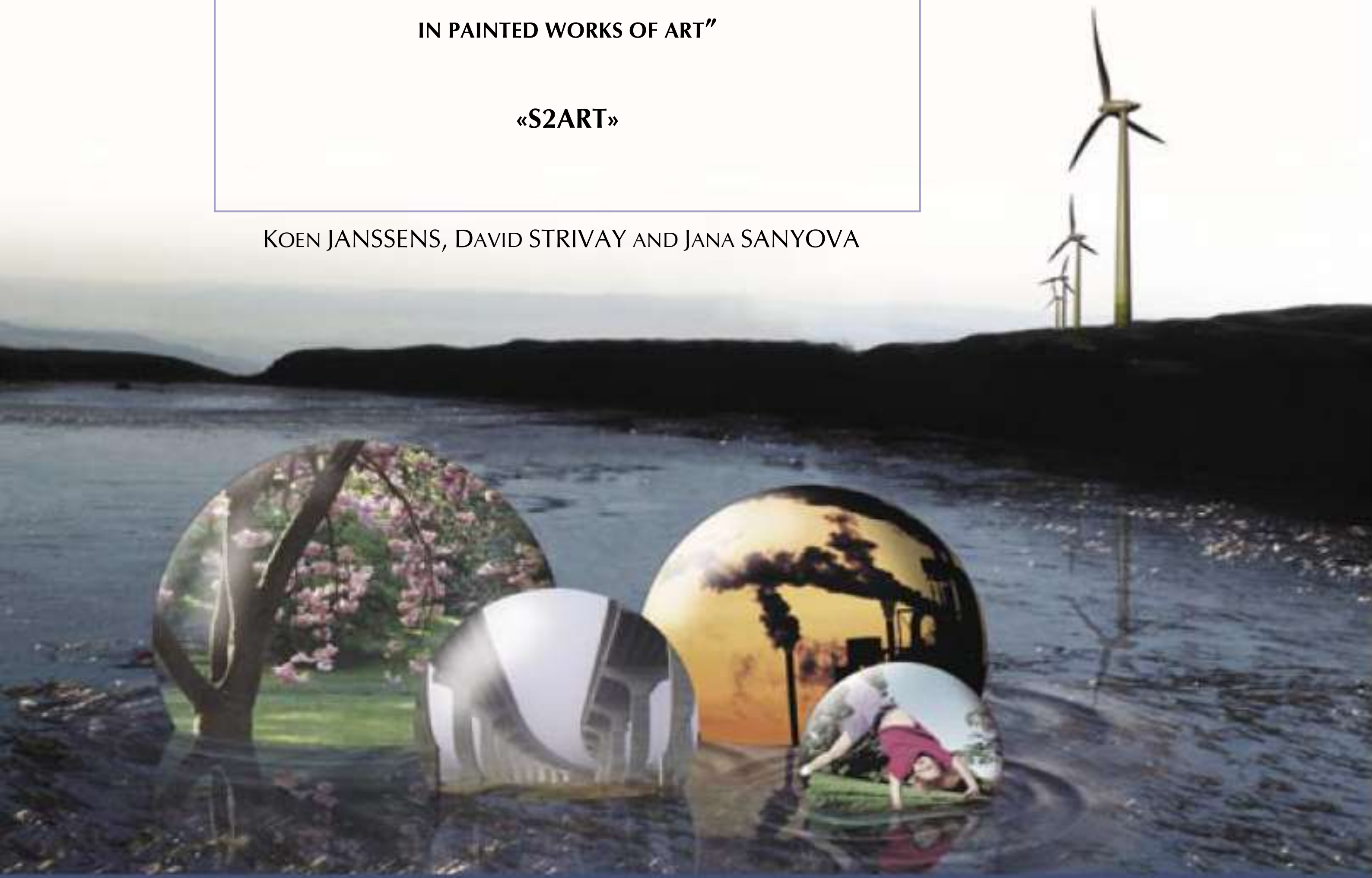
SSD

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

“LONG-TERM ROLE AND FATE OF METAL-SULFIDES IN PAINTED WORKS OF ART”

«S2ART»

KOEN JANSSENS, DAVID STRIVAY AND JANA SANYOVA



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(SSD)

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FINAL REPORT

LONG-TERM ROLE AND FATE OF METAL-SULFIDES IN PAINTED WORKS OF ART

"S2-ART"

SD/RI/04A

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SUMMARY

A. Context

Cultural Heritage has been defined by the UNESCO as *« the entire corpus of material signs – either artistic or symbolic- handed on by the past to each culture, and therefore, to the whole of humankind ».* Being the vehicle of our cultural identity, it is our responsibility to set its preservation as the corner stone of our cultural policies.

Our atmosphere has changed from pre-industrial times to our days. Particulate matter distribution and pollutants have evolved according to natural events but majorly due to anthropogenic activities. In any case, they have been incorporated to works of art mostly reinforcing their degradation processes.

Sulfide-based pigments may be noted on the list of endangered materials of Cultural Heritage Objects; the Table below lists a number of example.

Table 1. Various metallic sulphides used as pigments.

Colour	**Pigment**	**Formula**
White	Lithopone	ZnS
Yellow	Orpiment	As2S3
	Pararealgar	AsS
	Cadmium yellow	CdS
Orange	Realgar	As_2S_2
Red	Cinnabar/Vermillion	HgS
	Cadmium red	CdS
	Antimony sulphide	Sb2S3
Gold	Mosaic gold	SnS_2
Various	Neolor ®	CeS_2

These pigments are widespread in terms of time, space and substrate Their frailty due to their high reactivity, diminishes greatly their long-term durability and value. Hence, the S2-ART research project encompassed the study of the long-term evolution and degradation of metal-sulfides in painted works of art subjected to different atmospheric conditions.

B. Objectives

The main objectives of the project were:

- To characterise the present aerosols and evaluate their contribution to the degradation of metallic sulphide pigments in painted works of art and to assess the impact of future projected aerosols on metallic sulphide pigments;
- To evaluate the long-term evolution of the metallic sulphide pigments in the painted works of art and estimate the future progression of the degradation processes due to changes in the atmospheric composition.
- To propose and critically reflect on measures suitable for improving the indoor and

outdoor conservation of metallic sulphides, including measures to modify the indoor museum atmosphere.

- To produce a complete report with all the information gathered through this research, useful for policy makers and Cultural Heritage related institutions.

C. Conclusions

The project results include increased insights into the mechanisms of pigment degradation, into the types of chemicals that cause or catalyse these transformations and how air borne aerosol types may act as source of such chemicals. The role of cyclic changes in temperature and humidity in promoting transport of secondary chemicals to the surface of painted works of art has been elucidated. The effectiveness of measures designed to modify the museum atmosphere was measured.

The following significant project results can be listed:

Aerosol sampling and analysis in Belgian musea has pointed out that exposed paint surface of works of art can be in direct contact with a number of soluble salts. These include NaCl, $NaNO_3$, NH_4Cl, $(NH_4)_2SO_4$ and others. Gas analysis showed that also pollution gases such as HCl, NOx, SO_2 and NH_3, mainly the product of industrial and other combustion processes, are continuously present in the indoor atmosphere of musea.

Hygroscopic salts, when deposited on a paint surface, can cause small galvanic cells to be formed locally in which redox processes can occur. In the case the affected paint contains semi-conductor based pigments (such as is the case for vermillion red, red lead, cadmium yellow and chrome yellow and others) exposure to light can trigger the release of electrons and positive holes which in their turn can induce redox processes to occur.

Based on the examination of several representative paintings, it can be concluded that most sulfur-containing pigments suffer from chemical degradation induced by a combination of light and moisture exposure. In many cases, a combination of physical and chemical agents triggers unwanted chemical transformations. A prime physical agent is light, not only in the UV range but also of blue and green wavelengths. Another important circumstance driving secondary reactions is cyclical variations in relative humidity. Chemical agents implied in the formation of secondary products are various chlorine-containing salts and ammonia. In many cases, the secondary products that are formed cause the original paint layer to change color and/or to reduce its mechanical stability.

In view of the combined effect of short wavelength (UV + blue/green) light, humidity and salt components encountered in ambient aerosols, direct outdoor exposure of artworks painted with metal sufides should be avoided as much as possible. Isolation of these artworks from atmospheric moisture and particulate matter via transparent surface coatings is mandatory, as well as regular renewal of such coatings. Since next to UV light, also parts of the visual spectrum (such as blue and green light) stimulate the alteration of metal sulfide pigments, employing colorless UV-filtering coatings is likely only to have only a limited effect.

D. Contribution of the project in a context of scientific support to a sustainable development policy

In view of the conclusions arrived upon, a set of recommendations for improving museum atmospheric conditions and for related policies were formulated.

- Belgian musea and their curators should realize much more than now is the case that most painted works of art are subject to slow but relentless chemical transformations that are taking place either at or just below the visible paint surface. Continuous care should be taken to control/reduce the progression speed of such undesired changes.
- In particular, care should be taken to remove chloride-containing salts from the museum atmosphere and to limit the use of ammonia-containing cleaning products as much as possible.
- Many of the undesired chemical reactions of semi-conductor pigments and other artists' materials are being triggered by light, not only UV-radiation but also radiation in the visual range. Thus, special care should be taken to limit the illumination inside musea. In case LED-based energy-efficient lighting systems are installed, special care should be take to ensure that the new light sources do not emit more blue/green light than more conventional light sources.
- Belgian musea should give a higher priority to install state-of-the art air purification and air conditioning systems and maintain their operation at the desired specification. Such systems must not only regulate and stabilize the temperature and relative humidity to quasi-fixed values but also ensure that the ambient air is actively cleaned from airborne particles. This applies to both exhibition spaces, storage areas and more restricted spaces such as display cases and climate boxes.
- Musea should also seek to separate unprotected/uncovered surfaces of painted works of art from direct contact with the indoor museum atmosphere.

Thus, it appears also recommended that for musea of sufficient size, policy makers should allocate appropriate funds in order to enable the musea to

- install state-of the-art climatic systems ensuring stable conditions regarding lighting, temperature, relative humidity and atmospheric composition;
- employ competent, science-trained staff that (a) is able to periodically ascertain the correct atmospheric and lighting conditions in public exhibition spaces, artwork storage areas, display cases and climate boxes and (b) can objectively monitor the progress of unwanted chemical transformations at the surface of works of art via appropriate methods of analysis;
- systematically initiate restoration projects of all works of art in order to ensure that their paint surfaces remain isolated from external physicochemical influences.

E. Keywords

pigment degradation: vermillion red, red lead, chrome yellow, cadmium yellow, orpiment, realgar, relative humidity, UV-VIS light, chlorine, CO_2, H_2S

1 INTRODUCTION

The objectives of S_2ART research project were

- to investigate the chemical and physical behaviour of metal sulfide pigments; to study chemical degradation processes at the surface of paintings;
- to assess the impact of aerosols on metal sulfide pigments;
- to propose and critically reflect on measures suitable for improving the indoor and outdoor conservation of metallic sulphides, including measures to modify the indoor museum atmosphere.

In the project, the activities of the University of Antwerp were centered on the one hand on the characterization of the aerosols encountered in the ambient atmosphere of Belgian Musea. For this purpose, passive and active sampling of particulate matter in different musea was undertaken. These investigations allows to identify the presence of a number of seemingly innocuous chemical reagents that could potentially contribute to surface-modification of painted surface in musea. On the other hand, the chemical (in)stability of a series of S-containing and related pigments was studied as a function of exposure to physical and chemical environmental agents. Specifically, attention was focussed on the sulphidic pigments vermillion red and cadmium yellow. In a comparative perspective, also the reactivity of other red and yellow pigments, used by the same artists and for similar purposes such as Red Lead (minium) and Chrome Yellow was studied.

The activities of ULg were related to the study of the gaseous components present in the indoor atmosphere of Belgian musea and how these might influence the stability of paints realized with the pigments Cadmium Yellow and Yed. Their efforts were concentrated on the collection of the Musée de Beaux Arts de Liège (BAL).

KIK-IRPA focused on the characterization and determination of the degradation pathways and influencing-factors of Arsenic bearing sulphur-containing pigments. Especially natural orpiment is of interesting in this respect as most of its degradation pathways were still unclear. Three types of these pigments were the main focus of this work: two natural in crystalline form: yellow orpiment (As_2S_3) and reddish-orange realgar (As_4S_4). There is also an artificial amorphous form (g-As_xS_y) of which color is closely related to the arsenic and sulfur proportions (respectively x and y).

Where appropriate and where it added value, the project partners worked together to achieve common project goals or put results in a comparative perspective.

2 METHODOLOGY AND RESULTS

Pollutants (in gaseous, liquid or particulate form) contribute heavily to the deterioration of painting materials. The presence of gases such as SO_2, NO_x, peroxides or ozone may induce or catalyze degradation reactions. Though lately industrial emissions are being controlled and thus SO_2 emissions have decreased, NO_x levels tend to increase due to transportation exhausts. Soot and soil anchor easily to irregular surfaces providing adsorption and reaction sites for various gases. Other chemicals present in atmospheric aerosols such as ammonium ions, sea salt, nitrates, sulfates and organic compounds (including black or elemental carbon) may too interact with paints.

When atmospheric particles have been deposited on heritage materials, their possible adverse effects on the materials largely depend on their hygroscopic characteristics. Since water often plays a crucial role in degradation phenomena in general, and it probably promotes chemical reactions between particles and their deposition surface, the relative humidity is a decisive factor. All particles, even inert ones, can act as condensation nuclei, via adsorbing humidity from air, thus increasing their water content.[1] However, for insoluble particles such as silica, the water uptake is only significant in the extreme conditions of a supersaturated vapour. Water-soluble particles possess a moisture absorption capacity and already show a considerable water uptake under moderate conditions (unsaturated vapour).[2] These soluble particles have a strong affinity to water and possess the ability to attract and hold water from the environment. This hygroscopicity can be considered as one of their fundamental properties. On the one hand, it promotes particle growth when the particles are suspended in the air, thus increasing their settling velocity. On the other hand, hygroscopic particles attract water on the deposition surface, accelerating any degradation process favoured in humid conditions such as the oxidative degradation of paper and textile,[3,4] corrosion of metals, discoloration of pigments (Saunders & Kirby 2004), etc. Moreover, when a surface is soiled with a hygroscopic contaminant, the liquid film can easily adhere other particles that touch the surface, increasing the rate of particle deposition.[5]

The experimental activities of the S2-ART project can be divided up into two parts:
on the one hand studies related to the indoor atmospheric quality of Belgian musea and on the other hand investigations related to establishing the impact of atmospheric pollutants on painted works of art.

2.1 Study of atmospheric conditions in Belgian Musea

The internal atmosphere of a number of Belgian musea was studied on the one hand via aerosol sampling and characterization and on the other hand by means of gas analysis.

2.1.1 Gas analyses and particulate sampling at BAL [ULg]

Gas analysis. The Musée des Beaux Arts de Liège (BAL) is situated close to the river Meuse. The Meuse's plain has been for a long time an industrial centre, with mining activities (coal extraction) that go back twelve centuries in time, nowadays discontinued, and an iron and steel industry, which begun to decline in the late 1970's and came to an end in recent years. To this, a population of about 200.000 persons and heavy traffic needs to be added. The location of the museum thus offers the possibility to study the effects of pollutants such as SO_2, NO_x, peroxides or ozone (O_3).

Figure 1. Map of Belgium situating the city of Liege relative to the Belgian coal-producing regions (dd, 1968). Aerial photos of the city centre of Liège and the vicinity of the Musée des Beaux Arts.

A study was performed of the indoor atmosphere at the second floor of the BAL by monitoring the gases and suspended particle matter (aerosols). The temperature and relative humidity was monitored, while sampling campaigns of suspended particulate matter (aerosols) were conducted and atmospheric gases were measured within the gallery and the storage room of the building's second floor. For this purpose, two different devices were employed: a gas detector and a particle cascade impactor. Measuring periods ranged from 24h to 7 days.

The gas detector was an AdvanceSense instrument from GrayWolf Sensing Solutions with 2 different probes (TG-501 and TG-502), with can measure the following pollutant gases ClO_2, HCl, HCN, NO, H_2S, NH_3, O_3, NO_2, SO_2 and TVC (total volatile organic gasses) together with temperature and relative humidity. The limit of detection of this device is in the ppm range for NH_3, in the 0.1-1 ppm range for HCl, HCN, NO and SO_2 and below 0.01 ppm for ClO_2, H_2S, O_3, NO_2 and TVC. Gas concentrations can be measured in ppb or in $\mu g/m^3$.

In the figure below, as an example, typical monitoring traces resulting from gas analysis are shown, showing clear increases in NH_3 and SO2 during the morning rush hour period.

Comparison of similar traces recorded in exhibition and storage areas of BAL revealed that there is a large difference in stability of relative humidity (%RH), temperature, and the concentration of pollutant gases at different locations in this museum. For example, SO_2 is higher in the storage area while NH_3 is higher in the exhibition space.

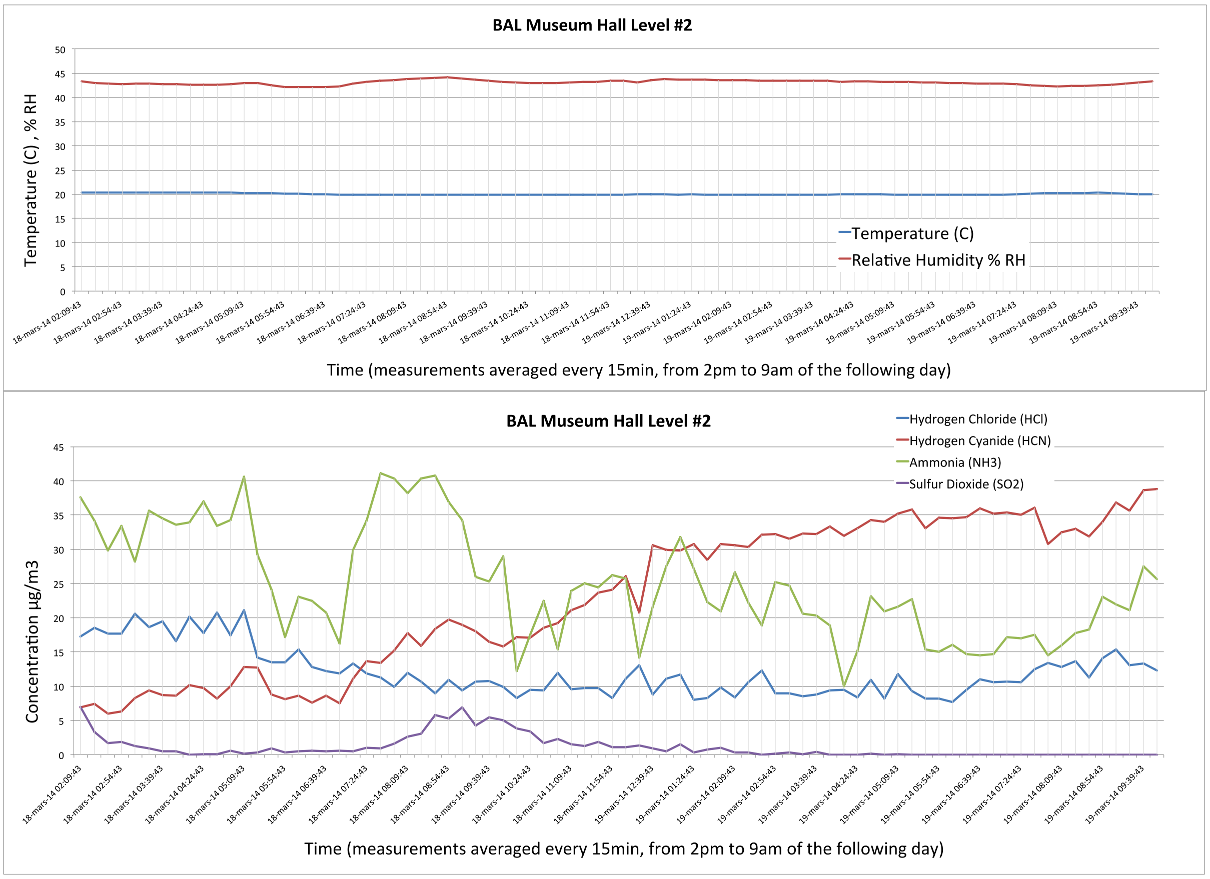


Figure 2. Time-dependent monitoring of (upper panel) the temperature and relative humidity and (lower) panel HCl, HCN, NH_3 and SO_2 in the second level exhibition hall of BAL (March 18 2014).

The totality of the measurements indicate that both temperature and relative humidity within the gallery at the 2nd floor of the BAL museum are correctly maintained. However, in the storage room of the same floor. Although the relative humidity is within the adequate range, the temperature is too low and should be better controlled. Non-controlled airflow sources from the outside to the inside of the building it should be revised and regulated. HCl, HCN, NH_3, H_2S and SO_2 were detected in the exhibition area, with hydrogen sulfide (H_2S) only appearing at the storage room.

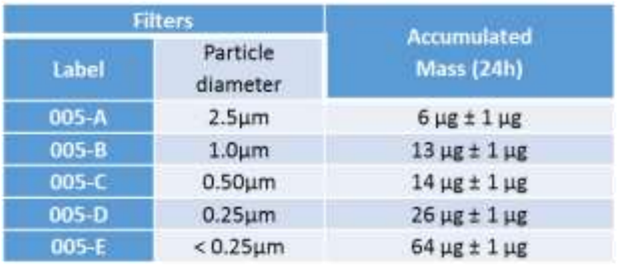
H_2S and SO_2 mainly originate from fuel combustion, industrial processes and transportation. Metal smelting can also form an important outdoor source of SO_2. These gases were particularly found in the storage room. The difference in H_2S and SO_2 content can be linked to differences in the quality of the ventilation systems and/or to the fact that air current entering the museum from outside is not adequately filtered.

In the gallery, higher values of hydrogen chloride (HCl) and ammonia (NH_3) are encountered. HCl typically originates from combustion processes or sea spray, but may also be introduced via cleaning products. Outdoor ammonia sources are livestock agriculture and fertilizers – which can be excluded if we take into account the surroundings of the museum. Indoor ammonia is also related to cleaning products, museum visitors, fresh emulsion adhesives and paints, and concrete. The entire building is made of concrete without any differences between the gallery and the storage room, and there was not any fresh paint or adhesives from which NH_3 might have been released into the gallery. The rate of visitors of the BAL museum in the second floor gallery would not justify the presence of this gas either. However, the museum possesses large windows and cleaning products for windows classically contain ammonia. In view of this, the elevated NH_3 levels were tentatively attributed to cleaning products. Most of the damage that ammonia may cause indoors, is associated with the production of ammonium salts which cause corrosion or a whitish deposit the surface of the works of art. These salts are formed by nucleation of ammonia with other compounds, such as sulfate or nitrate compounds, within fine particles.

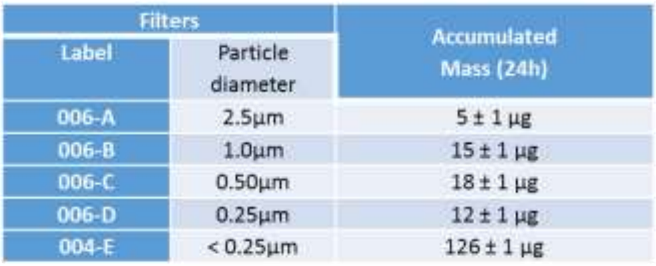
Particulate matter. In addition to the above measurements, also cascade impactor sampling was carried out at the same locations. Particle matter of aerodynamic diameter equal or smaller than 2.5µm ($PM_{2.5}$) in fractions of 2.5 µm, 1.0 µm, 0.50 µm, 0.25 µm and less than 0.25 µm was collected. These particles are the most dangerous in terms of degradation for museum objects. Due to their small sizes, these particles can lodge in the interstices of the object's surface, and they can remain for a few days suspended in the environment, unlike PM_{10}, which have shorter suspension time. Outdoors, PM2.5 particles are discharged directly from the atmosphere or formed within it. They include harmful compounds such as sulfates and nitrates, organic carbon (soot, oil smoke, tobacco smoke, petrol and diesel combustion), and sea salts (chloride). Most indoor generated particles in museums are composed of soil, dust and carpet and cloth fibres. These particles discolour or soil surfaces and serve as anchor to other compounds to produce chemical reactions.

As an example, the tables below list the collected aerosol mass within a period of 24h in the second floor exhibition area and the storage room area of the BAL museum.

Table 2. Collected aerosol mass within a period of 24h at (left) the second floor exhibition area (sample air volume: 12.96 m^3; total mass accumulated: 123 µg) and (right) the storage room area (sampled air volume: 12.96 m^3; total mass accumulated: 176 µg of the BAL museum.



Filters		Accumulated Mass (24h)
Label	Particle diameter	
005-A	2.5µm	6 µg ± 1 µg
005-B	1.0µm	13 µg ± 1 µg
005-C	0.50µm	14 µg ± 1 µg
005-D	0.25µm	26 µg ± 1 µg
005-E	< 0.25µm	64 µg ± 1 µg



Filters		Accumulated Mass (24h)
Label	Particle diameter	
006-A	2.5µm	5 ± 1 µg
006-B	1.0µm	15 ± 1 µg
006-C	0.50µm	18 ± 1 µg
006-D	0.25µm	12 ± 1 µg
004-E	< 0.25µm	126 ± 1 µg

The $PM_{2.5}$ levels obtained for the gallery (9.5 µg/m^3) are almost the double of what has been reported for a Harvard university office buildings (4.6-5.6 µg/m^3). The quantified adverse effects of these particles has been observed at doses of 10 µg/m^3 per year on horizontal surfaces and 50 µg/m^3 per year for vertical surfaces provided that conditions are 50–60% RH and 20–30°C.[6] The $PM_{2.5}$ levels obtained for the storage room are even higher than those of the gallery on the same floor. It can be concluded that the recorded particle matter $PM_{2.5}$ values are alarmingly high, especially within the storage room of the museum. It appears recommended that air filtering systems be regularly checked in order to reduce the PM concentration, and also to reduce the concentration of pollution gases entering the museum from outside.

A notable outcome is that a significant variation in atmospheric compostion (gases, particulates) between exhibition and storage areas of the museum BAL were observed and that the PM2.5 levels were alarmingly high.

2.1.2 Aerosol sampling and analysis at several Belgian Museum sites [UA]

In view of the analysis results obtained at BAL, aerosol sampling was carried out at a larger number of number of Belgian museum sites of different nature (closer and further away from the seasalt sources, historic and more modern buildings, urban and more rural settings) was performed with the aim of estimating the composition of the indoor museum atmosphere and its variability/dependence on a number of environmental influences.

Passive aerosol sampling was undertaken in the following musea:
- St. Augustine Church (Antwerp)
- Museum MAS (Antwerp)
- Rubenshuis Museum (Antwerp)
- MuZEE (Ostend)
- Japanese Tower (Brussels, suburbs)
- Museum of Art and History (Brussels, centre)

At the last three sites also active aerosol sampling was conducted.

Gravimetric analysis of the filters clearly shows a higher deposited mass on the horizontal filters compared to the vertical ones. The figure below provides an overview of the total deposited mass in all sites, an expected outcome since gravitational settling of large particles dominates on horizontal surfaces, whereas Brownian diffusion of fine particles prevails on vertical surfaces. Particles found on the horizontal surfaces can be very large and do not always fit within the definition of particulate matter (PM). Moreover, small particles often agglomerate on bigger particles (e.g., mineral particles, skin flakes, fibres).

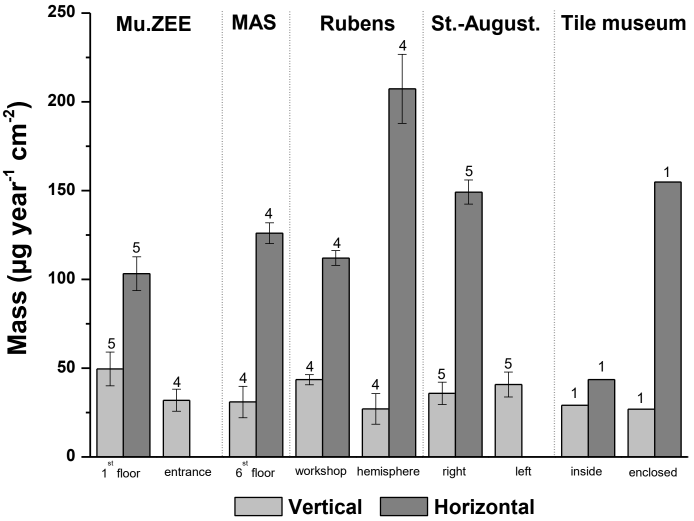


Figure 3. Typical aerosol loadings measured from horizontal and vertical passive samples located in various Belgian Musea compared to that in the Tile Museum, Lisbon, Portugal.

Ion-chromatographic analysis revealed that the predominant anions in the salts are Cl^-, NO_3^- and SO_4^{2-}, consistent with the literature on this topic. Among the passively sampled aerosols in the various museum site reveals differences in the relative abundance of e.g. NaCl and $NaNO_3$ between horizontal and vertical samplers were observed, likely induced by significant differences in grain size of these salts that are present in the museum air.

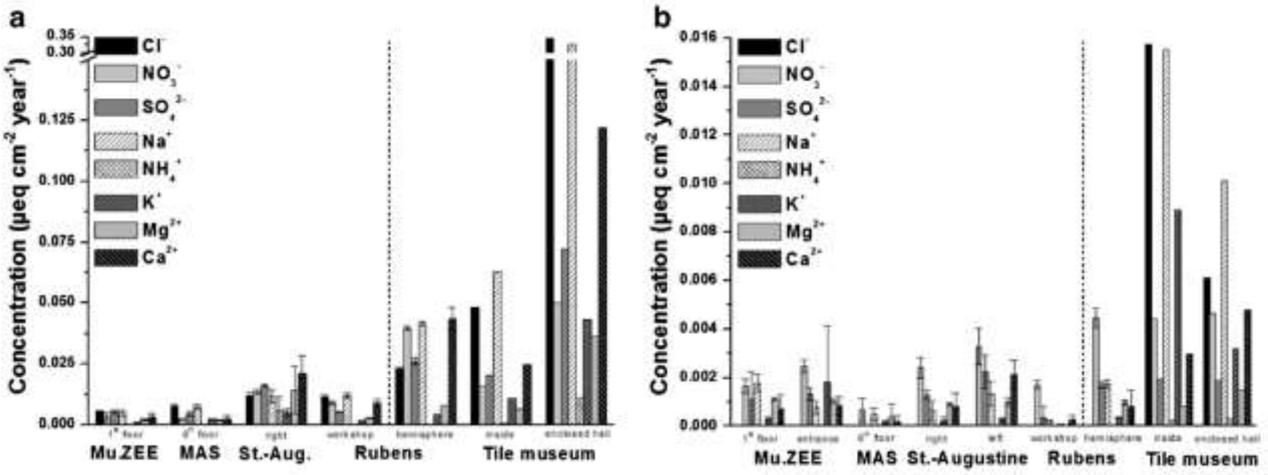


Figure 4. Concentration of the different anions and cations deposited on (a) horizontally and (b) vertically mounted aerosol filters.

The dashed line indicates the distinction between controlled and uncontrolled museum atmospheres. For horizontal surfaces, basically all anions are present, whereas for vertical surfaces nitrates mainly dominate. A clear trend is observed: on the horizontal filters, the detected Cl^- is mostly dominant, whereas on the vertical surfaces Cl^- is below the detection limit for all Belgian locations. The filters exposed in the Tile Museum in Lisbon, however, show relatively high Cl^- deposition on the vertical filters. This is probably due to the high ventilation rate and the seaside location of the Tile Museum, always experiencing freshly formed sea salt. Mu.ZEE, also located close to the sea, differs from the Tile

Museum by the presence of a climate control system. The remarkable difference between horizontal and vertical deposition finds its origin in the particle size. Small sea salt particles have a high surface-to-volume ratio, aging more rapidly compared to larger ones. Therefore, vertical surfaces will be enriched with aged sea salts as compared to horizontal surfaces. Deposition experiments in five southern Californian museums show analogous results: deposition rates for Cl^- on vertical surfaces were below the detection limit, whereas on horizontal surfaces, high Cl^--deposition rates were noticed. Sulfates were detected in all samples, except for the vertical filters in the MAS museum. The main origin of these sulfates are secondary reactions from anthropogenic SO_2-emissions.

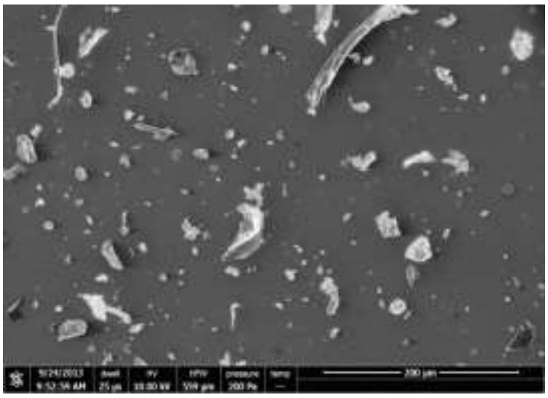
Publication: W. Anaf, L. Bencs, R. Van Grieken, K. Janssens, K. De Wael, *Indoor particulate matter in four Belgian heritage sites: Case studies on the deposition of dark-colored and hygroscopic particles,* Science of the Total Environment, **506** (2015) 361-368.

A notable outcome is that an abundant amount of Chlorides in encountered in most sampled musea, of which many acidic due to the presence of NH_4^+ ions and that, as expected, the deposition of horizontal surfaces is significantly higher than on vertical

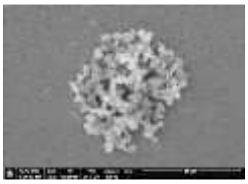
Individual particle analysis, performed by SEM-EDX on the collected particles revealed that particulate classes also reported in other museum indoor particulate investigations are encountered. Next to (acidic) salt particles of different types ($NaCl$, $NaNO_3$, Na_2SO_4, $MgCl_2$, NH_4OH, $(NH_4)_2SO_4$, NH_4HSO_4, NH_4Cl, $CaCO_3$, …), fossil fuel-combustion related particles are encountered. More details on these particulate classes can be found in Table 3 and 4 and the PhD thesis of W. Anaf. To study the effect of hygroscopic salt particles on paint surface more in detail, UV ageing of a series of paint surfaces sprayed with different (acidic and neutral salts) was performed. This resulted in a significant discolouration for specific combinations of salts and paints. SEM pictures of the salt spray particles revealed the recrystallization of the primary compounds as well as the formation of secondary compounds (e.g. $CdSO_4$, $(NH_4)_2Cd(SO_4)_2$) in some cases. This was confirmed via Raman analysis of some of the precipitates. Also a series of XANES measurements (point measurements and oxidation state-specific mapping) were performed on these samples, indicating that it is predominantly the hygroscopic properties of the salts, and to a far lesser extent their acidic or chelating nature that induce the surface discolouration.

A significant insight gained here is that on the surface of salt-sprayed paint surface, readily secondary products are formed in which Cl^- and NH_4^+ prominently are present as anionic or cationic partners to components that were originally part of the paint.

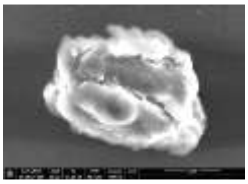
Table 3. Overview of particle morphologies and compositional classes encountered in the indoor-atmosphere of the Rubenshuis museum, Antwerp.



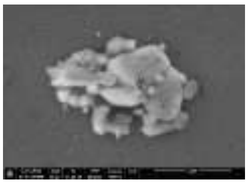
Overview



Sea salt, mainly NO_3^-

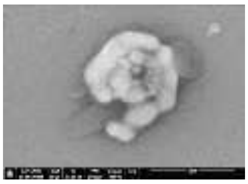


Carbonaceous

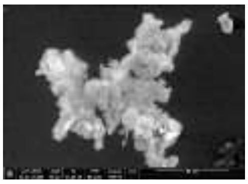


Sea salt, Cl^- and NO_3^-

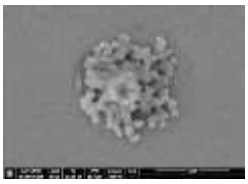
Carbonaceous



Sea salt, mainly NO_3^-



Gypsum



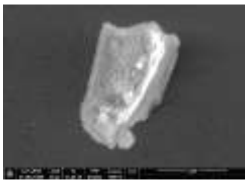
Sea salt, mainly NO_3^-

Calcium carbonate

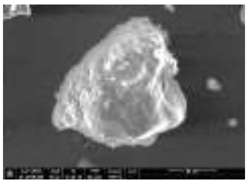
Calcium carbonate/chloride

Sea salt, Cl^- and NO_3^-

Calcium carbonate



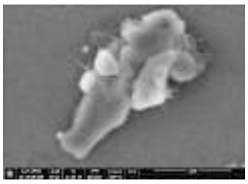
Carbonaceous



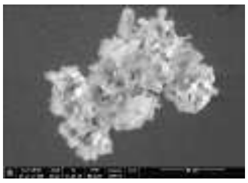
Mixed mineral

Biogenic, traces of salt

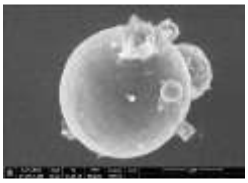
Carbonaceous



Sea salt, mainly NO_3^-

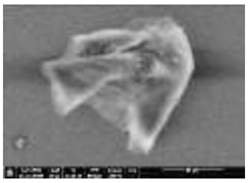


Gypsum, traces of iron

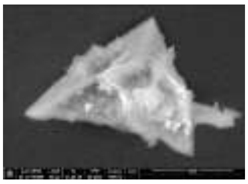


Iron-rich

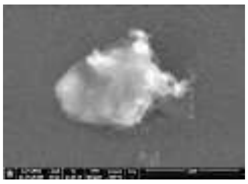
Carbonaceous (biogenic?)



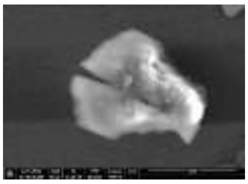
Carbonaceous (biogenic?)



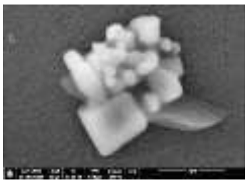
Calcium-rich mineral



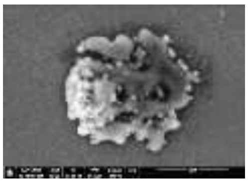
Carbonaceous (ammonium?)



Gypsum

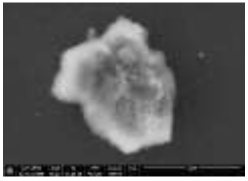


Sea salt, mainly NO_3^-



Sea salt, mainly NO_3^-

Iron-rich



Mineral (aluminosilicate)

Mineral (aluminosilicate)

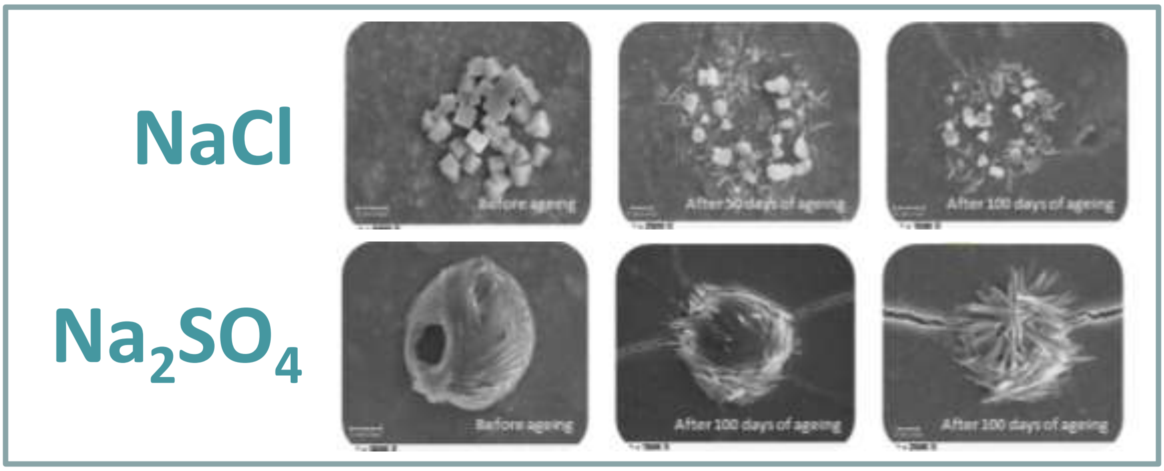


Figure 5. Scanning electron microscopy images of salt crystals at a CdS paint surface before ageing (left), after 50 (middle) and after 100 (right) days of ageing.

Table 4. Reconstruction of the mass balance, with classification of the measured ions into sea salts, mineral salts and ammonium salts at different Belgian museum sites

	Location		Mass	Sea salts	Mineral salts	Ammonium salts
			$\mu g\ cm^{-2}\ year^{-1}$	$\mu g\ cm^{-2}\ year^{-1}$	$\mu g\ cm^{-2}\ year^{-1}$	$\mu g\ cm^{-2}\ year^{-1}$
Horizontal	Mu.ZEE	1st floor	27.92 ± 2.56	0.46 ± 0.02	0.39 ± 0.12	0.12 ± 0.06
	MAS	6th floor	34.11 ± 1.58	0.72 ± 0.08	0.48 ± 0.16	-*
	St.-Augustine	Right	40.37 ± 1.85	1.15 ± 0.33	3.49 ± 0.71	-
	Rubens House	Workshop	30.31 ± 1.12	1.20 ± 0.12	1.00 ± 0.13	-
		Hemisphere	56.11 ± 5.26	4.58 ± 0.09	4.29 ± 0.49	-
	Tile Museum	Inside	43.55	5.00	1.91	0.05
		Enclosed hall	154.86	23.75	9.28	0.72
Vertical	Mu.ZEE	1st floor	13.41 ± 2.56	0.17 ± 0.04	-	-
		Entrance	8.64 ± 1.67	0.08 ± 0.01	0.15 ± 0.03	0.09 ± 0.03
	MAS	6th floor	8.38 ± 2.39	0.07 ± 0.02	0.01 ± 0.00	-
	St.-Augustine	Right	9.70 ± 1.71	0.11 ± 0.04	0.19 ± 0.02	-
		Left	11.02 ± 1.90	0.17 ± 0.06	0.28 ± 0.06	0.05 ± 0.01
	Rubens House	Workshop	11.77 ± 0.78	0.02 ± 0.00	-	0.11 ± 0.03
		Hemisphere	7.31 ± 2.34	0.24 ± 0.01	0.21 ± 0.04	0.14 ± 0.03
	Tile Museum	Inside	29.03	1.35	0.77	0.02
		Enclosed hall	26.92	0.93	0.41	0.02

* Insignificant concentrations.

Publication: W. Anaf, S. Trashin, O. Schalm, D. van Dorp, K. Janssens, K. De Wael, Electrochemical photodegradation study of semiconductor pigments: influence of environmental parameters, Analytical Chemistry, **86** (2014) 9742-8.

2.2 Pigment degradation studies: general aspects [UA]

To study the degradation behavior of various unstable artists' pigments under influence of various external physicochemical agents such as light of different wavelength and the chemicals encountered in the indoor atmosphere of musea, model samples of pure pigment powders or mixtures of them were prepared with and without different binders and subjected to accelerated aging under different conditions. Subsequently, the degradation products were identified via a combination of micro-analytical methods.

The pigment families studied included:
vermillion red (HgS) and Red lead (Pb_3O_4), both compounds being used from Antiquity to the mid 20th century by artists of varied style;
cadmium yellow (CdS), cadmium red ($CdSe_xS_{1-x}$) and chrome yellow ($PbCrO_4$/ $PbCr_{1-x}S_xO_4$), mostly employed from the late 19th to the early 20th century by impressionist and post-impressionist painters;
orpiment (As_2S_3) and realgar (As_4S_4), collectively known as Arsenic Sulfide pigments (As_xS_y), a series of pigments also employed since Antiquity.

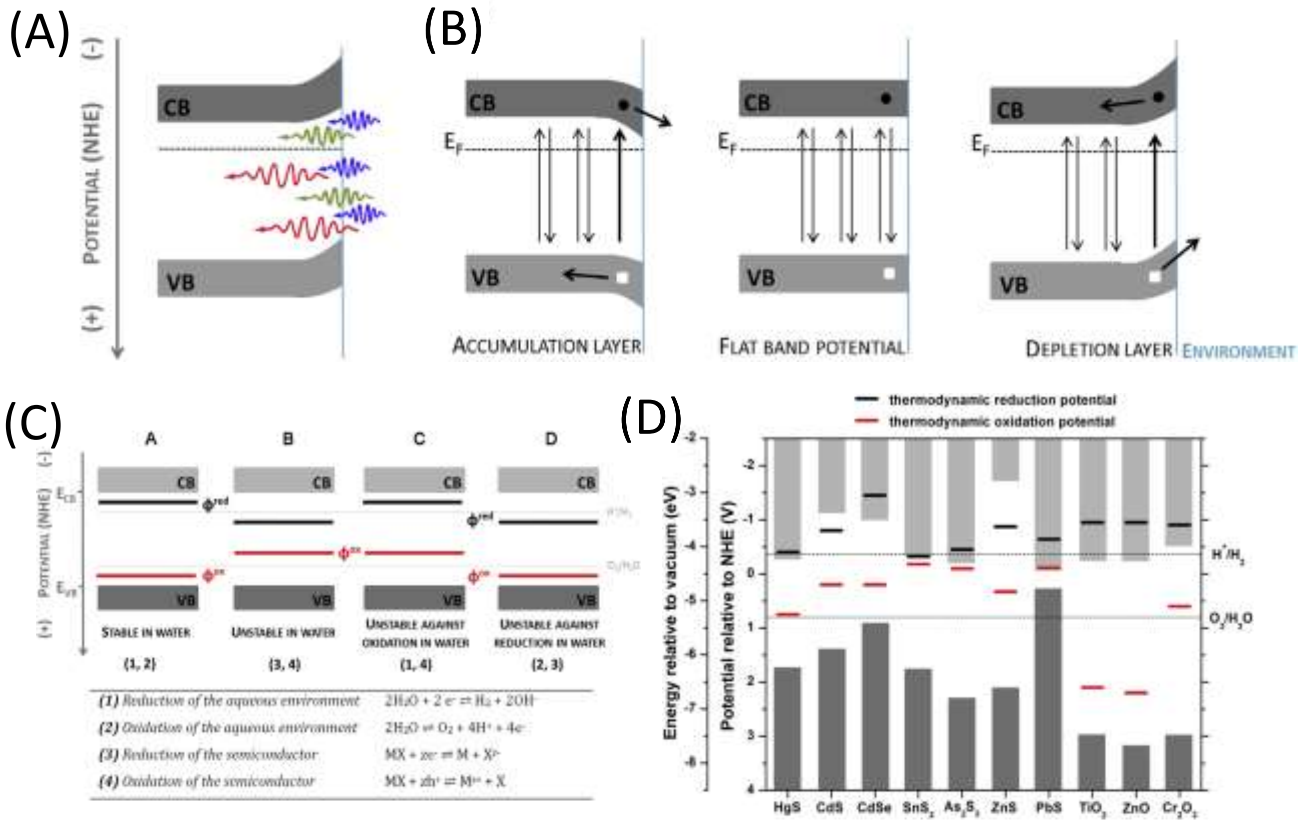
All these pigments suffer from chemical degradation induced by a combination of light and moisture exposure, albeit following different mechanisms of degradation. After an initial photo-induced redox reaction, in general several possibilities exist for the formation of secondary products.

For artificial degradation of model paint samples either 'traditional' ageing in a suitable ageing chamber with controlled light and relative humidity conditions or 'electrochemical monitoring' ageing where a laser of a particular color was employed to induced photo-catalytical reactions in the material being examined while the induced photocurrent and open clamp potential is recorded.

Via measurement of the photo-current, the semi-conductor pigments CdS, HgS, As_xS_y and Pb_3O_4 were found to be sensitive to blue and green light and, depending on the complexing ions available in the solution the paint is in contact with, can form different compounds. These were identified either via Raman microscopy, or via microbeam XANES and/or XRD. After the photo-induced reaction, therefore several other (precipitation or complexation) reaction steps may follow. These observations gave rise to several publications.

The fact that most affected pigments are semiconductors allows to generalize the conclusions derived from individual cases and predict the behavior of others in the same class of materials. Via this semi-conductor based model, the effect of aerosol particles on the above degradation reactions also can be rendered more understandable in qualitative terms: hygroscopic salt particles can created small galvanic cells on the paint surface in which diverse redox reactions can take place, depending on the charging of the material interfaces.

Publication: W. Anaf, O. Schalm, K. Janssens, K. De Wael, *Understanding the (in)stability of semiconductor pigments by a thermodynamic approach*, Dyes and Pigments, **113** (2014) 409-415.



(1) Reduction of the aqueous environment	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$
(2) Oxidation of the aqueous environment	$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$
(3) Reduction of the semiconductor	$MX + ze^- \rightleftharpoons M + X^{z-}$
(4) Oxidation of the semiconductor	$MX + zh^+ \rightleftharpoons M^{z+} + X$

Figure 6. (A) Indication of the penetration depth of blue (~450 nm), green (~510 nm) and red (~650 nm) light. (B) Band bending for n-type semiconductors under illumination: accumulation layer (negative surface charge), flat band potential and depletion layer (positive surface charge, most common for n-type semiconductors). Arrows indicate either recombination of generated electron-hole pairs, or charge separation in the presence of an electric field induced by band bending. (C) Schematic overview on the stability of semiconductors in water. Oxidation and reduction potentials of a semiconductor relative to the oxidation and reduction potential of H_2O. (D) Oxidation and reduction potentials relative to the Normal Hydrogen Electrode and vacuum level for relevant semiconductor pigments or pigment degradation products in aqueous solution at pH 7 (pH 8.5 for ZnO), plotted versus the valence (dark grey columns) and conduction (light grey columns) band edge positions at pH 7.

A significant insight gained here is that many pigments can be regarded as semiconductor materials that upon irradiation can release electrons and positive holes. These can trigger resp. reduction or oxidation reactions, either of the pigment itself of materials in its vicinity.

To support the sampling of degraded paint samples, on a number of the paintings mentioned in this report, MA-XRF scans were performed. An X-ray diffraction camera was integrated into an experimental setup for micro/macro-XRF/XRD. Results from this device were integrated into a paper devoted to new analytical methods for the characterization of painted cultural heritage artefacts.

Publication: S. Legrand, F. Vanmeert, G. Vandersnickt, M. Alfeld, W. De Nolf, J. Dik and K. Janssens, Examination of historical paintings by state-of-the-art hyperspectral imaging methods: from Scanning Infra-red Spectroscopy to Computed X-ray laminography, Heritage Science, 2 (2014) 13.

By means of chemically specific hyperspectral imaging methods, it becomes possible to visualize the distribution of secondary degradation products on the surface of works of art in a non-invasive/non-destructive manner. Systematic studies become possible.

2.3 Degradation study of the pigments Vermillion Red and Red Lead

2.3.1 Degradation of Vermillion Red [UA]

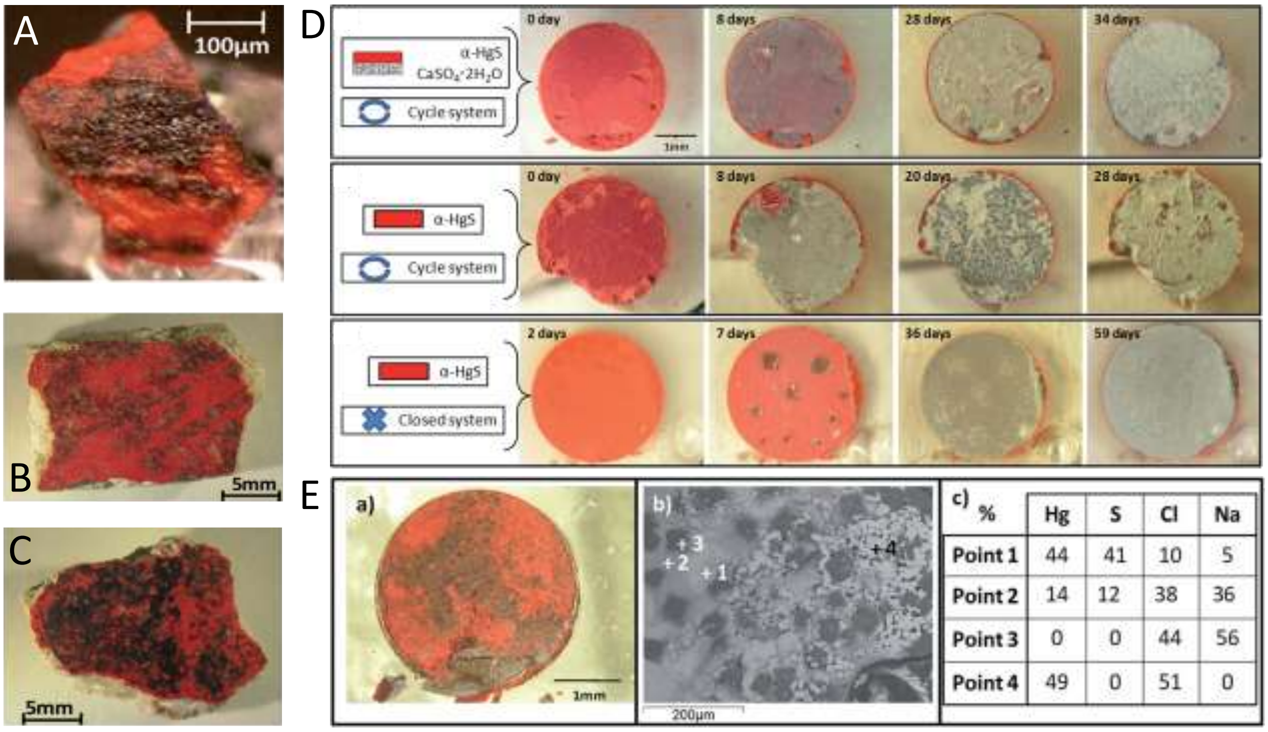
Vermilion red (α-HgS) is a very frequently used semi-conductor pigment from the neolithic period onwards. It has been mined prehistorically and historically in China, Japan, Europe, and the Americas to extract metallic mercury (Hg^0) for use in metallurgy, as a medicine or preservative, and as a red pigment for (body) painting and in ceramics.[7]

Chlorine and sulfur K-edge µ-XANES investigation were combined with µ-XRD to determine the alteration mechanism that causes red pigment to acquire a grayish-black aspect.[8] Paint fragments from works by P.P. Rubens and other 17th c. painters were examined.[9,10,11] Whereas elemental analyses of the degradation products revealed, along with mercury and sulfur, the presence of chlorine, XRD identified (in addition to α-HgS) calomel (Hg_2Cl_2) and the mercury-, sulfur-, and chlorine-containing minerals corderoite (α-$Hg_3S_2Cl_2$) and kenhsuite (γ-$Hg_3S_2Cl_2$). These observations are consistent with S- and Cl-edge XANES data. The resulting maps reveal a clear stratification between the primary mercury compounds (α-HgS) and the secondary species that arose from the interaction with environmental chlorine, leading the authors to hypothesize that α-HgS first takes up Cl, thereby converting into one or more $Hg_3S_2Cl_2$ phases. These light sensitive compounds, following the loss of sulfur atoms, can be transformed into Hg_2Cl_2, whereas sulfide ions oxidize into sulfate ions. The final step may involve the UV-induced disproportion of Hg_2Cl_2 to $HgCl_2$ and may cause metallic mercury to turn white calomel into a grayish-black substance. No evidence for this transformation could be found with X-ray methods however. To study in greater detail the principle environmental factors (light, presence of halides) influencing the instability of red mercury sulfide and to better understand the chemical equilibria governing the formation and evolution of the different degradation compounds, a thermodynamic study of the Hg-S-Cl-H_2O system was made in combination with theoretical considerations and experimental ageing experiments.

Publication: F. Da Pieve, C. Hogan, D. Lamoen, J. Verbeeck, F. Vanmeert, M. Radepont, M. Cotte, K. Janssens, X. Gonze, G. Van Tendeloo, *Casting Light on the Darkening of Colors in Historical Paintings*, Physical Review Letters, **111** (2013) 208302.

The degradation and discoloration of HgS is mainly caused by destabilising action of Cl-compounds.This converts HgS to Hg_2Cl_2 and causes formation of sulfates.

The latter were performed in O_2-rich and O_2-poor circumstances. From the results it could be concluded that Hg(0), α-$Hg_3S_2Cl_2$, and Hg_2Cl_2 can be formed from the reaction of α-HgS with ClO(g). Artificial ageing experiments were carried out on model samples following the conditions assessed in the first part, in order to reproduce natural ageing observed on red mercury sulfide. Similarly to degradation compounds detected on original works of art, mercury chlorine compounds such as calomel and corderoite were identified on the surface of α-HgS model samples, when exposed to light and a sodium hypochlorite solution. Together with these compounds, sulfates were detected as well, and more particularly gypsum ($CaSO_4.2H_2O$) when Ca was originally present in the model sample. These experiments also showed that light is a necessary factor to obtain degradation.



%	Hg	S	Cl	Na
Point 1	44	41	10	5
Point 2	14	12	38	36
Point 3	0	0	44	56
Point 4	49	0	51	0

Figure 7. Photographs of paint microfragments taken from: (A) *The Adoration of the Magi*, a painting by P. P. Rubens, Royal Museum of Fine Arts, Antwerp, Belgium; (B,C) a Roman fresco from *Villa delle Torre*, near Pompeii, Italy. (D) Pellets aged with NaOCl solution and light at different times of ageing: (top panel) two-layered vermillion|gypsum pellet, aged in a cyclic system; single-layered vermilion pellet, aged in (middle panel) cyclic and (bottom panel) closed system; (E) Visible and local backscattered electron (BSE) image of two-layered vermillion|NaCl pellet, aged with NaOCl in a closed system; the table shows quantitative SEM analyses results performed on the four points shown in the BSE image (in atomic percentage; Hg, S, Cl and Na concentrations were normalized to a total of 100%; C, O and Al data not shown here).

From the relevant Pourbaix diagrams, it follows that both calomel and corderoite can be formed at basic pH, which is consistent with their formation in the presence of NaOCl solution (pH 12) during artificial aging experiments. These compounds appear to be formed simultaneously but the visual aspect of the samples changed during the course of the ageing experiments, showing different steps and colors. In order to remain stable, corderoite needs chlorine to be always available as a reagent. In the case of aging in O_2-rich circumstances, corderoite after some time disappeared and was converted into calomel. It therefore appears that corderoite is an intermediate product in the reaction of the formation of calomel from α-HgS. Mapping of cross-sections obtained from the artificially aged samples revealed a multi-layered structure similar to the ones observed on altered works of art, with mercury chloride compounds on top of red mercury sulfide layers and sulfates at the surface of the samples. Compounds containing both S and Cl are found in intermediate layers. Concerning the visual aspect of the degradation of red mercury sulfide, the different compounds detected on the pellets and on historical paintings (calomel, corderoite, kenhsuite, gypsum) explain the observed white/purple colors, but not the black one. The attribution of the black colour to meta-cinnabar (β-HgS) turned out to be unfounded. Theoretical spectroscopic results have indicated that none of the minerals identified as degradation compounds on mercury sulfide samples is intrinsically gray or black.[12] The presence of elemental mercury was proposed as a by-product of the photo-induced mechanism that causes the darkening of the paintings. In some conditions, the formation of Hg^0 from HgS is indeed thermodynamically favorable. By means of electrochemical methods,[13,14] the formation of metallic mercury from HgS by the joint action of light and chloride ions could be experimentally demonstrated. All the above consideration could be brought together in the following sequence of chemical transformations:

$HgS \rightarrow \beta\text{-}Hg_3S_2Cl_2 \rightarrow \alpha\text{-}Hg_3S_2Cl_2, \gamma\text{-}Hg_3S_2Cl_2 \rightarrow Hg_2Cl_2 \rightarrow Hg^0 + HgCl_2$.

Publication: M. Radepont, Y. Coquinot, K. Janssens, J.-J. Ezrati, W. de Nolf and M. Cotte, *Thermodynamic and experimental study of the degradation of the red pigment mercury sulfide*, Journal of Analytical Atomic Spectrometry, **30** (2015) 599-612.

A sensitive electrochemical method, based on linear sweep voltammetry was used to provide a better insight into the final product of the degradation of HgS. By means of this method, we could finally demonstrate experimentally that HgS degradation leads to the formation of metallic Hg^0-nanodroplets, giving the paint material a dark/black aspect.

Publication: W. Anaf, K. Janssens, K. De Wael, *Formation of metallic mercury during photodegradation/photodarkening of α-HgS: electrochemical evidence*, Angewandte Chemie – International Edition, **52** (2013) 12568–12571.

The complete degradation mechanism of HgS, is a multistep process which can ultimately result in the formation of metallic Hg droplets.

2.3.2 Degradation of Red Lead [UA]

Minium or red lead (Pb_3O_4) is another frequently employed pigment since Antiquity. It contains both Pb^{2+} and Pb^{4+}-ions and has sometimes been observed to lose its red color. These transformations are either described as darkening of the pigment caused by the formation of either plattnerite ($\beta\text{-}PbO_2$) or galena (PbS) or as whitening by which red lead is converted into anglesite ($PbSO_4$) or (hydro)cerussite ($2PbCO_3.Pb(OH)_2$; $PbCO_3$). The degradation of minium is therefore also very much related to S-bearing compounds in its vicinity. By examining a degraded paint sample from Van Gogh's *Wheat stacks under a cloudy sky* (1889, KMM) by means of conventional 2D and tomographic XRPD, it was possible to elucidate the degradation mechanism of minium and identify a missing link compound (Vanmeert et al, 2015). The degradation process was understood to be induced by absorption of 550 nm (or shorter) wavelengths, promoting electrons from the valence to the conduction band of minium. These electrons may reduce Pb(+IV) to Pb(+II).

The *in situ* formed Pb^{2+} (perhaps in the form of PbO) then captures CO_2 (either atmospheric or the result of oxidation of the paint binding medium) to form various lead carbonates. Next to the frequently encountered cerussite and hydrocerussite, a very rare lead mineral, plumbonacrite ($3PbCO_3.Pb(OH)_2.PbO$), was revealed to be present. The location of this compound was revealed via XRPD-tomography of a hemispherical paint protrusion at which centre a partially degraded grain of minium was present. Evidence for the presence of a series of consecutive equilibria, gradually transforming plumbonacrite into cerussite via hydrocerussite was found. The influence of several parameters on the tendency towards degradation of minium such as (a) a surplus of PbO inside the red lead material itself, (b) the pH and (c) the concentration of available HCO_3^- or CO_3^{2-}-ions was investigated. For demonstrating the photoactivity of the pigment, an electrochemical setup with a minium-modified graphite electrode (C l Pb_3O_4) was used. It could be confirmed that minium behaves as a *p*-type semiconductor, photoactive during illumination and inactive in the dark. Raman measurements confirm the formation of degradation products. The photo activity of the semiconductor pigment is partly defined by the presence of PbO impurities; these introduce new states in the original band gap.

Publication: F. Vanmeert, G. Van der Snickt, K. Janssens, *Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting,* Angewandte Chemie – International Edition, **54** (2015) 3607-3610

Photo-activated minium can form different Pb^{2+}-carbonates. Next to cerussite and hydrocerussite these include plumbonacrite.

It was experimentally evidenced that the presence of PbO particles in minium leads to an upward shift of the valence band, reducing the band gap. Thus, upon photoexcitation, the electron/hole separation is more easily initialized. The PbO/Pb_3O_4 composite electrodes demonstrate a higher reductive photocurrent compared to the photocurrent registered at pure PbO or Pb_3O_4-modified electrodes. In the presence of bicarbonate ions, a significantly higher photoreduction current is recorded because the PbO that is formed *in situ* reacts further to become hydrocerussite. It could be shown that the presence of bicarbonates in the environment stimulates the photodecomposition process of minium and plays an important role in the degradation process.

Publication: E. Ayalew, K. Janssens and K. De Wael, *Unraveling the reactivity of minium towards bicarbonate and the role of lead oxides therein,* Analytical Chemistry, **88** (2016) 1564-1569.

The degradation mechanism of Red Lead involves take-up of HCO_3^- ions from the environment and is stimulated by excess PbO present in the minium pigment.

Degradation studies of the pigments Cadmium Yellow, Cadmium Red and Chrome Yellow

Cadmium yellow ($CdS/Cd_{1-x}Zn_xS$) refers to a class of yellow pigments frequently employed in the early 20th century by painters such as Henri Matisse, James Ensor, Edvard Munch and Vincent van Gogh. Cadmium and sulfur can be partially substituted to generate ternary phases with a wide range of colors from pale yellow to deep red. Among them, in $CdS_{1-x}Se_x$ solid solutions, the substitution of sulfur by selenium decreases the valence-to conduction energy gap, hereby modifying the color toward orange and red tonalities.[15],[16]
Of all the cadmium pigments, Cadmium Yellow (CdS) was the first to be synthesized. Proposed for artist's pigments in 1818, it was not commercially available until the 1840's. Cadmium oranges and reds where introduced shortly after, containing a solid solution of cadmium sulfide and cadmium selenide (general formula CdSeS). The first German patent depicting the fabrication process of CdSeS dates from 1892, but its application as a pigment is only described in 1909; date around which this material begins to be commercialized for artists' paintings. Its appearance seems to occur earlier in Germany (1907, De Haen) than in France (1909), England (after 1910) or the USA (1919), all in all indicating a limited presence until the 1920's. Further patents concerning improvements on its fabrication process are proposed until 1970, thus showing a variety of recipes.

2.3.3 Cadmium Red [ULg]

According to M. de Keijzer, Winsor & Newton began commercialising Cadmium Red in 1919, mentioning the use of the 1919 German patent corresponding to a "wet method" synthesis. There is proof that Claus & Fritz already sold it in Amsterdam in 1917, whereas Talens, first produced it in 1918. Lefranc & Bourgeois was already supplying it in France in 1911, and Charles Roberson & Co. (London) in London in 1912. The pigment was also produced earlier in time by Weimarfarbe GmbH, in Germany.

In the late 1920's, cadmium pigments co-precipitated with barium sulfate (BaSO4) made an appearance. This extender, which allowed reducing the pigment prices by half, was introduced within cadmium pigment formulations first in the USA (1926) and then in Europe, where patents date from1930 to 1940. Such formulations, also known as Cadmopones, are a fine physical mixture of chemical compounds but not a crystallographic one, which means that the addition of barium sulfate can be introduced alternatively by simple mechanical grinding of the pigment with BaSO4. However, this second procedure yields pigments of inferior quality than the ones obtained through co-precipitation in terms of durability. All in all, Cadmopones possess a mass tone equal to that of the pure pigment but lack the same tinting strength. Cadmium Red Lithopone (CdSeS·BaSO4) was introduced with great success due to its lower price and the possibility of manufacturing lighter shades.
Both Cadmium Red and Cadmium Red Lithopone are still being produced. They correspond to the following colour index numbers and formula:

Cadmium Red:	PR108 77202 CdSeS
Cadmium Red Lithopone:	PR108:1 77202:1 CdSeS *x*BaSO4

Other cadmium reds were introduced along the way: In 1950, briefly replacing CdSeS, a mercury cadmium sulfide (CdHgS, *aka* Mercadmium) was introduced due to a shortage of selenium as a consequence of WWII. The short lifespan of this pigment lasted only until 1960, when selenium became again available and the more toxic "cadmium red cinnabar" was abandoned.

Consultation of the data base of the Liège city museums allowed identifying 94 paintings in which metal sulfide containing pigments might be present. Both works of art in current exhibition and in museum storage spaces were considered for analysis. A screening campaign of the candidate paintings was conducted during the winter of 2014. This campaign consisted of a non-destructive non-invasive analysis with Energy-Dispersive X-Ray Fluorescence equipment (EDXRF) of the selected works of art, which allowed us to track down the presence of Cadmium Red. In the case of Cadmium Red, it shows the presence of cadmium, selenium and sulphur.

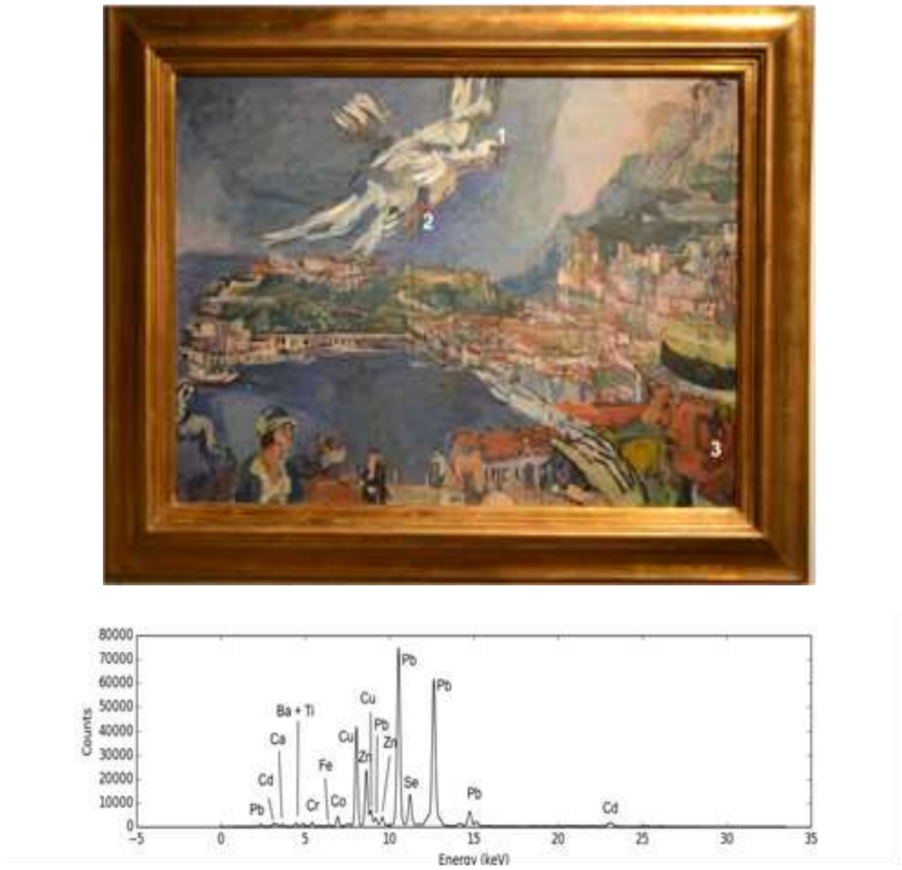


Figure 8. *Monte Carlo* (1925), by O. Kokoshka (Musée de Beaux Arts de Liège). CdSe was detected in the bird's claw and in the man's ear but not in the bird's eye.

In-situ cadmium sulfides (red and yellow) pigment identification was performed in half of the candidate paintings with EDXRF, through the presence of elements: S, (Se) and Cd. The following works of art containing cadmium red pigment were selected for examination:

- 21 Clédina Raphäel, Paysage mosan, 1914
- 30 Wouters Rik, Après-midi à Amsterdam, 1915
- 31 Carte Anto, Les aveugles, 1924

- 35 Flouquet Pierre-Louis, Femme à l'enfant, 1923
- 39 Scauflaire Elgar, Nature morte à l'étagère verte, 1933
- 53 Closon Henri Jean, Pas abolir – accomplir, 1934
- 54 Koenig Joseph, Portrait de Léon Koenig (fils de l'artiste), 1932
- 59 Lemaître Albert, Le bateau rouge, 1920
- 73 Maes Jacques, Marine, 1931
- 75 Kutter Joseph, Le clown, 1936
- 76 Kokoschka Oskar, Monte Carlo, 1925
- 86 Gorin Jean Albert, Composition no8, 1934
- 90 Guiette René, Puissance, 1893 (?)

In order to obtain a better understanding of the evolution of CdSe pigments, an extended study of CdSe pigments using mock-up samples was performed. Initially, three general methods of producing Cadmium Red were used:

- Reduction of cadmium selenate ($SeCdO_4$) or cadmium selenite ($SeCdO_3$).
- "Dry method": From the fusion of an adequate proportion of cadmium, selenium and sulfur powders in dry conditions, as explained in the patent by Morin and Janet (1909), where it is done in two stages: first heating the compounds up to 200 – 250°C in atmospheric conditions followed by calcination to 600°C within an inert atmosphere until the appropriate colour is observed. The colour depends not only on the calcination process but also on the granulometry of the reagents and ulterior grinding of the product. $CdSO_4(s)$ 100g + S(s) 10% + Se 5–7 % → CdSeS(s) 200 – 250°C

  Another modern dry method (patent by Cini and Melandri, 1971) employs heating of calcium sulfide and calcium selenide up to 450 – 500°C to obtain Cadmium Red.
- "Wet method": Bayer introduced this procedure in 1919, that involves the mixture of cadmium and selenium salts to form a precipitate from cadmium salt solutions with alkali and alkaline earth sulfides, with ulterior heating of the yellow precipitate to obtain the red hue. Thermal treatment has been later described at 300°C or 600°C depending on the recipe. Nowadays the procedures have evolved and new synthetic paths are being applied for its fabrication.

It could be established via XRD and Raman spectroscopy that Cadmium red, sold by color manufacturers in the early 20th century was a cadmium sulfoselenide. The hexagonal form is its most stable form. X-ray fluorescence analyses revealed that many other elements were also part of the composition of cadmium red, the most important being zinc and barium. It is assumed the zinc is in the form of a sulfide, a white compound, which would then allow the pigment to be diluted. The barium compound was identified via Raman spectroscopy as barium sulfate, a filler commonly used for a larger pigment production with a reduced concentration of the main elements of the pigment.

It could be concluded that the information provided by the historical color manufacturers is not always reliable or complete. The pigments of the Sennelier brand, described as pure and with the corresponding Color Index reference, actually contain barium sulfate and zinc. These therefore need to be regarded as Cadmium Lithopones instead of Cadmium

Red. It is therefore necessary to spectroscopically verify the composition of the pigments purchased from color manufacturers.

Accelerated aging of the different commercial cadmium reds was performed using the CEA (ULg) aging chamber. However, no alteration or degradation could be observed for Cadmium red. The experiments showed that the varnish applied to the paint protected it from environmental conditions, and thus protected the binder. The varnish therefore permits the preservation of the glossy appearance of the paint. When the paint is directly exposed to the environment, it becomes dull and loses its brightness. No reaction occurred on the pigment itself within the period of artificial exposure that was employed. Considering that the Musée de Beaux Arts in Liège is located within in the city centre, surrounded by an urban/industrial atmopshere containing pollutants such as SO_2, NO_x, peroxides or ozone (O_3), all reactive species that can degrade sulfide-based pigments, we can conclude that the currrent exhibition and storage conditions employed in the museum are adequate and that the Cadmium Red does not pose any conservation risk.

Cadmium red is a stable pigment, able to withstand oxidative influences from external chemical agents present in the museum atmosphere.

2.3.4 Cadmium Yellow [UA]

By employing a combination of S K-edge µ-XANES and µ-XRD, it could be established that the oxidation of the pigment cadmium yellow (α-CdS) to cadmium sulfate ($CdSO_4.H_2O$) (white/transparent) is the chemical transformation responsible for the loss of the bright yellow color in a painting by J. Ensor called "Stiff Life with Cauliflower".[17] By examining ins greater detail paint samples from a painting by Van Gogh called *Flowers in a Blue Vase* (1887, KMM), another chemical pathway was discovered to gives rise to the formation of an orange-grey superficial crust containing the grey/white mineral anglesite ($PbSO_4$) and cadmium oxalate. The different degradation pathways can be summarized:

1) simple oxidation, giving rise to transparent/whitish precipitates on the painting surface:

$$CdS + 2\,O_2 \rightarrow CdSO_4$$

2) oxidation followed by recombination with other ions, e.g. with oxalate and Pb^{2+} ions, resulting in an opaque, orange-grey crust to be formed on top of the surface:

$$CdS + 2O_2 + Pb^{2+} + OX^{2-} \rightarrow CdOX + PbSO_4$$

Publication: G. Van der Snickt, K. Janssens, J. Dik, W. De Nolf, F. Vanmeert, J. Jaroszewicz, M. Cotte, G. Falkenberg, L. Van der Loeff, *Combined use of Synchrotron Radiation Based Micro-X-ray Fluorescence, Micro-X-ray Diffraction, Micro-X-ray Absorption Near-Edge, and Micro-Fourier Transform Infrared Spectroscopies for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh*, Analytical Chemistry, 84 (2012) no. 23, 10221-10228.

Degradation of cadmium yellow can follow different paths but all involve the oxidation of the sulfidic ions to the sulfate form. The Cd^{2+} form different secondary compounds.

A similar strategy was employed to better understand the chemical and physical alterations of cadmium yellow (CdS) paints in Henri Matisse's *Le bonheur de vivre* (aka *The Joy of Life*, 1905-1906, The Barnes Foundation, Philadelphia, USA). These lead to fading, discoloration, chalking, flaking, and spalling of several regions of light to medium yellow paint. Similar secondary Cd-compounds such as $CdCO_3$, $CdSO_4.nH_2O$ and CdC_2O_4 (Cd-oxalate) as found in the Ensor and Van Gogh paintings could be identified. In thin sections of altered cadmium yellow paints from *Le bonheur de vivre* the distribution of various cadmium compounds confirms that cadmium carbonates and sulfates are photo-degradation products. On the other hand in *Flower Piece* (1906, H. Matisse, The Barnes Foundation), the cadmium carbonates appear to be remnants of the CdS manufacturing process, $CdCO_3$ being starting reagent.

Publication: E. Pouyet, M. Cotte, B. Fayard, M. Salome, F. Meirer, A. Mehta, E. Uffelman, A. Hull, F. Vanmeert, J. Kieffer, M. Burghammer, F. Sette, K. Janssens, J. Mass, *2D X-ray and FTIR micro-analysis of the degradation of cadmium yellow pigment in paintings of Henri Matisse*, Applied Physics A – Materials Science & Processing, **121** (2015) 967-98.

The degradation of cadmium yellow is influenced by synthesis residues present in the paint, among others $CdCl_2$ and $CdCO_3$.

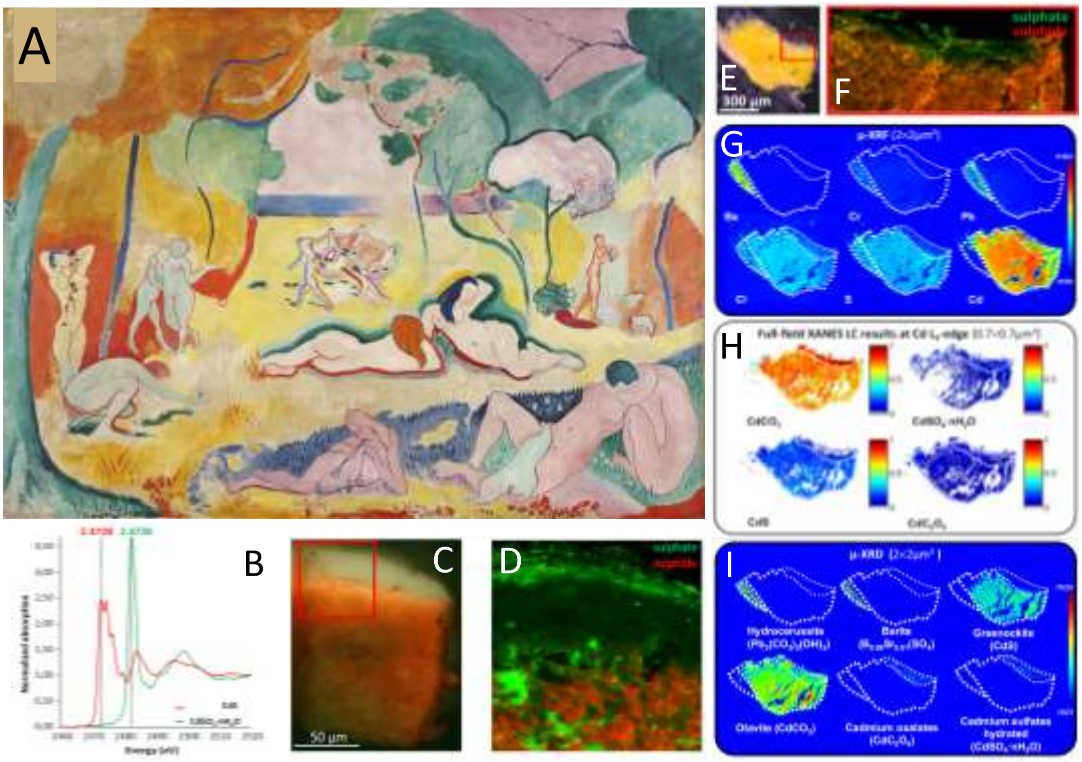


Figure 9. (A) *Le bonheur de vivre* (aka *The Joy of Life*, 1905-1906, oil on canvas, 176.5 x 240.7 cm, The Barnes Foundation, Philadelphia, BF719) by Henri Matisse; (B) S-Ka edge XANES of Cadmium yellow (CdS, in red) and its transparent/colourless oxidation product ($CdSO_4.nH_2O$, in green); (C,E) Optical photographs of paint cross sections taken from (A); (D,F) Compound sulfide (red)/sulfate (green) map of the areas indicated by the red rectangle in respectively (C) and (E) (step size: 1 x 1.2 μm^2); (G-I) XRF, full-field XANES and XRD maps of the sample shown in (E) showing the distribution of various primary and secondary paint components.

2.3.5 Chrome yellow: degradation-promoting role of Sulfur [UA]

Among the many colors employed by Vincent Van Gogh (and contemporary painters such as Monet and Gauguin) the use of yellow pigments becomes very important after 1885. While in his early period (1883-1885/6), he employed mainly Naples yellow (lead antimonate) or light hued earth pigments, in the second half of his career (when he works in Paris, Arles and St. Remy, 1885-1890), he frequently employs both chrome yellow and cadmium yellow.[18] As becomes clear from his correspondence,[19] chrome yellows are among Van Gogh's favored pigments, featuring in some of his most important paintings from the French period (1886-1890), such as for example the *Sunflowers* series of paintings. Already during his lifetime, Vincent van Gogh was aware of the lack of stability of chrome yellow.

To elucidate the reasons for the darkening of the originally bright *chrome yellow* (CY) paint in works by Van Gogh (see Figure 7), a combination of µ-XRF, S and Cr K-edge µ-XANES together with scanning transmission electron microscopy coupled to energy electron loss spectroscopy (STEM-EELS) has been employed.[20,21] The alteration proved to be caused by the surface reduction of Cr(+VI) to Cr(+III) but was very hard to document in a convincing manner using a combination of electron microscopy, Raman and FTIR spectromicroscopies only. In samples taken from various paintings and in artificially aged CY paint of that period, Cr(+III) species were found, usually at the boundary between the paint and varnish layers and in sulfur-rich areas (see Figure 7H). µ-XANES profiling and mapping (Figure7E-G) allowed to determine the superficial brown coating as being 2-3 µm in thickness and containing non-crystalline Cr(III) compounds such as $Cr_2O_3{\cdot}2H_2O$, $Cr_2(SO_4)_3{\cdot}H_2O$ and/or $(CH_3CO_2)_7Cr_3(OH)_2$.[20] The high sensitivity towards darkening of this material could be traced back to the presence of monoclinic and/or orthorhombic $PbCr_{1-x}S_xO_4$ ($0 \leq x \leq 0.8$) co-precipitate phases that are less stable than monoclinic (S-free) $PbCrO_4$ change from the monoclinic to the orthorhombic structure is observed in $PbCr_{1-x}S_xO_4$ when x exceeds 0.4.

An advanced form of high-resolution species specific mapping (by TEM-EELS) was employed to characterize a chrome yellow paint of ca 100 years old, during aging. This investigation showed very clearly how the product of the degradation, i.e. Cr_2O_3 is precipitating in the form of layers of 10-30 nm thickness on the outer surface of existing nanoparticles of $PbSO_4$ and $PbCrO_4$ that are originally present in (unstable) chrome yellow paint.

Publication: H.Y. Tan, H. Tian, J. Verbeeck, L. Monico, K. Janssens, G. Van Tendeloo, *Nanoscale Investigation of the Degradation Mechanism of a Historical Chrome Yellow Paint by Quantitative Electron Energy Loss spectroscopy Mapping of Chromium Species*, Angewandte Chemie – International Edition, **52** (2013) 11360-11363.

Sulfur-rich forms of chrome yellow are much more prone to spontaneous discoloration than sulfur-poor varieties. A nano-scale mechanism allows to explain the morphologiy of single and double shell core-shell particles.

The ageing of a series of *Chrome Yellow* model samples containing variable amounts of sulfate, revealed that the higher the sulfate level present, the more unstable the resulting pigment is. This effect causes the lighter varieties of chrome yellow to suffer the most from darkening. Irradiation with different bands of visible and UV light revealed that chrome yellow is especially sensitive to UV-VIS but also to blue light. This may have consequences for the lighting conditions in musea were paintings are on display containing sensitive subvarieties of chrome yellow. The results of this characterization were published in a series of papers. In this context, a large series of paint microsamples (ca 30) from paintings by Vincent Van Gogh were characterized by means of synchrotron methods. The results, clearly show the frequent presence of the unstable variant $PbCr_{1-x}S_xO_4$ in many paintings on the master.

Publication: L. Monico, K. Janssens, C. Miliani, G., Van der Snickt, G.; B.G. Brunetti, M. Cestelli Guidi, M. Radepont, M. Cotte, *The degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 3. Synthesis, characterization and detection of different crystal forms of the chrome yellow pigment*, Analytical Chemistry, **85** (2013) no. 2, 851-859.

Publication: L. Monico, K. Janssens, C. Miliani, G. Van der Snickt, B. Brunetti, M. Cestelli Guidi, M. Radepont, M. Cotte, *The degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 4. Artificial ageing of model samples of co-precipitates of lead chromate and lead sulfate*, Analytical Chemistry, **85** (2013), no. 2, 860-867.

Publication: L. Monico, K.H. Janssens, F. Vanmeert, M. Cotte, B.G. Brunetti, G. Van der Snickt, M. Leeuwestein, J. Salvant-Plisson, M. Menu, C. Miliani, *Degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 5. Artificial ageing of model samples of co-precipitates of lead chromate and lead sulfate*, Analytical Chemistry, **86** (2014) 10804-10811.

Sulfur-rich forms of chrome yellow, having a lighter hue than regular $PbCrO_4$, are frequently present in paintings by Van Gogh and contemporary artists and upon degradation, form thin superficial layer enriched in Cr(+III) at their surface.

Comparison of different types of museum light sources in relation to light-sensitive chrome yellow revealed that specific types of warm-LED lights, those emitting relatively few green and blue photons are inducing less damage that more conventional halogen light sources of the same emittance. However, lower quality LED illumination may have the inverse effect.

An irregularity in the wavelength dependence of light sensitive lead chromate lead to a systematic series of EPR-based measurements. These revealed the possible formation of Cr^{5+} species (which are very strong absorbers of green light) as part of the degradation process.

Publication: L. Monico, K. Janssens, M. Alfeld, M. Cotte, F. Vanmeert, C.G. Ryan, G. Falkenberg, D.L. Howard, B.G. Brunetti and C. Miliani, *Full spectral XANES imaging using the Maia detector array as a new tool for the study of the alteration process of chrome yellow pigments in paintings by Vincent van Gogh,* Journal of Analytical Atomic Spectrometry, **30** (2015) 613-626.

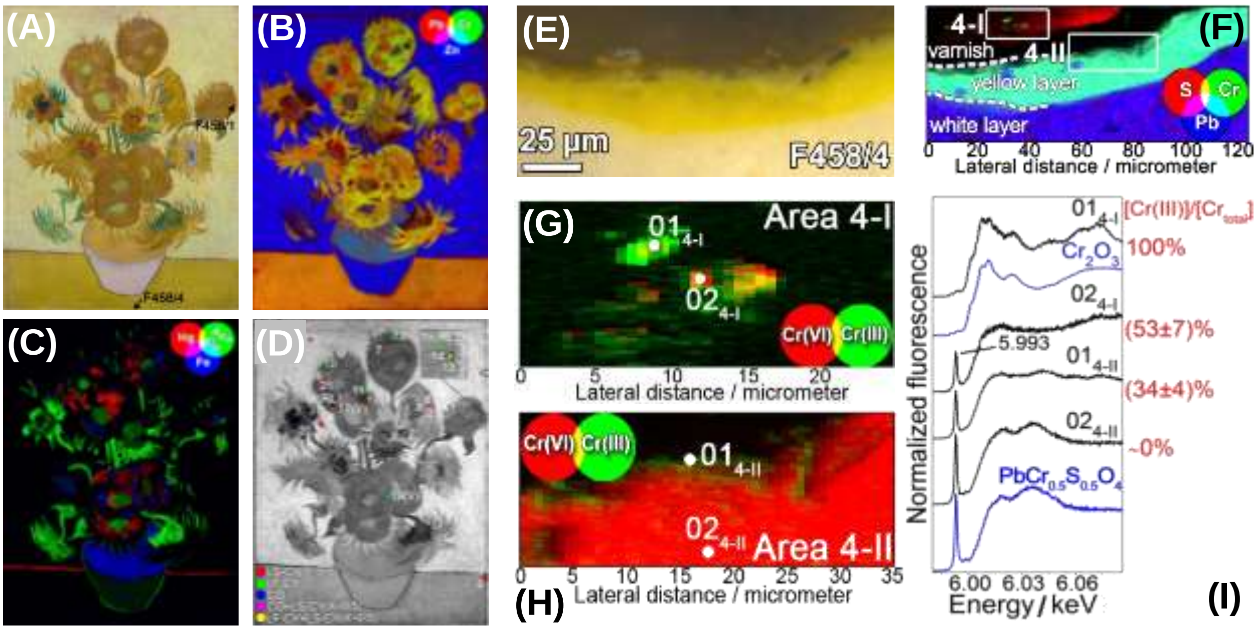


Figure 10. (A) Photograph of *Sunflowers* by Van Gogh (Arles, 1889; Van Gogh Museum, Amsterdam); sampling spots are also shown. RGB composite MA-XRF maps of (B) Pb/Cr/Zn and (C) Hg/As+Cu/Fe. (D) Raman and IR distribution of different CY types (LS-CY: light-sensitive chrome yellow ($PbCr_{1-x}S_xO_4$, with x>0.4); LF-CY: lightfast chrome yellow (monoclinic $PbCrO_4$); CO: chrome orange [$(1-x)PbCrO_4 \cdot xPbO$]). Triangles show the location of FTIR analyses;"V" and "RL" indicate spots containing also vermilion and red lead. The black circle denotes the location where only read lead was identified. (E) Photomicrograph detail of sample F458/4 where SR µ-XRF/µ-XANES analysis of (F-I) were performed. RGB SR µ-XRF images of (F) S/Cr/Pb [map size: 124×51.2 μm^2; pixel size (h×v): 1×0.25 μm^2; energy: 6.090 keV].(G-H) RG Cr(VI)/Cr(III) chemical state maps [pixel size (h×v): 0.7 ×0.2 μm^2] and (I) XANES spectra collected from areas indicated in (G-H). Maps of (G-H) were acquired in the regions shown in (F).

The reduction of chrome yellow pigments is not only triggered by UV light by also by green and blue wavelengths.

Four Van Gogh paintings were examined *in situ* with different mobile techniques such as portable XRF, reflection FTIR and portable Raman spectrometry. These paintings, all belonging to the collection of the Van Gogh Museum Amsterdam, include:

- Sunflowers (F458/1)
- Sunflowers Gone to Seed (F377/2)
- Bank of the Seine (F293/3)
- Portrait of Gauguin (X488/2).

The results of performing a series of mobile Raman, XRF and FTIR measurements on these paintings show that under the influence of light and humidity, S-rich chrome yellow varieties are prone to reduction, forming thin superficial layer of Cr(+III) degradation products.

Publication: L. Monico, K. Janssens, E. Hendriks, B.G. Brunetti, C. Miliani, *Raman study of different crystalline forms of $PbCrO_4$ and $PbCr_{1-x}S_xO_4$ solid solutions for the noninvasive identification of chrome yellows in paintings: a focus on works by Vincent van Gogh*, Journal of Raman Spectroscopy, **45** (2014) 1034-1045.

Publication: L. Monico, K. Janssens, E. Hendriks, F. Vanmeert, G. Van der Snickt, M. Cotte, G. Falkenberg, B.G. Brunetti, C. Miliani, *Evidence for Degradation of the Chrome Yellows in Van Gogh's Sunflowers: A Study Using Noninvasive In Situ Methods and Synchrotron-Radiation-Based X-ray Techniques*, Angewandte Chemie – International Edition, **54** (2015) 13923–13927.

Firm evidence for the presence of secondary Cr(+III) compounds on the surface of several Van Gogh paintings was found.

The combined effect of exposure to short wavelength light and seemingly innocuous atmospheric chemicals such as NaCl and related compounds on S-rich chrome yellow was investigated. One of the results is shown in the figure below. It is clearly visible that in the immediate vicinity of a NaCl crystal that deposited on the paint surface, the combined effect of both physical and chemical external agents can cause a very significant chemical degradation of the chrome-yellow containing paint.

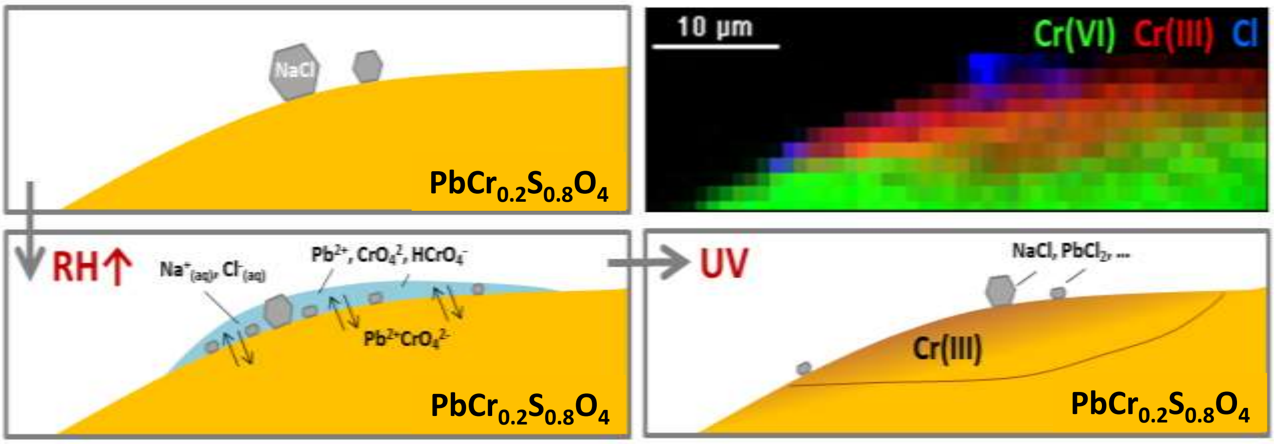


Figure 11. Ageing experiment of $PbCr_{0.2}S_{0.8}O_4$, covered with individual NaCl microcrystals before, during and after exposure to elevated levels of humidity and UV light. The XANES map shows the distributions of reduced Cr(+III) species (in red) in relation to the superficial remains of the NaCl crystals (in blue) and the original chromate material (green).

The formation of secondary Cr(+III) compounds on the surface of chromate paints can be readily induced by the joint action of individual NaCl crystals, humidity and UV-light.

2.4 Degradation studies of Arsenic Sulfide pigments [KIK-IRPA]

The decision to study the degradation pathways of orpiment was influenced by several factors: (1) Arsenic sulfide was and still remains extensively identified on many polychrome objects, from polychrome wood to paintings or manuscripts; (2) Natural orpiment has been less extensively studied than its red disulfide counterpart realgar; (3) The influence of light has been noted for many years but no fundamental studies have ever been conducted; (4) The incompatibility between arsenic sulfide and copper- or lead-based pigments is described but still remains unexplained.

Furthermore, arsenic sulfides are widely notorious for their instability toward light but, when found in artefacts, their degradation products are rarely identified. Consequently, questions arose. Are arsenic sulfides as light-sensitive as previously stated? Is their apparent (in)stability due to the binder? Is the lack of identification of degradation products due to the limitation of the apparatus available by museum/heritage scientists? All these problematic were relevant, not only for future scientific studies but also for conservators, preventive conservators or curators as expected results of this investigations include increased insights into the mechanisms of pigment degradation or the types of extrinsic factors that cause or catalyse these transformations. All of the information gathered during this research could therefore be used by the different parties for adapting conservation treatments or approaches as well as adjusting the storage or exhibition conditions of the arsenic-containing art objects.

Orpiment and realgar have been described as being incompatible with other pigments such as minium, verdigris or lead white, leading to their darkening. This has never been disputed as the darkening of minium or verdigris when found close by to arsenic sulfide pigments have been observed in painted artefacts. However, even if the darkened areas have been stated to be copper or lead sulfides, no scientific explanation has ever been given for this phenomenon. Therefore, this work also focused on investigating this singularity by looking at the pigments molecular level.

As mentioned previously, the initial focus of this work was on natural arsenic sulfide and especially natural orpiment. However, the identification of amorphous arsenic sulfide in several works of art broadened the aim of the study to a quite unexpected material. Therefore, along with understanding the stability and compatibility of crystalline arsenic sulfide, this works also aimed to find clues to characterize the amorphous materials and their manufacturing processes. Such information is of the foremost importance to understanding the changes in painting techniques from one period to another. Indeed, one can wonder, did amorphous arsenic sulfide take over the natural form due to a better stability? Were they used because of easy synthetic processes?

An extensive literature review was undertaken in order to understand better the use of Arsenic Sulfide pigments in cultural heritage as well as their properties regarding stability and aging. In addition, the different synthesis processes were considered, from a single melt of the crystalline material to the melt/quench according to industrial recipes.

The prepared pigments, together with the natural arsenic sulfides, orpiment and realgar were characterized by Raman spectroscopy. The assessment of the all forms arsenic sulfides stability was further investigated by microfadometry. The microscopic and spectroscopic characterization of both natural and artificial arsenic sulfides allowed to highlighted singularities allowing their differentiations, from size, shape, composition or presence of secondary peaks in spectroscopic techniques. The assessment of the different arsenic sulfides stability was further investigated by microfadometry.

One of the guideline in conducting this research was to give clues to conservators and heritage scientists on characterizing arsenic sulfides pigments and their degradation products in works of art. The investigation of the degradation products was carried out on the mockup paint samples by means of widely available techniques such as Raman or Fourier transform infrared (FTIR) spectroscopies, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) and the synchrotron-based micro X-ray absorption near edge structure (µ-XANES). This later technique was used to demonstrate the presence of arsenates in degraded arsenic-containing historical samples whereas not identified in previous Raman or FTIR studies. Along with spectroscopic methods, the electrochemical and colorimetric techniques were further used to study the stability, binder influence and incompatibility of arsenic sulfide pigments. The UV-Vis diffuse reflectance (UV-DR) spectroscopy was used to highlight the semiconducting nature of arsenic sulfide materials.

Finally, a combined Raman spectroscopy and µ-XANES study on both historical and mock-up paint samples permitted to venture a possible explanation regarding the darkening of copper- and lead-based pigments due to close by arsenic sulfides.

2.4.1 Synthesis and characterization of amorphous arsenic sulfide pigments

Throughout this research, Raman spectra presenting a broad band centred around 340 cm^{-1} were observed for compounds that were identified as arsenic sulfides by means of elemental analysis such as scanning electron microscopy coupled to energy dispersive X-ray analysis (SEM-EDX). The Raman findings appeared quite surprising as arsenic sulfide compounds are often categorized either as yellow natural orpiment (As_2S_3), orange-red natural realgar (As_4S_4) or yellow pararealgar (As_4S_4), the light-induced degradation of realgar; all compounds presenting well documented characteristic Raman spectra.[22,23,24,25] However, none of the compounds or known degradation products such as arsenic oxide appeared to match these references. After careful research extending into the infrared optics field, it appeared that the unexpected arsenic sulfide compounds corresponded to amorphous arsenic sulfide, a material very well known in the field of chalcogenide glasses for its semiconducting properties and its ability to transmit across a wide range of the infrared electromagnetic spectrum and already described as being used in works of art is the past.[26,27,28,29] Nonetheless, such material remains fairly unknown in the field of heritage science despite being mentioned in pigments encyclopaedias since the 14th century.[30]

A literature review focusing on amorphous arsenic sulfide in European, and particularly French, sources has been undertaken and gives a fair overview of the evolution of the amorphous arsenic sulfides production processes throughout time, from the simple sublimation of natural orpiment in the 14th-15th century to the precipitation of fine particles with the development of the wet chemistry in the 19th century. In order to understand better its use in cultural heritage as well as its properties regarding stability and aging, a synthesis of such material was considered and led to materials with various purities or compositions (Figure 12) before opting for an industrial procedure.

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Figure 12. Photographs of (a) ground natural orpiment, (b) ground natural realgar, (c) ground g-$As_{25}S_{75}$, (d) g-$As_{30}S_{70}$, (e) g-$As_{34}S_{66}$ and (f) g-$As_{40}S_{60}$.

From the literature review, trends regarding the production and use of artificial arsenic sulfides can be drawn. First of all, it is quite clear that two processes became available over time: the dry process (melting or sublimation of powdered materials) since the medieval times followed by a wet process after the development of wet chemistry in the 19th century.

From the first procedure description in the early 16th century Paduan manuscript to the 20th-century industrial manufactures, a clear evolution is witnessed within the dry processes. Amorphous arsenic sulfide was first obtained by melt or sublimation of natural pigments with or without external sources of arsenic and sulphur and, later on, by melt/quench or sublimation of arsenic oxide and sulphur mixtures. However, discrepancies regarding these recipes and especially the aim of the sulphur in the shading of the final material are observed. While it appeared clear from the industrial products that the more sulphur in the final product the more yellow, ancient recipes have advised to increase sulphur content in order to obtain darker hues. The purity of the dry-process amorphous arsenic sulfides mostly depends on the "baking" properties, allowing both the arsenic and the sulphur to react with each other when adequate temperatures are reached.

Regarding the amorphous pigment obtained through wet chemistry, the conversion degree and thus the purity of obtained product appears to depend mostly on the stoichiometry between the reactants and also on its purifying by filtering and rinsing in order to eliminate traces of arsenic oxide when it has not fully reacted.

Sulphur remnants are often observed in sulphur-rich amorphous arsenic sulfide pigments. Along with the presence of sulphur, realgar-like nano phases, which can be considered as crystalline nanophases included in the glassy matrix, can also be found (Figure 13). The latter peculiarities in the amorphous arsenic sulfide are often related to the experimental variables such as the raw materials, melting temperature or quenching time and can therefore be used to differentiate between different materials when found in artefacts.

Next to natural, crystalline orpiment (As_2S_3) and realgar (As_4S_4) also a glassy arsenic sulphide (g-As_xS_y) can be encountered in works of art.

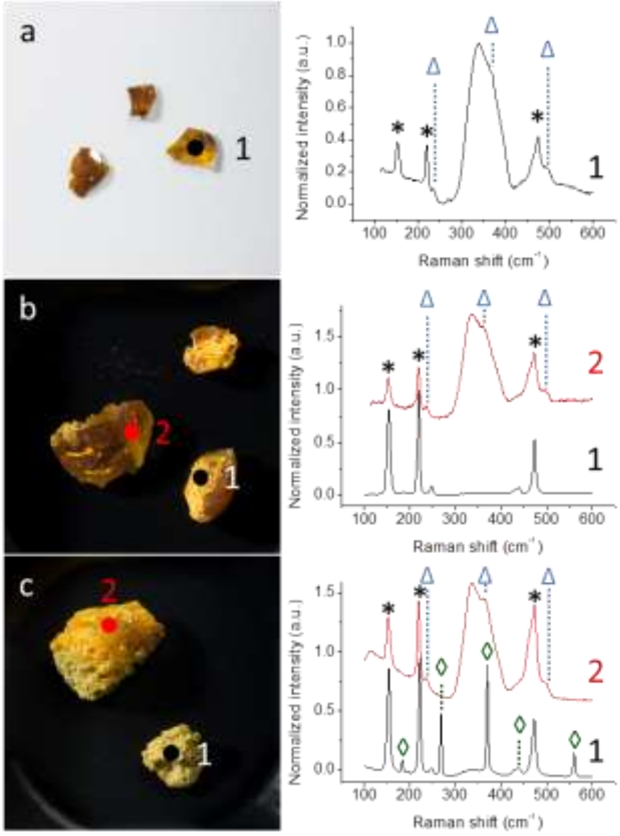

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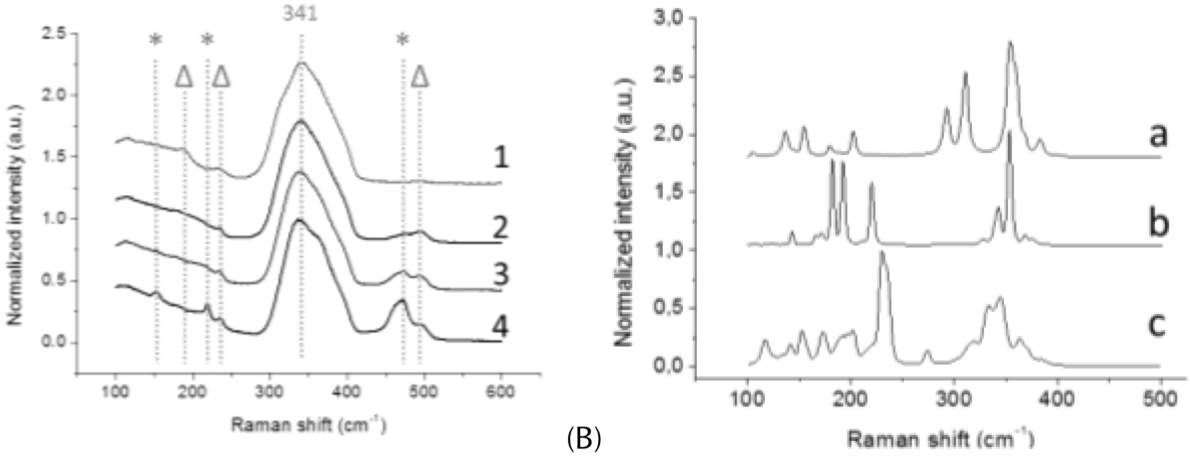
Figure 13. Photographs of the laboratory-synthetized amorphous arsenic sulfide according to different recipes (a, b and c) and the Raman spectra obtained on the associated material (location indicated by the red and black dots and the numbers refer to the underneath spectra). On the Raman spectra, asterisks (*) refer to the sulfur contributions while diamonds (◊) correspond to the arsenic oxide and triangles (Δ) to the realgar-like nano phases observed in the obtained amorphous materials. © KIK-IRPA, Brussels.



(A) (B)

Figure 14. (A) Raman spectra of (1) g-$As_{40}S_{60}$, (2) g-$As_{30}S_{70}$, (3) g-$As_{34}S_{66}$ and (4) g-$As_{25}S_{75}$. The asterisk (*) indicate the Raman bands characteristic for sulfur while the triangle (Δ) correspond to the bands characteristic for realgar-like nano phases; (B) of (a) natural orpiment, (b) natural realgar and (c) pararealgar, all obtained with a 785 nm laser excitation.

2.4.2 Mock-up samples and artificial aging

The long term evolution in the As-containing pigment type (natural vs. artificial) and the production techniques for the latter (diverse raw materials) can be used as indications regarding the period of an paint art object production. Therefore, such information can be relevant in order to better understand the context in which an art object has been created. Furthermore, being able to identify the arsenic sulfides as either natural or artificial may lead, due to their different nature, to various conclusions regarding the apparent (in)stability of the pigments as well as their interactions within the paint system or with the extrinsic elements such as light, humidity, gas or particulate matters. The influence of the light and the binding medium was studied further during this research through the realization and artificial aging of mock-up paint samples. The influence of the sulphur present within the pigment itself was, however, not assessed and should therefore be done as part as future research.

Two commercially available natural pigments (natural orpiment and natural realgar, both from Kremer Pigmente, Germany) as well as four amorphous laboratory-prepared artificial pigments of known compositions (g-$As_{40}S_{60}$, g-$As_{34}S_{66}$, g-$As_{30}S_{70}$ and g-$As_{25}S_{75}$) were considered (Figure 14A). The pigments were mixed together with selected binders in a 1 to 1 mass ratio and applied on a polycarbonate substrate or microscope glass slides for artificial aging and analysis purposes. One set of pure medium was prepared by depositing drops of the binding medium on a polycarbonate substrate.

The binders considered for the study were chosen based on historical context and by their identification in works of art when used with arsenic sulfide pigments. They were chosen as follow: glue, egg yolk, egg white, gum arabic, pre-polymerized linseed oil and Urushi lacquer, and are representative of most types of binders used from Antiquity to early 20th century (proteins, carbohydrates and lipids).

The prepared mock-up paint samples were artificially aged in order to accelerate their degradation while trying to rank the stability of the different forms of the pigments and assess the effect of the binding materials. The aging was carried out in an ATLAS Suntest CPS+ (Atlas Material Testing Technology LLC, Illinois, USA) equipped with a coated quartz and UV special glass simulating an outdoor light exposure. Samples were placed horizontally and perpendicular to the light source at around 35°C and 18 % relative humidity. They were aged for up to 20 weeks at a 650 W/m² and 175000 lux irradiation.

In order to determine relative differences in light sensitivity of the studied pigments and the binder influence on their degradation, a microfading tests was used. It uses an Oriel 75 watt Xenon arc lamp light source controlled by a universal arc lamp power supply and digital exposure control flux meter (Newport Corporation). The period of exposure is monitored with a probe that transforms the reflectance spectrum into color coordinates in real-time. A microfading test, results of which were expressed as a color change (ΔE), was achieved in 14 minutes.

2.4.3 Characterisation of arsenic sulfide pigments and their degradation products

When it comes to identifying arsenic sulfide pigments based on the elemental analysis and the color, the results can be easily misinterpreted. In characterization studies of arsenic sulfide pigments, there is actually a high probability that conclusions regarding the exact nature of the compounds present are drawn prematurely. In many cases, the encountered arsenic sulfide was recognized as being a mineral orpiment while in reality, it appears with further characterisation to be pararealgar - the yellow degradation phase of realgar. In others cases, distinction between natural and artificial arsenic sulfides was not remarked. The "artificial orpiment" question is much more complex than it seems. It can be produce following two different processes, wet and dry, and different starting material can be used.[31,32] This will always lead to arsenic sulfide pigments but their structure and properties can be different. Contradictions about the exact nature of arsenic sulfide pigments can also be found in published scientific literature or pigment encyclopaedias, sometimes confusing realgar with an arsenic sulfide glass of unknown composition.[33]

In order to understand the exact nature of the arsenic sulfide pigments, their composition and their characteristics, a multi-technique approach is often required. When analysing arsenic sulfide pigments, easily accessible laboratory-based techniques such as SEM-EDX, Raman and FTIR spectroscopies or polarized light microscopy allow access to valuable information regarding the nature of the pigment.[34,35,36,37,38]
As presented in Figure 14B, when only the nature of the pigment is foreseen – natural vs. artificial; orpiment vs. realgar vs. pararealgar, the information obtained by selected techniques such as Raman spectroscopy can be considered enough.[22,23,24,39] However, when artificial arsenic sulfide is found with Raman spectroscopy, further techniques such as polarized light microscopy or X-ray diffraction might be essential in order to understand better its fabrication processes.

Due to their abilities to characterize molecular features, spectroscopic techniques such as Raman or FTIR appear to be powerful techniques for the identification of selected degradation products. Raman will clearly highlight the presence of pararealgar or arsenic oxide based on their characteristic spectra that are different from that of the crystalline compounds (Figure 15a-c). Even if, FTIR will not allow the identification of arsenic sulfide species due to their transparency to the mid and far IR; it remains a suitable technique for highlighting arsenates (Figure 15d) and arsenic oxide (Figure 15e), two of the degradation products of arsenic sulfide pigments, when present in sufficient amount.

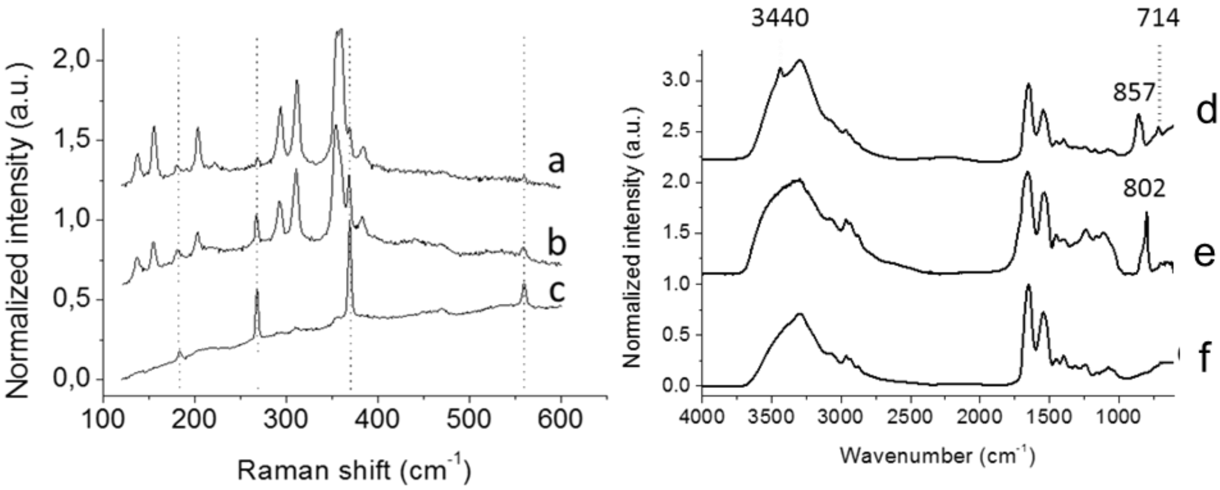


Figure 15. Raman spectra obtained on the degraded surface of (a) an Egyptian sarcophagus and (b and c) an Egyptian canopic jar presenting the characteristic bands for arsenic oxide (As_2O_3), one of the expected oxidation products of arsenic sulfide. Spectra d, e and f present FTIR spectra in transmission mode for (d) sodium arsenate, (e) arsenic oxide, both bound in (f) egg white protein binder. The characteristic wavenumbers are indicated.

Realgar first is converted to pararealgar prior to arsenolite formation; orpiment is directly converted to arsenolite.

Scanning electron microscopy coupled with an EDX detector, µ-Raman spectroscopy, polarized light microscopy and Fourier transform infrared spectroscopy have been used throughout this research as part of a multi technique approach to identify the arsenic sulfide pigment(s) used in various works of art as well as their degradation products.

Based on the size, shape and elemental composition of the particles (SEM-EDX data), the wavenumber and spectrum profile obtained in Raman and FTIR spectroscopy as well as the optical properties of the pigments in PLM, it appears possible to distinguish between natural and artificial arsenic sulfide pigments.

Satellite bands observed for amorphous arsenic sulfides in Raman spectroscopy may inform on the manufacturing process or initial material used. Indeed, when observed, sulphur and realgar-like nano phase bands may point toward an arsenic sulfide glass obtained through dry process (Figure 16). This can be further investigated by means of polarized light microscopy. The latter technique will demonstrate the use of sulphur and arsenic oxide rather than natural orpiment by assessing the lack of interference colours characteristic for natural pigments. On the other hand, the simultaneous presence of the characteristic signals for both natural and amorphous material in Raman spectroscopy (Figure 16) may indicate a synthesis by melt/sublimation of the natural pigment, either orpiment, realgar or pararealgar.[29]

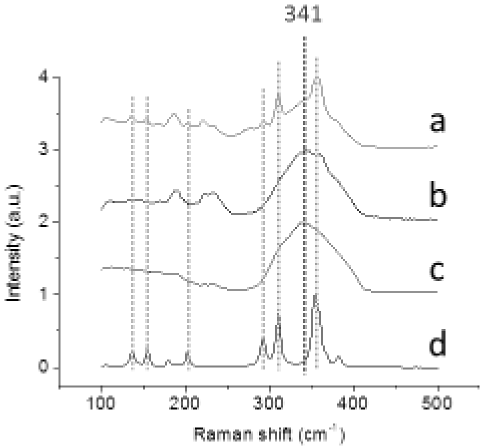


Figure 16. Raman spectra obtained on historical samples (a and b) and presenting the characteristics for amorphous arsenic sulfide (c) and natural orpiment (d).

Even though suited to identify other degradation products such as arsenate or sulfates, laboratory-available techniques, especially Raman and FTIR spectroscopies, often fail to characterize them. Indeed, even though these techniques are quite widespread in the cultural heritage field and have non-refutable advantages with respect to pigment and binder identification,[40,41,42,43] their detection limits for arsenic sulfide degradation products and especially arsenates are too low to allow their detection and identification. However, in the field of environmental science, the oxidation of As(III) (arsenite) into As(V) (arsenate) is often described; this transformation is instrumental for removal of As from the drinking water.[44,45,46] In recent years, it has been shown by means of microscopic and advanced spectroscopic techniques that the oxidation of the arsenic sulfide pigment in works of art continues when the initially formed oxidation product, water soluble arsenic oxide, is in the presence of moisture from the surrounding matrix and environment.[47,48] In this second step, arsenate compounds such as schultenite ($PbHAsO_4$) can be formed. However, up to now, this type of oxidation was not often identified in the cultural heritage field; mainly due to the limited speciation possibilities offered by the more conventional techniques for paint layer microanalysis such as Fourier transform infrared (FTIR) or Raman spectroscopies. Nevertheless, the recent development of more advanced methods of arsenic speciation analysis based on synchrotron radiation allows to clearly demonstrate the presence of As(V) compounds, likely in the form of arsenates, in historical samples.

Based on the XANES results and energy maps obtained, a qualitative difference in the stability of various types of arsenic sulfide pigments is supposed: the amorphous artificial form of orpiment is most likely more stable than the crystalline form. XANES examination of the amorphous glassy form revealed the presence of less arsenate among the degradation products in comparison to the crystalline equivalent. While XANES is not sufficiently specific to distinguish with some confidence among different arsenates, their occurrence as degradation products is consistent with the presence of compounds such as schultenite ($PbHAsO_4$).

Amorphous orpiment is more stable than the natural crystalline form.

A positive identification of this degradation compound by means of XRD, a more specific method of speciation, was realized on a 17th century painting by de Heem. Similar investigations are still on-going for various 17th century paintings showing realgar/orpiment discoloration.

Most of this research used widely available scientific techniques to investigate and reference the physical and chemical characteristics of arsenic sulfide pigments particles in different microscopic and spectroscopic techniques. Which makes this research of most interest for the heritage science community as it can be exported to most museum laboratories. The originality of this work was to use synchrotron radiation XANES in order to highlight the presence and image the fate of the arsenic sulfide pigments within the paint cross-sections. The findings have been published in various peer-reviewed publications, presented during several international conferences and will be available as part of Marc Vermeulen's doctoral dissertation.

Throughout the project, amorphous arsenic sulfide has been reported by Raman spectroscopy in numerous historical samples. This has been warmly welcomed by the community as most of the amorphous arsenic sulfide reported was either misidentified as natural arsenic sulfide or identified through optical techniques with the limitations that are the lack of knowledge of such materials or the artefacts induced by the optical devices. It is important to mentioned, that a research about sublimed arsenic sulfide pigments in paintings and polychromies was reported in the past,[29] but this work was focused on the production processes and did not report pure synthetized amorphous arsenic sulfide spectra.

Through this multi-analytical approach, natural orpiment, arsenic oxide, arsenate and amorphous arsenic sulfides were identified in various works of art:
Natural orpiment
Egyptian Canopic jar, unknown artist(s), 2033 – 1786 BC
Egyptian sarcophagus, unknown artist(s), 1059 – 945 BC
Saint Anne Trinity, unknown artist, 1400-1410
Enghien altarpiece, unknown artist(s) ca.1540
Oplinter altarpiece, unknown artist(s), ca. 1530
Bouvignes altarpiece, unknown artist(s), ca. 16th century
Lanaken altarpiece, unknown artist(s), 16th century
Descent from the Cross, Peter Paul Rubens (?),1577 – 1640
A stone cartouche with a garland of flowers, Daniël Seghers, ca. 1655

Couple in a garden, unknown artist, 18th century (?)
Arsenic oxide
Egyptian Canopic jar, unknown artist(s), 2033 – 1786 BC
Egyptian sarcophagus, unknown artist(s), 1059 – 945 BC
A stone cartouche with a garland of flowers, Daniël Seghers, ca. 1655
Arsenate
A stone cartouche with a garland of flowers, Daniël Seghers, Ca. 1655
Couple in a garden, unknown artist, 18th century
Amorphous arsenic sulfide
Couple in a garden, unknown artist, 18th century
(most likely sublimation of natural orpiment)
The Holy Family, Walter Pompe, 1730
(most likely sublimation of pararealgar)
Decorative panels of the Brussels Japanese Tower, 1900-1904
(several dry processes from arsenic oxide and sulphur)
Kirkarakawakami (Japanese style wallpaper), unknown artist(s), ca. 1900
(most likely dry process from arsenic oxide and sulphur)

Trends regarding the use of arsenic sulfide pigments as well as the synthesis of amorphous pigments can be drawn.
This work led to the publication "Identification of artificial orpiment in the interior decorations of the Japanese tower in Laeken, Brussels, Belgium" as well as several posters and oral presentations during national and international conferences.

In a representative series of artworks, oxidation products of As_xS_y in the form of arsenolate and arsenates were encountered.

2.4.4 Assessment of the stability, binder and light influence on the degradation of arsenic sulfide pigments

Stability. Over their time of use, arsenic sulfide pigments have been found mixed in various medium ranging from water-based Arabic gum (polysaccharide) to protein-based or oil-containing binders.[39,49,47] One of their main characteristic extensively described in manuscripts and painters manuals is their light sensitivity leading to the formation of white arsenic oxide often reported in artworks.[50,51,52,53,54,24] This transformation leads to a global loss of colour and transparency of the pictorial layer[55] and is described as a light fastness phenomenon.

While arsenic oxide and arsenate are identified as two of the degradation products of the natural pigments,[56,47,57] these products are often not observed in the degradation of the amorphous pigment. Indeed, when amorphous arsenic sulfides were identified in works of art, degradation products such as arsenic oxide were not identified nor mentioned.[49] This lack of degradation products leads to suppose their better stability compared to the crystalline forms, however, this lacks scientific evidences. Following the recent introduction of electrochemistry as a valuable tool to quickly assess the stability of semiconducting pigments such as vermilion (HgS) or minium (Pb_3O_4) by measuring the induced photo current upon monochromatic light illumination,[58,59,60] a similar approach had been used to assess the stability of natural orpiment, realgar and amorphous arsenic sulfides, all classified as semiconducting pigments.

The band gap energy of the studied materials, both crystalline and amorphous were measured by means of UV-Visible diffusive reflectance (UV-DR) spectroscopy and compared to one another as the value of their band gap may also be linked to their potential (in)stability. As all compounds have been found to be semi conducting materials, the evolution of their photo-induced current was measured and all three pigments proved to behave differently when exposed to a light source. While the photo activity of all pigments is initially high, it appears to decrease drastically within a short illumination time for both natural orpiment and amorphous arsenic sulfide. The drop in photo current observed for natural realgar is not as abrupt as the one observed for the two other pigments but lasts longer. For both natural orpiment and amorphous arsenic sulfide, the photo activity stabilises within the first few minutes of illumination while the photo current for natural realgar did not stabilize with the setup used. The amorphous form maintains however a rather important photo activity compared to the two crystalline forms which clearly illustrate the higher stability of the amorphous form compared to the crystalline ones (Figure 17a).

The light stability of all forms was further investigated by microfadometry using a much stronger light source than the one used in the electrochemical setup (750 W vs. ca. 30 mW, Figure 17b). Therefore, the data obtained for the microfadometric study is more representative of a long-lasting light exposure. The results obtained for the initial phase of the experiment is conclusive with the results of the electrochemical study: the amorphous form is more stable than the natural orpiment which is itself more stable than the natural realgar. However, when increasing the exposure time, the behaviour of amorphous arsenic sulfide changes and tends to match the behaviour of natural realgar. Therefore, it appears that on a short term scale amorphous arsenic sulfide is the most light-stable pigments of the three but is the least stable for longer exposure time.

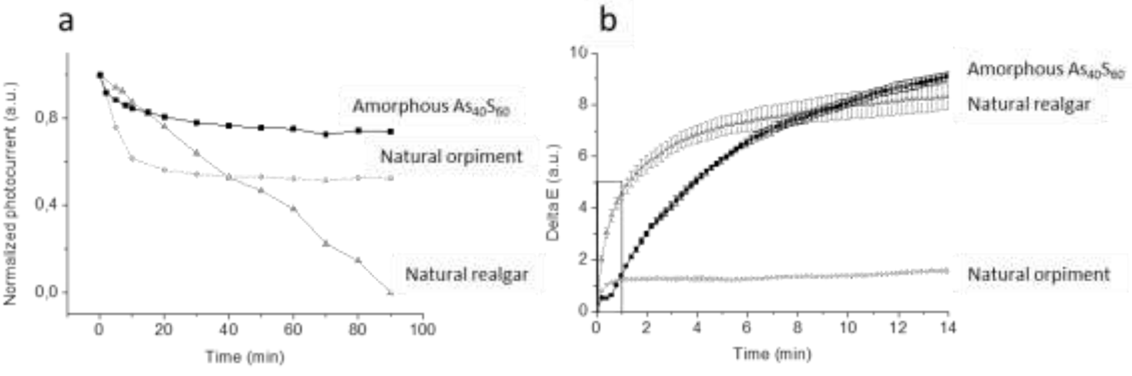


Figure 17. Evolution of the (a) normalized photocurrent (b) fading obtained for natural realgar, natural orpiment and amorphous $As_{40}S_{60}$

The initial stabilities have been explained by the crystalline and amorphous nature of the materials, the crystalline materials presenting more weak bonds easily breakable upon light-exposure than the strong covalent bonds present in the amorphous materials. The long-term behaviour of amorphous arsenic sulfide is however quite unexpected and would require more research.

Binder influence. In art works, arsenic sulfide pigments appear to behave differently depending on the medium in which they are bound. Degradation products have been mostly observed in oil based painted artefacts[48,57,56] but rarely in polysaccharide-based paintings such as in illuminated manuscripts.[61,62,63,64] This raised suppositions regarding the influence of the binding medium on the degradation of these pigments, both natural and artificial. Two series of mock-up paint samples composed of a 1:1 pigment/binder mixture were prepared and artificially aged for up to 20 weeks.

Since electrochemistry-based were found not be suitable to study this type of experiments, monitoring experiments were carried out with two alternative techniques: micro Fourier transform infrared spectroscopy (µ-FTIR) and micro x-ray absorption near edge structure (µ-XANES): the former to quantify the formation of arsenic oxide and the latter to follow the formation of sulfate.

For the FTIR measurements, micro samples of aged mock-up paint samples were flattened between two diamond cells and measured in transmission mode. The intensity ratios of the arsenic oxide over amide II (characteristic for the proteins present in egg yolk, egg white and glue) vibrational signal (Figure 18a) and of the arsenic oxide over the CH_2 vibration signal (characteristic for the lipids present in egg yolk and oil - Figure 18b) shows that not all binders will have the same influence on the aging of arsenic sulfide pigments.

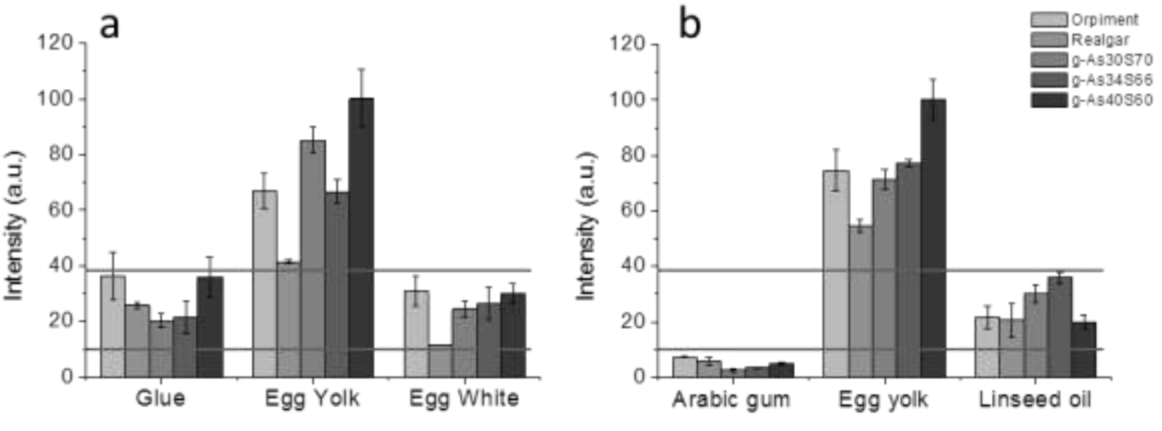


Figure 18. Bar histogram representing (a) the As_2O_3/Amide II and (b) the As_2O_3/aliphatic CH_2 area ratios in given medium for natural orpiment, natural realgar and three amorphous arsenic sulfide pigments of known arsenic and sulfur composition (30/70, 34/66 and 40/60) measured in transmitance FTIR.

Egg yolk is least suitable medium, causing the most arsenic oxide to be formed; pigment bound in gum Arabic will present the best conservation state in a dry environment. The XANES data (not shown) confirm the FTIR analyses.

The binding medium influences the speed of degradation of As_xS_y*.S-rich egg yolk stimulates the degradation much more than other binding media.*

The influence of light on the unbound reference pigments was investigated through Raman spectroscopy by looking at the $AsS_{3/2}$ light-sensitive bond. The pigments were exposed to monochromatic light (blue 405 nm and green 534 nm) and of different power (12 or 30 mW). By measuring the intensity decrease of the $AsS_{3/2}$ band, the sensitivity of arsenic sulfide pigments to certain light wavenumber and energies was identified (Figure 19).

Figure 19 clearly shows that the orpiment is mostly sensitive to the power of the light received as the most degradation is observed for 30 mW blue and green light illuminations (a and b). Almost no structural changes are observed for 12 mW blue light illumination (c) which is commonly said to be the most dangerous wavelength for pigments. However revealing, this study only took into consideration 2 specific wavelengths found in the visible range. It should be further investigated with more wavelengths in the visible range but also include UV illumination as well as external factors such like pollutants or humidity.

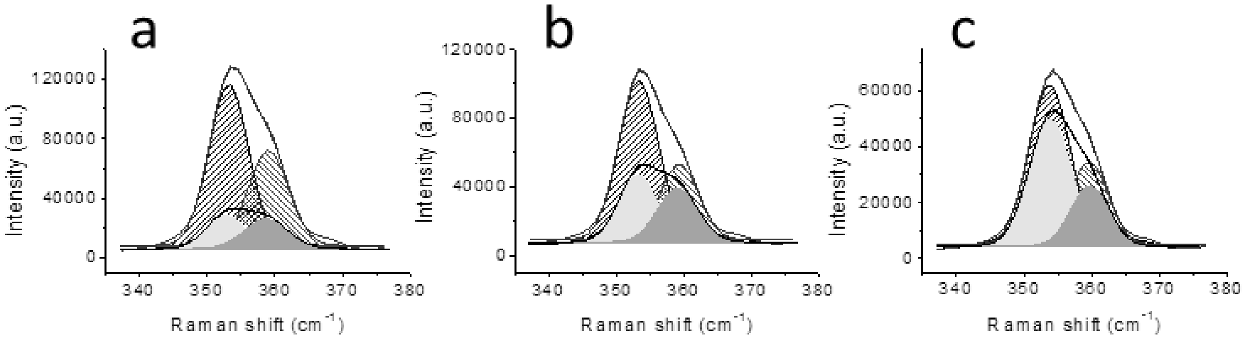


Figure 19. 335-378 cm^{-1} Raman spectral range of natural orpiment measured before (pattern) and after (plain colours) (a) 30 mW blue 405 nm, b) 30 mw green 534 nm and c) 12 mW blue 405 nm laser illumination. The peaks have been fitted as a sum of two Gaussians centred at 355 (light grey) and 359 cm^{-1} (dark grey). The patterned Gaussians correspond to the contributions for the non-aged samples while the plain Gaussians correspond to contributions for the aged samples.

Publication: M. Vermeulen, K. Janssens, J. Sanyova, C. McGlinchey, and K. De Wael, Assessing the stability of various arsenic sulfide pigments and influence of the binding media on their degradation by means of spectroscopic and electrochemical techniques, Dyes and Pigments (2017) *submitted.*

Natural orpiment is more efficiently degraded by blue than by green wavelengths.

2.4.5 Explaining the incompatibility between arsenic sulfide and copper- or lead-based pigments

Photo induced alterations, often combined with atmospheric factors, are well-known degradation processes observed during the degradation of arsenic sulfide pigments. These alterations are often visually identified through modification of the colour due to a change in redox state or formation of salts through complex reactions.[65,66,17,67] Arsenic-based pigments are then often described as easily oxidizing upon light exposure.[51,68] Upon ageing, they have often been pointed as the cause of darkening of close by copper- and lead based pigments due to the formation of copper sulfide (chalcocite, Cu_2S) or lead sulfide (galena, PbS) by reaction with a sulfide emitted by nearby orpiment (Figure 20).[68,69] While the exact origin and mechanism behind the formation of the sulfide ions essential for the reaction, still remained uncertain, it was well documented that natural orpiment transforms into white arsenic oxide, while natural realgar first turns into yellow pararealgar before oxidizing into arsenic oxide.[51,52,70,54,24,71]

The transformation of realgar to pararealgar is well described in the literature as a structural modification in which, under the influence of light and oxygen, a sulphur atom is inserted between two arsenic atoms of the realgar cage leading to a meta-phase (χ-phase, As_4S_5). This meta phase will later decompose with release of a sulphur radical by breaking an As-S-As bond and form a pararealgar As_4S_4 molecule.[72,73,74] Through the release of the sulphur radical, the process continues as a set of cyclic reaction in which the sulphur reacts with a molecule of realgar to produce a molecule of pararealgar whereupon a sulphur atom is produced and continues the process. The structural modification of the realgar cages has been reported in several studies.[24,75,72,71,76]

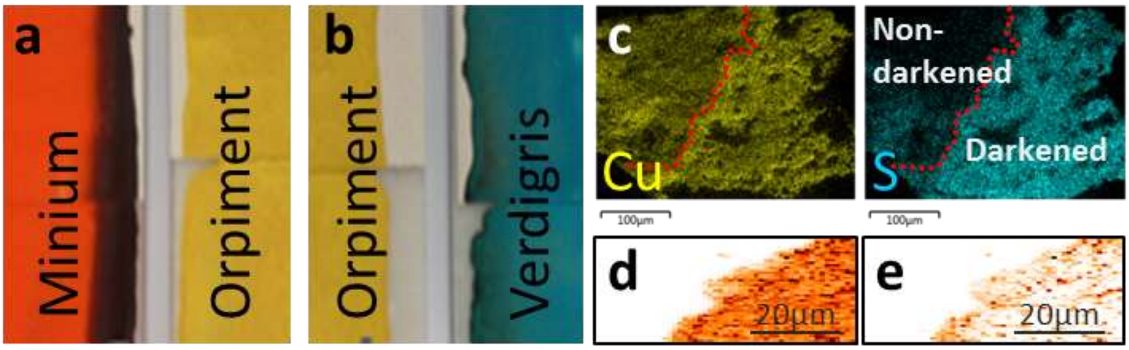


Figure 20. Mock-up paint samples of (a) minium and natural orpiment and (b) natural orpiment and verdigris all bond in sturgeon glue and stored contactless in a closed box. The areas of minium and verdigris closest to the orpiment appear darkened and present a significant larger amount of sulfur in its composition according to SEM-EDX analysis on the verdigris sample (c) and XRD maps of a cross sectioned sampe of darkened minium, showing (d) minium and (e) lead sulfide (galena) distribution.

Even though this photo-induced modification of the crystalline structure has been described quite extensively for realgar, a similar process has never been observed with natural orpiment. The degradation processes for the latter have indeed been quite overlooked and often described as a direct oxidation of the sulfide pigment into the arsenic oxide.[70,51]

Through this research project, the incompatibility of the arsenic sulfide and copper- or lead-based pigments has been explained by the formation of light-induced As-As bond (recorded in Raman spectroscopy) inducing the release of neutral sulphur atoms (S^0). (as indicated by XANES). The latter may interact with the surrounding atmosphere and environment to give H_2S gas or sulfates and lead to the formation of dark copper and lead sulfides.

This As-As bond has been identified on the surface of various historical samples bound in different media as well as in orpiment mock-up paint samples (Figure 21). Deeper in the pigment particles, the structural modification are not observed which clearly suggests a light-induced phenomenon. Moreover, in order to rule out a binder-induced possibility, novel tandem Raman-electrochemistry experiments were carried out on reference unbound natural orpiment and revealed the formation of As-As bind and a general decrease in the Raman signal which correspond to a loss in the pigment structure due to a breaking of the molecular bonds.

Publication: M. Vermeulen et al., "The darkening of copper- or lead-based pigments by arsenic sulfide pigments explained through a structural modification of natural orpiment: a spectroscopic and electrochemical study", (2017) *submitted*.

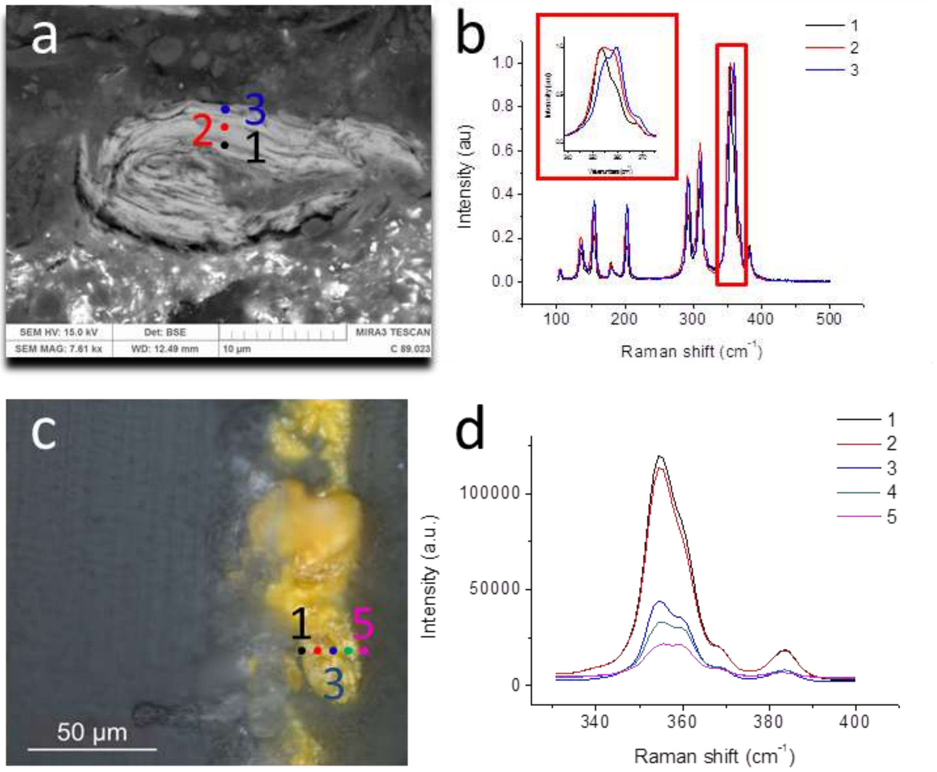
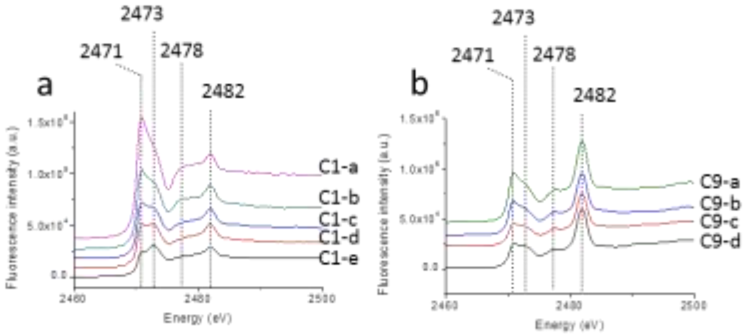


Figure 21. (a) SEM images of the analyzed natural orpiment from historical sample with the localization of Raman analyses (b) showing the broadening of the $AsS_{3/2}$ pyramid band due to the increase in the As-As band. (c) Visible light photograph of the mock-up paint sample with the localization of Raman analyses presented in (c) showing the broadening of the $AsS_{3/2}$ pyramid band of the orpiment and the overall decrease in the Raman signal.

The formation of sulfate ions and elemental sulphur in aged mock-up paint samples was investigated with XANES at synchrotron radiation facilities. This study highlighted in historical samples the greater presence of possible neutral sulphur atoms and sulfoxides in the outmost layers of the pigment particles (Figure 22). Combined with the known light-induced formation of radicals this pointed toward a release of elemental sulphur from the pigments particles due to the interaction between pigments and light.

Reduced S species (likely in the form H_2S) are responsible the incompatibility between AsxSy paint and paints containing minium and verdigris.



		C1	C9
Core	a	0.789	0.820
	b	0.865	0.822
	c	0.925	0.895
	d	1.003	0.939
Shell	e	1.256	n/a

Figure 22. XANES lines scans from core (C1-a and C9-a) to shell (C1-e and C9-d) for a) historical sample C1 and b) historical sample C9. Both line scan presents an increasing contribution for sulfur radical(s) at 2473 when moving toward the superficial layers of the pigment particles as presented by the ratio elemental sulfur to sulfides (intensity at 2473 eV/intensity at 2471 eV) in the table.

3 POLICY SUPPORT

3.1 Summary conclusions

The following significant project results, described in more detail in Section 2 were arrived at:

- Aerosol sampling and analysis in Belgian musea has pointed out that exposed paint surface of works of art can be in direct contact with a number of soluble salts. These include NaCl, $NaNO_3$, NH_4Cl, $(NH_4)_2SO_4$ and others. Gas analysis showed that also pollution gases such as HCl, NOx, SO_2 and NH_3, mainly the product of industrial and other combustion processes, are continuously present in the indoor atmosphere of musea.

- The hygroscopic salts, when deposited on a paint surface can cause small galvanic cells to be formed locally in which redox processes can occur. In the case the affected paint contains semi-conductor based pigments (such as is the case for vermillion red, red lead, cadmium yellow and chrome yellow and others) exposure to light can trigger the release of electrons and positive holes which in their turn can induce redox processes to occur.

- Based on the examination of several representative paintings (e.g., by Matisse, Van Gogh, Ensor, Rubens etc.), it can be concluded that the sulfur-containing yellow pigments cadmium yellow, chrome yellow and orpiment/realgar, all suffer from chemical degradation induced by a combination of light and moisture exposure, but that the mechanism causing the degradation is quite different. In some cases, a reduction of the central metal atom takes place while in other cases, an oxidation of the (sulfide) anion is the cause of the alteration. After these initial redox reactions, in general several possibilities exist for the formation of secondary products.

    - In the case of vermillion red (HgS), a complex degradation pathway is started when Cl^--ions enter the crystal lattice of the pigment, leading first to the formation of corderoite ($Hg_3S_2Cl_2$) and in second place to that of calomel (Hg_2Cl_2). A chemical equilibrium was demonstrated to exist between these two phases. Finally, the formation of metallic mercury nanodroplets (Hg^0) in combination with sulfates leads to the typical black + white/grey discoloration found of many Medieval and Baroque paintings.

    - The degradation of minium (Pb_3O_4) give rise to in situ formation of PbO which may become converted to plumbonacrite ($3PbCO_3.Pb(OH)_2.PbO$), hydrocerrusite ($2PbCO_3.Pb(OH)_2$)or cerrusite ($PbCO_3$). In the presence of Cl-, different chlorides such as Pb(OH)Cl and $PbCl_2$ may be formed. In the presence of sulfates, also $PbSO_4$ is a likely secondary product.

    - With cadmium yellow (CdS), a more simple reaction scheme is followed as the transformation is principally caused by the oxidation of the sulfidic ion to the sulfate form. Depending on the available counter ions, both Cd^{2+} and SO_4^{2-} can form different compounds, determining the mechanical properties, porosity and colour of the discolored paint. The beige otative ($CdCO_3$) may be formed in situ or remain behind after disappearance of the bright yellow color of CdS.

- Regarding cadmium red (CdS_xSe_{1-x}), no significant alteration or degradation has been observed in the paintings series studied in Liège musea. It appears that both the exhibition and storage conditions are adequate and that the pigment do not present any risk to the conservation of the paintings.

- For chrome yellow ($PbCrO_4$ and especially $PbCr_{1-x}S_xO_4$), a reduction of the Cr(VI) compound to Cr(III), possibly via Cr(V), takes place and the S-rich variant of the pigments is significantly more unstable than regular $PbCrO_4$. Both chemical agents such as salt particles and moisture and physical agents such as light from the UV to the green range of the EM spectrum are factors stimulating this alteration process.

- For orpiment (As_2S_3) and realgar (As_4S_4), the situation is more complex than anticipated due to the presence of both crystalline and amorphous/glassy forms of these pigments. The degradation pathway gives rise to the formation of As_2O_3 but the determining factors are still under study.

3.2 Recommendations regarding Sustainable Development Policy

In view of the above, it appears recommended that

- Belgian musea and their curators should realize much more than now is the case that most painted works of art are subject to slow but relentless chemical transformations that are taking place either at or just below the visible paint surface. Art works should therefore not be considered as static but rather as dynamic artefacts from the past that continuously interact with their environment. Since a continuous flux of material is emerging and entering the works of art, either in particulate or gaseous form, care should be taken to control such fluxes/keep them within certain boundaries.

- More in particular, care should be taken to remove chloride-containing salts from the museum atmosphere. In this project, the corroding/color modifying influence of Cl-compounds on various sulfur containing pigments such as vermillion red and cadmium yellow has been clearly demonstrated.

- Musea should also ensure that in their exhibition spaces, the use of ammonia-containing cleaning products is restricted as much as possible. Several of the secondary degradation products encountered in this project contain NH_3 or NH_4^+-ions as new ligands or counter-ions of the metals originally present in pigmented substances.

- Since many of the undesired chemical reactions of semi-conductor pigments and other artists' materials are being triggered by light, not only in the UV range but also in the blue-green visible wavelength range, special care should be taken to limit the illumination inside musea. Special care should be taken when new, energy-efficient lighting systems based on LED-lamps are installed that the output spectrum of these lamps does not contain more blue-green wavelengths than more tranditional lighting systems.

- Belgian musea should give a higher priority to install state-of-the art air purification and air conditioning systems and maintain their operation at the desired specification. Such systems must not only regulate and stabilize the temperature and relative humidity to quasi-fixed values but also ensure that the ambient air is actively cleaned from airborne particles. The latter, even those that have an innocuous chemical composition, have been shown to induced and/or accelerate chemical reactions at the surface of the artworks that lead to pigment degradation at the exposed surface of painted works of art.

- The attention musea give to maintaining appropriate atmospheric conditions in their public exhibition spaces should also be extended to the rooms where works of art are stored for extended periods of time.

- Musea should also seek to separate unprotected/uncovered surfaces of painted works of art from direct contact with the atmospheric components present in the visitor spaces of the museum. This can be done by more frequently following the established practice of placing works of art in (large or small) climate boxes within which the atmosphere can be kept constant and unpolluted. Via regular checks, care should be taken however that within such climate boxes, indeed the recommended conditions of relative humidity and temperature prevail.

- Since climate boxes limit the experience of the museum visitor in several manners, many painted works of art are not presented in such boxes. Neither are the majority of painted works of art shown behind protective/non-reflective glass panes. For painted works of art of which the varnished surface is the only layer protecting the paint from external physical or chemical agents, greater attention than now should be given to ensure that the varnish coat is able to block out particulate matter and moisture. As soon as a combination of these two external chemical agents can get into contact with the paint components, in a great many case, undesired chemical reactions can take place, leading to either unwanted discolorations of less of mechanical stability of the paint or both.

- In view of the combined effect of short wavelength (UV + blue/green) light, humidity and salt components encountered in ambient aerosols, direct outdoor exposure of artworks painted with metal sufide should be avoided as much as possible. Isolation of these artworks from atmospheric moisture and particulate matter via transparent surface coatings is mandatory, as well as regular renewal of such coatings. Since next to UV light, also parts of the visual spectrum (such as blue and green light) stimulate the alteration of metal sulfide pigments, employing colorless UV-filtering coatings is likely only to have a limited effect.

Thus, it appears also recommended that for musea of sufficient size, policy makers should allocate appropriate funds in order to enable the musea to

- install state-of the-art climatic systems ensuring stable conditions regarding lighting, temperature, relative humidity and atmospheric composition;

- employ competent, science-trained staff that (a) is able to periodically ascertain the correct atmospheric and lighting conditions in public exhibition spaces, artwork storage areas, display cases and climate boxes and (b) can objectively monitor the progress of unwanted chemical transformations at the surface of works of art via appropriate methods of analysis;

- systematically initiate restoration projects of all works of art in order to ensure that their paint surfaces remain isolated from external physicochemical influences.

4 DISSEMINATION AND VALORISATION

4.1 Organisation of concluding workshop

In July 2016, KIK-IRPA (J. Saynova) and UAntwerp (K. Janssens) jointly organized the conference "Chemistry in Cultural Heritage" (ca 150 pp.), a meeting where different aspects of chemical durability and sustainability of Cultural Heritage materials were discussed. Selected papers presented at this conference will appear is a special issue of the journal *Heritage Science* in 2017. D. Strivay (ULg) was a member of the Scientific Advisory Committee of this conference.

4.2 Invited lectures at International Scientific Conferences

- K. Janssens "The Role of Large Scale Facilities in Cultural Heritage Studies", invited discussion moderator, Gordon Research conference devoted to Scientific Research in Cultural Heritage, July 29-August 3 2012, Mount Snow, Vermont.
- K. Janssens, "Seeing What Others Cannot See: X-ray Based Imaging and Spectroscopy of Paintings and Painters Materials", Denver X-ray conference, 6-10 August 2012, Denver, Colorado, USA.
- K. Janssens, "X-ray Micro- and Nanoprobe for the Characterization of Artists' Pigments and Paintings", International Conference on X-ray Optics and Microanalysis, 2-6 September 2013, Hamburg, Germany.
- K. Janssens was invited to participate in an expert meeting on "Integrating Imaging and Analytical Technologies for Conservation Practice", 10-12 September 2013, The Getty Conservation Institute, Los Angeles, CA, USA
- K. Janssens, "Cultural Heritage and X-rays: Non-destructive Imaging and Spectroscopy of Pigments and Paintings", EuroAnalysis, 25-29 August 2013, Warsaw, Poland
- K. Janssens, "Macroscopic XRF imaging of paintings: possibilities, limitations and comparison to other imaging methods", TechnArt, 23-26 September 2013, Amsterdam, the Netherlands
- K. Janssens, "X-ray Spectroscopy and Imaging of Painted Works of Art: from the Nanometer to the Meter Scale", SciX2013, 29 Sept-4 Oct. 2013, Milwaukee, MI, USA
- K. Janssens, "Non-destructive investigations of artifacts at EU heritage scale", Final Meeting of CHARISMA, Cultural Heritage Advanced Research Infrastructures: 5-6 March 2014, Firenze, Italy
- K. Janssens, L. Monico, C. Miliani, G. Van der Snickt, F. Vanmeert, M. Alfeld, B. Brunetti, M. Cotte, G. Falkenberg and E. Hendriks, 'Hierarchical' examination of paintings by V. van Gogh using several X-ray-based methods of investigation", 5th Meeting X-ray and other techniques in investigations of the objects of Cultural Heritage, 14-17 May 2014, Krakow, Poland.
- K. Janssens, G. Van der Snickt, S. Legrand, E. D'Angelo, L. Depuydt, B. De Volder, H. Dubois, N. Laquière, C. Mehagnoul, M. Postec, F. Rosier, J. Sanyova and G. Steyaert, "The use of MA-XRF for better understanding the paint layer buildup in the two donor portraits of 'Adoration of the Mystic Lamb' (1430-1432) by Jan and Hubert Van Eyck", European X-ray Analysis Society Meeting (EXRS-2014), 15-20 June 2014, Bologna, Italy.

- K. Janssens, "X-ray based imaging and spectroscopy of paintings by V. Van Gogh from the dm to the µm level", CHEMCH, 1-5 July 2014, Vienna, Austria.
- K. Janssens, L. Monico, C. Miliani, G. Van der Snickt, F. Vanmeert, M. Alfeld, B. Brunetti, M. Cotte, G. Falkenberg and E. Hendriks, "Hierarchical' Examination of Paintings by V. van Gogh using Several X-ray Based Methods of Investigation", Denver X-ray Conference, 28 July-1 August 2014, Big Sky, Montana, USA.
- K. Janssens, L. Monico, C. Miliani, G. Van der Snickt, F. Vanmeert, M. Alfeld, B. Brunetti, M. Cotte, G. Falkenberg and E. Hendriks, 'Degradation of painters pigments and their examination via X-ray based methods", ALMA Interdisciplinary Conference, 11-15 November 2014, Prague, Czech Republic
- K. Janssens, "X-ray based analysis of pigment and painting alterations", IUCA Conference "Science & Past 2014", 26-28 November 2014, Zaragosa, Spain.
- K. Janssens, "From MA-XRF to MA-XRD and MA-FTIR: a survey of possibilities and limitations", AAAS Meeting, 12-16 February 2015, San José, CA, USA.
- K. Janssens, "X-ray Micro Imaging in Cultural Heritage Studies", 21 January 2016, SOLEIL User's Meeting, Palaiseau, France.
- K. Janssens, "X-ray based in-situ and ex-situ studies of chemical degradation phenomena in cultural heritage artefacts", 39th International Conference on VUV and X-ray Physics 2016, 3-8 July 2016, Basel, Switserland.
- K. Janssens, Expanding MA-XRF with MA-XRPD: More information on past and future appearing on the horizon, Gordon Research Conference, 31 July-3 August 2016, Newry, Maine, USA
- K. Janssens, "Spectroscopic X-ray imaging for studying alterations at and below the surface of fine art paintings, stained glass windows and illuminated manuscripts", Denver X-ray conference, 3-5 August 2016, Chicago, Ill., USA
- K. Janssens, "Micro-XRPD, XRPD tomography and MA-XRPD: three related methods to better understand structural alterations in cultural heritage materials", European Crystallography Meeting, 28 August-1 September 2016, Zürich, Switserland.

4.3 Oral presentations during international scientific conferences

- L. Monico et al. "Study of the Degradation Process of Chrome Yellow Pigments in Paintings by Vincent van Gogh and Its Contemporaries Through the Combined use of Synchrotron X-ray Spectromicroscopy and Conventional Spectroscopic Methods: the role of sulfate anions", Synchrotron radiation in Art and Archaeometry (SR2A) 2012 - New York (USA), 5th-8th June 2012.
- L. Monico, K. Janssens, F. Vanmeert et al., "Van Gogh and alteration of chrome yellow pigments: new Cr speciation studies by using the Maia X-ray detector", International Conference on X-ray Optics and Microanalysis, 2-6 September 2013, Hamburg, Germany
- L. Monico, K. Janssens, F. Vanmeert et al., "Non-invasive in situ spectroscopic techniques and synchrotron radiation-based X-ray methods to examine the state of conservation of chrome yellow pigments in Van Gogh's Sunflowers", Synchrotron Radiation in Art and Archaeology, 9-12 September 2014, Paris, France.
- F. Vanmeert, K. Janssens, G. Van der Snickt, "X-ray powder diffraction mapping and tomography for analysis of (degraded) paint layer systems", Synchrotron Radiation in Art and Archaeology, 9-12 September 2014, Paris, France.

- F. Vanmeert, S. De Meyer, W. De Nolf, G. Van der Snickt, S. Legrand, K. Janssens, "Macroscopic XRF/XRPD Scanning System for Non-Destructive Examination of Oil Paintings and Other Cultural Heritage Artefacts", Denver X-ray Conference, 28 July-1 August 2014, Big Sky, Montana, USA.
- W. Anaf, A.E. Meteke F. Vanmeert, K. De Wael, K. Janssens, M. Vermeulen, J. Sanyova, H. Calvo del Castillo, D. Strivay, "Salts on the surface: Exposed paint surfaces degrade faster under the influence of fine dust, European Materials Research Society (EMRS) Spring Meeting, May 11-15 2015, Lille, France.
- G. Nuyts, F. Vanmeert, M. Alfeld, G. Van der Snickt, W. De Nolf, K. Janssens, J. Titanah, D. Lamoen, H. Tan, J. Verbeeck, A. Van Loon, P. Noble, J. Dik, "Degraded smalt in 17th C. paintings: an investigation at multiple length scales", TechnArt 2015, 27-30 April 2015, Catania, Italy.
- L. Monico, K. Janssens, M. Cotte, A. Romani, L. Sorace, C. Grazia, B. Brunetti and C. Miliani, "New insights into the visible light effects on the darkening of chrome yellows and a first evidence of Cr(V)-species", Technart 2015, 5-10 April 2015, Catania, Italy.
- M. Vermeulen, C. Poleunis, P. Bertrand, A. Delcorte and J. Sanyova. "The use of Argon Cluster Bombardment for the Surface Preparation of Paint Cross-Sections for Analysis by ToF-SIMS", ECASIA'13, Cagliary (Italy) October 2013
- W. Anaf, A.E. Meteke, F. Vanmeert, K. De Wael, K. Janssens, M. Vermeulen, J. Sanyova, H. Calvo del Castillo and D. Strivay. "Salts on the surface: Exposed paint surfaces degrade faster under the influence of fine dust", E-MRS Spring meeting 2015, Lille (France) May 2015.
- M. Vermeulen, J. Sanyova, K. Janssens and K. De Wael. "Studying the degradation of arsenic sulfide pigments by the use of tandem Raman spectroscopy-electrochemistry", RAA2015, Wroclaw (Poland) September 2015
- M. Vermeulen, J. Sanyova, G. Nuyts and K. Janssens. "The use of XANES for the investigation of the degradation process of arsenic sulfide pigments in different binding media," Journée de contact du FNRS group synchrotron, Namur (Belgium) November 2015
- M. Vermeulen, J. Sanyova, G. Nuyts, K. De Wael and K. Janssens. "Stability and influence of the binding medium on arsenic sulfide pigments' degradation investigated by spectroscopic and electrochemical techniques", ChemCH2016, Brussels (Belgium) July 2016

4.4 Poster presentations during international scientific conferences

- G. Van der Snickt et al., "Combined synchrotron radiation-based µ-XRF, µ-XRD, µ-XANES and µ-FTIR reveals an alternative degradation pathway of the pigment cadmium yellow (CdS) in a painting by Van Gogh", ISEAC2012 (International Symposium on Environmental Analytical Chemistry), Antwerp, 21-25/05/2012.
- G. Van der Snickt et al., "Combined use of synchrotron radiation-based µ-XRF, µ-XRD, µ-XANES and µ-FTIR reveals an alternative degradation pathway of the pigment cadmium yellow (CdS) in a painting by Van Gogh", YOCOCU (Youth in Conservation of Cultural Heritage), Antwerp, 18-20 June 2012.
- L. Monico et al., "Chrome yellow ($PbCrO_4$, $PbCr_{1-x}S_xO_4$): the role of sulfate anions on the degradation process of these class of pigments and their detection in paintings by Vincent van Gogh and its contemporaries through the combined use of Synchrotron X-ray and conventional spectroscopic methods", YOCOCU (Youth in Conservation of Cultural Heritage), Antwerp, 18-20 June 2012.

- L. Monico et al., "The degradation process of chrome yellows: a focus on the reactivity between different forms of chrome yellows and the oil binder", Symposium "Issues in Contemporary Oil Paint" – Amersfoort (The Netherlands), 28th-29th March 2013.
- F. Vanmeert, S. Legrand, L. Monico, K. Janssens, "X-ray beam induced alterations to cultural heritage materials", International Conference on X-ray Optics and Microanalysis, 2-6 September 2013, Hamburg, Germany
- F. Vanmeert, S. Legrand, L. Monico, K. Janssens, "X-ray beam induced alterations to cultural heritage materials", Synchrotron and Neutron Workshop (SYNEW2013), 28/11/2013, Antwerp, Belgium
- M. Vermeulen, C. Poleunis, F. Vanmeert, K. Janssens and J. Sanyova. "Characterization of the artificial orpiment in the interior decorations of the Japanese tower in Laeken, Brussels", ChemCH2014, Vienna (Austria), July 2014
- M. Vermeulen and J. Sanyova "The synthesis of artificial arsenic sulfide in the laboratory according to ancient processes", E-MRS Spring meeting 2015, Lille (France) May 2015.
- F. Vanmeert, K. Janssens, G. Van der Snickt, "Degradation of minium in a Van Gogh painting investigated with X-ray power diffraction tomography", DESY User's meeting, 28-29 January 2015, Hamburg, Germany.
- F. Vanmeert, K. Janssens, G. Van der Snickt, "Degradation of minium in a Van Gogh painting investigated with X-ray power diffraction tomography", Synchrotron and Neutron Workshop (SYNEW2015), 01/06/2015, Utrecht, Netherlands.
- M. Vermeulen, J. Sanyova, K. Janssens and K. De Wael. "Fast degradation and monitoring of arsenic sulfide pigments with Raman spectroscopy-electrochemistry", InART2016, Ghent (Belgium), March 2016.
- J. Sanyova, L. Delvaux and M. Vermeulen. "An unexpected use of benzoin resin in an Egyptian wooden canopic jar of the Middle Kingdom revealed by FTIR and (py)-GCMS", ChemCH2016, Brussels (Belgium), July 2016.
- M. Vermeulen, J. Sanyova, K. De Wael, C. McGlinchey and K. Janssens. "Alteration of arsenic sulfide artists' pigments: a spectroscopic and electrochemical study", GRC Scientific Methods in Cultural Heritage, Newry (ME, USA) August 2016.
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4.5 PhD theses

In the frame of this project, several PhD thesis were prepared.

Willemien Anaf prepared a PhD thesis entitled "Influence of fine dust of Cultural Heritage artefacts". It was supervised by professors Koen Janssens and Karolien De Wael (University of Antwerp) and defended in the fall of 2014.

Frederik Vanmeert prepared a PhD thesis entitled "Micro- and Macro-XRPD, essential tools for the study of pigment degradation mechanisms" was prepared by Frederik Vanmeert. It was supervised by professors Koen Janssens and Karolien De Wael (University of Antwerp). The dissertation of this work is being finalized (spring 2017).

Marc Vermeulen prepared a PhD thesis entitled "*Natural and amorphous arsenic sulfide pigments: characterization, degradation and influence of the binding medium*". It was supervised by Dr. Jana Sanyova (KIK-IRPA) and professors Koen Janssens and Karolien

De Wael (University of Antwerp). The dissertation of this work is being finalized (spring 2017).

4.6 Attention in the General Press

On several occasions, the research activities themselves and its results drew the attention of the general press, both inside and outside Belgium. Below, a few examples related to the degradation of Vermillion Red (HgS) in a painting by P.P. Rubens (Oct. 2013) are shown.

Paintings turning black? Blame mercury

Salty air and light produce liquid metal from red paint pigment.

Davide Castelvecchi, highlight in Nature News (doi:10.1038/nature.2013.13887),4 October 2013

Mercury released from the red pigment in Adoration of the Magi (Peter Paul Rubens, 1624) has formed black stains in some places. (Koninklijk Museum voor Schone Kunsten, Antwerp/Giraudon/The Bridgeman Art Library)

The pigment vermilion has been a favourite of artists for centuries, but it is notorious for turning black as it degrades over time. But the source of the black colouring, found in works ranging from ancient Roman frescoes to the baroque paintings by Peter Paul Rubens, has been unclear. Now researchers have shown that the culprit is elemental mercury, which forms under exposure to light and chlorine ions in the air. The finding is the first step to devising a way for conservators to prevent further degradation of historic masterpieces.

Vermilion, also known as cinnabar, is a mineral made of the elements sulphur and mercury. In 2005 Katrien Keune, a chemist at the University of Amsterdam, and her colleagues showed that the compound can be broken down through a series of chemical reactions initiated by chlorine ions — which are especially abundant in the air near the sea — together with light[1].

Keune and her team suggested that the ultimate product of this reaction was pure mercury, the liquid used in old-fashioned thermometers. Its accumulation in microscopic pores and crevices in the paint could be responsible for the blackening effect.

But their theory was hard to prove — metallic mercury is volatile, so determining whether it has formed in a given reaction is difficult, says Koen Janssens, a chemist at the University of Antwerp in Belgium, and a co-author of the latest study[2]. "It's gone before you are able to analyse it," he says.

To prove that the altered cinnabar was elemental, or 'metallic', mercury, lead author Karolien De Wael and her team placed the pigment on a platinum surface and dipped it in water that contained chloride ions. When the researchers cast laser light on the mineral, it turned black (see inset in picture below). By applying an electric voltage, the mercury ions were released from the pigment into the water. Moreover, the voltage required was precisely that required for metallic mercury to release ions, De Wael says. The results were published this week in Angewandte Chemie.

Keune says the team's demonstration that the black material is metallic mercury is convincing, and will be "extremely valuable" for determining how to best store and exhibit works of art.

Janssens agrees that knowing the exact cause of vermilion's blackening might help conservators to prevent it. Keeping paintings in the dark is not an option, but keeping chlorine from reaching the pigment should be possible, for instance by making sure that the protective layer of varnish does its job properly.

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De Standaard, 8 Oct 2013

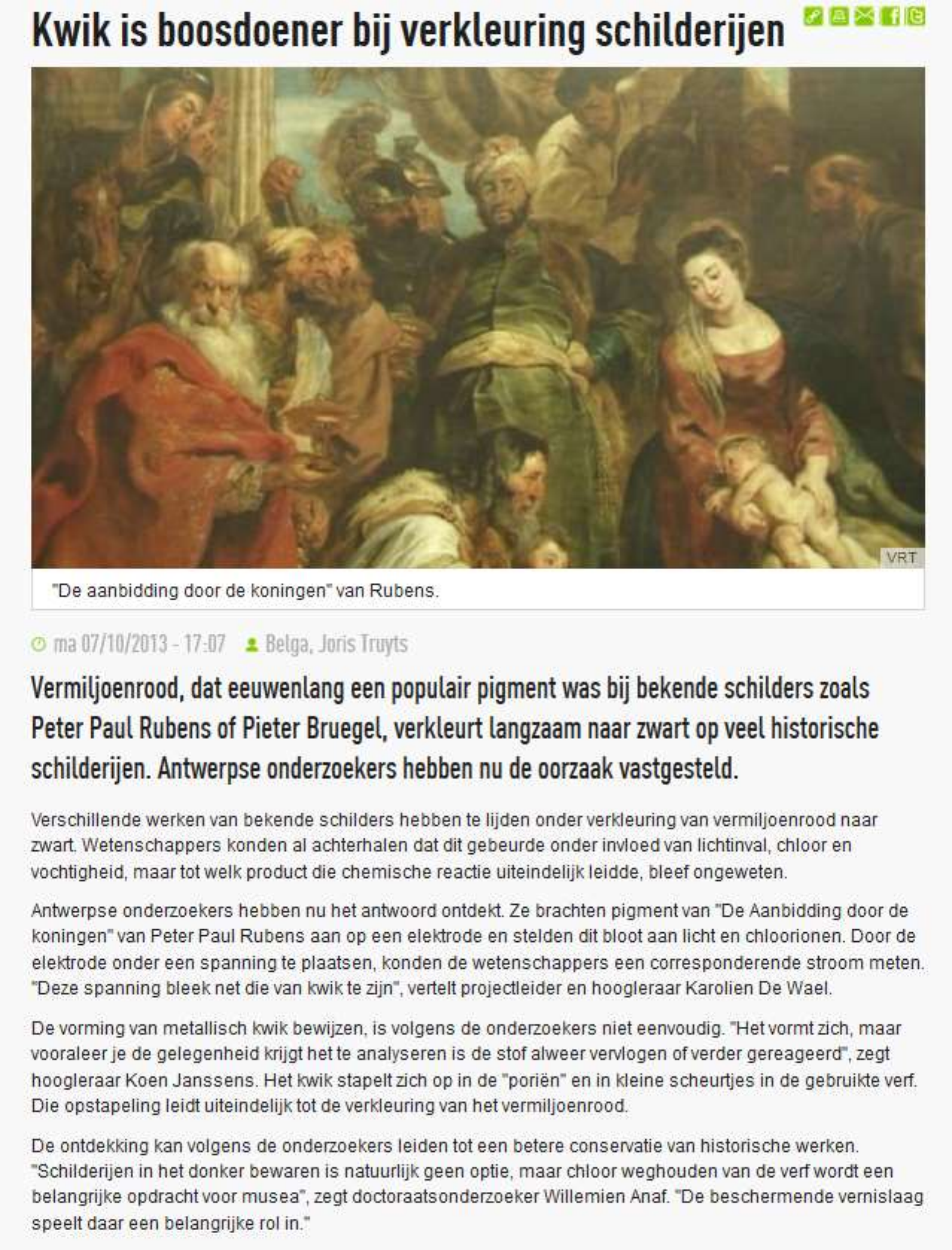
OOK DAT NOG

Schilderijen wenen kwikzilveren tranen

Karolien De Wael en Koen Janssens van de Universiteit Antwerpen ontdekten hoe de bekende kleurstof vermiljoenrood naar zwart verkleurt – een probleem dat zowel opduikt bij de fresco's in Pompeï als in de schilderijen van Bruegel en Rubens. Sinds de negentiende eeuw vervingen de schilders daarom vermiljoen door cadmiumrood. Vermiljoen, bij de geologen bekend als cinnaber, is een sulfide van kwik.

Onder invloed van licht, chloor en vocht wordt vermiljoen omgezet in een zwart kwiksulfide. De Antwerpse chemici plaatsten vermiljoen op een elektrode, bestookten het met licht en chloor en maten de elektrische effecten. Daaruit blijkt dat er zuiver metallisch kwik ontstaat. Dat was niet eenvoudig te bewijzen, want metallisch kwik vervliegt. Voor hun onderzoek hadden ze verfschilfers gekregen van *De aanbidding door de koningen* van Pieter Paul Rubens in het Koninklijk Museum voor Schone Kunsten Antwerpen. 'Eigenlijk kun je zeggen dat dit schilderij kwikzilveren tranen huilt.' Het kwik stapelt zich op in de poriën in de verf, waar het verdampt of verder reageert. Het eindresultaat is zwart, melden de chemici in het vakblad *Angewandte Chemie*. Vernis beschermt tegen chloor, geven ze nog mee. (rel)

In vermiljoen duiken na verloop van tijd zwarte puntjes op.



Kwik is boosdoener bij verkleuring schilderijen

"De aanbidding door de koningen" van Rubens.

ma 07/10/2013 - 17:07 Belga, Joris Truyts

Vermiljoenrood, dat eeuwenlang een populair pigment was bij bekende schilders zoals Peter Paul Rubens of Pieter Bruegel, verkleurt langzaam naar zwart op veel historische schilderijen. Antwerpse onderzoekers hebben nu de oorzaak vastgesteld.

Verschillende werken van bekende schilders hebben te lijden onder verkleuring van vermiljoenrood naar zwart. Wetenschappers konden al achterhalen dat dit gebeurde onder invloed van lichtinval, chloor en vochtigheid, maar tot welk product die chemische reactie uiteindelijk leidde, bleef ongeweten.

Antwerpse onderzoekers hebben nu het antwoord ontdekt. Ze brachten pigment van "De Aanbidding door de koningen" van Peter Paul Rubens aan op een elektrode en stelden dit bloot aan licht en chloorionen. Door de elektrode onder een spanning te plaatsen, konden de wetenschappers een corresponderende stroom meten. "Deze spanning bleek net die van kwik te zijn", vertelt projectleider en hoogleraar Karolien De Wael.

De vorming van metallisch kwik bewijzen, is volgens de onderzoekers niet eenvoudig. "Het vormt zich, maar vooraleer je de gelegenheid krijgt het te analyseren is de stof alweer vervlogen of verder gereageerd", zegt hoogleraar Koen Janssens. Het kwik stapelt zich op in de "poriën" en in kleine scheurtjes in de gebruikte verf. Die opstapeling leidt uiteindelijk tot de verkleuring van het vermiljoenrood.

De ontdekking kan volgens de onderzoekers leiden tot een betere conservatie van historische werken. "Schilderijen in het donker bewaren is natuurlijk geen optie, maar chloor weghouden van de verf wordt een belangrijke opdracht voor musea", zegt doctoraatsonderzoeker Willemien Anaf. "De beschermende vernislaag speelt daar een belangrijke rol in."

5 PUBLICATIONS

Peer-review publications

2012

- G. Van der Snickt, K. Janssens, J. Dik, W. De Nolf, F. Vanmeert, J. Jaroszewicz, M. Cotte, G. Falkenberg, L. Van der Loeff, Combined use of Synchrotron Radiation Based Micro-X-ray Fluorescence, Micro-X-ray Diffraction, Micro-X-ray Absorption Near-Edge, and Micro-Fourier Transform Infrared Spectroscopies for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh, Analytical Chemistry, 84 (2012) 10221-10228.doi: 10.1021/ac3015627

2013

- Da Pieve, C. Hogan, D. Lamoen, J. Verbeeck, F. Vanmeert, M. Radepont, M. Cotte, K. Janssens, X. Gonze, G. Van Tendeloo, Casting Light on the Darkening of Colors in Historical Paintings, Physical Review Letters, 111 (2013) 208302.doi: 10.1103/PhysRevLett.111.208302.
- H.Y. Tan, H. Tian, J. Verbeeck, L. Monico, K. Janssens, G. Van Tendeloo, Nanoscale Investigation of the Degradation Mechanism of a Historical Chrome Yellow Paint by Quantitative Electron Energy Loss spectroscopy Mapping of Chromium Species, Angewandte Chemie-International Edition, 52 (2013) 11360-11363. doi: 10.1002/anie.201305753.
- W. Anaf, K. Janssens, K. De Wael, Formation of metallic mercury during photodegradation/photodarkening of α-HgS: electrochemical evidence, Angewandte Chemie-International Edition, 52 (2013) 12568–12571. doi: 10.1002/anie.201303977.
- L. Monico, K. Janssens, C. Miliani, G., Van der Snickt, G.; B.G. Brunetti, M. Cestelli Guidi, M. Radepont, M. Cotte, The degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 3. Synthesis, characterization and detection of different crystal forms of the chrome yellow pigment, Analytical Chemistry, 85 (2013) 851-859. doi:10.1021/ac302158b
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- K. Janssens, M. Alfeld, G. Van der Snickt, W. De Nolf, F. Vanmeert, M. Radepont, L. Monico, J. Dik, M. Cotte, G. Falkenberg, C. Miliani, B. Brunetti, The Use of Synchrotron Radiation for the Characterization of Artists' Pigments and Paintings, Annual Reviews of Analytical Chemistry, 6 (2013) 399-425. doi: 10.1146/annurev-anchem-062012-092702.

2014

- W. De Nolf, F. Vanmeert, K. Janssens, XRDUA: crystalline phase distribution maps by two-dimensional scanning and tomographic (micro) X-ray powder diffraction, Journal of Applied Crystallography, 47 (2014) 1107-1117. doi: 10.1107/S1600576714008218
- W. Anaf, O. Schalm, K. Janssens, K. De Wael, Understanding the (in)stability of semiconductor pigments by a thermodynamic approach, Dyes and Pigments, 113 (2014) 409-415. doi: 10.1016/j.dyepig.2014.09.015

- W. Anaf, S. Trashin, O. Schalm, D. van Dorp, K. Janssens, K. De Wael, Electrochemical photodegradation study of semiconductor pigments: influence of environmental parameters, Analytical Chemistry, 86 (2014) 9742-8. doi: 0.1021/ac502303z.
- L. Monico, C. Miliani, K. Janssens, E. Hendriks, M. Geldof, B.G. Brunetti, Raman study of $PbCr_{1-x}S_xO_4$ solid solutions: implications for the non-invasive identification of chrome yellows in paintings, J. Raman Spectrocopy, 45 (2014) 1034-1045. doi: 10.1002/jrs.4548
- S. Legrand, F. Vanmeert, G. Vandersnickt, M. Alfeld, W. De Nolf, J. Dik and K. Janssens, Examination of historical paintings by state-of-the-art hyperspectral imaging methods: from Scanning Infra-red Spectroscopy to Computed X-ray laminography, Heritage Science, 2 (2014) 13. doi: 10.1186/2050-7445-2-13.
- K. Janssens, M. Alfeld, G. Van der Snickt, W. De Nolf, F. Vanmeert, L. Monico, S. Legrand, J. Dik, M. Cotte, G. Falkenberg, L.van der Loeff, M. Leeuwenstein, E. Hendriks, "Examination of Vincent Van Gogh's paintings and pigments by means of state-of-the-art analytical methods", Chapter 18 in: "Art & Science", A. Sgamelotti, B. Brunetti, C. Miliani (Eds.), Royal Society of Chemistry, London (2014).

2015

- M. Radepont, Y. Coquinot, K. Janssens, J.-J. Ezrati, W. de Nolf and M. Cotte, Thermodynamic and experimental study of the degradation of the red pigment mercury sulfide, Journal of Analytical Atomic Spectrometry, 30 (2015) 599-612. doi: 10.1039/c4ja00372a.
- L. Monico, K. Janssens, M. Alfeld, M. Cotte, F. Vanmeert, C.G. Ryan, G. Falkenberg, D.L. Howard, B.G. Brunetti and C. Miliani, Full spectral XANES imaging using the Maia detector array as a new tool for the study of the alteration process of chrome yellow pigments in paintings by Vincent van Gogh, Journal of Analytical Atomic Spectrometry, 30 (2015) 613-626. doi: 10.1039/c4ja00419a.
- F. Vanmeert, G. Van der Snickt, K. Janssens, Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting, Angewandte Chemie International Edition, 54 (2015) 3607-3610. doi: 10.1002/anie.201411691.
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7 ANNEXES

The annexes are available on our website

http://www.belspo.be/belspo/SSD/science/pr_risk_en.stm

ANNEX 1 : COPY OF THE PUBLICATIONS

ANNEX 2 : MINUTES OF THE FOLLOW-UP COMMITTEE MEETINGS

The follow-up committee was composed in the following manner:

- Karolien De Wael, UA, Antwerp, B
- Nico Broers, ESA St-Luc, Liège, B
- Jean-Marie Gay, Musées de Liège, B
- Patrick Bertrand, UCL, Louvain-la-Neuve, B
- Joris Dik, Dept. Of Materials Science, TUDelft, NL
- Klaas Jan van den Berg, RCE, Amsterdam, NL
- Philippe Walter, UPMC, Paris, F
- Veronique Rouchon, CRCC, Paris, F
- Marika Spring, National Gallery Laboratory, London, UK
- Mark Richter, University of Glasgow, UK
- Guenther Grundmand, Technische Universität München.

Next to a limited number of general meetings, various smaller meetings were held with a few or even individual members of the Advisory Committee, usually during, just before or just after other events.

Discussions were held for example:
- between K. Janssens, J. Dik, M. Spring, and K.J. Van den Berg at the 'Late Rembrandt' conference, National Gallery London, November 2014 re. degradation of minium and cadmium yellow
- between K. Janssens and R. Van Grieken at the Technart Conference, Catania, April 2015 regarding the average aerosol composition in Western-Europe, indoor and outdoor.
- between J. Saynova, M. Spring, B. Brunetti in the margin of the preparatory discussions of the Iperion.CH network of the EU, regarding arsenic sulhide pigments
- between D. Strivay, Ph. Walter at the LAMS (UMPC, Paris) concerning evaluation of the pigment ageing (Paris, January 2015)

- between D. Strivay, Ph. Walter during the Pittcon conference (New Orleans, March 2015) regarding the effect of chemical agents on modern pigments.
- between D. Strivay, Ph. Walter during the International School of Structural and Molecular Archaeology “Hubert Curien“ (Erice, April 2015) regarding the effect of chemical agents on commonly occurring pigments such as lead white.
- between K. Janssens, K.-J. Van den Berg and J. Dik regarding the painting ‘Sunflowers’ of the Van Gogh Museum, Amserdam (December 2016).
- Regular meetings between D. Strivay, Nico Broers and J.-M. Gay on degradation and preservation of modern art paintings in Liège museum collections.
- regular meetings between K. Janssens and J. Dik regarding degradation studies of 17th and 19th C. paintings.

The input of the follow-up committee is general considered to be very useful and inspiring.

KIK-IRPA [P3] organized on March 19th 2014 a meeting with new members of the follow-up committee professor Mark Richter from the University of Glasgow (UK) and professor emeritus Guenter Grundmann, from the Technische Universität of Munich (Germany), both highly specialized in the arsenic sulfide pigments, having a large experience with the characterisation and synthesis of this kind of pigments. During the meeting, held at the laboratory of the KIK-IRPA, the finding of the amorphous orpiment in the decoration of the Brussels' Japanese tower was discussed. The coordinator of the project, Koen Janssens participated to the meeting as well. The advices of both specialists during the meeting as well during later contact were very useful for the orientation of the further research on the arsenic sulfides.

ANNEX 3 : Nederlandse samenvatting / résumé français

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