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D3.3. Procedures and application of artificial ageing

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List of definitions & abbreviations

Abbreviation	Definition
HPLC	High Pressure Liquid Chromatography
GC	Gas Chromatography
IR	InfraRed
FTIR	Fourier Transform Infrared Spectroscopy
RTI	Reflectance Transformation Imaging
QUV	Q-Lab Corporation Ultra Violet
UV	Ultra Violet
RH	Relative Humidity
WP	Work Package

Executive Summary

This report summarizes and presents the methodology followed in order to age the materials under investigation *via* artificial accelerated ageing. The materials of interest in the Scan4Reco project consist of paintings from Byzantine iconography and metallic objects (silver and copper) from Medieval and Renaissance metalworks. The document presents the literature and reference sources that describe the rationale behind artificial ageing as well as the most common ageing procedures applied in the fields of interest. On this basis, the ageing procedures to be applied to the historical reconstructions prepared in Scan4Reco and described in D3.2 are selected and described in Paragraph 5.

Table of Contents

List of figures

List of figures

1. Introduction

Among the objectives of the Scan4Reco project, there are the development of a spatio-temporal simulation software for research and visualization porpoises, as well as of a decision supporting system to help in the planning of restoration interventions. To these aims, it is fundamental to achieve a reliable description of the outmost surface structure, appearance, and chemical features of art objects as well as their changes upon weathering. Information on the ageing mechanisms and on the changes the materials undergo with ageing and exposure are to be taken both from the literature and from the application of accelerated ageing procedure to historical reconstructions (mock-ups) prepared in T3.2 of WP3.

1.1 Purpose of this report

This report aims to provide adequate information for the ageing and weathering of mock-up samples of both painting and metals prepared in T3.2 and described in D3.2. During a restoration or monitoring work, a very important need for conservators is to have as much as possible insights into the behaviour of pictorial and metallic materials, including their physical chemical properties, the associated ageing effects and the results of restoration intervention. In their daily activity, scholars usually apply scientific methods to check the surface structure and appearance, as well as to identify the various material properties of surface and underlying layers. People involved in curatorial work and in preservation/conservation tasks need to characterize the state of conservation of an artwork, to classify the level of preservation, and to make predictions about the future. In this scenario, it is of extreme importance to have tools to produce digital representations and models of visual surface appearance and material properties, and to understand how they evolve over time and under particular environmental conditions. To obtain repeatable and reliable data and models and to check the goodness of the developed representation, it is necessary to perform such studies on mock-ups prepared in the laboratory and aged under controlled conditions. This is also pointed out by end-users in the EUR/MC/04 in project’s deliverable ***D2.3. Scientific end-user and public requirements***:

EUR/MC/04	**Inducing changes of surface structure, appearance and chemical-physical properties**	**Important**
The surface of CH assets as well as their chemical-physical properties undergoes changes due to different factors. General factors affecting the surface changes of painting and metal objects are (as ranked by the questionnaire respondents): - Temperature and relative humidity cycles - Restoration procedures (cleaning, application of protective coatings etc.) - Exposure to outdoor environmental agents - Interaction with UV radiation - Chemical reactions with pollutants - Application of coating or over-painting layers The impact such factors have on the CH objects is strongly related to display conditions and to restoration and maintenance operations. Therefore, it is of fundamental importance to provide decision makers with suitable tools to support their exhibition and preservation strategies.		

1.2 Work package interdependencies

This work builds on the work package 3 (T3.1). In the related deliverable D3.1 “Material related booklet” the basic materials under investigation and their properties were described. The review of the properties and the behavior of painting materials of Byzantine icons and of silver and copper alloy Medieval and Renaissance works of art led to the preparation of the respective reference samples (T3.2). Subsequently, the reference samples will be subjected to artificial ageing (T3.3) and simultaneous monitoring of their state in order to collect reference data supporting the extraction of the material specific ageing models (T3.4). Another contribution of the reference data collection is the production of a ground truth dataset for the calibration of the scanning techniques (WP4). Moreover, the reference dataset will be used for training of the simulation algorithms to be developed in WP5.

2. Rationale

2.1 Aims of accelerated ageing

So-called accelerated-ageing tests are carried out for three major purposes [1]. The first is to establish in a conveniently short time the relative ranking of materials, or physical combinations of materials, with respect to their chemical stability or physical durability. The second is to estimate or “predict” long-term behavior of material systems under expected conditions of use. Thirdly, processes of deterioration are speeded up in the laboratory in order to elucidate the chemical reactions involved (the “mechanism” of the degradation) and the physical consequences thereof. Depending on the scope of accelerated ageing, tests can be run under suitable conditions for the purpose. When experiments are conducted for ranking materials, the conditions chosen can be more harsh than normal use ones. For long-term prediction of lifetime, a more careful choice of conditions must be done in order to take into account all the factors affecting the degradation as well as possible synergistic effects. For mechanism studies, it is sometimes convenient to have a single ageing agent or a simplified system in order to make clear the influence of each factor.

The three main factors, which cause weather degradation, are light, heat and moisture. These primary factors can be used to describe the exposure conditions in a broad sense. For every weathering test, in either the laboratory or outdoors, at least one of the three factors plays a role in material degradation. Secondary factors on degradation are those influenced by specific local climatic conditions or special materials property requirements, e.g. stress caused by movement such as expansion and contraction of different substrates.

In the art conservation field, the effort to conduct sensible accelerated-ageing tests can be seen as an attempt in forecasting the effects of certain conservation and restoration treatments. Photochemical and thermal ageing aspects, as well as the effects of other environmental factors such as humidity or outdoor and indoor generated air pollutants, are studied on museum and archival materials.

When running an accelerated ageing experiment, a concern is on the choice of properties to be monitored as indication of the extent of ageing. This is a critical issue since relying on measurement of one chemical property of one particular component of the system to follow the course of ageing can lead to wrong conclusions. Opposing reactions—cross-linking and chain breaking, yellowing and bleaching—can take place concurrently. Hence, there is always the question of whether the particular chemical property chosen will provide a true indicator of the moment when an unacceptable change will have taken place. An important point to be considered in choosing the property to measure is to select one, depending on the objectives, that will either (a) change markedly at a very early stage, (b) change dramatically near the time of failure, or (c) change in a predictable manner throughout the entire useful life span of the material being tested.

When laboratory-ageing tests are aimed at predicting the condition of a material at a future time, it is fundamental to achieve a full understanding of the ageing mechanism, i.e. whether it is linear, slow down, or speed up in time. The basic approach to the problem of nonlinear as well as linear changes in properties with time involves the extensive subject of the kinetics of change (namely, the study of the rates at which reactions occur and the influence of conditions—temperature, humidity, concentration of reactants—on the rates).

When only one principal chemical reaction is responsible for the change being monitored, an interpretation in terms of chemical kinetics often serves rather well. However, when more than one chemical process is going on in the course of ageing, and this is the usual case, one can expect to encounter confusing degradation data. For example, in the action of light on ordinary paper, the lignin component may darken under the influence of ultraviolet radiation emitted by a particular light source. At the same time, another component of the paper, the discolored remnants of the degradation of cellulose and hemicelluloses, may be bleached either by visible or ultraviolet radiation. Alternatively, additional discoloration may occur through the action of temperature and humidity. Thus, both bleaching of certain components and discoloration of others can be going on at the same time. In this situation, the net discoloration measured at any given time will depend on which of these chemical processes is the dominant one under the particular conditions of illumination, temperature, and humidity.

Whenever the particular change in a property (yellowness, fading) is the result of more than one chemical process—and, as stated, most outward manifestations of deterioration are just that—it is logical to expect that a rise in temperature, an increase in humidity, or a change in the relative severity of ultraviolet radiation will not speed up each of the underlying chemical steps to the same extent.

Few degradation processes in the heritage materials follow a zero order kinetics, i.e. have properties changing in a linear manner in time. Cases can indeed be found in which the rate of deterioration is constant, as for example the formation of C9 dicarboxylic acid, a decomposition product in linseed oil paints exposed to ultraviolet radiation. One must always check, however, to verify whether the rate is only apparently linear over the relatively short period of the experiment or whether, if the test were carried out over a much longer period, the rate would be found not to be constant. Situations frequently occur in which a process appears linear but if the very first moments of change are observed, an initial change may be noted that is particularly rapid. The presence of an induction time or a rapid initial process may go unnoticed and this can alter significantly the overall description of the whole degradation mechanism and rate.

As mentioned, when a single, rather well-defined, chemical substance or process is studied, it is usually a relatively easy task to describe the course of its deterioration by a well-known kinetic equation. The fading of dyes in solution, for example, has been extensively studied and repeatedly found to obey first-order kinetics (i.e. a monotonic behavior over time). However, textiles, paints, varnishes, and adhesives represent complex mixtures of substances and one finds that specific chemical constituents and their general physical properties usually deteriorate in a manner that is not constant or even monotonic from time zero up to the point where all useful properties are lost. Most materials tend to deteriorate in stages, which may often be considered in terms of specific chemical-process steps designated as initiation, propagation, and termination reactions. There may also be specific subsidiary reactions such as inhibition or chain transfer in free-radical processes. In the alkaline degradation of oxidized cellulose, a “chain-stopping” chemical reaction has long been known.

Because substances tend to deteriorate not in a linear fashion, it is important, in designing and conducting accelerated-ageing tests, that the character of the overall pattern of changes in physical properties or specific chemical substances with time be determined up to the point of failure.

2.2 Artificial vs. natural ageing

In many cases, durability of materials and their behavior are tested under natural ageing conditions by exposing them outdoors or indoors in the proper environment where they are supposed to be in their lifetime. However, it is often necessary to determine more rapidly the effects of light, heat and moisture on the physical, chemical and optical properties of materials with artificial accelerated weathering or artificial accelerated irradiation exposures that use specific laboratory light sources. Exposure of materials in laboratory ageing devices are conducted in more controlled conditions than found in natural conditions and are aimed at both studying the effect of single weathering factors and accelerating material degradation and product failure. Relating results from accelerated weathering or artificial accelerated irradiation exposures to those obtained in actual-use conditions is difficult because of variability in both types of exposure and because laboratory tests do not reproduce all the exposure stresses experienced by materials exposed in actual-environment conditions [2]. In addition, the increase in rate of degradation by the accelerated test compared with natural exposure conditions varies with the type of material and its formulation. No single laboratory exposure test can be considered as a total simulation of natural exposures. These vary on a broad range depending on differences in solar radiation, time of wetness, temperature, pollutants and other factors. Therefore, even if results from specific accelerated weathering are useful for comparing the relative durability of materials exposed in a particular location and for understanding the weathering mechanism, it cannot be assumed that they are useful for determining the durability and the ageing behavior of materials in their exposure conditions. In other words, it is not trivial to satisfactorily demonstrate the correlation of the behavior under accelerated and normal conditions [3]. Many elaborate mathematical treatments have been applied to determining how well the results of accelerated ageing tests correspond with the behavior of materials during outdoor ageing [4]. However, examples of extensive data on indoor ageing under normal museum or outdoor conditions that correlate with accelerated tests are extremely rare. Even though it is very tempting, it is invalid to assign to all materials a “general acceleration factor” relating x hours or megajoules of radiant exposure in an ageing device to y months or years of actual exposure.

Acceleration factors are material-dependent and can differ significantly for each material and for different formulation or combination of materials. Moreover, acceleration factors calculated based on the ratio of irradiance between a laboratory light source and solar irradiation do not take into consideration the effects of temperature, moisture and differences in spectral power distribution between the laboratory light source and solar radiation. The very frequent cycling between high and low specimen temperatures as well as unrealistic levels of moisture in the accelerated tests can produce effects that do not reproduce the actual effects of natural exposure (conditions of overstress can lead to a different mechanism of change). The absence of biological agents as well as of minor pollutants can also lead to unrealistic ageing. Even though many different accelerated ageing procedures and evaluation methods have been proposed in the past for predicting the stability and the behavior of various kinds of materials stored under ambient conditions, this kind of approach is now very debated. For example, the assumption that elevated ageing temperatures only accelerate the reactions responsible for natural ageing, without altering significantly their nature, which was the base of many past studies, has been abandoned.

Acceleration factors determined for a specific formulation of a material are valid but only if they are based on a sufficient number of separate outdoor and indoor environmental tests and accelerated weathering exposures so that results used to relate times in each exposure can be analyzed using statistical methods. Despite the above-mentioned problems and limitations of artificial ageing tests, they are indispensable to estimate the life expectancy of materials or at least to rank their relative stabilities.

3. Artificial ageing: requirements and state of the art

Although artificial ageing tests have been used as a general research tool in the past decades, several questions regarding the practical aspects remain, as these tests have proven to have a number of intrinsic problems which have to be considered both when designing the trial and its analysis, and when estimating the significance and accuracy of the results [5].

As stated above, the main factors affecting ageing and weathering of material are light, heat and humidity. Therefore, these are the three parameters that are most often controlled in accelerated ageing devices. Sunlight, particularly the ultraviolet portion of the solar spectrum is very frequently responsible for the initiation of weathering degradation. The shorter wavelengths possessing higher photon energies are more strongly absorbed in most organic materials, and have a greater potential to break chemical bonds in those materials. In some cases, materials do not absorb short wavelength light, the absorption, however, can occur through the impurities and additives present in the material. To simulate a particular environment, knowledge on the distribution of the wavelengths present and their intensities is paramount. Sunlight varies in intensity and spectral energy distribution, with season, location and atmospheric effects such as aerosols or pollutants. Accelerated test conditions must be consistent with real exposure conditions in order to apply to the development and application of a prediction model. The photodegradation of organic materials is a result of the absorbed radiant energy causing scission of chemical bonds and subsequent formation of reactive groups; the short wavelengths available in the UVB region of many light sources can break bonds with higher energy than can the wavelengths found in sunlight. Therefore, the absorption of short wavelengths that do not exist in sunlight and the degradation they produce may ultimately lead to alternative chemical degradation pathways [6]. In addition, if there is a deficiency in a wavelength when compared to sunlight, a similar type of effect may occur. Light sources available on the market consist mainly of xenon arc, carbon arc and fluorescent.

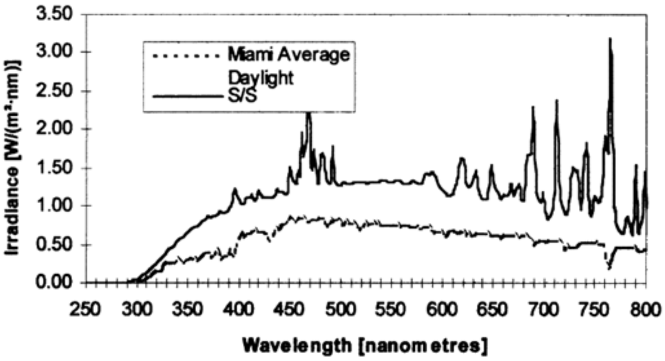

Figure 1*:* Xenon arc with borosilicate inner and outer filters vs miami, average optimum daylight.

For most applications, the xenon arc spectrum modified with specific filters gives a good simulation of sunlight. Figure 1 shows the xenon arc spectrum and its relationship to the sunlight spectrum [7].

Other kind of lamps of common use are fluorescent UV ones. Fluorescent UVA lamps are available with a choice of spectral power distribution that vary significantly. UVA 340 has actual peak emissions at 343 nm and mostly applies to the short and middle UV wavelength region of the daylight (Figure 2). UVA 351 lamps is peaked at 351 nm and is used for the short and middle UV wavelength region of the daylight, which has been filtered through a window glass (Figure 3).

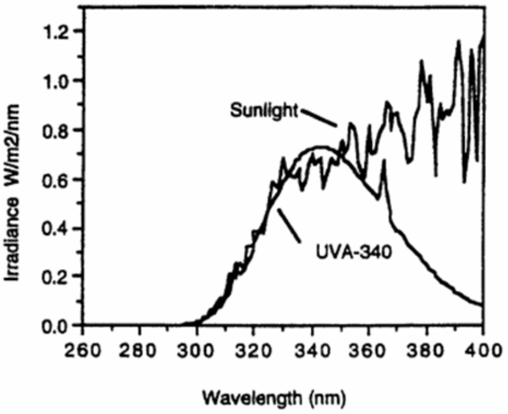

Figure 2.Spectral power distributions of UVA - 340 lamp and sunlight.

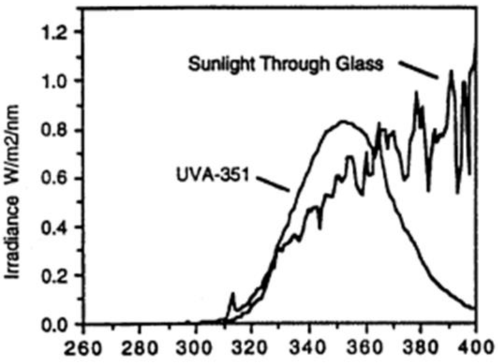

Figure 3. Spectral power distribution of UVA 351 lamp and sunlight distribution through window glass.

Two factors are of main importance when selecting a light source for accelerated testing. Firstly, the spectrum should at best have a cut off at the same or very similar wavelength to that of the actual exposure environment, since short wavelengths present in an artificial source can induce unnatural chemical degradation and provide an erroneous test result. In addition it is also desirable to make sure that the full sunlight spectrum is simulated. Secondly, the intensity of the irradiance level should be controlled and maintained at the set level. The ‘average optimum daylight’ for Miami, a spectrum often used as reference, has been measured using a spectroradiometer. Measurements were made at periods throughout the day at the spring equinox, and the average data was taken. If the *Miami average optimum daylight* curve is used as a baseline reference for sunlight, a setting of 0.35 W/msq/nm can be used to simulate sunlight intensity. Acceleration of photodegradation has been achieved by even further increase the irradiance level, however it has been found that this acceleration technique may also lead to unnatural chemical degradation if the level is too high.

Many sources emit radiation that does not have the same range or distribution of wavelengths as that found in daylight. The visible and ultraviolet radiation in the sunlight that reaches the earth has little energy in wavelengths shorter than about 290 nm; when this passes through ordinary window glass, little below 315 nm is present [1 and references therein]. Hence, in studies related to museum problems, wavelengths below 315 nm are generally inappropriate.

The question regularly arises concerning just how much the rate of photochemical deterioration can be speeded up by various light sources while at the same time satisfactorily reflecting the behavior that occurs under normal conditions of use. This issue has led to the shared statement that “the degree of correlation between natural and artificial ageing seems to be inversely related to the degree of acceleration” [8].

Some researchers suggest that an acceleration factor of five to ten times would represent an acceptable level [9] and that the ultraviolet intensity should “not exceed more than three times the standard solar intensity in a given climatic zone” [10].

Many accelerated-aging tests expose samples continuously to lamp emission, whereas under natural conditions exposure takes place under alternate periods of daylight and darkness. The conditions of continuous exposure produce different results from those observable under alternating conditions, even if this aspect of testing is not very clear [1 and references therein]. In fact, an increase in sample temperature caused by intense and continuous illumination tends to lower the moisture content of samples. The result would be that, for a given number of milliwatt x hours of exposure to alternating light and dark, the average moisture content of the samples would be higher than under conditions of constant illumination. Fading or other photochemical damage is often dependent upon moisture content. Another way in which alternating conditions can seriously affect the results is if expansion and contraction play an important part in the change of physical and mechanical properties of the samples.

Another important factor of acceleration is heat. To get comparable conditions of heat, a frequently reported parameter is the ‘Black Panel Temperature’ that theoretically represents the maximum surface temperature achieved during exposure. The most commonly used outdoor black panel sensor is a black coated steel panel with a thermocouple fixed to either the front or the back of the panel. Some black panels are constructed using resistance temperature detectors. The primary function of the black panel in a weathering device is to be used to control the temperature in that device and to set it to reproduce actual exposure conditions. This more realistically describe the specimen condition than if the ambient temperature were used.

The presence of water may be necessary for some degradation reactions to occur, depending on the material being tested. Water causes damage to materials by both physical and chemical processes. Absorption of water into a material, from humid air or surface deposition causes a volume expansion causing stresses within the material. A wet period followed by a dry period then causes a volume contraction of the surface layers setting up more stresses within the material. Cycling of such stresses can eventually result in fatigue, setting the stage for further chemical and mechanical change or degradation. In the case of metal surfaces, water promotes the onset of corrosion reactions. Water may be delivered to the surface of a specimen in several forms; water represented as relative humidity; rainwater; water formed at the surface of the specimen as dew or condensation. In accelerated weathering, water is applied to the panel in similar processes. Relative humidity should be controlled at the appropriate level. Spray cycles may be used to simulate rainfall, and condensation may also be possible depending on the desired simulation.

Apart from the three environmental agents, light, heat and water, gaseous and saline pollutants can play a fundamental role in degradation, as well as particulate matter. Gas air pollutants of importance for degradation are SO_2, NO_x, HCl, HF, O_3, as well as H_2SO_4, HNO_3. Dry and wet depositions are the processes for bulk transportation of the pollutant to a surface. When gaseous and particulate species accumulate directly on a surface this is called dry deposition. Wet deposition is when the pollutants are incorporated into a cloud droplet form and then deposited as falling precipitation. Gas concentration and wind velocity are two of the main factors that affect the interaction of gaseous pollutants with the exposed surface, but also other factors are important, such as the wetness time. For example, the SO_2 deposition on to a dry calcareous stone is dependent on humidity but is also an order of magnitude smaller than deposition onto a wet surface [11]. The cause of this is probably the transportation of the soluble product away from reaction sites leaving a ‘fresh’ surface for further reaction. This indicates the importance of time of wetness when formulating models and damage functions for material degradation. The time of wetness has to be measured, or calculated from the frequency and duration of actual rain events.

In the presence of multiple pollutants, synergistic interactions may occur. For example, SO_2 and NO_2 degrade calcareous materials individually but when combined the effect is greater than the sum of the individual degradation rates [12]. Care must be taken in relating environmental data directly to degradation rates when the mechanisms are not fully understood.

4. Artificial ageing procedures

In order to set properly the artificial ageing experiment of the materials tested in Scan4Reco (paints, metals and coatings), the main ISO standards for paints, varnishes and metals are reviewed in the following. Despite these rules have been set for industrial checks and comparison of the performance of different in-service materials, they can provide useful recommendations on the setting of an accelerated ageing experiment aimed at pretending the actual ageing of heritage materials in their regular display conditions. Many scientific papers in the conservation science field deal with accelerated ageing of painting materials, metals and coatings. These papers are mostly aimed at reproducing accurately the features of naturally aged objects of art in order to understand the factors affecting their degradation/ageing, to test new analytical techniques for their investigation and to develop new restoration/preservation strategies. Some papers have been selected among the most significant ones and the ageing procedures that the authors have applied are summarized herein.

The ISO standards and the literature references will guide the selection of the ageing procedures for the Scan4Reco project.

4.1 Procedures of artificial ageing for painting materials

The main guidelines for the application of artificial ageing for painting materials are to be found in two basic ISO standards, i.e. ISO16474-1:2013 Paint and Varnishes-Methods of exposure to laboratory light sources-Part 1:General guidance, and ISO16474-2:2013 Paint and Varnishes-Methods of exposure to laboratory light sources-Part 1: Xenon-arc lamp**.**

In the mentioned ISO standards, specimens are exposed to laboratory light sources under controlled environmental conditions. The ISO 16474-1 deals with the requirements for laboratory exposure devices (see paragraph 3 of this report), the form, number, size and preparation of mock-up samples, the test conditions and procedure, the periods of exposure and evaluation of results. The standard indicates that a careful exposure must take into account irradiance, temperature, humidity and moisture and gives some specifications for them.

Ageing encompasses a set of physiochemical process that paintings undergo within months to years of their making. Initially, the paint, which is a mixture of pigments in a binder or a mixture of binders, undergoes drying, which leads to the formation of a polymeric matrix. Longer-term ageing leads to various different phenomena, and these have been studied extensively on easel and panel paintings [13 and references therein]. In lipidic binders, the most commonly observed process is the oxidative degradation of un-saturated fatty acids, resulting in the formation of mono- and di-carboxylic acids with varying chain lengths. The smaller acids and glycerol evaporate from the surface of the paintings, while the longer-chain di-carboxylic acids form 3D polymeric networks with the pigments, with the mono-carboxylic acids acting as terminal groups. This phenomenon of cross-linking strengthens the paint layer and prevents its breakdown. However, depending on environmental conditions, the mono-carboxylic acids can form soaps with lead pigments, which migrate to the top layer and frequently form protrusions. The hydrolysis of polysaturated triglycerides is known to happen over a time-span of 50–100 years, and, in the advanced stages of degradation, lead soaps form semi-crystalline structures, which eventually flake off. In general, degradation processes cause paint films to become thinner and more transparent to light, which is then absorbed by the support layer, making the painting appear darker.

Compared to their lipidic counterparts, the ageing of proteinaceous binders is a lot less well understood. Colombini et al. [14] carried out extensive analysis on proteinaceous binders using HPLC and GC in conjunction with UV–visible or IR spectroscopy. These authors found that the composition of the fresh and aged proteinaceous binders did not vary significantly and this is the main reason for the scarcity of literature on artificial ageing on protein-based media. However, on ageing, these binders form cross-linked polymers with the cations from the pigments.

While proteinaceous binding media are observed to be relatively stable, not much work has been done to understand their ageing. Manzano et al. recently carried out studies on mixtures of lipidic paint binders using Raman spectroscopy and chemometrics [15], during which they identified a need to study the ageing of proteinaceous binders, but observed no systematic chemical changes under accelerated ageing with UV light. In their work, these authors focused on the evaluation of the accelerated ageing process – represented by the UV light exposure – of proteinaceous binding materials in simulated pictorial samples both when proteins were single and when they were in a complex matrix. The painting materials chosen for the study (gypsum, egg albumin, jersey cow casein, rabbit epidermis collagen, linseed oil, white lead pigment and terpenic resin) were representative of proteinaceous and lipid binders, inorganic pigments and varnish used for many years and throughout historical epochs. They used for accelerated test a high-speed exposure unit SUNTEST CPS, Heraeus, equipped with a Xenon lamp; a special UV glass filter was used for limiting the radiation at wavelengths greater than 295 nm, corresponding to outdoor solar exposure. Irradiance was set at 765 Wm^{-2}, and the maximum and minimum temperatures of the samples were maintained between 30–35 °C and 15–20% relative humidity.

In a paper aimed at assessing the capability of microspectrofluorometry to identify and distinguish between different binding media used in works of art, by investigating their endogenous fluorescence properties in the presence or in the absence of mineral pigments, Matteini et al. [16] prepared mixtures of different binding media (animal glue, whole egg, defatted milk and linseed oil) with several pigments and laid the mixtures onto microscope glass slides. Accelerated photo-ageing of these specimens was conducted for a 600 hours period using a Xenon lamp equipped with an "outdoor filter" ($\lambda > 280$ nm) for simulating outdoor exposure (Solarbox 3000e, Co.Fo.Me.Gra, Milan, Italy) and fixing the BST (Black Standard Temperature) at 40 ◦C. The stressing conditions used in these two works account for their aim to induce changes that the analytical technique tested should have discriminated. None of them tried to reproduce actual exposure conditions for painting that is museum or church environment.

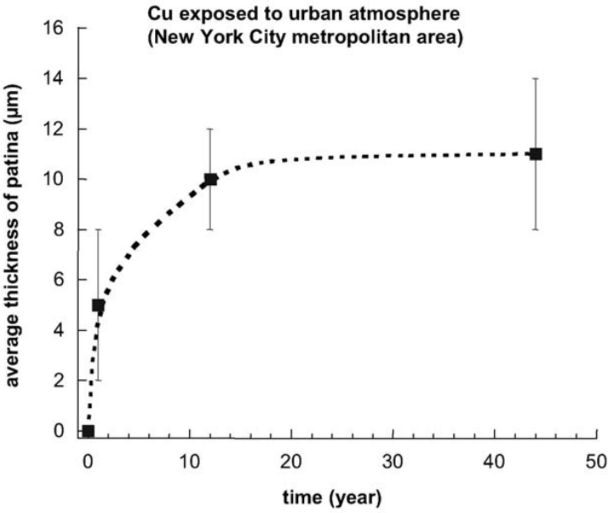

Figure 4: time corrosion curve (average penetration) (from J.P. Franey, M.E. Davis, Metallographic studies of the copper patina formed in the atmosphere, Corrosion Science 27 (7) (1987) 659–668.)

In general, the data in the literature highlight that, in the absence of particular stressing conditions or photosensitiving agents, proteins are relatively stable to oxidation with respect to other painting materials such as lipids and terpenic resins, and that their alterations are often more ascribable to the action of humidity and to the effect of cleaning procedures with aggressive alkaline solvents. However, photoxidation processes involving free radicals formation, have been reported to affect the most sensitive amino-acids, his, met, tyr, cys, lys, ser, and in particular trp [14 and references therein]. Moreover, physical changes, such as, swelling or shrinkage phenomena, due to variations of humidity and temperature, can cause loss of adhesion and cohesion of the paint film.

In the museum field, photochemical damage is often assessed by measuring the surface color change resulting from light exposure. Data on the rate of fading caused by a particular light source over a relatively long time period were extrapolated to suggest a rough order-of-magnitude extent of change over the shorter time of exposure to photoflash. This approach builds on the assumption that the reciprocity principle is applicable.

The physical basis for the reciprocity principle is that the determining factor responsible for change is the total amount of energy absorbed by the object rather than the rate at which the energy is absorbed. Using this principle, the same extent of fading should occur, for example, if an object is illuminated at 5 lux for 100 hours or 50 lux for 10 hours. Some experimental results [17], however, indicate that reciprocity failure occurs with the use of high-intensity lamps during accelerated-aging trials.

Most inorganic pigments are acknowledged to be very light stable, with a few well-known exceptions that include vermilion, lead(II) oxide, lead chromate, Prussian blues, and some copper greens [18 and references therein].

For example, the darkening of vermilion is due to conversion of the pigment from one crystalline form to another, and/or to the presence of certain inorganic salt impurities. Well-made vermilion would resist change in a carbon-arc Atlas Fade-Ometer for more than 600 hours, whereas some brands change significantly in less than 100 hours. For Prussian blue, the composition of the pigment appears to have been rather variable and its durability to have varied as a result. It has been rated moderately durable when tested by exposure to five hundred hours of summer sunlight, or durable when exposed to six months of 104 lux radiation from daylight fluorescent tubes.

Fluctuating relative humidity and temperature stress materials also from a mechanical point of view. RH variations are mostly responsible for many damages [18]. A change in RH may cause warping, splitting, delamination and other dimensional changes in moisture-absorbing, or hygroscopic, materials (wood, ivory, skin and other organic materials). Seasonal slow drifts, allowing slow equilibrium, are less harmful than abrupt changes. Of course, the extent of damage depends on the material and sometimes which part is exposed. In some display conditions, the surfaces may feel daily changes, causing stress within the structure. Few museum objects respond significantly to fluctuations under an hour in duration. Many objects take days, weeks or even months to respond. Because of the long time required for many organic materials to reach moisture equilibrium with their environment, seasonal cycles may be the most important operative cycles, but small RH fluctuations can lead to fatigue in materials. For some materials, each cycle causes tiny fractures to grow. Deterioration increases as cracks are opened further. The amount of mechanical damage is directly related to the type of material, the constraint on the material and amount of RH change. Small changes cause small effects. If tension climbs in a constrained material it eventually reaches a breaking point. For example, wood needs room to expand and contract when RH fluctuates. If a wood panel is nailed into a frame, it will split. If it is placed in a groove, without glue, with space for expansion and contraction, it probably will not crack.

4.2 Procedures of artificial ageing for metals and their coatings

Since the corrosion of metals is a very important issue which has significant economic consequences for industry, many studies exist that are aimed at understanding the mechanism of corrosion in different environments and the performance of different protective coatings. A review of the most significant publications that deal with ageing metals is presented herein, with a particular focus on metals in the heritage field.

4.2.1 Copper alloys

Bronze art works may exhibit complex and heterogeneous corroded structures, depending on the composition and the microstructures of bronzes, the corrosivity of the environment, and other factors. The formation process of bronze patinas in natural environments is mainly related to the decuprification phenomenon, the selective dissolution of copper, connected to an internal oxidation of the alloys. The main factors affecting the alteration phenomena of outdoor bronzes are the following:

External factors:

- Chemical composition of the atmosphere
- Humidity as moisture or rain (promoting factor)
- Sun irradiance (effect of UV and temperature)
- Exposure to other environmental agents, like wind

Internal factors:

- Type of metal or alloy
- Type and structure of corrosion products
- Casting defects
- Exposure of the different portions of the object

In a not polluted environment, the reaction of oxygen with the metal surface forms a thin and compact reddish oxide (cuprite) that tends to form a film well adhering to the metal. It provides a sort of protection to the underlying metal (dry corrosion). When the moisture content is low and a thin (10-100 Å) and discontinuous water film occurs on the surface, cuprite can be transformed into basic carbonates, like malachite. Malachite and other carbonates form green patina with a protective action. The electrochemical corrosion, however, is the main mechanism through which water acts (wet corrosion), with the formation of batteries.

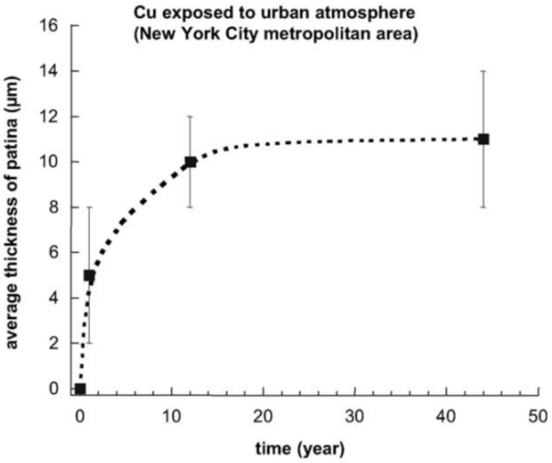

Figure 5. Time corrosion curve (average penetration) (from J.P. Franey, M.E. Davis, Metallographic studies of the copper patina formed in the atmosphere, Corrosion Science 27 (7) (1987) 659–668.)

The objects in their environments reach a steady-state regime, i.e. the thickness of ancient bronze alteration layer is not a function of the time of exposure. This is confirmed by comparing long-term corrosion tests on copper and copper-base alloys exposed in different natural corrosive environments with archaeological samples. The average penetration of the corrosion with respect to time of exposure follows globally a parabolic law (Figure 4) in a great number of natural environmental conditions.

The aspect of an outdoor weathered bronze sculpture is affected by many factors. The early formation of a cuprite layer can provide a certain protection and slow down the corrosion. On the other hand, a corrosive process, which produces green soluble corrosion products, leads to the formation of a non-protective layer. These compounds can be solubilized and produce an electrolyte solution on the surface. A sculpture conserved outdoor for at least two decades show on the surface alternate patches and strips of dark and light green. These areas are related to variable grades of the surface, presence of undercuts, sheltered areas and fully exposed areas.

To sum-up, on outdoor bronze sculptures the following situations are observed:

1. Black and smooth surfaces, sometimes with brownish or green aspect, representative of the original bronze surface, with an underlying cuprite layer. They are composed of cupriet and atacamite;
2. Thick black crust overlapping a light green layer and a cuprite layer. The black crust contains soot. It is composed of quartz, atacamite, paratacamite, feldspars and sometime copper hydroxysulphates;
3. Orange or brown cuprite layer (in recent sculptures). Orange strips are also present, due to the leaching of the alteration layer with the solubilisation of the outer layers;
4. Black areas surrounded by light green corroded areas (Figure 5).

5. Corroded rough areas with light green color. These areas are hit by the rainfall or are vertical portions exposed to strong winds. They are composed of cuprite and brochantite (copper hydroxysulphates).

Figure 6: Black and light green areas.

Because of all the aforementioned reasons, the bronze and brass outdoor heritage objects are usually protected to slow down the corrosion rate.

Accelerated corrosion conditions are used to test how the alloy composition and the protective coating properties affect the behaviour of outdoor protected and unprotected bronze surfaces. Since it has been shown that in real outdoor bronze monuments, the corrosion behaviour is strongly influenced by the exposure geometry (sheltered and unsheltered areas with respect to the action of rainfall), it is necessary to simulate both sheltered and unsheltered conditions. Different devices have been developed to simulate outdoor conditions in the laboratory. Each of them presents limitations and drawbacks and is designed in order to reproduce particular aspects of the corrosion process, like the leaching action of the rain and the effects of stagnant water.

The oldest and most wildly used method for laboratory accelerated corrosion testing is maybe the continuous neutral salt spray test. Although used extensively for the purposes of qualification testing, results from continuous salt spray testing seldom correlate well with in-service performance. Combining salt spray exposure with humidity cycling between a high humidity level and a low humidity level (wet and dry cycling) results in a better correlation with in-service performance at normal outdoor conditions of metal surfaces. A number of cyclic accelerated corrosion tests based on this principle have been developed and standardised. The complexity of such tests, however, varies and so the requirements on test equipment. To get better control of the factors determining the rate of corrosion and relevance to in-service corrosion performance advanced systems have come into use. Certain air pollutants as sulphur dioxide, nitrogen dioxide, hydrogen sulphide, and chlorine present in air as trace substances promote corrosion of metals under high humidity conditions and need to be taken into consideration in the evaluation of corrosion resistance of products that are especially sensitive to corrosion failures such as electronic devices. High humidity exposure tests in the presence of such air pollutants are therefore frequently used in the qualification of electronic products with respect to corrosion resistance. Corrosion effects may appear at air volume fractions of pollutants less than of 10^{-6} . The conduct of air pollutant corrosion tests, therefore, requires very special kind of test equipment. Moreover, mixtures of polluting gases are often used to simulate synergistic effects. Condensation tests are often used for the testing of organic coatings because they may induce damage caused by swelling and out-leakage of additives.

An important reference is the ISO/TR 16335 technical report *Corrosion of metals and alloys – Corrosion tests in artificial atmospheres – Guidelines for selection of accelerated corrosion test for product qualification.* It is applicable for the selection of suitable accelerated atmospheric corrosion tests for qualification of products with metallic materials without or with permanent corrosion protection or temporary corrosion protection. The main purpose of this technical report is to present a framework for comparing the different accelerated corrosion test methods, which presently are available as international standards. The suitability of a test method varies with the requirements set by the intended application of the product. The methods listed in the report include: continuous salt spray tests, tests with alternating immersion of test objects in a salt solution followed by drying or intermittent salt spraying and drying, tests with cyclic variation of humidity (dry/wet) and including also steps of salt spraying, tests with continuous exposure to atmospheres with low concentrations of corrosion promoting gases and at moderately high humidity, tests with continuous exposure to atmospheres with higher concentrations of corrosion promoting gases and at higher humidity including also steps of drying and short period of salt spraying, high humidity test. There is increasing trend to use cyclic tests since their results – mainly the type and character of degradation- are similar as in various natural conditions. The most relevant cycling tests that applies properly to metals and alloys as well as to organic coatings on them involve the exposure to humidity and to salt spraying (ISO 14993, ISO 16151, ISO 16701, ISO 21207) [19]. The ISO 14993 involves cyclic exposure of test specimens to a mist of salt solution, to drying conditions, and to periods of high humidity It reproduces the corrosion that occurs in outdoor salt-contaminated environments. The specimens are sprayed with a NaCl solution (50 g/l, 35°C) during two hours. Then a phase of dry conditions follows, where the specimens are kept at temperature = 60 °C and relative humidity < 30 % RH for 4 hours. The third phase is exposure to wet conditions (Temperature = 50 °C Relative Humidity > 95% RH) for two hours. The specimens are supported in the rack 20° to the vertical.

The ISO 16151 specifies two test methods A and B, which involve cyclic exposure of test specimens to a mist of acidified salt solution, to drying conditions, and to periods of high humidity. Method A applies to metals and their alloys, and organic coatings on metallic materials. Times and conditions do not differ from those of ISO 14993, but for the fact that the salt solution is acidified down to pH=3.5.

The ISO 16701 refers to accelerated corrosion test involving exposure under controlled conditions of humidity and intermittent spraying of salt solution. The method is especially suitable for comparative testing in the optimization of surface treatment systems. It is recommended to simulate corrosion on open surfaces. It includes many steps:

Step 1) Exposure at 35 °C and 95 % RH for 4 h.

Step 2) Exposure at 35 °C to a linear reduction of relative humidity with time from 95 % RH to 50 % RH over a total period of 2 h.

Step 3) Exposure at 35 °C and at 50 % RH for 4 h.

Step 4) Exposure at 35 °C to a linear increase of relative humidity with time from 50 % RH to 95 % RH over a total period of 2 h.

Step 5) Spraying of the test objects inside the climate chamber at 35 °C with a sodium chloride solution (concentration 10 g/litre and pH = 4,2) at a linear downward flow rate of 15 mm/h for 15 min.

Step 6) Exposure at 35 °C for 1 h 45 min with the relative humidity set point at 95 % - 99 % RH in such a way that the test objects remain wet.

The ISO 21207 describes two cyclic corrosion test methods involving a short period of neutral salt spray testing, followed by drying and a longer time of exposure to an air flow containing corrosion promoting gaseous pollutants and high humidity. The methods are intended for use in assessing the corrosion resistance of products with metals in environments where there is a significant influence of chloride ions, mainly as sodium chloride from marine sources or by winter road de-icing salt, and from corrosion promoting gases from industrial or traffic air pollution. One method in the standard includes a) neutral salt spray testing (for 2 h in a mist of a salt solution containing a mass fraction of 5 % of sodium chloride at 35 °C, followed by drying for 22 h in a standard laboratory climate, and b) exposure for 120 h in a test atmosphere containing a mixture of corrosion promoting gases, (NO_2 + SO_2) at a relative humidity of 95 % and at a temperature of 25 °C, followed by drying for 24 h in a standard laboratory climate.

The above-mentioned standards and guidelines are especially developed for testing materials for industry and setting comparative tests in particularly harsh environments where metallic parts are in service. Nevertheless, they can provide useful indication to set conditions for accelerated weathering of metals and alloys of interest in the heritage field. In the most relevant scientific literature on metallic heritage, many variations are proposed for the ageing of metal specimens that focus on different degradation factors.

In [20], Chiavari et al. develop the dropping test method, where the atmospheric exposure is simulated through a cyclic exposure of the alloy to a precipitation runoff with an artificial rain periodically dripped on the sample. It means that this test simulates a severe runoff condition with a solution reproducing natural acid rain.

The device consists on a support inclined at 45° where the samples are mounted. The support is pierced in order to pass pipes carrying the artificial rain using a pump system. The leaching solutions are collected under the support and then analyzed. A synthetic rain containing the same quantities of the main inorganic and organic ions as in natural rain of a particular site and in a particular time of the year is usually used.

In [21], the authors propose a comparative study between naturally exposed bronze specimen and artificially aged ones. The ageing technique consists of wetting and drying cycles where the specimens were periodically dipped (no run-off is taken into account in this study, i.e., the specimens were cyclically immersed in the same weathering solution at each cycle) either in synthetic or in natural rain: 50 min of immersion, 10 min of drying. The device is made of glass cells, each made up of two interconnected cylindrical chambers. In the first chamber, the suspended specimens do not touch each other, neither the cell walls. A timer regulates a compressed air flux pulling the solution alternatively into the two chambers. The volume of the ageing solution is 0.6 L in each cell. The weathering periods had a maximal length of 40 days for each series of tests. Each test was performed at room temperature. An example of composition of synthetic rain is Cl^- (1.27mg/L), NO_3^- (4.64mg/L), NH_4^+(1.06mg/L), $SO_4^{=}$(1.9mg/L), $HCOO^-$ (0.05mg/L), CH_3COO^- (0.23mg/L), Na^+(0.53mg/L), Ca^{2+}(0.34mg/L), pH = 4.25. Even though the authors introduced some more components (i.e. organic compounds) into the formulation of the synthetic rain in an attempt to reproduce better the weathering behaviour of an outdoors bronze, the results showed slightly different corrosion behaviours in the exposure to both natural and synthetic rain. The natural rain seems to have a composition that favours the growth of a more passivating film, thinner but more uniform than the film grown in the artificial rain. This very accurate study provides a meaningful example of the difficulty to achieve a good laboratory reproducibility of the corrosive conditions determined by a natural acid rain.

In [22], the influence of different exposure conditions, i.e. stagnant and leaching acid rains, are reproduced on bronze specimens by using the following protocol: stagnant conditions, which simulate sheltered areas on the sculpture, are assessed by wet/ dry test, during which the coupon is cyclically immersed in stagnant artificial rain. Rainfall runoff conditions, simulating unsheltered areas on the sculpture, are assessed with the DROP test, during which artificial rain is periodically dripped onto the metal surface of the coupons. The overall duration of the test is 30 days. In this work, a good agreement was found between the results obtained from laboratory tests and those obtained from real samples.

A further interesting experiment is described in the report WEATHERING OF TREATMENTS FOR BRONZE CONSERVATION Results of natural and artificial weathering Work performed for the European Project ARTECH – Access, Research and Technology for the conservation of the European Cultural Heritage [23]. Aim of the work presented here was the study of different protective coatings for bronzes. Due to the different nature of the treatments under study the artificial weathering had two parts: (I) UV radiation exposition to promote degradation of treatments and (II) a salt solution exposition in a salt fog chamber to promote corrosion. In the first part of the procedure, UV exposure was carried out according to the standard EN ISO 11341 in a Xenon-arc radiation chamber, for the second part, a salt spray chamber was used for the acid salt solution exposure, following the standard ISO 9227 exposure conditions definition and the sprayed solution had the following composition: NaCl (0,5 g/L + $(NH_4)_2SO_4$ (3,5 g/L), with a pH close to 4,5 in order to be approximated to the urban rain water composition. The treated samples were exposed alternatively to the UV radiation and to the salt solution, for periods of two weeks in each test chamber, till having reached a total of 2000 h of exposition.

4.2.2 Silver Alloys

Atmospheric corrosion of silver occurs in the presence of moisture, since the water layers adsorbed on the surface provide the medium to adsorb atmospheric gases. Gases that can be involved in indoor atmospheric corrosion can be O_2, O_3, H_2O_2, H_2S, COS (carbonyl sulphide), SO_2, HCl, Cl_2, HCHO, HCOOH and CH_3COOH. Sulphides, both in the form of H_2S and COS, are the most harmful pollutants to silver objects, the concentration in the environment that attacks silver being very low, to the extent of 0.2 ppb. The tarnishing reaction mechanisms are:

$$8Ag + 4HS^- \leftrightarrow 4Ag_2S + 2H_2 + 4e-$$

$$0_2 + 2H_2O + 4e- \leftrightarrow 4OH^-$$

Typical indoor levels for hydrogen sulphides (50-100 ppt) and carbonyl sulphides (300-500 ppt) are enough to cause tarnishing, the rate of which is increased as the RH and the level of other pollutants (i.e. NO_2, O_3, Cl_2) rise. Their synergistic effects are, however, small in typical concentrations of the gases. Silver chloride is also found as a corrosion product of silver. Chlorine gas and sodium chloride react with silver to produce silver chloride.

In a very comprehensive paper [24], Reedy et al. tested three coatings commonly used for protection of silver artefacts housed indoors (Agateen, Paraloid B-72, and Paraloid B-48N) and ranked their performance. The authors developed ageing protocols to be relevant to conservation practice, while also incorporating industry testing techniques. A variety of test specimens were used to check for effects of complex geometry and silver alloy composition, and to measure changes occurring on the silver beneath the coatings as well as changes of the coatings themselves. Accelerated test methods were used to compare the relative merits of the three coatings in their ability to protect silver substrates against corrosive pollutants typically found in museums and historic houses. Since objects in museums and historic houses are not normally exposed to high levels of UV light, but rather are more likely to be exposed to elevated temperatures and high humidity, these tests combined the latter destructive factors. The most common environmental pollutants, which are off-gassing products in storage or display case materials may affect coated metals. Therefore, the tests included exposure to common indoor pollutants such as hydrogen sulfide, sulfur dioxide, ozone, formaldehyde and acetic acid. Two chambers were used, one for a wet environment and one for a dry environment; a movable sample holder was constructed so samples could easily be rotated between the two chambers minimizing the handling. Each of the two chambers was constructed using a sealed glass aquarium, set into an insulated plywood box. The removable sample holder was built of Plexiglas; all samples were hung or set into place on this holder, and moved at the appropriate periods from the wet environment chamber to the drier one. In the wet environment chamber, conditions were maintained at 50°C and 100% RH. A shallow pan of water provided the RH; and heat was introduced with a hot air gun (hair dryer) set into a hole cut into the plywood box. The second chamber was maintained at typical room temperature and RH conditions. Room conditions were not strictly controlled, but were constantly measured (with RH between 50-60% and temperature between 20-21° C).

To take into account possible synergistic effect, the accelerated tests exposed specimens to a ‘cocktail’ of volatile pollutants, as well as to fluctuating temperature and relative humidity that may cause stress on the coatings.

The following pollutants were produced and introduced into the first test chamber with elevated temperature and RH:

(1) H_2S, produced with 1% Na_2S, using 1 gram in 300 mL water with pH adjusted to 7.0; the entire solution was placed in a 500 mL beaker inside the test chamber.

(2) $S0_2$, produced using 0.01 gram of $NaHS0_3$ plus 10 drops of 3% H_2S0_4 in a small weighing boat inside the test chamber. The following pollutants were introduced in the second, dry test chamber, with room temperature conditions.

(3) Ozone was produced by running an ozone generator at the lowest output for 3 minutes at about 10 ppm into the test chamber; producing an ozone level of about 1 ppm (0_3 will decompose to 0_2 in the test chamber). Ozone can have a direct oxidative effect on coatings, so does not need the high humidity to cause deterioration.

(4) Acetic acid, introduced with 1 mL of 10% acetic acid dispensed into filter paper laying in the bottom of the test chamber.

(5) Formaldehyde, introduced as 1 mL of 10% formaldehyde dispensed onto filter paper laying in the bottom of the test chamber.

A very interesting work is focused on the assessment of the representativity and reproducibility of artificially corroded silver mock-ups in order to evaluate the suitability of their use as samples for testing conservation procedures [25]. In this work, sterling silver samples were artificially aged in five different environments. The samples were exposed to uncontrolled ambient air at different locations (e.g. residential and laboratory environments) and to three accelerated ageing methods in a gaseous or liquid environment under controlled conditions.

These tests showed different results in morphology, microstructure, composition, thickness and the interface between bulk and corrosion layer. A first accelerated sulfidation procedure in a Na_2S solution alternated with exposure to air, resulted in a fast corrosion rate and an even corrosion layer formation with several S-species. A second series of sulfidation in a controlled gas environment of H_2S and SO_2 developed a thin but uneven corrosion layer, mainly consisting of oxides. A third corrosion methodology used was based on the thioacetamide method. This resulted in an even and relative thick corrosion layer, comparable to the Na_2S/aeration sulfidation system. However, the interface between the corrosion layer and the bulk is importantly different, showing severe voids.

Analyses demonstrated that the composition and microstructure of the corrosion layers were strongly dependent on the sulfidation method used and copper was found to be an important element present in all sulfide layers analyzed. Therefore, artificially corroded sterling silver is not necessarily representative for naturally tarnished historical objects and the extrapolation of the cleaning results obtained on dummies to historical objects must be performed with care.

5. Selection and application of artificial ageing in Scan4Reco

As reported above [1, 8], scholars agree on the difficulty of reproducing in an ageing chamber the actual environmental conditions affecting the degradation of materials and, consequently, to set a good correlation between natural and artificial ageing. Thus the choice of the ageing procedures in Scan4Reco is not aimed at pretending the natural environment where artworks are exposed but, rather, at inducing degradation to train and calibrate the Scan4Reco predictive system and eventually to validate it. The calibration will occur through measurements of surface and sub-surface properties before, during and at the end of the ageing process. For this reason, when two replicas are available, each set of parameters will be aged with a different choice of parameters, in order to explore the effect of a wider range of combination of variables.

5.1 Ageing of painting samples

To account for chemical, visual and mechanical deterioration induced by light, temperature and humidity fluctuations in a not heated/conditioned historical building, like a church, where Byzantine icon have been and/or are stored for long an ageing apparatus (Angelantoni ACS GTS60) equipped with a mercury vapor lamp HSW-400W E40. Since the spectral emission of the mercury vapor lamp includes the lines listed in Table 1, a glass filter will be used to cut shorter wavelengths (ordinary window glass passes about 90% of the light above 350 nm, but blocks over 90% of the light below 300 nm).

Table 1: emission lines of the vapor mercury lamp

Wavelength (nm)	Color
184.45	ultraviolet (UVC)
253.7	ultraviolet (UVC)
365.4	ultraviolet (UVA)

404.7	violet
435.8	blue
546.1	green
578.2	yellow-orange

The temperature and the humidity will be decreased and increased periodically in order to simulate the seasons of the years within the time cycle of the 2 weeks. Temperature will range between 48 °C and 60°C and relative humidity between 40% and 60%.

A total amount of 6 cycles is planned.

Check of visual, chemical and physical properties before ageing (T0) is done with the following components of the project:

HW/VISDEPTH – Acquisition of 3D of surfaces with variable extent of gloss and reflectivity.

HW/ACOUSMIC - Structural characteristics of the samples.

HW/FTIR- Molecular fingerprint of the coating polymer and the corrosion products.

HW/RAMAN- Molecular fingerprint of the coating polymer and the corrosion products.

HW/UVSPEC- UV and visible emission properties of the coated and uncoated surfaces

HW/MPROF - Quantitative measurements of the surface texture and roughness at micrometric level

HW/HDMSRI- Check of the surface appearance of material samples

HW/MSRTI- Check of the surface appearance of material samples

HW/IRCAM- Check of the IR reflectance of material samples

HW/XRF- In-depth check of the elemental composition of material samples

Further checks will be done every two weeks with the abbreviated list of techniques:

HW/VISDEPTH – Acquisition of 3D of surfaces with variable extent of gloss and reflectivity.

HW/ACOUSMIC - Structural characteristics of the samples.

HW/FTIR- Molecular fingerprint of the coating polymer and the corrosion products.

HW/RAMAN- Molecular fingerprint of the coating polymer and the corrosion products.

HW/UVSPEC- UV and visible emission properties of the coated and uncoated surfaces

HW/IRCAM- Check of the IR reflectance of material samples

A full check will be repeated halfway of the ageing period and at the end.

5.2 Ageing of copper alloys

Since Scan4Reco needs to test the effect not only of weathering bronze but also the effect of environmental outdoor parameters (i.e. sunlight, humidity, rain and heat) on the protective coating, an ageing chamber equipped with fluorescent ultraviolet (UVA) lamp, condensing humidity device and water spray will be used (QUV spray chamber).

The chamber simulates the outdoor moisture by heating water on the bottom of the chamber to obtain superheated steam filling the test chamber. Samples are fixed on the wall of the test chamber (Figure 7). Thus, the sample surface is exposed to the ambient air of test chamber while the other side of the sample is exposed to the natural environment, which has a cooling effect. The temperature difference between internal and external surfaces of the sample leads to the test surfaces always have drips caused by condensation process.

The condensation process automatically purifies the ordinary tap water used in the system. This is because the process of evaporating and condensing the water onto the specimens is actually a distillation process, which removes all impurities. The chamber conveniently accommodates up to 48 specimens (size 75mm x 150mm). In Table 2, the dimensions and operating temperature ranges are reported.

Dimension(W×D×H)	137x53x135 cm
Temp. range	50°C~75°C
Condensation Temp.	40°C~60°C

Table 2. Characteristics of QUV spray chamber used for ageing of bronze samples.

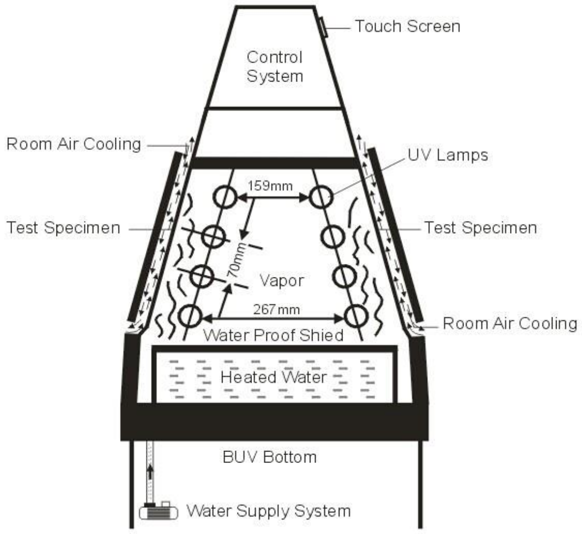

Figure 7: Scheme of the QUV spray chamber

The lamp irradiance is checked by a calibration radiometer; the radiometer is periodically calibrated (a calibration certificate is released by the company according to the requirement of ISO9001)

The bronze samples are described in project’ deliverable D3.2: one is not coated, while 18 are coated with two replicas for each sample (two identical sets) to allow for a better statistics.

The cycle applied on SET1 is:

- 4 hours dry conditions (T= 60°C) UV exposure to simulate sunshine exposure
- 4 hours wet conditions (T=40°C , RH=90%) dark
- manual spraying every 6 cycles with solution A, imitating an acidic rain.

Solution A composition: Cl^- (1.27mg/L), NO_3^- (4.64mg/L), NH_4^+(1.06mg/L), $SO_4^{=}$(1.9mg/L), $HCOO^-$ (0.05mg/L), CH_3COO^- (0.23mg/L), Na^+(0.53mg/L), Ca^{2+}(0.34mg/L), pH = 4.25. The total time of cycling is 12 weeks.

The same cycle is applied to SET2, with the difference that no solution is sprayed. This set will experienced only dew and not sprayed water. The aim is to mimic sheltered surfaces, exposed to sunshine and dew but not to direct rainfall.

The bronze samples are checked before ageing (T0) with a set of techniques that allow the detection of both chemical and physical features of the samples and their changes:

HW/VISDEPTH – Acquisition of 3D of surfaces with variable extent of gloss and reflectivity.

HW/ACOUSMIC - Structural characteristics of the samples.

HW/FTIR- Molecular fingerprint of the coating polymer and the corrosion products.

HW/RAMAN- Molecular fingerprint of the coating polymer and the corrosion products.

HW/UVSPEC- UV and visible emission properties of the coated and uncoated surfaces

HW/MPROF - Quantitative measurements of the surface texture and roughness at micrometric level

HW/HDMSRI- Check of the surface appearance of material samples

HW/MSRTI- Check of the surface appearance of material samples

In the Scan4Reco pipeline, ageing of samples is in the second stage, after measurements at T0 (not aged samples). The ageing will be carried out gradually in order to allow measurements to be done at intermediate times.

An abbreviated check will be done after 3 and 9 weeks, while the full-list check will be repeated after 6 weeks and at the end of the process.

The abbreviated check includes:

HW/FTIR- Molecular fingerprint of the coating polymer and the corrosion products.

HW/RAMAN- Molecular fingerprint of the coating polymer and the corrosion products.

HW/MPROF - Quantitative measurements of the surface texture and roughness at micrometric level

HW/HDMSRI- Check of the surface appearance of material samples

HW/MSRTI- Check of the surface appearance of material samples

5.3 Ageing of silver alloys

The ageing of silver items is dominated by the interaction of silver with S-bearing compounds in the environment. Humidity conditions affect the speed of the reaction as well. Silver objects are usually exhibited in showcases or rooms with UV-screened windows and the UV effect on the ageing of the protective coating can be neglected. Silver samples will be exposed to a humid H_2S containing environment, produced in an ageing unit. The variable will be the H_2S concentration. The ageing unit consists of a dessicator (figure 7) where the required concentrations of H_2S is achieved either by introducing H_2S from a gas cylinder (SAMPLE SET 1, H_2S concentration A) or by the decomposition of Na_2S from a solution at pH=7 (SAMPLE SET 2, H_2S concentration B). Humidity and temperature will be measured inside the unit. A total amount of 100 hours exposure will be reached.

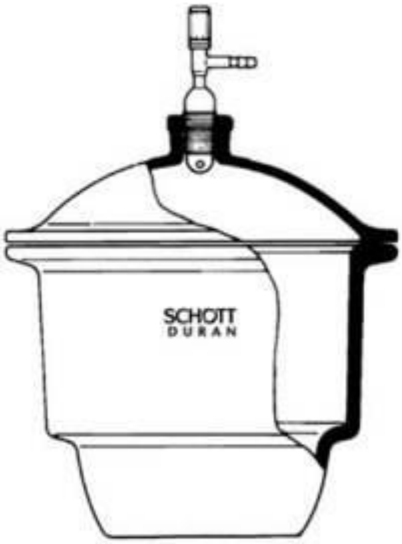

Figure 8: Ageing unit for tarnishing of silver

The surface and sub-surfaces probes applied before the tarnishing experiment (T0) are:

HW/VISDEPTH – Acquisition of 3D of surfaces with variable extent of gloss and reflectivity.

HW/ACOUSMIC - Structural characteristics of the samples.

HW/FTIR- Molecular fingerprint of the coating polymer and the corrosion products.

HW/RAMAN- Molecular fingerprint of the coating polymer and the corrosion products.

HW/UVSPEC- UV and visible emission properties of the coated and uncoated surfaces

HW/MPROF - Quantitative measurements of the surface texture and roughness at micrometric level

HW/HDMSRI- Check of the surface appearance of material samples

HW/MSRTI- Check of the surface appearance of material samples

The aging will be carried out gradually in order to allow measurements to be done at intermediate times.

To account for the early stages of the blackening process, close checks will be done after 4 (T1) and 10 (T2) hours exposure with the full-list probes.

Further checks will follow at 24, 48 and 72 hours, again with all the probes.

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