauer published a work on the identification of the odour of books showing over 70 products as acetaldehyde, toluene and cyclo hexanol derivates (Buchbauer, Jirovesz et al. 1995). Accelerated ageing studies of paper by Soares and Rodrigues showed that 2-furfuraldehyde, 5-hydroxy methyl furaldehyde, 2-furfurol, 5 methyl- 2- furfural and 2- acetyl furan were released (Soares and Rodrigues 1998). Some of these VOC are similar to those that are released for the use of iron gall inks as shown by Penders at the first Iron gall ink meeting.

Based on the different works and theories of ageing of paper, the emission of VOC is obvious and main volatiles that paper may emit due to ageing are formaldehyde, formic acid, acetic acid and furfural. These components can be absorbed again by the collection. Once absorbed these components may cause the acidic catalysed hydrolysis of the cellulose and hemicelluloses as presented above (Ramalho, Dupont et al. 2010). However, following the latest discussion based on results presented at the IAQ2010 conference in Chalon-sur-Saone followed by the discussion at the COST D42 workgroup meeting, it was concluded that only formic acid will rapidly react with cellulose resulting in severe deterioration. The effect of acetic acid and other components mentioned above is smaller (Tetreault, Begin et al. 2010). More research on VOC role in paper deterioration is therefore needed.

In case lignin is present in the material, many other reactions can take place generating the specific odour of old paper. For example, by means of some oxidation in presence of NO_2 or in presence of transition metals, vanilla can be formed (Fengel and Wegener 1989). In case formaldehyde is present, a condensation reaction with lignin components and formaldehyde can take place, enhancing the brittleness of the paper matrix.

Based on recent work by Strlič et al. it was also concluded that VOC are generated in the presence of lignin and alum-rosin sizing volatiles. Especially the presence of rosin is responsible for paper deterioration. Components as hexanal, furfural, acetic acid and butanol were identified. Also the ageing of paper without lignin generates formic acid, acetic acid and glycoic acid. These compounds might react with the indoor environment in the gas phase, but also they may be adsorbed inside the paper causing ageing and others degradation products (Fenech, Strlič et al. 2010; Strlič, Thomas et al. 2010).

Finally, it is not only the absolute concentration of a certain pollutant which is decisive for the damage potential: the interaction between pollutants and their synergetic effect as well as the damage function related to temperature and especially humidity should be taken into account and are quite complex indeed. Here we should not disregard the role of water, present in the paper matrix as well in the indoor environment.

Acknowledgements

This work was made possible thanks to the support of the European Science Foundation and especially the COST action D42: *EnviArt*.

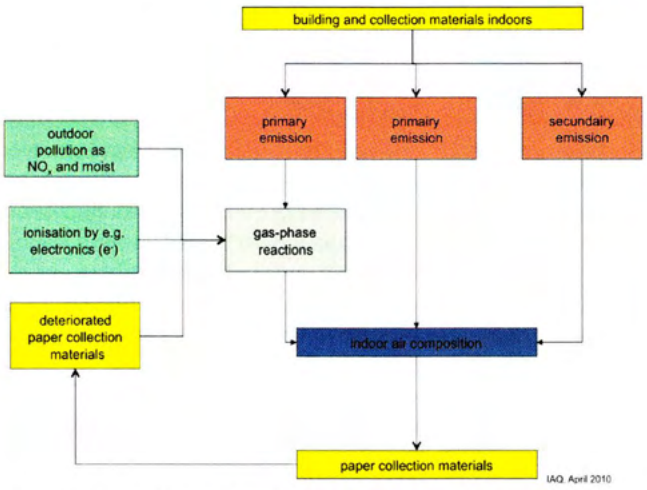


Fig. 7 - Proposed scheme of the role of the indoor air quality on paper ageing, based on Uhde and Salthammer (2007). Here the paper collection emits volatiles and form a 'new' part of the collection. The deteriorated collection will be a part not only of the new collection, but also it will involve directly the gas-phase reactions in case other pollutants are present.

References

Adler, E., 1977. "Lignin chemistry. Past, present and future." Wood Science & Technology 11: 169-218.

Akim, E. L., 1978. Changes in Cellulose Structure during Manufacture and Converting of Paper. Cellulose Chemistry and Technology, ASC.

Anonymous, 2008. "IMPACT." Retrieved April 28, 2010, from http://www.ucl.ac.uk/sustainableheritage/impact/index.htm.

Buchbauer, G., L. Jirovesz, et al., 1995. "On the Odour of Old Books." Journal of Pulp and Paper Science 21(11): J398-J400.

Fellers, C., T. Iversen, et al., 1989. Ageing/Degradation of Paper, A literature Survey, FoU-projectet for Papperkonservering Report 1E.

Fenech, A., M. Strlič , et al., 2010. Volatile aldehydes in libraries and archives. 9th Indoor Air Quality meeting. Chalon-sur-Saone, France, IAQ.

Fengel, D. and G. Wegener, 1989. WOOD, Chemistry, Ultrastructure and Reactions. Berlin, Walter de Gruyter.

Grøntoft, T., 2004. Deposition of gaseous pollutants to indoor surfaces. Time, humidity and temperature dependent deposition of O_3, NO_2 and SO_2. Measurements and modelling. Faculty of Mathematics and Natural Sciences. Oslo, University of Oslo. Ph.D.

Gustafsson, H., 1992. Building materials identified as major sources for indoor air pollutants. Stockholm, Swedish Council for Building research: 72.

Havermans, J., 2010. The Dutch Archival Act and Harmonisation. 9th Indoor Air Quality meeting. Chalon-sur-Saone, France, IAQ.

Havermans, J. B. G. A., 1995. Environmental influences on the deterioration of paper. Delft, Rotterdam, Barjesteh, Meeuwes & Co.

Havermans, J. B. G. A., 1996. Effects of air pollutants on the accelerated ageing of cellulose based materials. International Congress on Environment / Climate, Rome, Italy.

Havermans, J. B. G. A., Deventer, J. P. V., et al., 1994. The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper. EC/DGXII/STEP Project CT 90-0100, TNO, Delft, The Netherlands.

Havermans, J. B. G. A., W. L. Genuit, et al., 2001. Emission of Volatile Organic Compounds From Deacidified Paper. EAS 2001 Conservation Science Annual, Atlantic City, EAS.

Havermans, J. B. G. A. and H. Porck, 2002. Natural ageing of paper: Characterisation of differences between identical copies of books stored in the New York Public Library and the National Library of The Netherlands. ARSAG2002, Paris, France, ARSAG.

Havermans, J. B. G. A. and T. A. G. Steemers, 2005. Air pollution and its prevention. Ageing and stabilisation of paper. M. Strlič and J. Kolar. Ljubljana, National and University Library: 165-179.

Iversen, T. and J. Kolar, 1991. Effects of nitrogen dioxide on paper, FoU-projektet för Papperskonservering, Report No. 5. National Archives.

Johansson, A., 2000. Air pollution and Paper Deterioration. Department of Chemistry, Inorganic Chemistry. Goteborg, Goteborg University: 80.

Kimberly, A. E., 1932. "Deteriorative effect of sulfur dioxide upon paper in an atmosphere of constant humidity and temperature." U.S. Bureau of Standards Journal of Research 8 (February): 159-171.

Laivins, G. and A. Scallan, 1993. "Mechanism of Hornification of Wood Pulps" (Baker, C. F., ed): Products of Papermaking 2, 1235-1260.

Lanting, R. W., 1989. Preventive conservation of archives and books: air pollution, TNO, Delft, The Netherlands.

Lanting, R. W., E. H. P. Logtenberg, et al., 1985. Ageing and deterioration of cellulose containing materials by air pollutants. A literature review, TNO, Delft, The Netherlands.

Nevell, T. P., 1963. Oxidation. Methods in Carbohydrate Chemistry. R. L. Whistler, J. W. Green, J. N. BeMiller and M. L. Wolfrom. New York, Academic Press. III: Cellulose: 168-169.

Penders, N. J. C. M., J. B. G. A. Havermans, et al., 2000. Emission of volatile organic compounds from objects written with and without iron gall ink and ink components. The Iron Gall Ink Meeting, Newcastle, U.K., University of Northhumbria.

Ramalho, O., A.-L. Dupont, et al., 2010. Relationship between the emission of volatile organic compounds from paper and cellulose degradation. 9th Indoor Air Quality meeting. Chalon-sur-Saone, France, IAQ.

Sjöström, E., 1993. Wood Chemistry. Fundamentals and Applications. Boston, Academic Press, INC.

Soares, S. and E. Rodrigues, 1998. Monitoring cellulose paper insulation by accelerated aging experiments. Proc. Int. Symp. Nat. Polym. Compos., 2nd, Embrapa Agricultural Instrumentation, Sao Carlos, Brazil.

Strlič , M., J. Thomas, et al., 2010. The scent of degradation: VOCs as a source of information. 9th Indoor Air Quality meeting. Chalon-sur-Saone, France, IAQ.

Tetreault, J., P. Begin, et al., 2010. Carbonyl vapours and their impact on paper degradation. 9th Indoor Air Quality meeting. Chalon-sur-Saone, France, IAQ.

Uhde, E. and T. Salthammer, 2007. "Impact of reaction products from building materials and furnishings on indoor air quality - A review of recent advances in indoor chemistry." Atmospheric Environment 41: 3111-3128.

Wiesner, J., 1887. "The influence of gas lightning on the rapid discoloration of wood-made papers." Dingler's Polyt. J. 266: 181-184.

Chapter 12
Surface protection of porous inorganic materials

Vasco Fassina

1. Short historic overview of stone protection in buildings and outdoor sculptures

Archival documents and ancient treatises can provide information on the knowledge about the decay and durability of stones, on the measures adopted to prevent stone from weathering and on the surface finishes that could have had protective or aesthetic functions.

Vitruvius[1]and Pliny[2] are the best sources of information on Greek and Roman antiquity. The protective aim for the finish layers to be applied to brick or stone buildings is clearly stated in Vitruvius's De Architectura. The extensive remains of the surface finishes on many Roman buildings as well as on columns, cornices, capitals stone-made show that this use was widespread mainly for aesthetic reasons e.g. to imitate marble. According to Pliny's text marble did not have any finish treatment, but particular attention was dedicated to its polishing to obtain a shining surface. According to Pliny and Vitruvius the polished marble received a final wax treatment with the aim to increase the brilliancy of the marble rather than for protection. The resistance of wax to the action of those considered as the main cause of stone decay was well known, in fact the encaustic painting of ships was said not to be spoilt by the action of the sun, nor by salt water or winds. Nevertheless, it is not specifically said what the purpose of the wax treatment of marble was.

In Vitruvius and Pliny time the relatively new Roman buildings did not show the symptoms of deterioration and for this reason alteration of marble was never considered and the necessity for protection and maintenance is never specifically stated. On the contrary these authors considered marble the most resistant material to be frequently mentioned as a hard material, not easily deteriorated like soft limestone. Only starting from XIX century the best scientists of that time acquired the knowledge that marble is subject to decay processes.

The chemical analyses of paint residues on many monumental Medieval sculptures all over Europe show that most of them were originally completely painted. In ancient treatises by Eraclius[3], Cennini[4] and the Livres de Métieres[5] there are clear instructions for painting stone sculptures and above all clear statements that stone sculptures must always be polychromed.

According to Rossi Manaresi 1993) the taste for complete polychromy was probably common in Northern Europe as well as in the North of Italy. On the contrary in the centre of Italy, especially in Tuscany, the reopening of the ancient Carrara marble quarries (closed in V century) and the re-use of antique marble imported from Rome assumes an emblematic importance as a link to antique Rome and as a symbol of power. As a matter of fact, the better preserved sculptures bear witness that, in Tuscany, gold and colour were used for ornamentation, while most of the surface of the marble sculptures were left unpainted, just as occurred in ancient Rome. From the above considerations it can be established that the practice of painting stone sculptures was mainly for aesthetic reason other than for stone protection, nevertheless it also had protective effect.

During Renaissance period we have evidence that some architects like Leon Battista Alberti[6] recognized that ancient marble monuments were affected by deterioration processes mainly on the areas exposed to rainwater. The extensive use of plaster and stucco to coat walls and architectural elements built in brick or soft stones (tuff, limestone, sandstone ect.) was primarily aesthetic, to imitate marble or other shining stone or to make coloured finishes. According to Rossi Manaresi 1993) the protective effect of these surface coats is never specifically stated, but it was certainly obtained.

In the archival documents the citations about the use of organic materials such as oil, egg white and wax, added in the mixture of plaster and stucco, or applied on the finished surface was a frequent practice, but no explanations about the purpose of these additives was mentioned, perhaps their use could be that of increasing durability.

As regards the statue polychromy its use declined and only gilded decorations were still applied, mainly on marble sculptures, at least during the XV and XVI centuries. The polishing of marble and final shining with wax was mentioned in a contract drawn up for work in a Baroque church in Rome. In Marciana manuscript[7] of XVI century more detailed information on varnishes containing colophony, honey, sandarac, nut oil, incense and other organic materials were reported. The examination of samples taken from the Portal of San Petronio in Bologna showed the presence of a film containing wax, oil and resin confirming the citations quoted in ancient documents. However we cannot say if this treatment was for protective or aesthetic purposes. According to Rossi Manaresi 1993) the first explicit mention of stone treatment with the declared purpose of protection is dated 1567 for the Public Palace of Louvain, which being built in porous stone very sensitive to frost, in order to prevent any damage "the habit of painting with oil was adopted"[8].

At the beginning of XIX century mention of the use of oil or wax as water repellent treatment for preservation purposes were found in archival documents:

-Ferrara's Cathedral was oiled according to a well known traditional procedure of stone conservation,

-Venice manuscript in 1816 mentioned plastering statues with melted wax,

-Venetian custom of protecting marble by rubbing its sur-

face with pigskin,

-Bolognese custom of preserving sandstone by application of egg white or tar oil.

In the second part of XIX century many different methods for preserving stone were proposed and they consisted mainly in the application of complex mixtures including the most fanciful ingredients forming a thick opaque coat as shown by the results of analytical researches carried out on Roman marble monuments in Rome, on the Portal of San Petronio in Bologna or on the sculptures of Wiligelmo in the Ferrara Cathedral (Rossi Manaresi, 1993).

Since 1840 there has been a long succession of proposed stone preservatives. Some of them have been followed sooner or later, by scaling of the treated surfaces and have done more harm than good. According to many authors 1963) the main reason for failing was the difficulty for protective substance to penetrate far enough to give the protection looked for.

It is generally accepted that water, salts, air pollutants, microorganisms are agents of deterioration for stone and related building materials and that it is desirable to keep materials, as much as possible, free from their presence (Lewin, 1966).

A complete overview of the numerous proposals for stone preservation presented in a century of experimentation, investigation and field testing needed an appropriate discussion which cannot be included in this paper due to lack of space.

2. The present state of art for the preservation of stone materials

The increasing pollution of urban atmosphere has strongly reduced the effectiveness of traditional organic products (oils, waxes and others) as well as inorganic ones (lime, silicates and fluosilicates). Inorganic consolidation materials, e.g. fluosilicates were at first introduced by Kessler in 1883 and after alternate events were re-introduced by Sanpaolesi in the period from 1940 to 1970 (Sanpaolesi, 1966).

In the early 1960's, synthesised polymers were enthusiastically accepted as soon as they appeared on the market, both for laboratory testing and for direct application on monuments. These new materials seemed promising for the conservation of architectural surfaces (Van Hess, 1996).

The products used were essentially acrylic resins, polysiloxanes, oligomeric alkyl-alkoxy-silanes, mixtures of acrylic resins and alkoxy-silanes (Alessandrini & Tabasso, 1993; Butlin et al., 1995)).

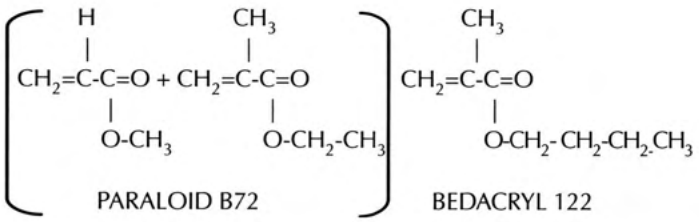
The difference between consolidation and chemical protection become clearer starting from 1970's. Consolidation is a deep impregnation of the product to improve the cohesion of decayed material and adhesion between it and the substratum. The aim will be an improvement in resistance to deterioration processes.

Protection is defined as an operation whose purpose is to slow down the decay processes. As previously said since the beginning of XIX century many scientists had the consciousness that the principal causes of the deterioration of stone materials were related to the presence of water. Specifically the associated effects of water, like transport and crystallization of water soluble salts that come from the components of the stone materials themselves, or from air pollution and the freezing and thawing cycles are responsible for stone decay. Thus, the primary function of a protective is to prevent the access of water (rain, condensation, etc.) to the internal structure of stone materials. As previously mentioned throughout history, a range of protective materials has been applied to exposed surfaces to prevent the ingress of water including oils, waxes, sacrificial layers and renders (Charola, 2003). At present, mostly synthetic products are used. Modern methods of organic synthesis guarantee the constant composition and reproducibile properties of protective compounds. Moreover, synthetic products are free of all the impurities that hinder the use of natural substances and are more versatile, because they can be appropriately modified and adapted to specific purposes.

Before to consider the most recent water repellent products used for stone protection let us make a review of the types of synthetic organic compounds introduced on the market.

Acrylic resins were well known as industrial adhesives and for this reason they were among the first compounds tested for restoration purposes when consolidation of building materials was necessary.

The most important and widespread acrylic resin was polymethyl methacrylate (PMMA) which is transparent and resistant to UV light, but having a high glass transition temperature (Tg) could not be used in solution as a consolidant. To decrease the Tg a mixture of monomers can be used, such as copolymers of ethyl methacrylate and methyl acrylate, commercially available as Paraloid B72 (in Europe) or Acryloid B72 (in USA), or poly butyl methacrylate (Bedacryl 122).



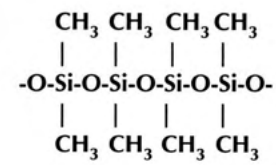
Methyl acrylate + ethyl methacrylate buthyl methacrylate

As no chemical reaction occurs among stone materials and such acrylic polymers, the latter remain soluble and may be extracted from the stone substrate and therefore the consolidation can be considered reversible. As regards protective action against water there are two reasons to dishearten its use for outdoor applications: the mild hydrophobic character of acrylic resins and their swelling properties when they remain in contact for a long time with water (Charola et al., 1985).

The second type of protectives is based on microcrystalline waxes: i) linear paraffins with low melting temperatures, ii) microcrystalline waxes based on cycloparaffins and isoparaffins that have a higher melting temperatures (70-90°C) than natural waxes. Sometimes, polyethylene waxes synthesized for this purpose are used. Their water repellence is comparable with that of polyethylene and as they do not react with the substrate they do not lose their solubility and they are regarded as reversible (Penati, 1993).

The third type of protectives is formed by silicon resins which act not only as consolidants, but also as protectives due to their marked hydrophobic character.

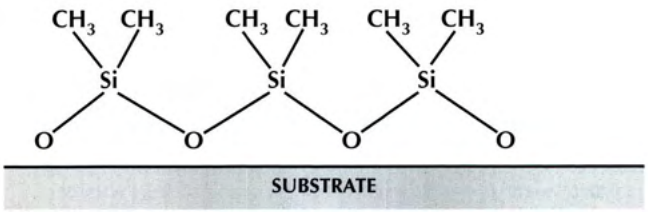
The most frequently used compounds are poly (methylsiloxanes):



whose molar masses are between 2000 and 3000, dissolved in

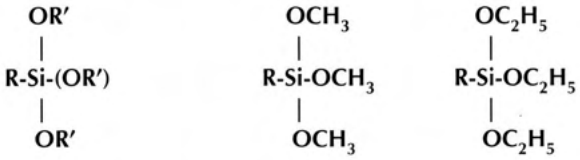
organic solvents. Substituting methyl groups with aliphatic groups, poly (alkyl siloxanes) were prepared that are more stable under alkaline conditions.

As the bonds of a silicone atom assume a tetrahedral configuration the polymer chains adhere to the substrate with electronegative oxygen atoms leaving the non-polar methyl group on the external side thus forming a hydrophobic barrier against the water:



In order to increase the molar masses of the products and their adhesion to the substrate alkoxyl groups can be introduced into polysiloxane chains, preferable at the ends of the chains. Hydrolysis of alkoxyl group produces Si-OH silanol groups that can either react with one another (thus increasing the molar mass of the protective) or with the siliceous substances in the substrate, thus increasing the interfacial adhesion.

Alkylalkoxysilanes having a lower molar masses with respect to the polysiloxane before mentioned can penetrate more into the stone structure (Lewin & Wheeler, 1985):



The alkoxy group –OR' can be either $-O-CH_3$ (Alkyl trimethoxy silane) or $-O-C_2H_5$ (alkyl triethoxy silane). Methyl is almost always used as the group –R. Due to their low molar masses, the alkyl alkoxysilanes have low viscosities, can be diluted with alcohols, can easily penetrate into the stone structure, and may be used on humid walls. The alkoxy group hydrolyzes in the presence of moisture, forming silanol Si-OH groups that either can produce more or less crosslinked polysiloxane chains, or can create bonds with the substrate (Fig. 1).

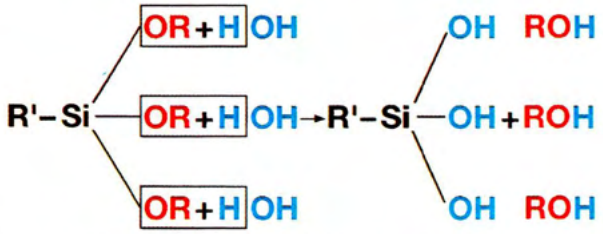
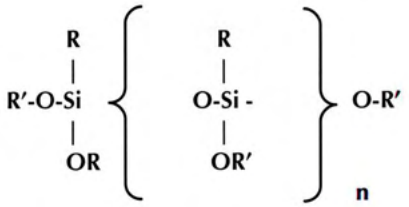


Fig. 1 - The alkoxy groups are easily hydrolyzed by moisture forming silanol groups.

The applications of alkyl alkoxy silanes are limited by two factors: i) their evaporation prior to hydrolysis and condensation may amount to 20-40%; ii) they can be washed down with rain water.

To mitigate these problems, products with higher molar mass can be prepared, preferably by means of partial polymerization. If a known amount of water is added to alkyl alkoxy silanes, a certain percentage of alkoxy groups is hydrolyzed, and Si-O-Si siloxane groups are introduced. In this way alkyl alkoxy silanes are prepared:



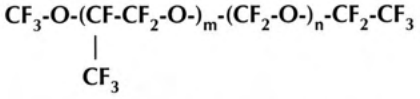
n<4 siloxane oligomers

n>4 siloxane polymers

The oligomers offer the advantages and characteristics of silanes, but their losses due to evaporation remain very low. The polymers do not differ too much from silicone resins, but they can bond to substrates and/or enhance their molar masses.

Among silicone compounds only the silicone resins maintain their solubility and reversibility, while all the other products are bound by chemical bonds to the stone substrates, and constitute a three- dimensional insoluble structures.

The last type of protective is related to fluorine-containing compounds that are characterized by the highest degree of water repellence. In order to use fluorine polymers as protectives, copolymers must be prepared containing ether oxygen, which give flexibility and mobility to the polymer chains.



As perfluoropolyethers do not crosslink during their application they can be repeatedly dissolved remaining reversible, but the shortcoming is that slowly they can be removed from stone materials by running water. To minimize perfluoropolyethers migration some terminal polar groups such as carboxylic or amids, which can react with the substrate, have been introduced (Piacenti at al. 1992). Recently some other researches were carried out to obtain different fluoro compounds for protection of monumental buildings (Aglietto et al., 2000; Botteghi et al, 1992; Fassina, 2004; Matteoli at el., 1995)

3. What is the meaning of protection and what are the functions of a protective?

As previously defined protection has the purpose to slow down the decay processes by applying chemical substances able to create a barrier towards atmospheric pollutants and rainwater. This operation is generally carried out after consolidation to extend its effectiveness and can sometimes substitute the consolidation process when the stone is sound and it is only superficially decayed.

The key function of a water repellent is to prevent penetration of liquid water through capillary action into porous materials by changing the surface properties of the material to which it is applied (Figs. 2, 3,4).

Although the main reason is to prevent water penetration the assessment of the performance should also include:

-the resistance against the attack of pollutants,

-the resistance against biological growth,

-damage occurring after treatment and the relation between treatment and damage

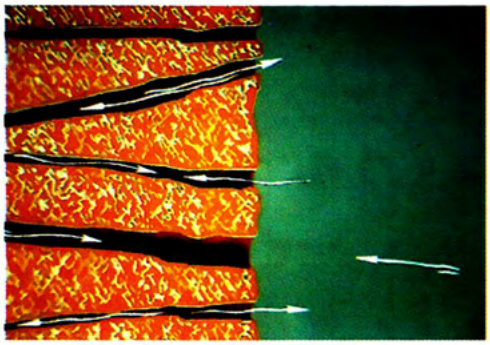


Fig. 2 - In a porous building material moisture can enter from the outside and at the same time can escape from the inside.

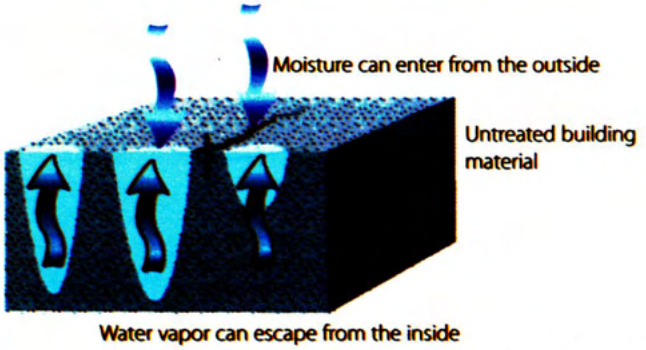


Fig. 3 - In a porous building material moisture can enter from the outside and at the same time can escape from the inside.

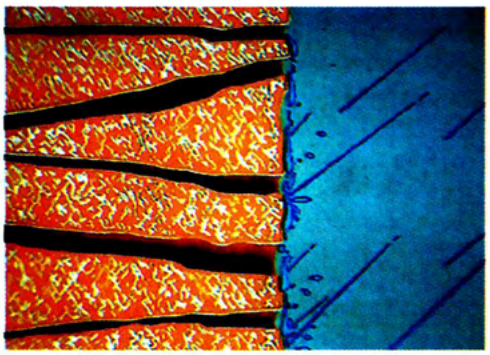


Fig. 4 - External liquid water cannot enter the pores, while water vapour generated from within the structure can still escape. The structure remains transpirant.

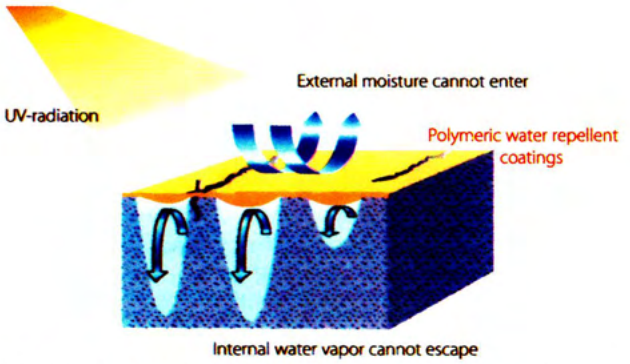


Fig. 5 - Film forming coatings are based on large size polymeric water repellent coatings able to seal the pores of the substrate. Liquid water is kept out, but water vapor generated from within remains trapped, causing more damage. In addition the surface coating is subject to degradation by UV radiation, eventually breaking down the coating and allowing water to penetrate once again.

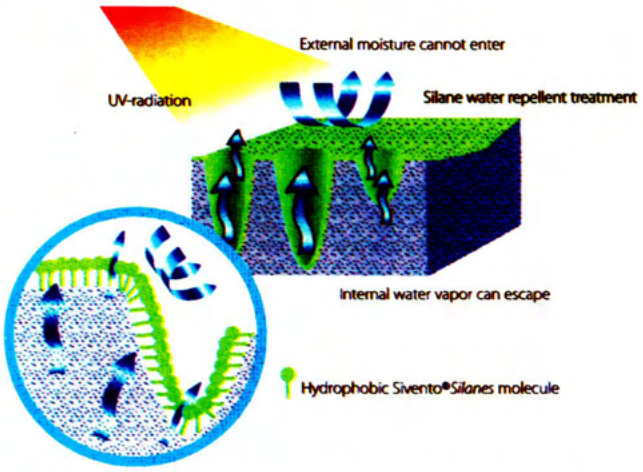


Fig. 6 - Silanes are smaller than the pores of the substrate and penetrate into the building material and bond chemically to the surface, rendering it hydrophobic. External liquid water cannot enter the pores, while water vapour generated from within the structure can still escape. The structure remains transpirant. Because they are inside the pores silanes are not affected by UV radiation.

In general a protective product should fulfill the following requirements (Many authors, 1985):

-chemical inertia towards the substrate,

-not produce harmful by-products even a long time after the application,

-good chemical stability toward atmospheric pollutants and oxygen,

-good chemical stability to ultraviolet radiation,

-low liquid water absorption,

-high water vapor permeability,

-minimum change in the chromatic properties of the substrate,

-good solubility in organic solvents even after ageing.

The water repellence of a material is related to the differences in the surface tensions of the material and water. As a consequence the critical surface tension of protective products should be considered because a liquid is wetting and diffusing into the porous material if its surface tension is lower than that of the substrate (Penati, 1993). Natural products used in the past have a practically paraffinic-like structure similar to polyethylene. From literature data polymers based on fluorine and silicone show even stronger water repellency than natural products. Protective materials forming an external impermeable film are not suitable (Fig. 5), on the contrary they should be penetrating into the porous structure and leaving water vapour transmission and at the same time preventing liquid water ingress from outside (Fig. 6). For this reason the protective polymers should be in a rubber-like state at ambient temperatures, which means that their glass transition temperature should be around room temperature. This means that during thermal expansion and contraction the protectives will not produce stresses on the capillary walls. As regards solvent no phase separations should occur with increasing concentrations of the polymer (due to evaporation of the solvent in the pores after application), but a single-phase system has to be preserved up to the complete evaporation of the solvent. When a blend of two polymers is used their solubility parameters should be similar to prevent their separation during the evaporation of the solvent (Paul & Newman, 1978).

Nowadays the most popular water repellent agents belong to the family of alkyl silicon products. i.e. alkylsiliconates, alkyl silanes, siloxanes, polysiloxanes and silicone resins. Organo-silicon products originate from ethylsilicate which was developed in the mid-nineteenth century in Europe, but commercial development started in USA in 1943 by Dow Corning Corporation and three years later by General Electric Company. In the mid-twentieth century water repellents for protection of building materials were commercialized in USA and Europe. Because of their chemical structure which is very similar to quartz, they possess properties that predestine them for this task (Hager, 1996). Silicon-based water repellent are penetrating within capillary structure where they react with water and develop a chemically bond-

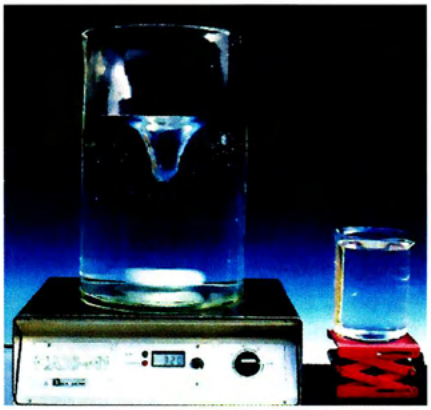


Fig. 7 - Water dispersion preparation. The big beaker contains water, while the small one contains the silane.

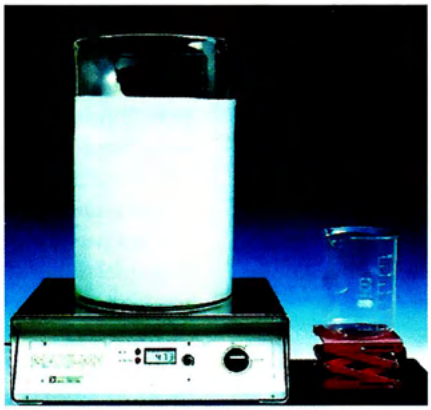


Fig. 8 - Soon after mixing of silane with water a milky solution is formed.

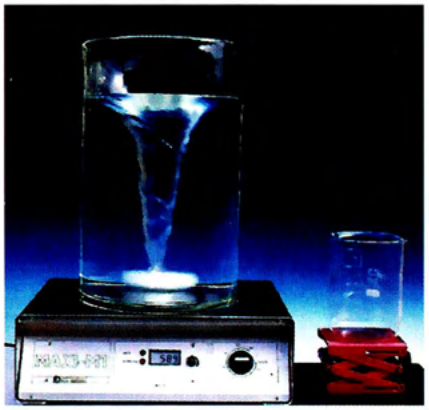


Fig. 9 - Silane water dispersion becomes transparent and remains active and stable for 24 hours.

ed silicone resin network on the walls of the pores and capillaries.

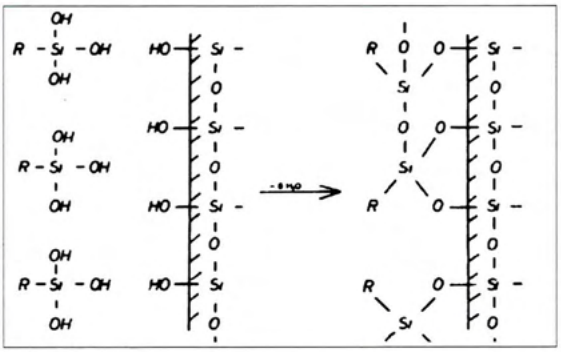
Commercially available siloxanes are designed to last also on alkaline substrates. In keeping with their hydrophobic nature, silanes and siloxanes are soluble to an almost unlimited extent in organic solvents. As a logical consequence in the 1980's the industry has started to develop methods to bring silanes and siloxanes into aqueous systems. Water dispersions of these materials made their appearance on the market around 1990's because increased environmental concerns regarding solvents used in the earlier formulations. Nowadays there are two different types available: silicon micro-emulsions and emulsions. In the case of micro-emulsion the solvent-free mixture of silanes, siloxanes and surfactants emulsify spontaneously in water to yield ready-to-use silicone micro-emulsions with particle sizes between 50 and 100 nm. A disadvantage is the instability of micro-emulsion: it has to be used within 24 hours after dilution. An alternative approach is the preparation of emulsions (Figs. 7, 8, 9).

All the products up to now mentioned are applied as liquids and for practical application two steps are required to reach the required amount of active substance inside the substrate. Generally with liquid impregnants a major concern is to know the quantity of the material which has finally been applied especially for vertical exposed surfaces. To overcome this situation a creamy impregnating system can be applied with the advantage that contrarily to the conventional low viscosity impregnants they can be applied even on vertical surfaces and ceilings without the material trickling or dripping off in an uncontrolled way. While the contact time of common liquid products is in the range of 10-20 seconds this can be extended with creams to a range of 30 minutes and more. The reaction is the same as previously seen for liquid or micro-emulsion solutions and silanoles can either polymerize and/or react on the capillaries' walls forming a water-repellent silicon-resin network there. A creamy product can be applied by brush, lambskin roller or spatula to small areas, but generally it is preferable sprayed by an airless process onto the substrate. Depending on the absorbency of the substrate, usually 200 g/m^2 are adequate, applied in a single operation with no waste. After it has penetrated the milky white cream layer disappears completely. Impregnation creams can be formulated to provide the greatest penetration depth of the active ingredient into the mineral substrate. The thixotropic consistency of the product ensures a long contact time of the silane/siloxane active ingredients with the surface thus improving penetration depth. Of course penetration depth depends on the absorption properties of the mineral substrate as well as the concentration of the active ingredient. Silane/siloxane creamy products have the same performance of the most common impregnating agents at least by only a one step application.

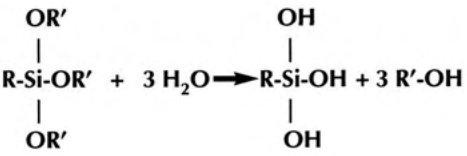
3.1 Mechanism

Hydrophobic impregnation of building materials is able to create a water-repellent finish by impregnating building surfaces with solutions of particular substances. Interfaces have special properties which lead to the development of very specific forces of attraction or repulsion. At the surfaces of inorganic mineral substances there are forces of attraction on water molecules and this is particularly pronounced in the case of silicates. Thus the film of water on the surface of quartz glass can only be removed at relatively high temperatures.

Thus if a substance is made water-repellent by hydrophobic impregnation, it means that interfacial forces are changed, i.e. attraction forces are changed into repelling forces. How to do this? One way is the application of boundary surfaces to the existing surfaces. Impregnation takes place with the addition of a hydrophobic substance and after evaporating the solvent a thin coat of the hydrophobic substance is left behind on the boundary surfaces of the pores and the capillaries, where it exerts a water-repellent action. For alkoxysilanes it is reasonable to expect the following reaction behaviour at the interfacial surfaces of building materials (Figs. 10 a, b).



Figs. 10 a,b - Silanol groups are bound to the substrate, while alkyl groups are oriented toward the external side thus forming an umbrella to rainwater.



Silanoles can react with hydroxyl groups of the silicate lattice (left-side represent the silicate lattice) and consequently produce surface compounds on the boundary surfaces of the mineral substances which in turn have a water-repellent action (Fig. 11).

Silanoles can also react with the adjacent molecules leading to the formation of polysiloxanes (Fig. 12).

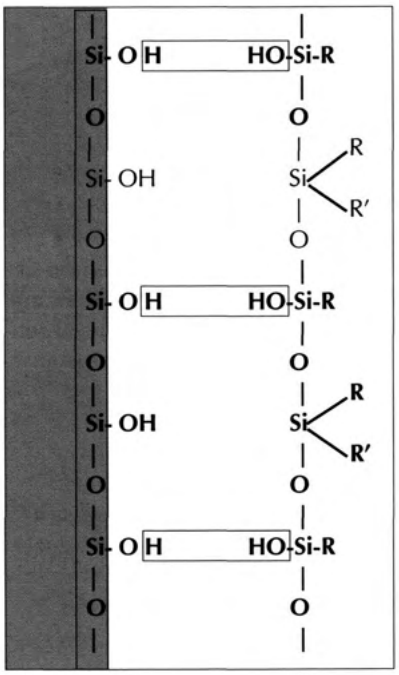


Fig. 11 - Surface treated with reactive silicon resins.

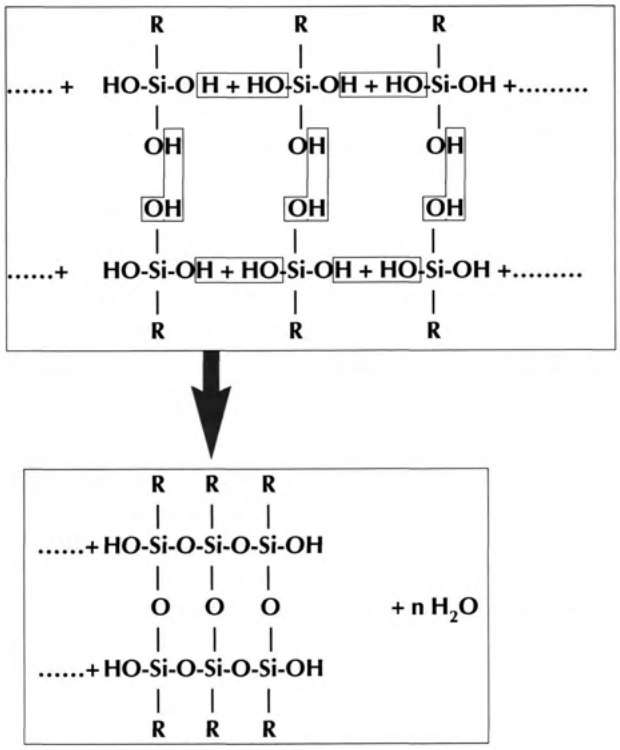


Fig. 12 - Polysiloxane formation through the polycondensation of silanes.

Under natural conditions the two reactions now described are competitive in particular the following parameters: pH value, OH supply, moisture can influence one or other reaction. This leads to a short-chain polysiloxane which is connected to the silicate lattice. The chain length is dependent on the reaction conditions.

As silane molecules are very small, about 1 mμ, they are able to penetrate virtually all the pores and capillaries occurring in building materials resulting in a very great depth of penetration. As the covalent bond to the silicate lattice is of the same order of magnitude as the forces holding together the silicate lattice a very great resistance to chemical action is imparted to the hydrophobic surface compound.

As previously discussed the production of a silane hydrophobic treatment is producing a short-chain polysiloxane anchored to the substrate by very strong chemical bonds. Alternatively to the in situ oligomer formation it is possible to introduce short-chain polysiloxanes into the cavities and anchoring them to the boundary surfaces. Short chain are still soluble in alcohols (due to their low molecular weight) and can form chemical bonds with the OH groups of the silicate lattice via reactive groups. The difference between the two treatment procedures is that in one the polysiloxane is formed in situ whilst in the other it is formed before application to the surface. In both cases it bonds chemically to the surface and penetrates layers of moisture. The depth of penetration of pure silanes is naturally greater, the question is as to whether it is always necessary. There are also far more possibilities of reaction with the substrate in the case of silanes, which is shown by the reduced alkali of impregnations with reactive polysiloxanes. However, cases exist where such an extremely good resistance to alkali action is not required, i.e. whenever the substrate is only slightly alkaline, e.g. in the case of weathered brickwork.

3.2 Influence of the formulation

In general studies have found that emulsions provide protection similar to solvent-based formulations although they show lower penetration depths. It has also been suggested that the presence of salts within porous materials may de-stabilize the emulsion of water-borne products (Ciabach, 1996). Water based formulations show lower performance than solvent-based ones when subjected to free-thaw cycling (Fort Gonzales et al., 2000).

Even for solvent-based formulations, different results are observed depending on the degree of polymerization: commercial siloxane products may lose initial hydrophobicity faster than a silane formulation, it provides better long-term protection for granites and limestones. Recently silicon-based creams formulations seem to have been developed to obtain good penetration depth in low porosity concrete, but until now not yet sufficient researches have been carried out to extend their uses to stone or bricks materials.

3.3 Influence of the alkyl group

The hydrophobicity imparted to silicon-based compounds depends on the alkyl group attached to Si atom. Performance can be improved, in particular alkali-resistance, if molar masses of alkyl group is increased. In commercial product methyl group can be substituted with propyl, butyl or octyl groups (De Witte et al, 1983). Studies carried out with commercial alkyl silanes containing only methyl, or either iso-butyl or n-octyl groups, showed that the porosity of the stone was critical in determining the performance of the water repellent, based on

the amount of moisture remaining in test samples of dense and porous sandstones. Only octyl-containing silanes, or synthetically produced pentyl and exyl silanes provided relative water repellency for denser stones (Grobe et al., 1994). According to some studies stones with smaller pores require a larger alkyl group to counteract the stronger "forces" of finer capillaries that tend to retain moisture. Smaller pores in the range of pore diameters 3.5-17 μm seem to have more influence on the water repellent performance than the total porosity of the substrate (De Witte et al. 1995).

According to Charola (2003) other studies showed that replacement of some methyl groups by longer alkyl groups was not as significant for performance as the substrate (brick and limestones) when evaluated artificial weathering (De Witte et al., 1983). This was also confirmed in field tests performed for different stones weathered in either an urban or an industrial environment (Bruchertseifer et al., 1996).

3.4 Influence of the substrate

Possible interaction between the support and the protective product can be reasonable expected and consequently there is a need to investigate on the influence of the chemical nature of the substrate on the polymerization reactions taking place by using polymeric substances. In some studies a difference in the behavior of products used on the same substrates was observed. This was interpreted as an active role played by the substrate respect to the different substances applied. For example silicate compounds (montmorillonites, bentonites, kaolinites and other clay minerals) can strongly influence, activating and accelerating, polymerization processes. When using silanes for impregnation it should be taken into account that the polymerization reaction is competing with the evaporation rate of the liquid. As a consequence, environmental conditions for application are critical but, so far, cannot be defined a priori. According to Charola (2003) studies have shown that water-based emulsions of siloxanes are more susceptible to the moisture content within the substrate than solvent-based formulations, although other studies highlight that this is dependent on the substrate. The strong variability in the composition and texture of natural stones is strongly influencing the performance of the treatment and in general water repellent substances perform well when applied to bricks while on limestones they have an erratic behavior.

Sometimes the hydrophobization is improved if the silicon-based water repellent was applied in mixture with a silicate ester thus suggesting that the silicate consolidant is improving the homogeneity of the substrate as well as is acting as an anchor for the water repellent (Charola, 2003).

3.5 Influence of the application technique

The application method can influence the water repellent performance and the durability of the treatment, in fact it can strongly influence the penetration depth. As a consequence the developing a good application method is of paramount importance for the success of the treatment. The difficult in achieving this is demonstrated by the years of research spent in improving the systems (Charola, 2003). Good penetration has been achieved even in dense concrete when application procedures, i.e. number of sprayings and/or subsequent sprayings, were adjusted to the conditions of the substrate, such as the amount of moisture present. An improvement for dense materials such as concrete is the use of a thickened water repellent which is sprayed or brushed on as a cream. This allows for longer contact times between the agent and the surface resulting in increased capillary absorption. Box technology the water repellent floods on the concrete surface for a minimum time pre-determined experimentally for the particular concrete.

Even under laboratory conditions it was found that only capillary absorption, as compared to brushing or spraying, gave reproducible results (Matteoli, 1993, Berardi et al., 2000).

3.6 Durability of hydrophobization

For economic and practical reason, a good water repellent should stay efficient as long as possible, but it is currently recognized that treatment with these agents should be considered as a periodic intervention to be included in routine maintenance rather than as a definitive treatment (Delgado Rodrigues and Charola, 1996). The durability of a water repellent is not only influenced by the chemical composition of the water repellent product, the typology of the substrate, the depth of penetration, but also by external factors which interacting with the chemical compound can reduce the ability to prevent water penetration.

According to some authors (Wendler & Snethlage 1988) in Germany the durability of water repellent treatments based on silicon-containing products seems to have an average lifetime of 7 years, while some others reported longer lasting treatments, about 15 years (Wendler et al., 1991). The latter evaluation was also confirmed by our recent measurements carried out, after 16 years since the protective application on the brick-wall masonry of the external façade (on the internal side the Last Judgement frescoes of Giotto's is present) of the Scrovegni Chapel, in Padua (Fassina et al., 1998). Studies carried out by Fort Gonzales et al. (2000) and Wendler 1997) seem to indicate that silicon-based compounds are not susceptible to UV radiation and the loss of water-repellency can be attributed to soiling of the treated surface through deposition of hydrophilic particles (Wendler, 1995). In fact long-term exposure of samples exposed to direct rain maintained better surface water-repellency than those in sheltered position were dust accumulated (Von Plewe et al., 1996).

A comparison on different stones treated with a propyl-octyl silane and methyl-octyl siloxane exposed in urban and industrial environments for 8 years showed that silane maintained its hydrophobicity far better than siloxane (Bruchertseifer et al. 1995).

Moisture content in the substrate can influence positively or negatively the performance of water-based emulsions (Charola, 2003). Most performance evaluation data for water repellents were obtained by artificial weathering tests which vary greatly in design. Artificial weathering encompasses different ageing techniques such as cycles of:

-temperature and relative humidity,
-freeze and thaw,
-salt crystallization,
-or exposure to UV radiation and/or to pollutants.

The control tests to be used after the weathering have to be chosen in accordance to the specific ageing cycles. The relationship between real and artificial weathering remains poorly defined and hence the development of artificial ageing processes to mimic real weathering is still a challenge. It is hoped that continued researches in the comparison of the phenomena resulting from real and laboratory ageing situations will provide the means of identifying the relation between them.

4. Assessment of effectiveness and performance of surface treatments with protective substances for porous inorganic materials

Today conservation science imposes that consolidant and or protective substances should be applied onto the surface of cultural property only after they have gone through a series of laboratory tests. As these products have not been specifically conceived for historical buildings thus they need appropriate experimentation before use. Only in a fewer cases their characteristics account for the specificity required for historical buildings (Fassina, 2006).

According to Delgado & Charola (1996) although hydrophobicity is a surface property, it is commonly considered that a certain in-depth anchoring capacity is a positive factor and therefore the depth of penetration has been considered a parameter to be taken into account for assessing the efficacy of water repellents.

The amount of absorbed product may be taken as an indirect evaluation of the penetration capacity, but more direct determinations have been used by different authors when appropriate element tracers are present (Delgado & Charola, 1996). For instance SEM-EDS analysis, can be used to visualize directly the interaction between the protective and the substrate. In particular EDS elemental distribution maps of tracer elements allow the visualization of the treatment's distribution. Another property related to the depth of penetration is the change in pore size distribution in the area where the product has been applied.

In general, laboratory evaluation of stone treatments should assess their efficacy, harmfulness and durability. Whereas efficacy can be regarded as the short-term performance of the product, durability refers to its long-term behaviour. Harmfulness encompasses all the undesirable effects that a treatment might induce in the treated material (Delgado & Charola, 1996).

In order to get information about the properties and the behavior of the protective products it is necessary to establish the significant parameters that should be considered as well as the standard test methods permitting the measurements of these parameters.

For the evaluation of the water repellent used in the treatments of porous inorganic materials the following chemical-physical characteristics should be considered:

-ability to prevent or to minimize the water absorption,

-hydrophobicity of the substrate,

-ability of water vapour to escape from the surface.

An analysis on the existing procedures and a literature survey allowed to have an image on how water repellent agents are tested nowadays. First of all there is a lack of information about the formulation available and how well they perform as a function of the various materials encountered in practice. Furthermore the absence of recognized test procedures results in the impossibility to obtain objective technical information which would/should be comparable for the very large number of products available on the market (Pien & Vanhellemont, 2003). The investigated test procedures show a wide diversity in test parameters caused by different building habits in different countries. The lack of criteria for the evaluation of the performance can cause some problems:

-difficulty to have an objective comparison among the performance obtainable with the use of protective products actually present on the market,

-difficulty to establish an appropriate methodology for each product,

-difficulty to have an evaluation of the efficacy of protection,

-uncertainty to have a protocol for bidding.

First of all the assessment of different protective substances needs to individuate:

-significant parameters for measuring the modification of surface physical behavior introduced by the application of the treatment;

-standardized and reproducible test methods for each parameter;

-limit of acceptability.

The need to assess in a proper way the performance of protective substances is currently been developed in the Working Group 3 "Evaluation of methods and products for conservation works" in the framework of European Committee for Standardization CEN/TC 346-Conservation of Cultural Property. According to the WG3 the following parameters have been considered (Fassina, 2008):

1. Determination of water absorption by capillarity, EN 15801.
2. Determination of static contact angle, EN 15802.
3. Determination of water vapour permeability (δp), EN 15803.
4. Colour measurement of surfaces, prEN 15886.
5. Determination of drying properties
6. Measurement of water absorption under low pressure

The most common undesirable changes associated to water repellent treatments are colour changes, water vapour permeability reduction, variations in the drying behavior, increasing in hygric dilation, acceleration in the bio-organisms growth.

The control of water vapour permeability aims at ensuring that enough "breathing" capacity remains in the material after hydrophobisation.

The drying of water-saturated specimens should not change after treatment. The treatment should certainly not retard the evaporation of liquid water once it has entered into the stone.

Hydric dilation is the expansion of the specimen when subjected to prolonged contact with liquid water. High relative humidity exposure will produce a similar expansion which is called hygric dilation.

The evaluation of water repellent products applied on stone materials should be carried out according to the following steps:

- specimen preparation
- measurements of the above parameters before the treatment,
- determination of the duration of the treatment and of the methodology of application of the product to evaluate,
- measurements of the above parameters after the treatment,
- artificial weathering using different ageing techniques,
- measurements of the above parameters after each ageing techniques

4.1 Methodology of application

Stone materials can be impregnated satisfactorily when the protective product is characterized by a low viscosity, a proper surface tension and a small contact angle on the substrate. Generally the increase of molar mass of a dissolved polymer has to be compensated by an adequate decrease in its concentration to maintain the appropriate viscosity of the solution.

In practice to accelerate the process of impregnation the stone material is firstly impregnated with the pure solvent which is much more penetrating than the polymer solution, and successively the diffusion of the polymer from the solution into the solvent is favoured by the presence of the solvent previously applied.

Apart from differences in the testing facilities available in various research laboratories and the problems of information

exchange due to the variation of the testing protocols, there are many other factors influencing the final behaviour of the treated materials. Among them can be mentioned the sizes and shapes of the testing specimens, the concentration of the product tested and the type of solvent used in its preparation, the application procedure, the environmental conditions during the curing of the treated specimens.

For the case of application procedures some researchers prefer to simulate in situ application methods by using spraying or brushing techniques. But the usually small dimensions of the testing specimens drastically reduce the possibility of making this a representative sample and the extreme difficulty of applying the product in a reproducible manner eliminates the advantages of this approach.

About the treatment methodology a review on published papers show that different application techniques were used by: brushing; spraying; immersion; capillary rise absorption, cream.

Sometimes the application techniques are not specified, but only the amount of product after drying:

- the time of application is extremely variable, but in most cases they are the same for different lithotypes and chemicals in the frame of the same research;
- preliminary conditioning of the samples is often reported, but it is carried out in very different conditions;
- the amount of product in the sample is often reported, but the condition are very different;
- the evaluation of the efficiency is reported in relation to the capillary absorption and more rarely in relation to contact angle and the water absorption at low pressure (Karsten tube or pipe);
- generally treatments by capillarity, brush or spray are carried out to only on one face, with the exception of one paper which involves 4-6 sides of the specimen.

Brushing can be discarded because it depends upon the skill of the operator. In fact, brushing results in differences in the quantity of product applied on various samples and a scarce homogeneity of the treatment, producing zones containing different thickness of protective product in the same sample.

Spraying can also be discarded because of the small sizes of the samples and the small quantity of the product to be applied, two factors that cause significant losses of product in the surrounding environment, and considerable difficulties in treatment operations. Totally immersion of the specimen produces homogeneous penetration, but has a drawback to create some difficulties for air to escape.

The method producing the most homogeneous and reproducible results is the capillarity treatment, supporting the side to be treated on a multilayer filter paper, which is soaked with protective solution. In this way, sufficiently uniform applications of various protective products were obtained without problems related to the skill of the operator performing the treatment.

Which is the best time of application? What is the optimum quantity to be applied to the samples of the various litho types?

The type and the extent of protection offered by the various products to be tested could easily vary according to the quantity of product applied. Therefore, the use of the same quantities of different protective products does not necessarily imply the achievement of similar protection. The protection might also vary from different lithotype, since each lithotype requires a specific adequate quantity of protective material.

According to producer companies a short time should be advisable because it simulates quite well the real application conditions. A drawback to simulate real conditions is the difficulty to have reproducible conditions. In fact, the external environment presents very variable condition of temperature and relative humidity which could influence in a different way the efficacy of application and some negative results, by using the above test methods, could be ascribed to the difficult to have standard and reproducible conditions. It is not reasonable and correct to evaluate different products by using a treatment methodology which is not reproducible.

As said before the best way to apply protective products is to use the capillary rise absorption. About the duration time of treatment it should be decided by making some preliminary tests at different times and calculating every time the efficiency of protection (see the meaning later).

As regards the use of siloxane treatment the environmental conditions, that should be appropriate to have polymerisation of the compound, have to be taken into consideration. Generally the usual laboratory measurements need to dry specimens, but this create unfavourable environmental conditions for polymerisation occurrence and therefore specimens before treatment request a conditioning at appropriate humidity values for at least 24 hours in order to supply moist conditions which are favouring the hydrolysis and the subsequent polymerization of siloxane. Specimens are conditioned for 24 hrs at 25°C and 50% RH and successively are put on a multilayer filter paper of 1 cm of thickness soaked up almost to its top with protective solution, the samples should be laid in contact with the face on which the parameters should be measured before treatment. After the chosen time, samples should be turned, placed again on the bed and completely covered for 5' with the protective product up to 1 cm over the sample surface. The samples should be then dried still in this upside down position resting on small glass beads for 30 days in the laboratory (Many authors, UNI 10921, 2001; Matteoli et al., 1995).

As regards the duration of the treatment it depends on the following factors:

- chemical composition and concentration of the product,
- chemical composition of the solvent and the evaporation rate,
- pore size distributionosity of stone material

4.2 Determination of the amount of protective product

The weight of the product absorbed generally tends to decrease in time both because of the slow evaporation of the solvent and, in the case of silicon-based products, because of their progressive polymerisation (Many authors, 1993).

The porosity and the solvent evaporation rate influences strongly the weight decrease of the specimen: high porous stones show a rapid evaporation rate.

Experiments carried out by different laboratories highlights that the influence of environmental parameters is particularly important during treatment. Differences in relative humidity of the environment influence the moisture content of the specimen and consequently the absorption kinetic of protective product and its polymerisation rate.

Specimen is weighted before and after the treatment having the care to allow the complete evaporation of the solvent. This is obtained when the specimen weight has reached a constant value.

4.3 Determination of water absorption by capillarity - EN 15801 (CEN TC 346/WG3)

This measure allows to evaluate the kinetics of water absorption and the amount of water absorbed by means of the capillary rising process. This test is significant to evaluate the efficacy of the water repellent both after short and long times.

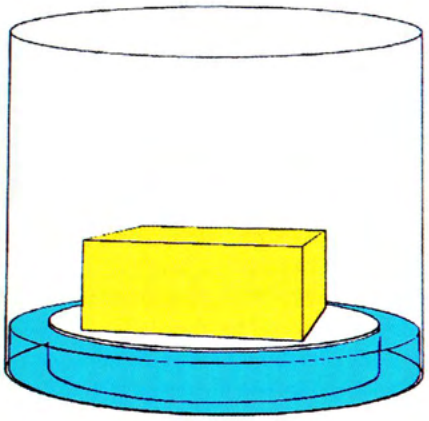


Fig. 13 - Specimen in contact with a multilayer filter paper.

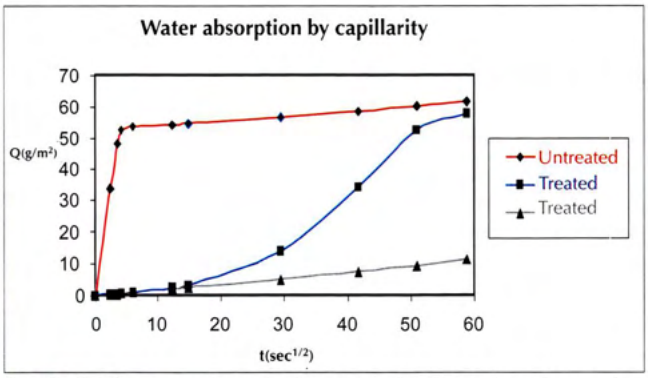


Fig. 15 - Capillary water absorption for untreated and treated specimens with three different products.

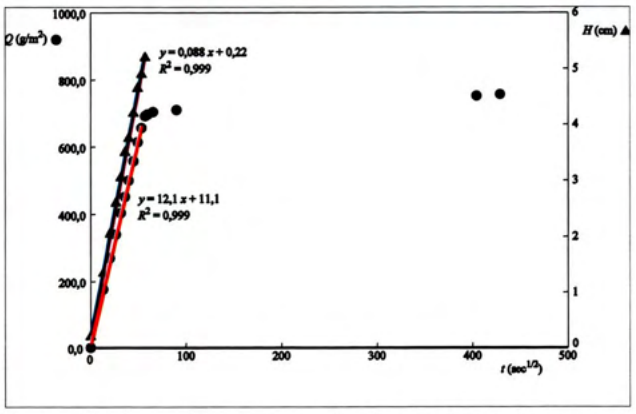


Fig. 14 - Graph reporting the water absorbed by the specimen per unit area (Qi) versus $(t_i)^{1/2}$. Example of calculation of the capillary water absorption coefficient (AC = 12,1 g/m² sec $^{1/2}$ - full dots) and capillary water penetration coefficient (B = 0.088 cm/sec$^{1/2}$ - full triangles). Cylindrical specimen: height = 5cm; diameter = 4cm)

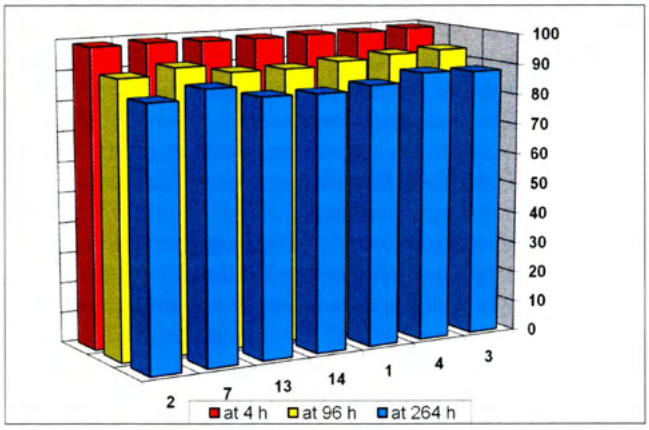


Fig. 16 - Protection efficiency PD_C (%) at different times: 4 hrs red; 96 hrs yellow; 264 hrs blue histograms. After 4 days the protection efficiency is still higher than 90% (yellow histograms). Numbers in the abscissa represent different samples.

Capillary water absorption is obtained when the specimen comes into contact with a multilayer filter paper that is completely saturated with water (Fig. 13). The amount of water taken from the specimen is determined by weighing it at different times. At a certain point, the water content reaches an asymptotic value.

The capillary water absorption coefficient (AC) is the slope of the linear section of the curve obtained plotting the mass change per unit area (Q_i) versus time $(t_i)^{1/2}$, and shall be calculated by linear regression, using at least 5 successive aligned points. The shape of the curve and the inclination of the linear section of the curve provide an indication of the kinetic of water absorption, which is dependent on the pore size distribution of the lithotype considered (Fig. 14). A good reproducibility is generally obtained for most of porous materials. Only in few cases especially for low porous material, where the amount of water absorbed is very low, the reproducibility is influenced by the skill of the operator.

Untreated samples show generally a very fast water absorption rate in the initial stage and then the water uptake rate strongly decreases and slowly reaches an asymptotic value. The last represents the maximum amount of absorbed water and is significant of the porosity accessible to water.

After treatment the change of inclination of the linear section shows the decrease of absorption rate, while the second part of the curve can give indication about the distribution of the product: on the surface or inside the material (Fig. 15).

Finally it is important to underline that the evaluation of the efficacy of the water repellent is not only based on absorption coefficient, but also on the kinetic of the absorption curve. Very frequently different products can have the same AC but show different curve shape after long times.

Protection degree by capillarity; untreated **PD_C**

The assessment of the effectiveness of the treatment regarding water absorption (defined as protection degree) is carried out by comparing the amount of water absorbed before (WA_{bt}) and after the treatment (WA_{at}) according to the following formula:

$$PD_C\ (\%) = \frac{WA_{bt} - WA_{at}}{WA_{bt}} \cdot 100$$

The protection degree obtained after a long time of water absorption gives an indication of the resistance to water penetration exerted by the protective.

Values of PDc close to hundred percent mean that the protective applied is efficiently preventing water uptake (Fig. 16).

4.4 Measurement of water absorption at low pressure (WALP) by pipe method (CEN TC 346/WG3)

This test method provides a simple means for measuring the rate at which water moves through a porous materials. The test is performed by measuring the volume of water absorbed on a fixed surface under low pressure and within a specified time. This test can be performed at the site or in the laboratory and can be used to measure vertical and horizontal water transport. Penetration of driving rain into wall surfaces results in horizontal transport. Under actual conditions, the amount of rain penetration depends on prevailing wind conditions as well as on the composition and condition of the exposed surfaces. The device used is the pipe-like apparatus designed for vertical sur-

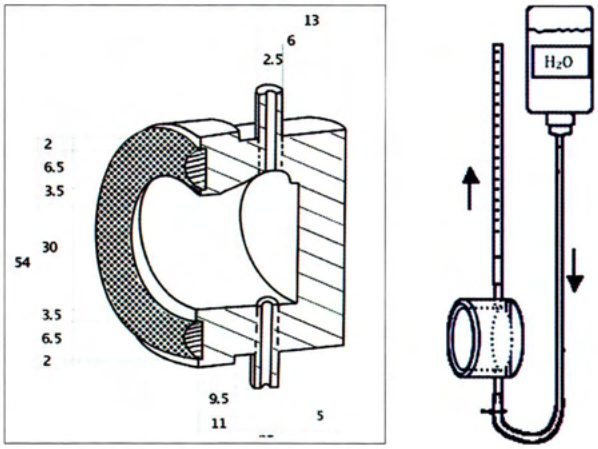


Fig. 17 - Pipe-like apparatus with the water supply from the bottom.

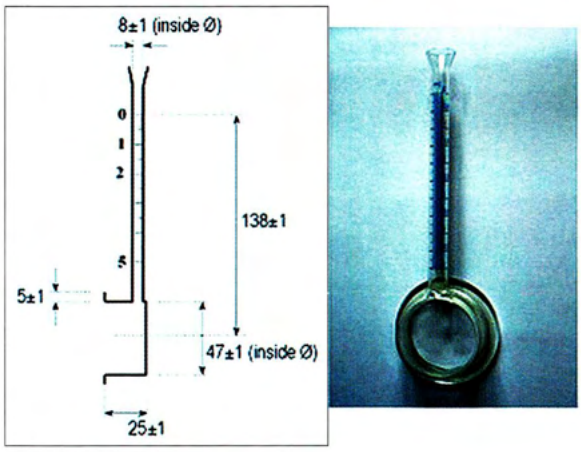


Fig. 18. Karsten tube.

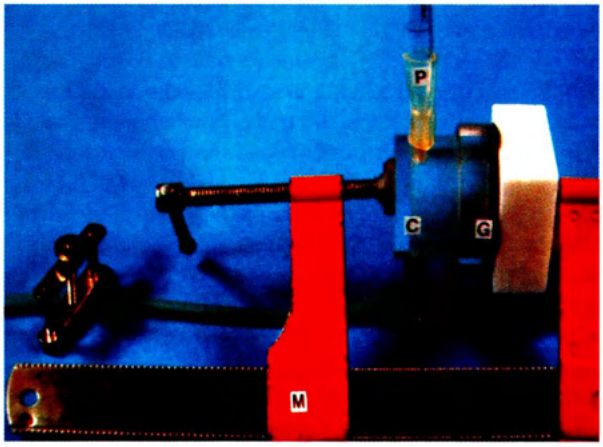


Fig. 19 - Typical system to use the pipe-like device in laboratory.

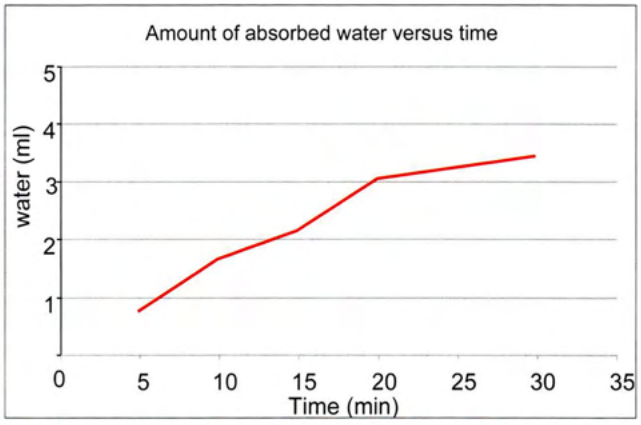


Fig. 20 - Measurement of water absorption at low pressure for untreated sample.

faces and is formed by a cylindrical vessel whose open extremity can be applied to the stone surface by the interposition of a sealing ring (Figs. 17, 18, 19). The cylinder wall has two opposite holes, one of them allows water to be supplied from the bottom, while the upper one is connected to a graduated pipe.

The quantity of water absorbed by the material during a specified period of time is read directly from the graduated tube (Fig. 20). The periods of time appropriate for the test depend on the porosity of the material on which the measurement is being made.

$$WA_{LP} = \frac{WA_{30} - WA_5}{S}$$

WA_{30}=Water absorption at 30 minutes
WA_5 =Water absorption at 5 minutes
S = contact area between sample and pipe set

Protection degree at low pressure $\mathbf{PD_{LP}}$

The protection degree at low pressure can be evaluated by using the following formula:

$$PD_{LP}\,(\%) = \frac{(WA_{LP})_{bt} - (WA_{LP})_{at}}{(WA_{LP})_{bt}} \quad 100$$

PD_{LP} =protection degree at low pressure
$(WA_{LP})_{bt}$ =Water absorption before treatment
$(WA_{LP})_{at}$ =Water absorption after treatment

4.5 Measurements of drying properties (CEN/TC 346/WG3)

Evaporation takes place if there is a moisture gradient between the ambient air and the material. The conditions for drying discussed here are limited to a one-dimensional flow of moisture running to the surface where the water evaporates (Knofel et al., 1982). The time-dependent weight loss can be divided into two periods:

Period 1: it is characterized by the transport of liquid water to the surface followed by evaporation. The surface remains wet allowing evaporation to continue at a constant rate, if water moves to the surface quickly enough to compensate for the loss of evaporation. The water content $\boldsymbol{\psi}$ close to the surface is greater than the critical humidity $\boldsymbol{\psi_{kr}}$. The following relation holds:

$$q = \beta\,(p_o - p_1)$$

where **q** is the amount of evaporated water; $\boldsymbol{\beta}$ is the coefficient of the water vapour conductivity of the surface; $\mathbf{p_o}$ is the water vapour pressure at the surface, $\mathbf{p_1}$ is water vapour pressure of the ambient air. In this period the weight loss **q** is linear related to time. Here the evaporation depends only on the environmental conditions and is independent of the physical structure of the material.

When the amount of water brought to the surface becomes too small to keep the surface wet, the rate of evaporation decreases.

Period 2: transport of liquid water to the surface is no longer possible and only the less efficient vapour diffusion mechanism remains available according to a concave curve.

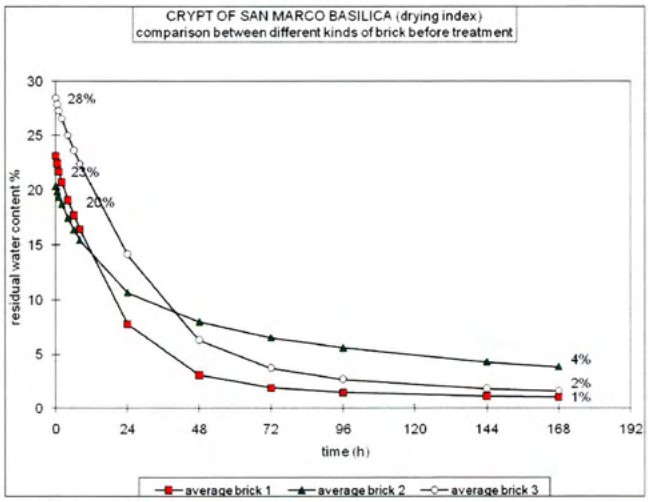


Fig. 21 - Evaporation curves for three different categories of brick characterised by different porosity.

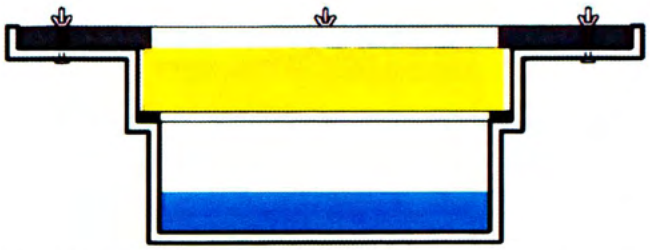


Fig. 22 - Device for measurement of water vapour permeability. The bottom of the container is filled with water; the sample is closing the box and the water vapour is forced to pass through the sample. The driving force is the gradient of partial pressure between inside and outside the box.

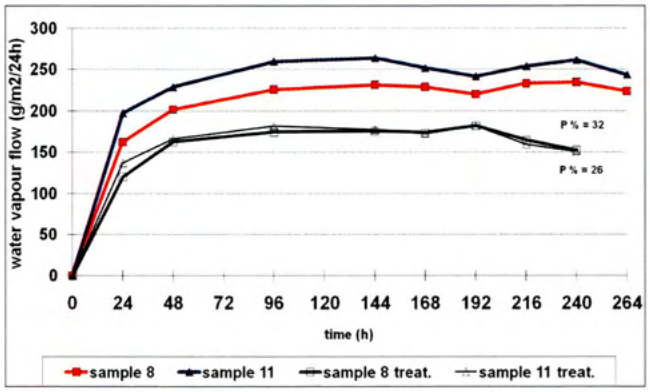


Fig. 23 - Water vapour permeability: comparison before and after treatment. The water vapour reduction is 26 and 32 % for the brick samples considered (sample 8 and 11).

The water content is lower than ψ_{kr}. The following relation holds:

$$q = \delta/d\ (p_1 - p_2)$$

where **q** is the amount of evaporated water; δ is the coefficient of water vapour conductivity of the material; **d** is the thickness of the layer which water vapour passes through; and p_1, p_2 are water vapour pressures at both sides of the layer. The drying processes in period 2 can be explained as follows: the water flow through the capillary system is lower than the amount of water which evaporates. Therefore, the level of pore water moves more and more into the interior of the material, and the water evaporates within the pore space leaving it via water vapour diffusion. The weight loss **q** during period 2 is exponentially time dependent. The time of drying is dependent on the relative humidity and the wind velocity at a given temperature. In the same way for a given material ψ_{kr} is influenced by the wind velocity and the relative humidity of the air.

The moisture content corresponding to the discontinuity is called *knick-point water content*.

The experiments yield information about the velocity of water release and the amount of residual water remaining after a certain time. The sample previously saturated with water, is placed into a box that contains silica gel to maintain a dry environment. It is weighed from time to time to determine the amount of evaporated water (Fig. 21). During the first eight hours specimens are weighted every hour and afterwards twice a day for at least one week. Water evaporation occurs in controlled conditions and its amount is recorded in a graph.

4.6 Determination of water vapour permeability (δ_p) - EN 15803 (CEN TC 346/WG3)

This measure show the amount of water vapour passing through the specimen over time in static conditions. A flux of water vapour through the specimen occurs when there is a difference in the partial pressure between the two opposite surfaces of the specimen.

To reach this condition, each sample is fitted like a "plug" into a suitable box with a small amount of distilled water at its bottom; then the box is placed in a desiccator containing silica gel in sufficient amount to absorb water vapour during the test (Fig. 22).

As air temperature strongly influences the difference in vapour partial pressure between specimen surfaces, it is strictly controlled. When stationary conditions are reached, the water vapour flux (in g/m^2 for 24 hrs) is calculated by measuring the weigh loss of the box every 24 hrs. The stationary conditions are generally reached after some days. (In the graph after four days, Fig. 23). Specimens shall be prepared in a way that the parallel test faces are perpendicular to the direction of water vapour flow. The thickness of the specimens will influence the time to reach the equilibrium as well as the precision of the test method.

The assessment of the reduction of water vapour permeability $\mathbf{WV_{red}}$ is obtained by comparing the flux of water vapour before (Φbt) and after the treatment (Φat) with the following formula:

$$\mathbf{WV_{red}}\,(\%) = \frac{\Phi bt - \Phi at}{\Phi bt}\ 100$$

Low values of WV_{red} indicates that the applied product gives a minimum interference to water vapour flux, so it is preferable to use protective products giving the minimum water vapour reduction.

4.7 Determination of static contact angle - EN 15802 (CEN/TC 346/WG3)

This measure offers a means of assessing the degree of water-repellence on the surface.

The contact angle θ of a liquid on a surface is widely used to predict wetting and adhesion properties of the solid by calculating its solid-vapour surface tension. The contact angle θ of a liquid on a surface is frequently used to estimate the wetting properties of the solid by calculating its solid-liquid-vapour surface tension.

Its definition is based on the equilibrium of a drop on an

ideal (i.e. flat, horizontal, smooth, homogeneous, isotropic and rigid) surface, according to the Young relationship:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

where γ_{SV} is the solid-vapour interfacial tension, γ_{LV} is the solid-liquid interfacial tension and γ_{SL} is the liquid-vapour surface tension.

Looking at a cross-section of a drop on a solid, θ is the inclusive angle between the direction of γ_{SL} and the direction of γ_{LV}, tangent to the external surface of the drop, with the vertex at the three-phase liquid-solid-vapour intersection. Looking at a cross-section of a drop on a solid, θ is the inclusive angle between vector γ_{SL} and vector γ_{LV}, tangent to the external surface of the drop and having its vertex at the of three-phase system (Fig. 24).

Under these hypotheses, a contact angle corresponds to the thermodynamic value that minimizes the surface free energy.

Contact angle smaller than 90° indicates a hydrophilic surface, while contact angle higher than 90° indicates a hydrophobic one. Hydrophobic surfaces after treatment should have contact angles exceeding at least 100° (Fig. 25).

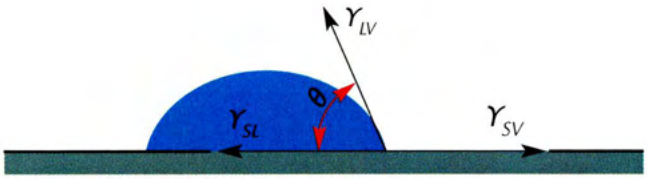


Fig. 24 - Contact angle θ for a hydrophilic surface.

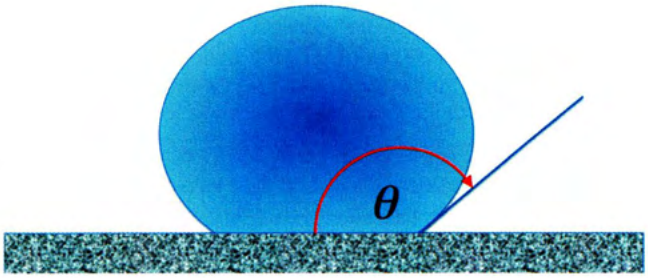


Fig. 25 - Contact angle θ for a hydrophobic surface, e.g. after treatment.

4.8 Measurements of colour surfaces - pr EN 15886 (CEN TC 346/WG3)

The measure of colour surface of a specimen can be performed by measuring the colour coordinates of the object according to International methods defined by the Commission Internationale de l'Eclairage CIE. The colour is represented in a "colour space", where any colour in the visible range is defined by the three coordinates: L*(lightness-darkness), a*(redness-greeness), b*(yellowness-blueness) are considered (Fig. 26).

The diameter of the measuring area and the equipment shall be appropriate to the type of material under investigation, and the size of the specimen or object. Heterogeneous surfaces may be measured using a measuring area with a diameter as large as possible, in order to compensate for variations in colour and texture, and to even out structural unevenness on the surface of the specimen or object, thus imitating the human visual process. Uniform specimens or object with or without well-defined areas of different appearance (such as dark veins on light marble) may be measured with a much smaller 1mm) measuring field diameter to avoid (or define) any areas of inhomogeneity.

When the number of readings has been determined, the measuring points for the after-treatment colour measurement shall be localized by reference spatial coordinates in order to ensure precise repeated measurements. A grid delimiting the measurement field may be useful for this purpose, depending on specimen size.

The calculation of total colour differences ΔE^* between two colours (L^*_1 a^*_1 b^*_1 and L^*_2 a^*_2 b^*_2) is the geometrical distance between their positions in the CIELAB colour space. It is calculated using the following equation:

$$\Delta E^*_{1,2} = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})}$$

where:

$\Delta L^* = L^*_1 - L^*_2$; corresponds to the lightness difference
$\Delta a^* = a^*_1 - a^*_2$; corresponds to the red/green difference
$\Delta b^* = b^*_1 - b^*_2$; corresponds to the yellow/blue difference

ΔE^* values close to zero means that no undesirable colour changes occurred. Less restrictive conditions with colour changes ΔE^* less than 2 are acceptable because they correspond to the perception of human eye.

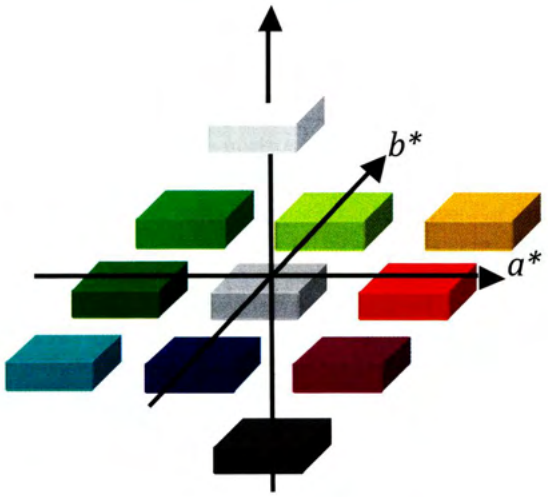


*Fig. 26 - L*a*b* colour space.*
L=the lightness coordinate. The scale for L* ranges from 0 (black) to 100 (white).*
a=the red/green ccordinate. +a* indicating redness and –a* indicating greenness.*
B=the yellow/blue coordinate. +b* indicating yellowness and –b* indicating blueness.*

Note

[1] Vitruvius, De architectura, Introduction to book VII, II, c. VII, VI.

[2] Plinius, Naturalis Historia, XXXIII, XXXV, XXXVI.

[3] Eraclius, De coloribus et artibus romanorum, book III, n. XXV, in M.P. Merrifield, Original treatises on the art of painting, ed. New York 1967, pp.230-231.

[4] C. Cennini, Il libro dell'arte, c. XCIV, CLVI, CLXXIV, ed. Vicenza 1971, pp. 102, 162, 190-191.

[5] E. Boileau, Livres des Métieres, (1268) quoted by M. Aubert, Il trionfo del gotico, Milano 1964, pp. 71-74.

[6] Leon Battista Alberti, De re edificatoria, I, II, III, V, VIII, IX.

[7] The Marciana Manuscript, in Merrifield, Original treatises on the art of painting, ed. New York 1967, p. 631.

[8] This information was given by L. Guicciardini in 1567 and quoted by V. Manikowsky, Die Denkmalpledge, 12, 7, 1910, pp. 51-54.

References

Aglietto, M., Castelvetro, V., Ciardelli, F., Matteoli, U., Botteghi, C., Chiantore, O., Lazzari, M., Alessandrini, G., Peruzzi, R., Toniolo, L. & Fassina, V., 2000. An integrated approach to design fluorosubstituted 'smart' polymers for protection of monumental buildings, Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19-24, 2000, ed. V. Fassina, Elsevier, Amsterdam, pp. 209-214.

Aldi, A., Alessandrini, G., Casarino, A., Pedemonte, E., & Peruzzi, R., 1995. Evaluation of the effectiveness of protective treatments for slate from the val di Lavagna (ITALY), Int. Colloquium "Methods of evaluating products for the conservation of porous building materials in monuments, ICCROM, Rome 19-21 June 1995, pp. 285-300.

Alessandrini, G. & Laurenzi Tabasso, M., 1993. The protection of stone: the current situation in Italy and the Mediterranean countries, Science and Technology for Cultural Heritage, 2, 191-199.

Alessandrini, G., Fassina, V. & Matteoli, U., 1993. Round table: The protection of stone materials. The state of art. Science and Technology for Cultural Heritage, 2, 213-220.

Appolonia, L., Fassina, V., Matteoli, U., Mecchi, A.M., Nugari, M.P., Pinna, D., Peruzzi, R., Salvadori, O., Santamaria, U., Scala, A., & Tiano, P., 1995. Methodology for the evaluation of protective products for stone materials. Part II: Experimental tests on treated samples, in International Colloquium Methods for evaluating products for the conservation of porous building materials in monuments, Rome 19-21 June 1995, pp. 301-316.

Berardi, E., Mecchi, A.M., Calia, A., & Lettieri, M., 2000. Trattamenti idrorepellenti su alcune pietre calcaree pugliesi a differente porosità, in Galan, E., Apariccio, P., & Miras, A., eds. Protection and Conservation of the Cultural Heritage of the Mediterranean Cities, Proceedings of the 5th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Univerdidad de Sevilla, Sevilla, 5-8 April 2000, pp. 217-218.

Botteghi, C., Matteoli, U., Paganelli, S., Arbizzani, R., Ciardelli, F., Aglietto, M., Taburoni E & Fassina, V., 1992. Polyfluoroalkylmethacrylates as materials for the protection of stones, Science and Technology for Cultural Heritage, 1, pp. 111-122.

Bruchertseifer, C., Bruggerhoff, S., Grobe, J., & Gotze, H.J., 1996. DRIFT Investigation of sylilated natural stone, molecular surface information and macroscopic features, in Riederer, J., ed., Proceedings of the 8th International Congress on Deterioration and Conservation of Stone, Berlin, pp. 1223-1231.

Bruchertseifer, C., Bruggerhoff, S., Grobe, J. & Stoppek-Langner, K., 1995. Long term exposure of treated natural stone. Development and first results of a testing concept, in Wittmann, F.H., Siemes, A.J.M. and Verhoef, L.G.W., eds., Proceedings of the First International Symposium on Surface Treatment of Building Materials with Water Repellent Agents, Delft, University of Technology, Faculty of Architecture, Delft, pp. 27/1-27/11.

Butlin, R.N., Yates, T.J.S. & Martin, C., 1995. Comparison of traditional and Modern Treatments for Conserving Stone, in International Colloquium Methods for evaluating products for the conservation of porous building materials in monuments, Rome 19-21 June 1995, pp. 111-119.

Charola, A. E., 1995. Water repellent treatments for building stones: A practical overview. In: APT Bulletin, 24, (2-3), pp. 10-17.

Charola, A. E. 2003. Water repellents and other protective treatments: a critical review, International Journal for Restoration of Buildings and Monuments, 9, n.1, 3-22.

Charola, A.E., Laurenzi Tabasso, M., & Santamaria, U. 1985. The effect of water on the hydrophobic properties of an acrylic resin. In Preprints of the 5th Congress on Deterioration and Conservation of Stone, Lausanne, 739-747.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Determination of water absorption by capillarity, European Standard - EN 15801, December 2009.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Determination of static contact angle, European Standard - EN 15802, December 2009.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Determination of water vapour permeability (δ_p) European Standard - EN 15803, December 2009.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Colour measurements of surfaces, European Standard - prEN 15886, under publication in 2010.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Measurement of water absorption at low pressure, draft document under discussion.

CEN TC 346/WG3-Conservation of Cultural Property-Test methods-Measurement of drying properties, draft document under discussion.

Charola, A. E., 1995. Water repellent treatments for building stones: A practical overview. In: APT Bulletin, 24, (2-3), pp. 10-17.

Charola, A. E., 2003. Water repellents and other protective treatments: a critical review, International Journal for Restoration of Buildings and Monuments, 9, n.1, 3-22.

Charola, A.E., Laurenzi Tabasso, M., & Santamaria, U. 1985. The effect of water on the hydrophobic properties of an acrylic resin. In Preprints of the 5th Congress on Deterioration and Conservation of Stone, Lausanne, 739-747.

Ciabach, J. & Lukaszewicz, J. M., 1993. Silicone emulsion concentrate VP 1311 as a water repellent for natural stone. In Proceedings of the International UNESCO/RILEM Congress on Conservation of Stone and other materials. M.J. Thiel ed. E. & FN Spon, London, 697-704.

De Clercq, H. & De Witte, E., 2002. Effectiveness of commercial silicon based water repellents applied under different conditions, in International Journal for Restoration of Buildings and Monuments, 8, 2002, n. 2-3, pp. 149-164.

Delgado Rodrigues, J., Charola A.E., 1996. General report on water repellents, Science and Technology for Cultural Heritage, 5, 93-103.

De Witte, E., Verheyen, A., De Bruyn, R. & Pien, A., 1993. Surface protectants for stone materials: the current situation in Northern Europe, Science and Technology for Cultural Heritage, 2, 173-181.

De Witte, E., De Clerq, H., De Bruyn, R. & Pien, A., 1995. Systematic testing of water repellent agents, in Wittmann, F.H. Siemes, A.J.M. and Verhoef, L.G.W., eds., Proceedings of the First International Symposium on surface treatment of building materials with water repellent agents, Delft, University of Technology, Faculty of Architecture, Delft, pp. 501-510.

De Witte, E., Florquin, S. & Terfve, A., 1983, The efficiency of water repellents for historic buildings, Wittmann, F.H. ed., Materials Science and Restoration, Filderstadt, pp. 131-135.

Fassina, V., Borsella, S., Naccari, A. & Favaro, M., 1998. Water repellent treatment on the brick wall of the external facade of the Scrovegni Chapel in Padua, in Conservation of Historic brick structure, ed N.S. Baer, S. Fitz, E.A. Livingstone, Donhead Publishing Ltd, pp. 294-310.

Fassina, V., Arbizzani, R., Naccari, A. & Favaro M., 1998. Brick Masonry of the Crypt of San Marco Basilica - evaluation of on-site desalination experiments and laboratory consolidation treatments, in Conservation of Historic Brick Structures, ed. N.S. Baer, S. Fitz and

R.A. Livingston, Donhead Publishing ltd, pp. 407-426.

Fassina, V., 2004. Evaluation of fluorinated polymeric acrylic materials used as stone protective in historical buildings, 5th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Lisbon, April 7-10, 2004, pp. 413-417.

Fassina, V., 2004. Evaluation of multifunctional fluoropolymers ad hoc designed for stoned protection of monuments, 10th International Congress on Deterioration and Conservation of Stone, Stockholm, June 27-July 2, 2004, pp. 503-510.

Fassina, V., 2006. Criteri metodologici di valutazione dei protettivi e risultati di laboratorio sulla sperimentazione delle facciate affrescate di Feltre, in Facciate dipinte: verifiche sui protettivi e metodologie innovative di pulitura a Feltre e nel Veneto orientale, a cura di A.M. Spiazzi, V. Fassina, F. Magani, Il Prato, 2006, pp. 7-14.

Fassina, V., 2008. Il comitato europeo di normativa CEN/TC 346 Conservazione dei Beni Culturali, in La normativa per i Beni Culturali, a cura di G. Alessandrini e V. Fassina, Kermes, Luglio-settembre 2008, XXI, pp. 14-30.

Fort Gonzales, R., Lopez de Azcona, M.C., Mingarro Martin, F., Alvarez de Burgo Ballester, M., & Rodriguez blanco, J., 2000. A comparative study of the efficiency of siloxanes, methacrylates and microwaxes-based treatments applied to stone materials of the Royal Palace of Madrid Spain, Fassina, V., ed., Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, vol. II, Elsevier, pp. 254-243.

Geich, H., 2004. Recent development in protecting facades with silicones, Proceedings of the 10th

International Congress on Deterioration and conservation of Stone, Stockholm June 27-Luly 2, 2004, pp. 363-369.

Grobe, J., Boos, M., Fabis, R. & Gotze, H.J. 1994. Trocknungserhalten hydrophobierter Baustoffe und penetrationseigenschaften siliciumorganisher Steinschutzmittel, Snethlage, R., ed., Jahresberichte Steinzerfall-Steinkonsiervierung 1992, Berlin, pp. 103-112.

Hager, R., 1996. Silicones for concrete protection. Proceedings of the International Congress

Concrete in the Service of Mankind, University of Dundee, Scotland, UK 1996.

Kessler, J. L., 1883. A process for hardening soft limestones by means of the fluosilicates of insoluble oxides. Comptes Rendus, Academie des Sciences, Institut de France, 96, pp. 1317-19.

Knofel, D.K., Hoffmann, D. & Snethlage, R., 1982. Physico-chemical weathering reactions as a formulary for time-lapsing ageing tests, TC 58-VPM Rilem Committee.

Laurenzi Tabasso, M. & Simon, S., 2006.Testing methods and criteria for the selection/evaluation of products for the conservation of porous building materials, Review in Conservation, N. 7, 2006, pp. 67-82.

Lewin, S. Z., 1966. The Preservation of Natural Stone, 1839-1965, an Annotated Bibliography, Art and Archaeology Technical Abstracts, 6, n. 1, pp. 185-277.

Lewin, S. Z. & Wheeler, G.S., 1985. Alkoxysilane chemistry and stone conservation. In Preprints of the 5th International Congress on Deterioration and Conservation of Stone, Lausanne, pp. 831-834.

Many authors, 1963. Building Research Station Digest First Series, Report n. 128.

Many authors, Normal 20/85, 1985, Interventi conservativi: progettazione, esecuzione e valutazione preventive, Raccomandazioni Normal, ICR CNR.

Many authors, UNI 10921, 2001. Natural and artificial stones, water repellents, application on samples and determination of their properties in laboratory, Milano.

Many authors, Commissione Normal, Sottogruppo sperimentazione protettivi 1993 "Metodologia per la valutazione di prodotti impiegati come protettivi per materiale lapideo"-Parte I -Tests e trattamento dei campioni, L'Edilizia, 7, pp. 57-71.

Matteoli, U., 1993. Methodology for the evaluation of stone treatments, Science and Technology for Cultural Heritage, 2, pp. 205-211.

Matteoli, U., Aglietto, M., Fassina, V., Botteghi, C., & Ciardelli, F., 1995. Modulation of structural and stone protective properties of fluorinated methacrylate polymers, International Colloquium on "Methods of evaluating products for the Conservation of porous building materials in monuments, ICCROM, Rome, 19-21 June 1995, pp. 373-388.

Paul, D. R. & Newman, S., 1978. Polymer Blends, Academic Press, New York.

Penati, A., 1993. Protectives for stone materials: the present state of art, Science and Technology for Cultural Heritage, 2, pp. 141-147.

Piacenti, F., 1993. Conservation materials for stone used between the industrial revolution and 1950, Science and Technology for Cultural Heritage, 2, 1993, pp. 161-163.

Piacenti, F., Camaiti, M., Brocchi, T. & Scala, A., 1992. Protection of stone by perfluoropolyethers. Preprints of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, pp. 1223-1230.

Pien, A. & Vanhellemont, Y., 2003. A comparison of European test procedures for water-repellent products, International Journal for Restoration of Buildings and Monuments, 9, n.1, pp. 79-96.

Rossi Manaresi R., 1993. Stone protection from antiquity to the beginning of the industrial revolution, Science and Technology for Cultural Heritage, 2, pp. 149-159.

Sanpaolesi, P., 1966. Metodo di indurimento delle pietre dell'architettura. Istituto di Restauro dei Monumenti, Facoltà di Architettura dell'Università di Firenze, pp. 68.

Sasse, H.R. & Snethlage, R., 1997. Methods for the Evaluation of Stone Conservation Treatments, Saving Our Architectural Heritage: The Conservation of Historic Stone Structures, N.S Baer and R Snethlage eds., pp. 223-243.

Van Hees, R.P.J., 1996. Evaluation of the performance of surface treatments for the conservation of historic brick masonry, in Protection and Conservation of the European Cultural Heritage, Research report n. 7, p. 205.

Von Plewe-Leise, E., Warscheid, T., & Leisen, H., 1996. Studies of Long term behavior of conservation agents and microbial contamination on twenty years exposed treated sandstone cubes, in Riederer, J., ed., Proceedings of the 8th International Congress on deterioration and Conservation of Stone, Berlin, pp. 1029-1037.

Wendler, E., Klemm, D.D. & Snethlage R., 1991. Consolidation and hydrophobic treatment of natural stone, in Baker, J.M., Nixon, P.J., Majumbar, A.J., & Davies, H., eds., Durability of Building Materials and Components, London, pp. 201-213.

Wendler, E., 1997. New materials and approaches for the Conservation of Stone, in Baer, N.S., Snethlage, R., eds., Saving Our Cultural Heritage. The Conservation of Historic Stone Structures, Chichester, pp. 181-196.

Wendler, E., 1995. Treatment of porous building material with water repellent agents-Restoration or Protection? Case studies on efficiency and durability, Wittmann, F.H. Siemes, A.J.M. and Verhoef, L.G.W. eds., Proceedings of the 1st International Symposium on Surface Treatment of Building materials with water repellent agents, Delft University of Technology, Delft, pp. 25/1-25/11.

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