"LUCHTANALYSE IN MUSEA VOOR PREVENTIEVE CONSERVATIE"

René Van Grieken, Dept. Chemie, Univ. Antwerpen **CONSERVATION** = maintaining a work of art in « good condition »

In addition to intrinsic parameters, often ENVIRONMENTAL FACTORS are important for conservation, even indoors (museums).

Improving the environmental conditions (micro-climate and chemical pollution) around a work of art is now popular and called:

« PREVENTIVE CONSERVATION »

PREVENTIVE CONSERVATION is defined as: "the mitigation of deterioration and damage to cultural property through the formulation and implementation of policies and procedures for the following: appropriate environmental conditions; handling and maintenance procedures for storage, exhibition, packing, transport, and use; integrated pest management; emergency preparedness and response; and reformatting/duplication, etc."

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Major culprit for damage to buildings (LIMESTONE, MARBLE) has been sulphur dioxide (from thermal power plants and heavy industry) which transforms calcite into gypsum ! But SO₂ now much lower...

= "black crust"

Sulphur dioxide is no longer a problem (- 85% in Belgium)

- But other gases (like nitrogen oxides) and PARTICLES (natural and pollution) have not decreased...
- And INDOOR atmosphere has become relatively more important



Soiling by particles of Michelangelo's Sistene Chapel in Vatican

Slide from Dario Camuffo, CNR, Padua

Air quality studies (preventive conservation) in... *20 museums in Europe (including Correr Museum, Venice, Italy; Wawel Castle, Cracow, Poland; Plantin-Moretus Museum, Antwerp), Morocco, Brazil, Argentina, Japan, USA (Metropolitan Museum, New York) *In cathedrals (France, Germany) with medieval stained glass windows and small mountain churches with valuable cultural heritage (Poland, Italy) *In caves with prehistoric wall painting in Spain

and Italy

*Alhambra in Granada, Spain

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In each case, the intention was to evaluate the indoor air quality (mostly particles collected on filters or in impactor deposits; also some gases), to identify the sources of harmful pollutants, and to propose remedies ("preventive conservation") !!!

- For characterizing indoor atmospheric particles and their sources, we use mostly:
- Ion chromatography for ionic analysis
- Gas chromatography- mass spectrometry for organics
- Aethalometry for soot determination
- Gravimetry for total mass per m³
- X-RAY FLUORESCENCE (energy dispersive; polarized beam) for bulk (on loaded filters) elemental analysis
- MICRO ANALYSIS FOR INDIVIDUAL MICRO-PARTICLE CHARACTERISATION (when you see elements sitting together in one single particle, it is usually much easier to identify the source and source process): mostly automated electron probe X-ray micro-analysis and micro-Raman spectrometry

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Monitoring pollution damage to cultural heritage



Tools used for sampling campaigns

Aethalometer Black carbon



Berner-type impactor Single particles

> Attention1 FRAGILEI

Harvard-type impactor Particulate matter, 3 fractions: PM1.0, PM2.5, PM10

Radiello (Passive diffusion samplers) NO_2 and SO_2





IDENTIFICATION OF AIR PARTICLE SOURCES IN MANY MUSEUMS IN EUROPE

(1) Correr Museum, Venice, Italy

Classical Museum (limestone): Problems with darkening of Bellini paintings



Bulk aerosol concentration (by XRF)



Individual particle characterisation by electron probe X-ray **microanalysis** Correr Museum: gypsum particles, calcium-rich particles, calcium-silicon particles, aluminosilicates, sea salt

Calcium-rich particles more abundant with windows closed, no visitors, etc. Plaster on the walls in Bellini rooms is deteriorating (old or bad quality?) and releasing Ca-rich particles
These particles deposit on the paintings and are embedded

-These particles adsorb soot and turn dark

SOLUTION: Renew plaster or cover plaster with a suitable paint !!

= Preventive conservation based on chemical analysis (Correr Museum, Venice, Italy)

Other example: Environmental analysis concerning the conservation of the fantastic rock wall paintings in the CAVE OF ALTAMIRA, Northern Spain

15,000 years old !!!

Only discovered in 1879...



Joan Miro said: « Art has been in decadence since the bisonts of Altamira »

Prehistoric art is now fading away; plus sometimes white deposit





Different hypotheses about the deterioration:

-external air pollution (new factories and power plant in area)?

-physical erosion of paint by percolation water?

-biological activity? (but no light = no algae)

-effect of visitors? 3000 visitors/day in 1970s; limited to 30/d in the 1990s

ALTAMIRA CAVE:

ELECTRON PROBE X-RAY MICROANALYSIS ON AEROSOL SAMPLES

Particle type	Outdoors	Entrance hall	Main cave with paintings
Sea salt	70 %	0 %	0 %
Ca-rich	4 %	20 %	23 %
Alumino- silicate	6 %	33 %	34 %

NO INFLUENCE OF OUTDOOR AIR...

Altamira: dripping water samples (water that has run over the paintings) Suspended particles: mainly Ca-rich and aluminosilicate particles, No paint (iron-oxide; charcoal) particles •High concentration of Total Organic Carbon: up to 5 ppm !!!??? === clue for microbiologists !!! Noted high colonisation by different microorganisms


Hill was used as a limestone quarry in 19th century; now perfect funnel for rainwater

CAVE

Later there were many cows on the grass here

5 m rock only

Organic material (from cow dung and plants) in the percolating water serves as food for microorganisms

3000 visitors per day in the 1970s; until recently 30 were still allowed per day

- •Influence of visitors: calculation of Ca (bi)carbonate equilibria:
- \Rightarrow calcite corrosion still 78 times enhanced due to short visits of 30 persons per day due to CO₂ and H₂O release

Now: Altamira cave is completely closed for public: copy has been built in museum And the cows have been displaced....

Metropolitan Museum of Art in New York

ΗΑΤSΗΕΡSUΤ

OM QUEEN





White deposits were noticed in and on showcases in some sections of the museum. After cleaning they re-appear quickly! *Sources? Problem with indoor emissions, particle filtration?*

Ion Chromatography shows that the deposit is rich in nitrate:

- Ammonium nitrate from fertilizers in Central Park?
- Sodium nitrate from the reaction of seasalt wit nitrogen oxides from traffic?

The particles were mostly NaNO₃. Hence: improve filtration !!

E.g. Wawel castle in Cracow, Poland

- Enormous importance
- for national history
- of Poland
- Nearly 1 million visitors
- per year





Many great Arrases from Flanders (getting stained)





Much NaCl in indoor air in winter on days with visitors: far from sea: salt from deicing access paths. Hence manual deicing !!!

Much soot anytime from traffic ! Hence close leaks and reduce cars !!!



Finest example of Islamic art in Europe More than 3 million visitors per year **UNESCO** World Cultural Heritage since 1984





- Construction started in the 11th century and ended in 1492 (Christian conquest of Granada).
- Official residence of Nasrid dynasty (1238-1492); zenith of Islamic culture in Europe.
- 27 towers, 7 palaces, spas, cemetery, etc.
- Since 1492, construction (e.g., Renaissance Palace of Charles V), restorations and now mass tourism, all definitively altering its original aspect.





Harvard (PM₁; PM₁₀), May (7 size fractions), Aethalometer (soot)

Large particles

PM₁₀ = soil dust, rich in calcite, dolomite and silicates,

and sea salts, especially NaNO₃ (= seaspray that has reacted with nitrogen oxides from traffic !). Hygroscopic salts ! Soil particles = suspension of local soil, plus North African dust in summer.



Sahara dust intrusion in June above 50 µg/m³ EU norm)

<u>Heavy metals</u> From diesel exhaust (V and Ni) and tire tread emissions (Cu, Cr, Pb and Zn).

INDIVIDUAL PARTICLES



INDIVIDUAL PARTICLES



$NaCl + SO_2 - Na_2SO_4$

$NaCl + NO_x ---- NaNO_3$

<u>Small particles (most penetrating)</u> PM₁ = mostly ammonium sulphates and (in winter) ammonium nitrate (these are acidic and hygroscopic !!!) and soot. Soot = 20-40% of total PM_1 ; highest concentrations on working days during morning traffic jams, and at the beginning of the evening hours (weekends).





Soiling

- Esthetic threshhold: 35%
- $PM_{10} < 30 \ \mu g \cdot m^{-3}$
- EC < 2–3 μ g·m⁻³
- Economic/perception
- Historical value
- Relief: More difficult restauration

Soot is black, staining and reactive.

No cars through "Gate of the Pomegranates" in Alhambra park. At present, soot concentration around 2 μ g/m³; expected to rise up to 8 µg/m³ or more, as found at similarly steep streets with dense traffic, if gate is reopened. Considerable impact on the levels of soot and other vehicle derived pollutants inside the Nasrid palaces?

Deterioriating air quality factors:

- Sahara dust erosion
- Salt from the sea
- TRAFFIC:
 - NaNO₃ which is formed by reaction of nitrogen oxides with seasalt
 - Soot
- Preventive conservation: Reduce traffic especially around Alhambra; wait for soot filters and catalytic converters for soot (EU)

MUCH WORK HAS BEEN DONE ON THE INTERACTION OF POLLUTION GASES WITH CULTURAL HERITAGE ITEMS, BUT NOT AT ALL FOR PARTICLES... (except sea salt corrosion for metals)

E.g. cementation to and reaction with underlying material?