

# ***Probing the alteration processes of artists' pigments in paintings by synchrotron radiation-based X-ray methods and vibrational spectroscopies***

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**Frederik Vanmeert**  
**Geert Van der Snickt**



# Chromatic alteration of yellow pigments

Darkening of chrome yellows  
( $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ )

Discoloration of cadmium  
yellows ( $\text{CdS}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$ )



- 1 - What is the alteration mechanism of a specific class of pigments?
- 2 - What are the factors that trigger their transformations?

- Developing strategies to prevent/mitigate the degradation processes.
- Optimizing the conservation practices of the long-term storage of paintings.

# Methodological approach



**Macro-scale**  
Imaging/mapping techniques:  
MA-XRF, MA-XRD,  
Vis-hyperspectral...

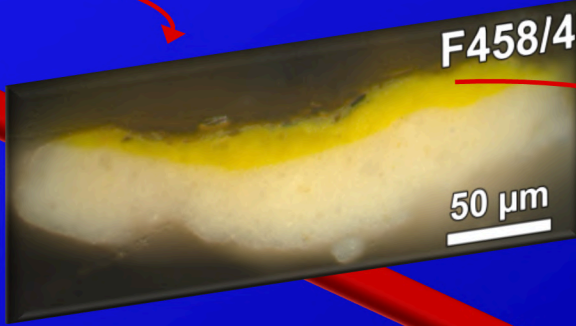
*Paintings: heterogeneous and composite systems, in the most of cases composed of multi layers, whose thickness can achieve values down to the sub-micrometers.*

**Top-down MULTIMETHOD and MULTISCALE experimental approach**

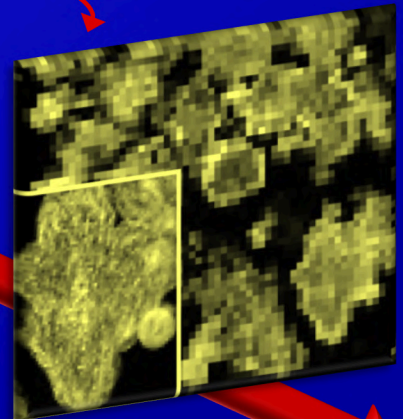


**Meso-scale**  
Non-invasive single point FTIR, Raman analysis

**Micro-scale**  
SR-based X-ray methods  
 $\mu$ -FTIR,  $\mu$ -Raman  
(Bench-top equipments)



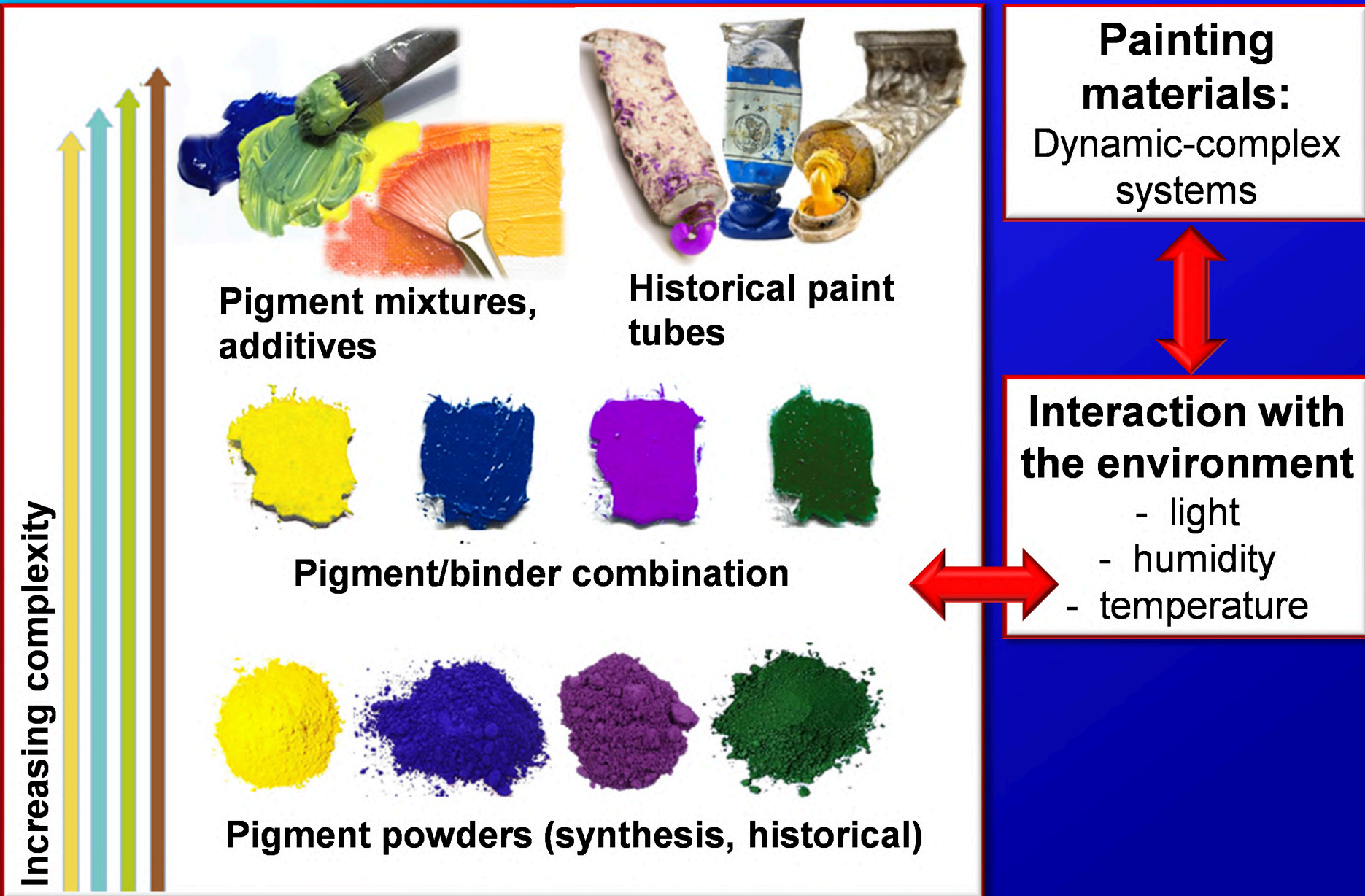
**Nano-scale**  
STEM-EDX/EELS




Length-scale

# Pigments & mock-up paints: a bottom up approach

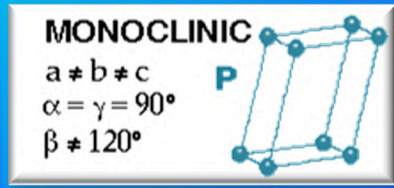
- We need to take the complex and make it simpler



The background is a reproduction of Vincent van Gogh's painting 'Sunflowers'. It depicts several sunflowers in various stages of bloom, with vibrant yellow petals and dark brown centers. The brushwork is thick and expressive, characteristic of the Impressionist style. The overall color palette is dominated by yellows and browns, with some green leaves and stems. Overlaid on the center of the painting is a text block in a bold, red, italicized font.

***Chrome yellows:  
bright yellows that turn dark***

# Lead chromate-based pigments: chemical properties



- x = 0.0
- x = 0.2
- x = 0.4
- x = 0.6
- x = 0.8
- x = 0.9
- x = 1.0

**PbCrO<sub>4</sub>·PbO**  
chrome orange

**PbCrO<sub>4</sub>**

**PbCr<sub>1-x</sub>S<sub>x</sub>O<sub>4</sub>**  
coprecipitates

**PbSO<sub>4</sub>**

solubility

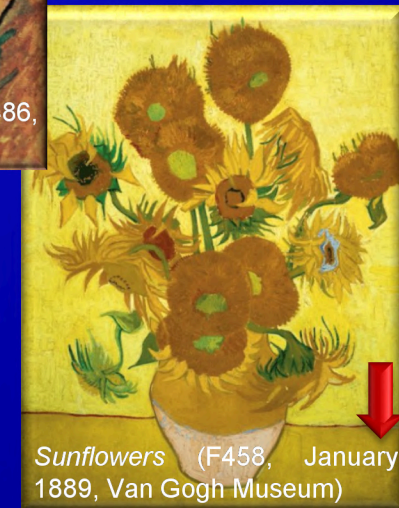
$K_{ps} = 1.7 \cdot 10^{-14}$   
 $s \sim 5 \cdot 10^{-7} \text{ mol/L}$

$K_{ps} = 4.5 \cdot 10^{-8}$   
 $s \sim 2 \cdot 10^{-4} \text{ mol/L}$



# Darkening of chrome yellow pigments\*

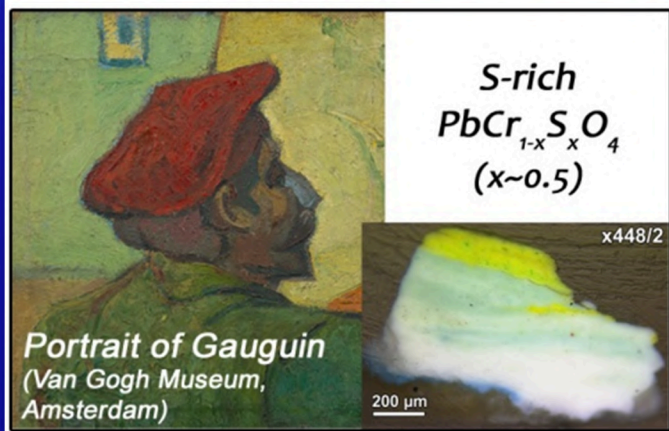
- Characterized by low photochemical stability.



\*L. Monico *et al.*, *Anal. Chem.* 83 (2011) 1224-1231; L. Monico *et al.*, *Anal. Chem.* 85 (2013) 851-859; L. Monico *et al.*, *Anal. Chem.* 86 (2014) 10804-10811; L. Monico *et al.*, *JAAS* 30 (2015) 613-626; L. Monico *et al.*, *Angew. Chem. Int. Ed.* (2015) 54, 13923-13927.

# Characterization of different chrome yellow types

- Possibility to distinguish among different forms of chrome yellows by means of mid-FTIR, Raman and XRD



analytical  
chemistry

ARTICLE

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## 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

Letizia Monico,<sup>†,‡</sup> Koen Janssens,<sup>\*,‡</sup> Costanza Miliani,<sup>§</sup> Brunetto Giovanni Brunetti,<sup>†,§</sup> Manuela Vagnini,<sup>||</sup> Frederik Vanmeert,<sup>‡</sup> Gerald Falkenberg,<sup>⊥</sup> Artem Abakumov,<sup>@</sup> Yinggang Lu,<sup>@</sup> He Tian,<sup>@</sup> Johan Verbeeck,<sup>@</sup> Marie Radepont,<sup>‡,#</sup> Marine Cotte,<sup>#,∇</sup> Ella Hendriks,<sup>○</sup> Muriel Geldof,<sup>◆</sup> Luuk van der Loeff,<sup>||</sup> Johanna Salvant,<sup>□</sup> and Michel Menu<sup>□</sup>

[dx.doi.org/10.1021/ac302158b](https://doi.org/10.1021/ac302158b) | *Anal. Chem.* 2013, 85, 851–859

Research article

Journal of  
RAMAN  
SPECTROSCOPY

## 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<sup>†</sup>

Letizia Monico,<sup>a,b</sup> Koen Janssens,<sup>b</sup> Ella Hendriks,<sup>c</sup> Brunetto G. Brunetti,<sup>d,a</sup> and Costanza Miliani<sup>a,d,\*</sup>

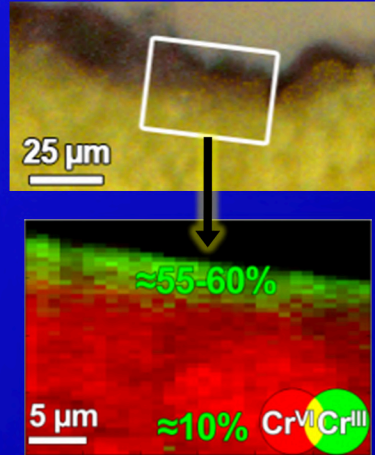
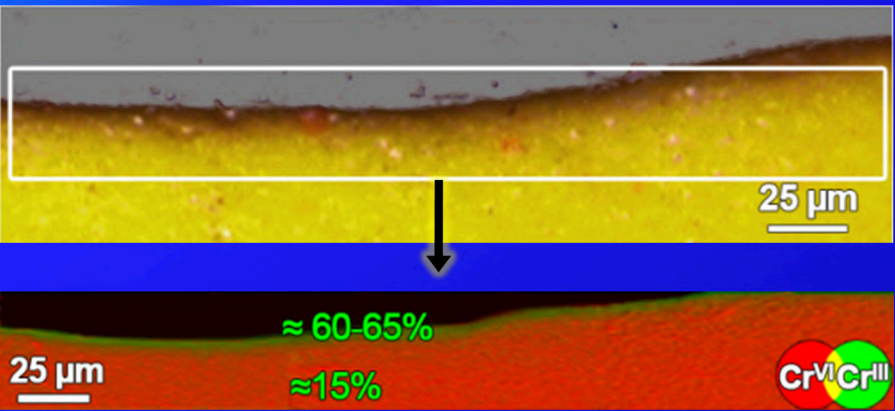
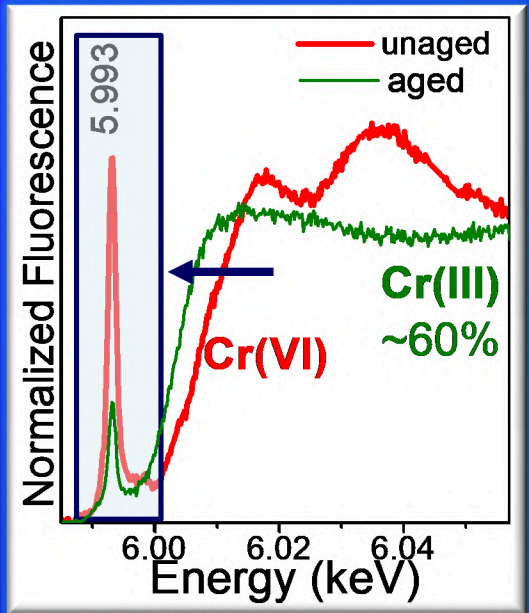
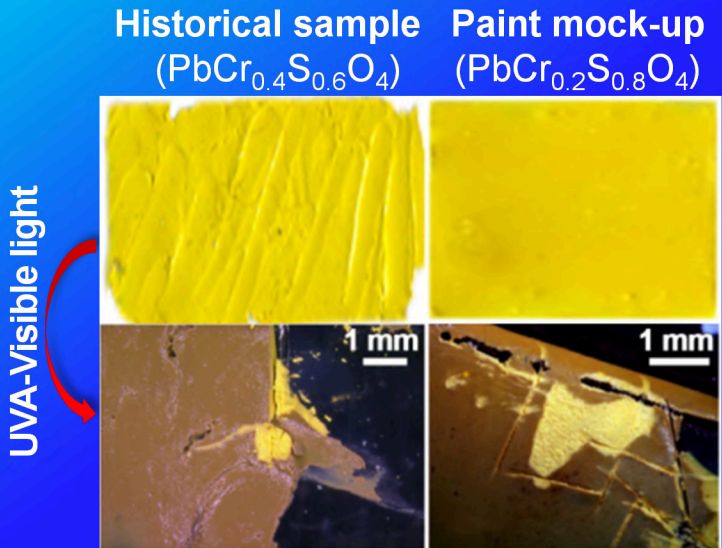
*J. Raman Spectrosc.* 2014, 45, 1034–1045





# S-rich historical sample and mock-up paint

Reproduction of the same alteration process as observed on the historical sample



**EPR analysis: detection of Cr<sup>V</sup>-compounds**

\*L. Monico *et al.*, Anal. Chem. 83 (2011) 1214–1223; L. Monico *et al.*, Anal. Chem. 85 (2013) 860-867; L. Monico *et al.*, JAAS 30 (2015) 1500-1510; L. Monico *et al.*, Microchem. J. 124 (2016) 272-282.

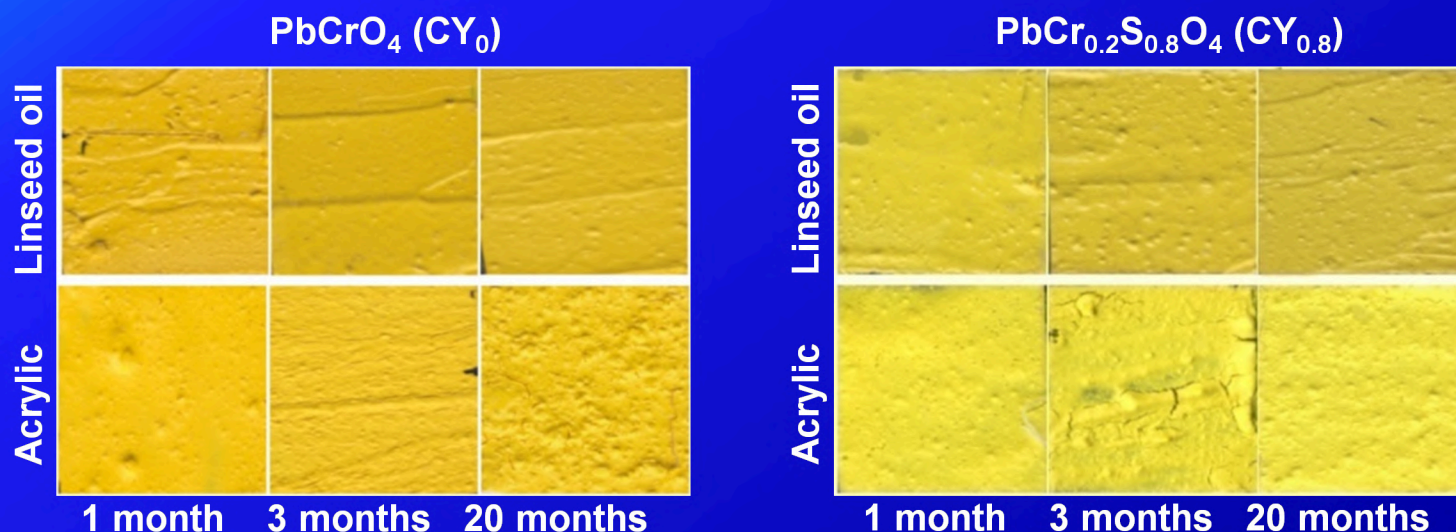
# Effects of the binding medium: naturally aged mock-ups\*

## Disclosing the Binding Medium Effects and the Pigment Solubility in the (Photo)reduction Process of Chrome Yellows ( $\text{PbCrO}_4$ / $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ )

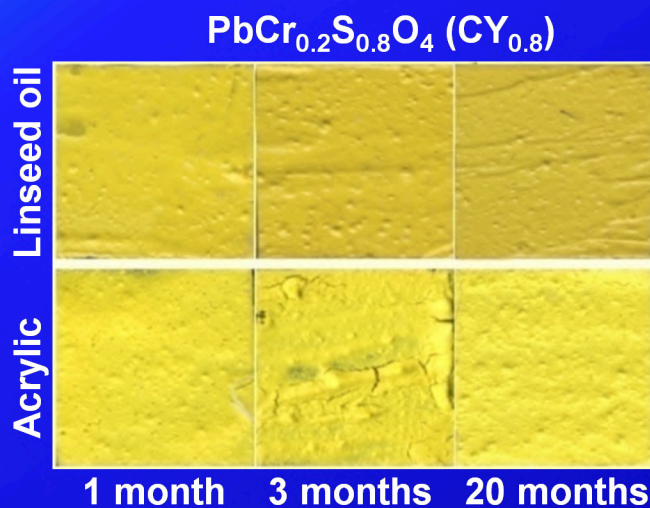
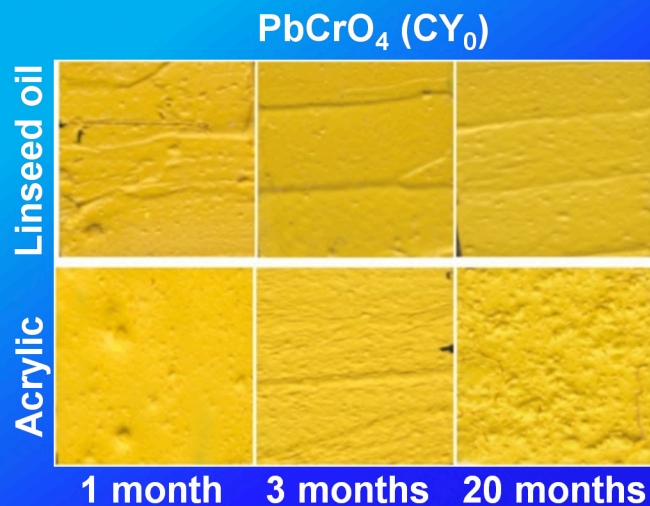
Letizia Monico,<sup>\*,†,‡,§</sup> Lorenzo Sorace,<sup>||</sup> Marine Cotte,<sup>⊥,#</sup> Wout de Nolf,<sup>⊥</sup> Koen Janssens,<sup>§</sup>  
Aldo Romani,<sup>†,‡</sup> and Costanza Miliani<sup>‡,†</sup>

DOI: 10.1021/acsomega.8b03669

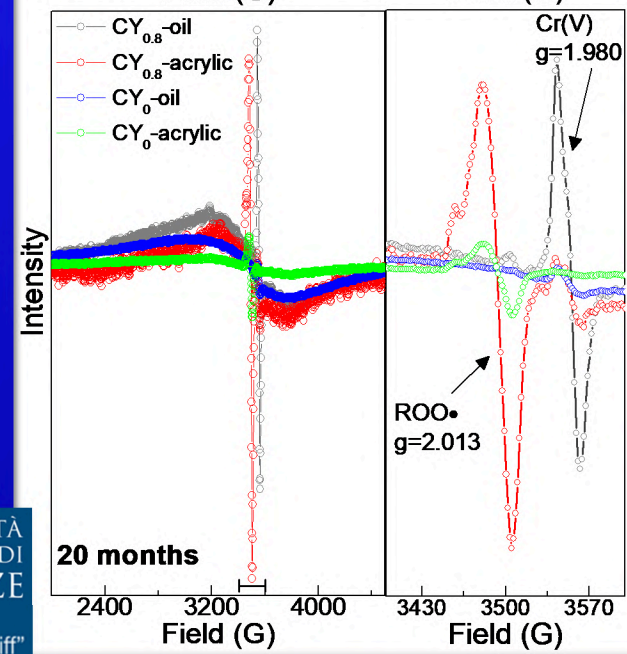
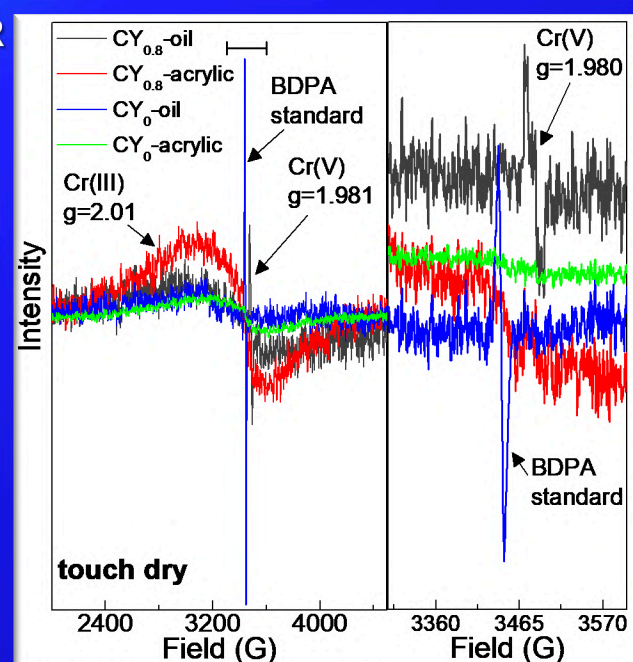
ACS Omega 2019, 4, 6607–6619



# Effects of the binding medium: naturally aged mock-ups\*

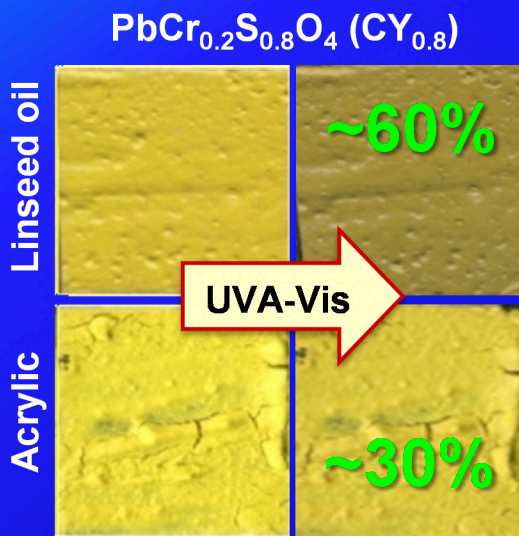
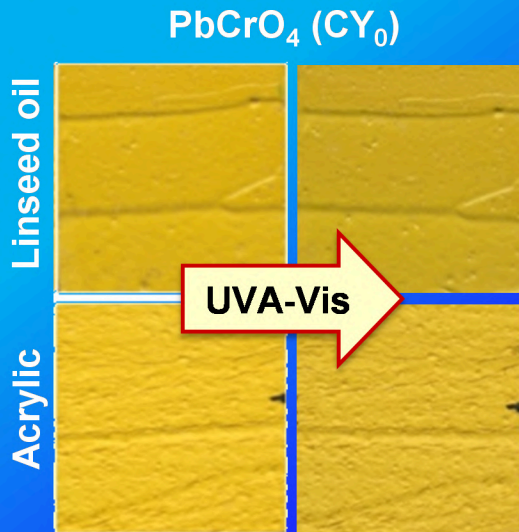


EPR

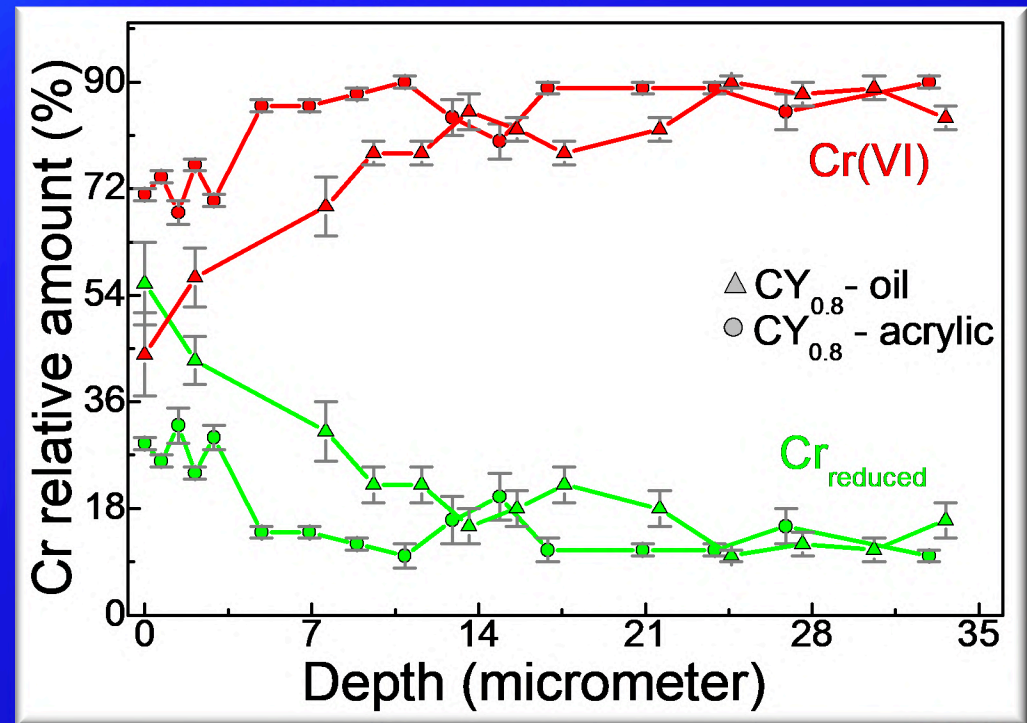


\* L. Monico, L. Sorace, M. Cotte, W. de Nolf, K. Janssens, A. Romani, C. Miliani, "Disclosing the Binding Medium Effects and the Pigment Solubility in the (Photo) reduction Process of Chrome Yellows ( $\text{PbCrO}_4/\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ )", ACS Omega 4 (2019) 6607-6619.

# Effects of the binding medium: light-exposed mock-ups\*



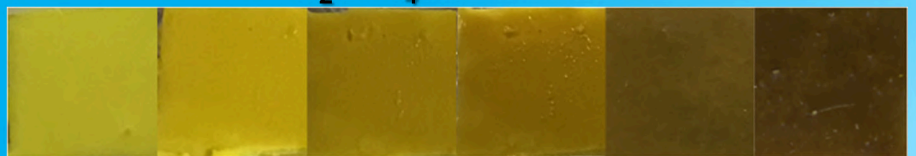
Cr K-edge  $\mu$ -XANES spectroscopy



\* L. Monico, L. Sorace, M. Cotte, W. de Nolf, K. Janssens, A. Romani, C. Miliani, "Disclosing the Binding Medium Effects and the Pigment Solubility in the (Photo) reduction Process of Chrome Yellows (PbCrO<sub>4</sub>/PbCr<sub>1-x</sub>S<sub>x</sub>O<sub>4</sub>)", ACS Omega 4 (2019) 6607-6619.

# Effects of the Pigment's Solubility\*

$K_2CrO_4$ -linseed oil

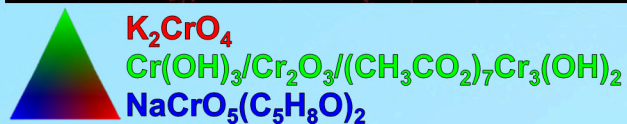
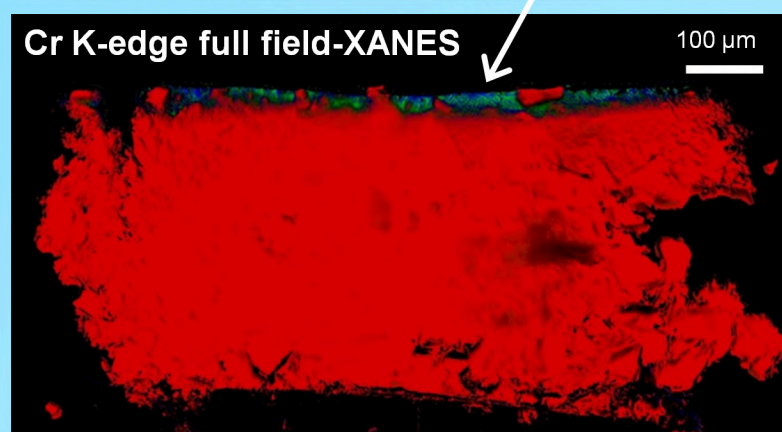
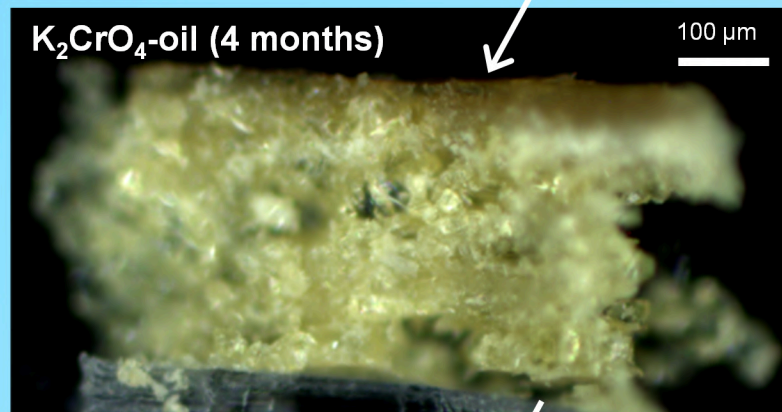
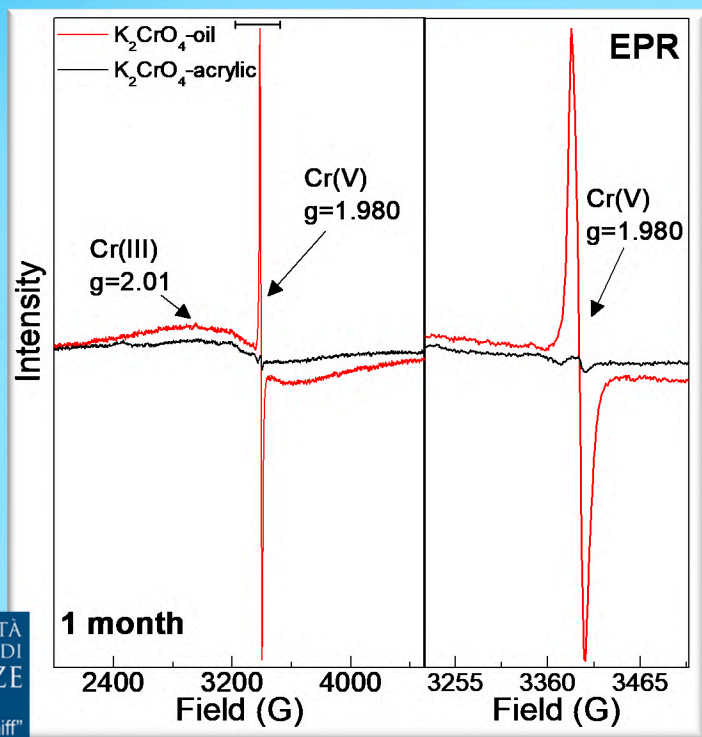


0 days    2 days    5 days    8 days    4 months    10 months

$K_2CrO_4$ -acrylic



0 days    2 days    5 days    8 days    4 months



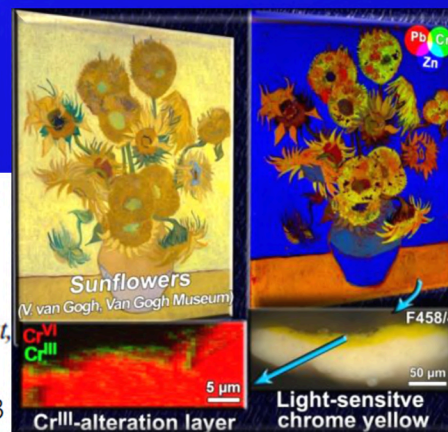
# Van Gogh's Sunflowers (Amsterdam version)

Angewandte  
Chemie

## 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

Letizia Monico,\* Koen Janssens, Ella Hendriks, Frederik Vanmeert, Geert Van der Snickt, Marine Cotte, Gerald Falkenberg, Brunetto Giovanni Brunetti, and Costanza Miliani

Angew. Chem. 2015, 127, 14129–14133

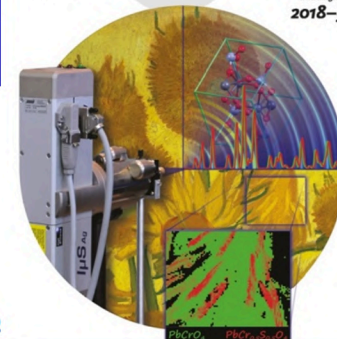


## Chemical Mapping by Macroscopic X-ray Powder Diffraction (MA-XRPD) of Van Gogh's Sunflowers: Identification of Areas with Higher Degradation Risk

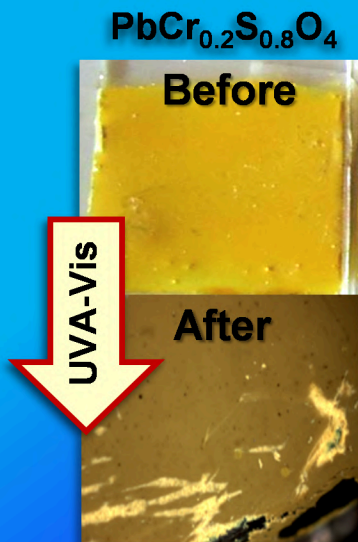
Frederik Vanmeert,\* Ella Hendriks, Geert Van der Snickt, Letizia Monico, Joris Dik, and Koen Janssens

Angew. Chem. Int. Ed. 2018, 57, 7418–7422

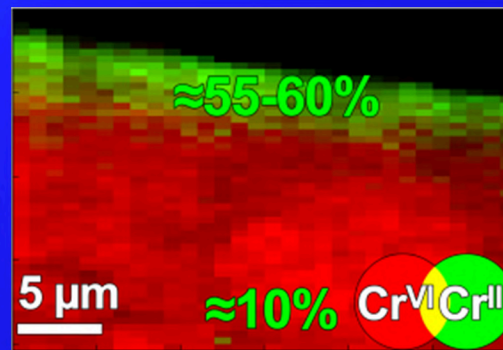
A Journal of the Gesellschaft Deutscher Chemiker  
Angewandte  
Chemie  
International Edition  
www.angewandte.org  
2018–57/25



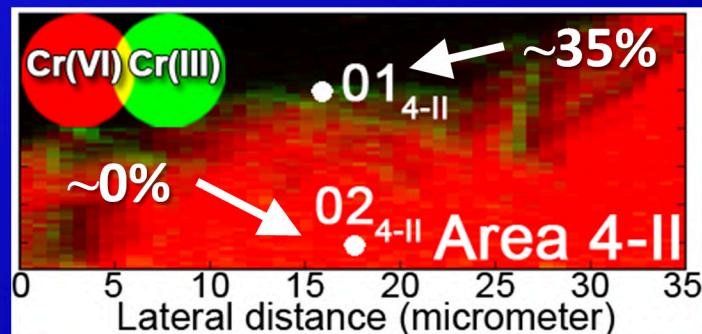
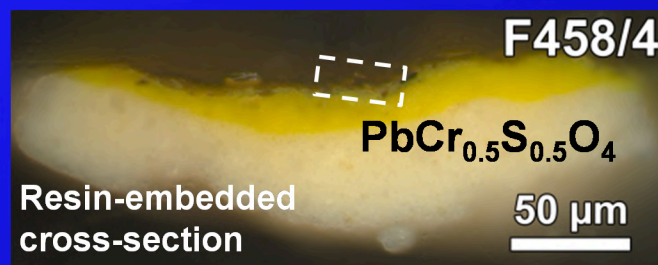
# Cr speciation analysis of original paint micro-samples



Thin section  
(thickness: ~5 μm)



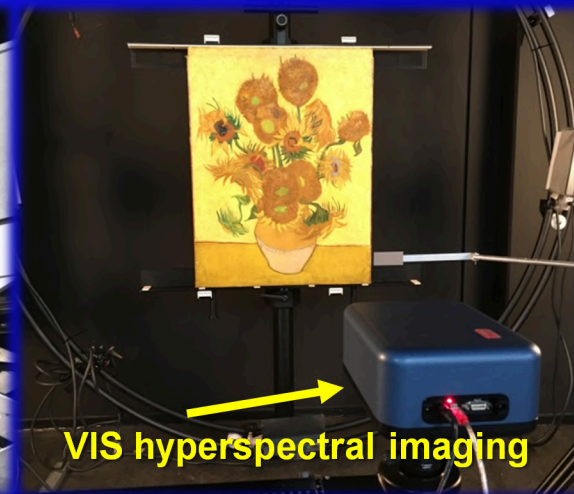
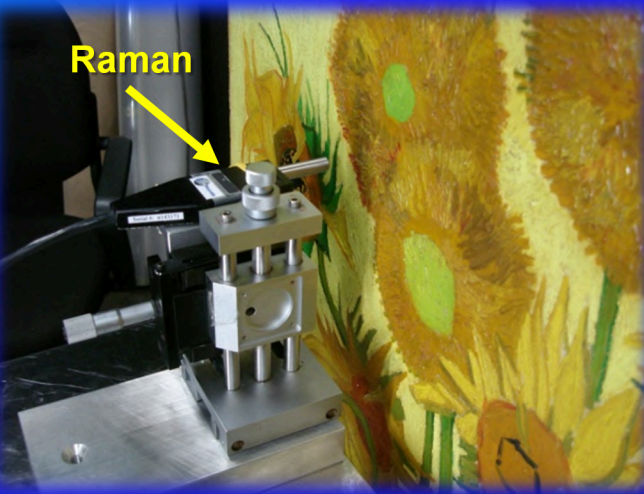
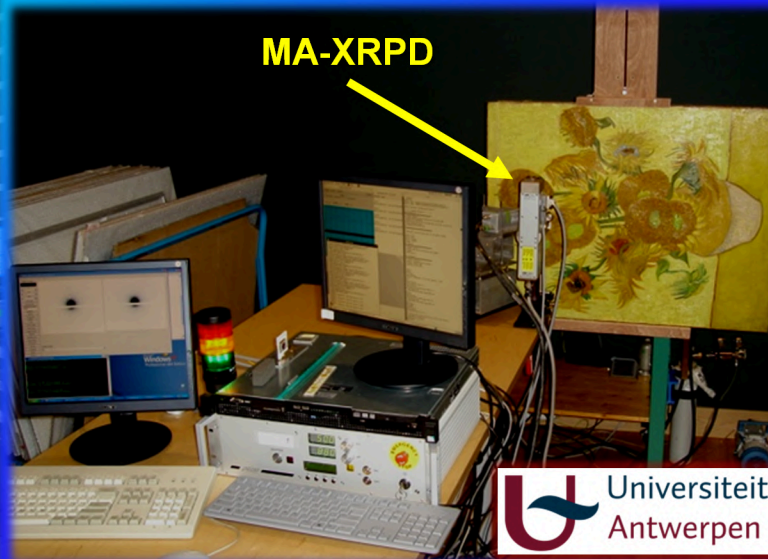
step size (h×v): 0.8×0.3 μm<sup>2</sup>  
 dwell time: 100 ms/pixel  
 Energy: 5.993-6.1 keV



step size (h×v): 0.7×0.2 μm<sup>2</sup>  
 dwell time: 100 ms/pixel  
 Energy: 5.993-6.1 keV



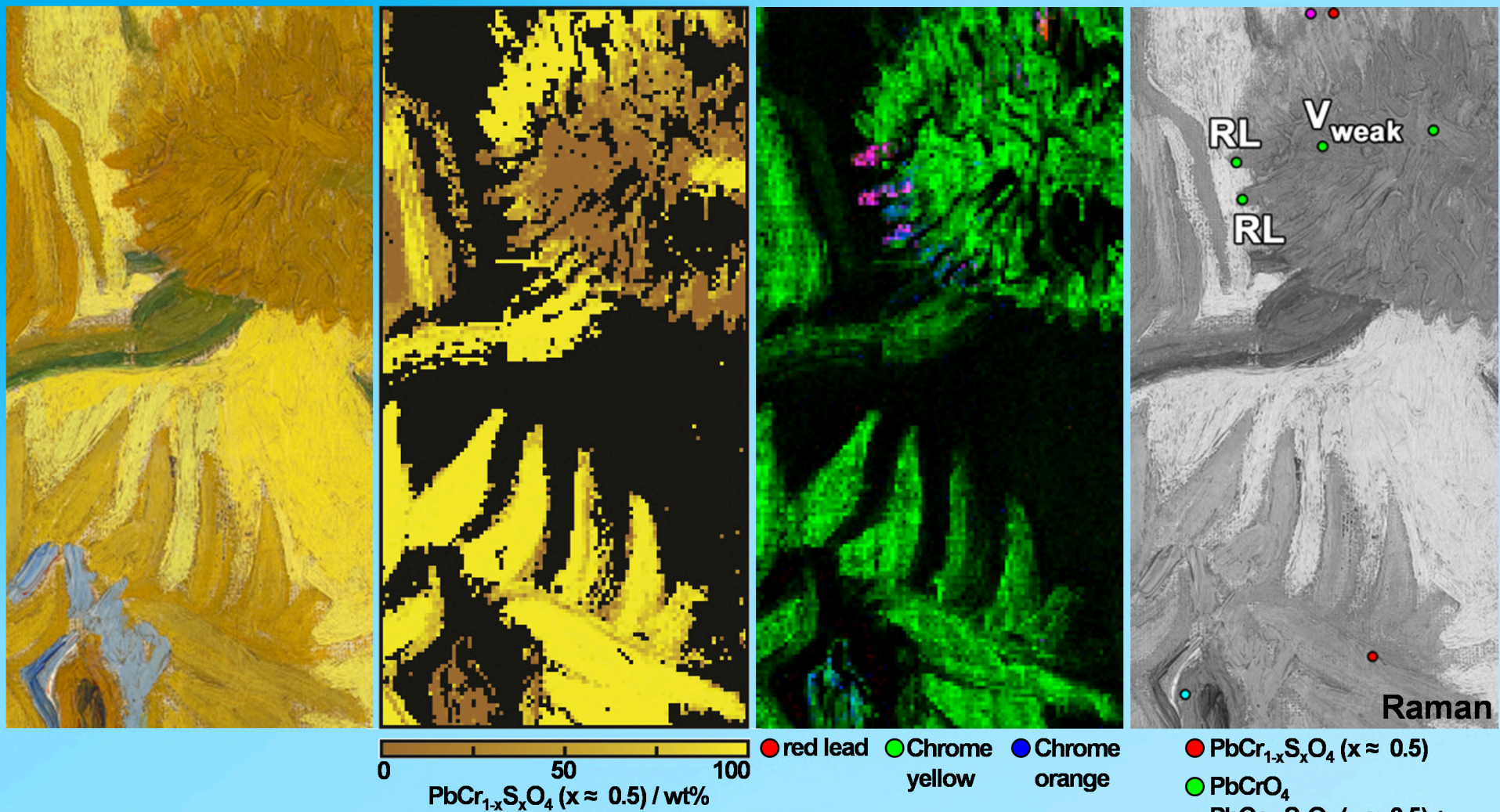
# Non-invasive in situ investigations



## MA-XRF/XRPD, reflection mid-FITR, Raman, Vis-hyperspectral

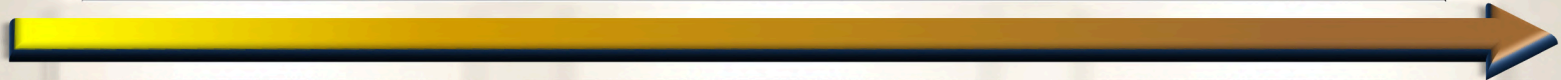
- Identification and distribution of different chrome yellow types and some of the corresponding degradation compounds;
- Detection of other pigments.

# MA-XRPD and Raman distributions of different chrome yellow types



**Chemical Mapping by Macroscopic X-ray Powder Diffraction (MA-XRPD) of Van Gogh's *Sunflowers*: Identification of Areas with Higher Degradation Risk**

Frederik Vanmeert,\* Ella Hendriks, Geert Van der Snickt, Letizia Monico, Joris Dik, and Koen Janssens  
*Angew. Chem. Int. Ed.* 2018, 57, 7418–7422



**LOOKING BACKWARDS**

how colors looked from the moment the painting was finished?



**LOOKING INTO THE FUTURE**

What we can do now for preventing the color changes?

# Acknowledgments

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  - IPERION-CH (H2020-INFRAIA-2014-2015, Grant No. 654028)
  - CHARISMA (EU FP7 programme, Grant No 228330)
  - project AMIS-Dipartimenti di Eccellenza 2018-2022 (funded by MIUR and University of Perugia)
  - program “Ricerca di Base 2017” (University of Perugia)
  - ESRF (exps. EC-504, EC-799, EC-1051, HG-18, HG-26, HG-32, HG-64, HG-95 and in-house beamtimes)
  - DESY/PETRA III (exps. I-20120312 EC, I-20130221 EC, I-20140760 EC, H-20000043 and I-20160126 EC)
  - FWO (Brussels) (projects no. G.0C12.13, G.0704.08 and G.01769.09)
  - BELSPO (Brussels) “S2-ART” (SD04A)
  - GOA “SOLARPAIN” (Research Fund Antwerp University: BOF-2015)
  - Fund Inbev-Baillet Latour (Brussels)