ALBA SYNCHROTRON:
NEW TOOLS FOR MATERIALS CHARACTERIZATION
ALBA November 13-14th 2014

X-Ray Absorption Spectroscopy at CLÆSS

Marta Ávila

CLÆSS - Core Level Absorption and Emission Spectroscopies

Outline

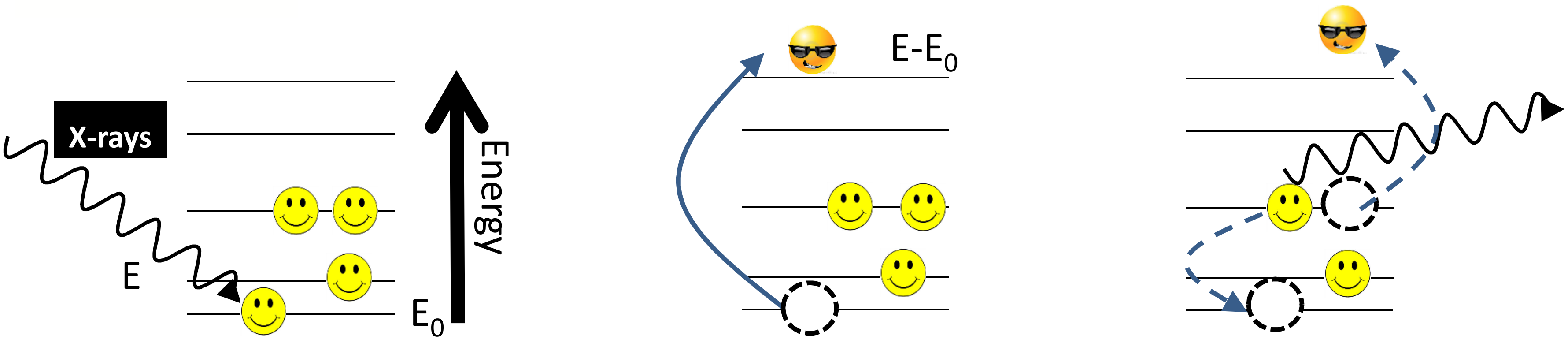
1. What is x-ray absorption spectroscopy (XAS)?
2. What can be used for?
3. Applications

1. What is X-ray absorption spectroscopy?

Peter BEHRENS

Trends Anal.Chem., v.11, n.7, p.237-244, 1992.

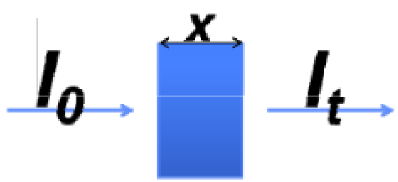
1. What is X-ray absorption spectroscopy?



An incident x-ray of energy E is absorbed, exciting a core electron of binding energy E_0

emitting a photo-electron with kinetic energy (E-E0), to some unoccupied state

The core state is filled (1 or 2 fs later), ejecting a fluorescent x-ray or an Auger electron



Absorption

Lambert-Beer: $I_t = I_0\, e^{-\mu x}$

$\mu x = -\ln(I/I_0)$

μ = x-ray absorption coefficient

x = thickness of the sample

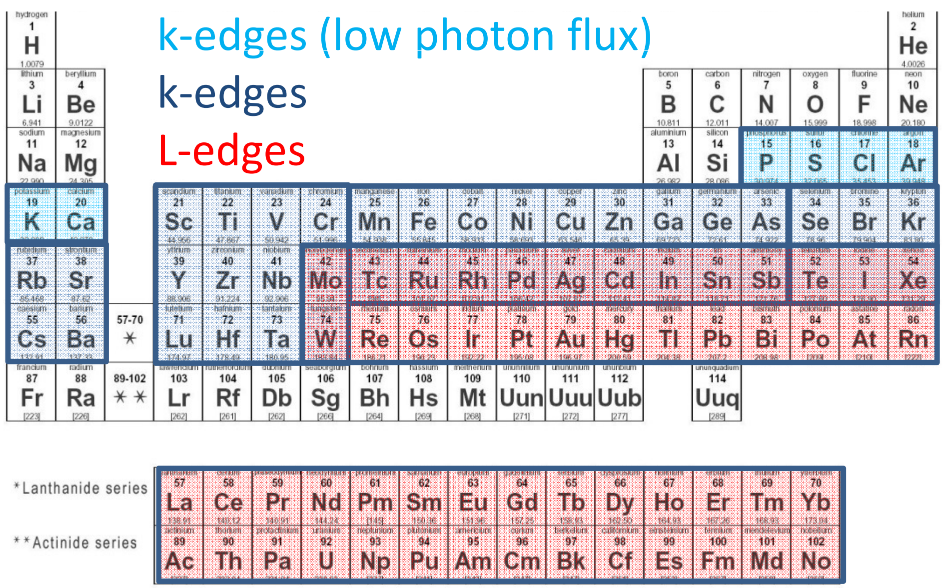
Fluorescence

Auger electrons

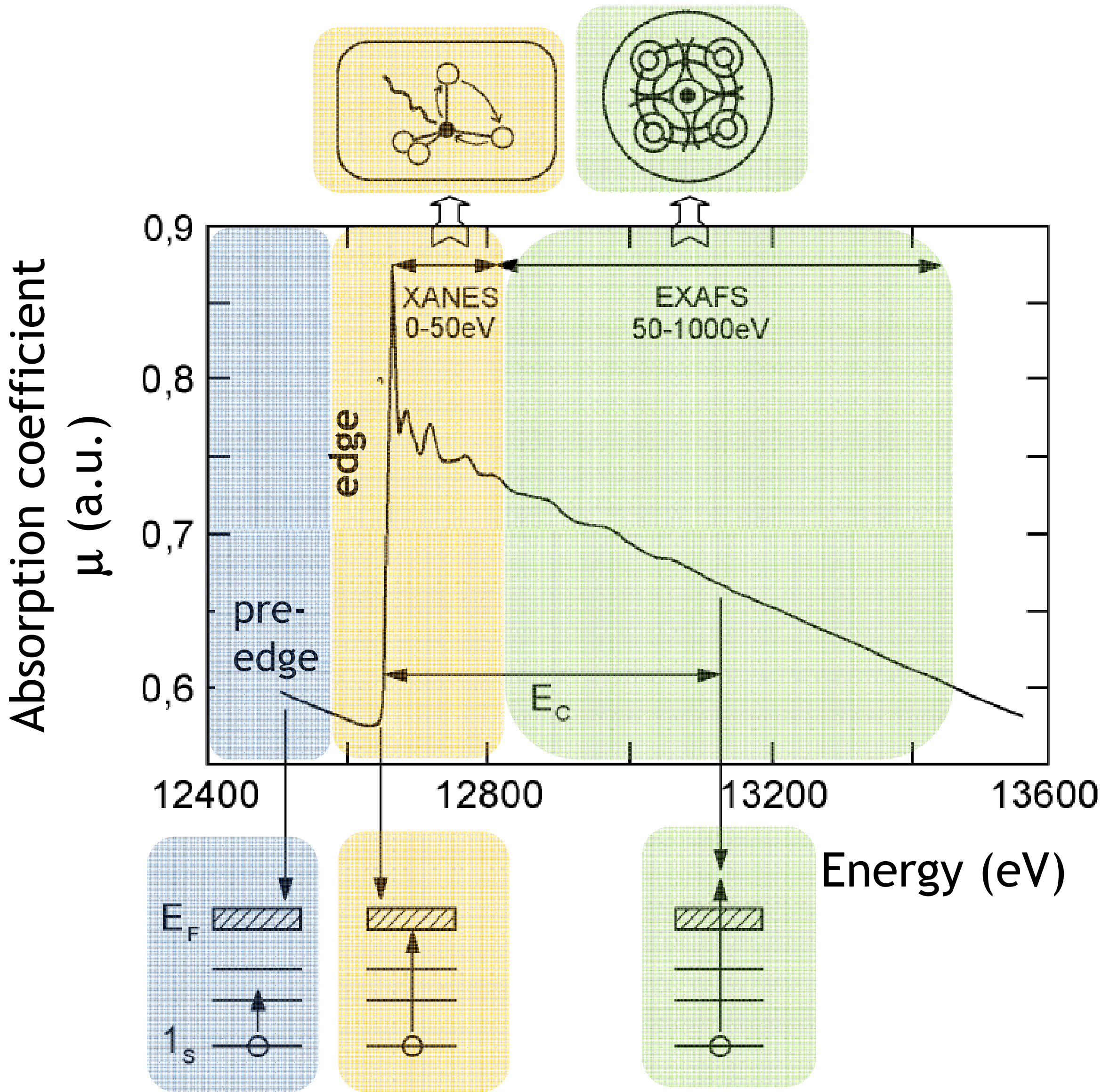
Proportional to absorption

1. What is X-ray absorption spectroscopy?

- ❑ XAS is element specific
- ❑ Can be measured in diluted or concentrated systems
- ❑ The study of disordered systems is possible (local probe)



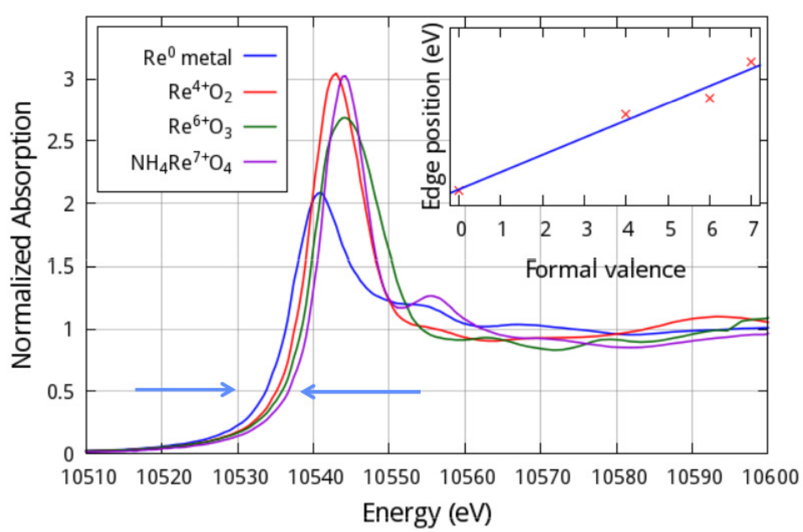
1. What is X-ray absorption spectroscopy?

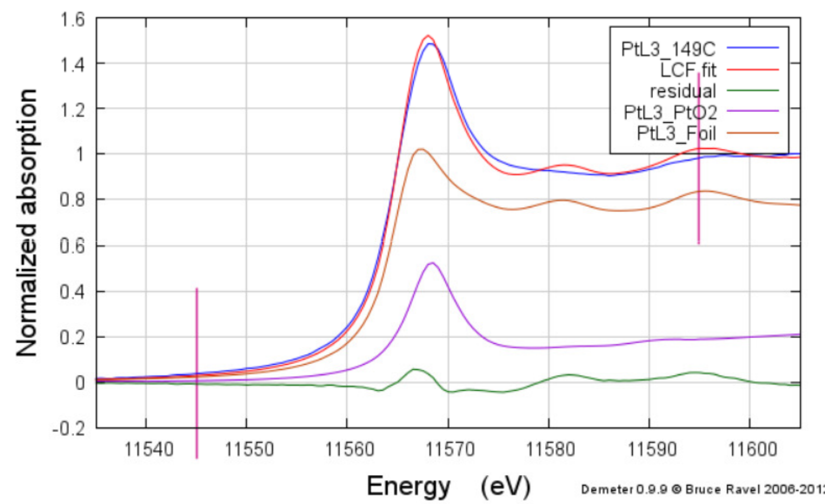


1. What is X-ray absorption spectroscopy?

XANES (X-ray Absorption Near Edge Structure)

- The position of the absorption edge is different for different **oxidation states**. Charged elements require higher energy to remove the electrons causing the edge to shift.
- Linear combination fitting (LCF) using standards to reproduce the measured spectrum to determine the **relative amount of each standard** in the measured spectrum.



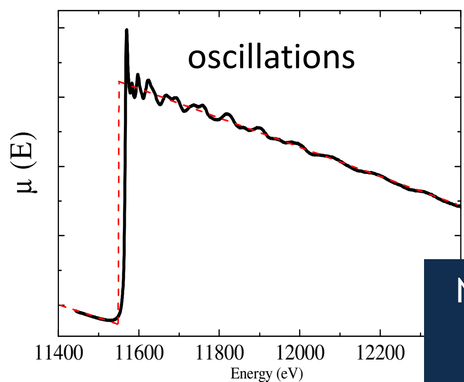


Good knowledge of your sample, **standards should be a good representation** of Pt species in the sample.

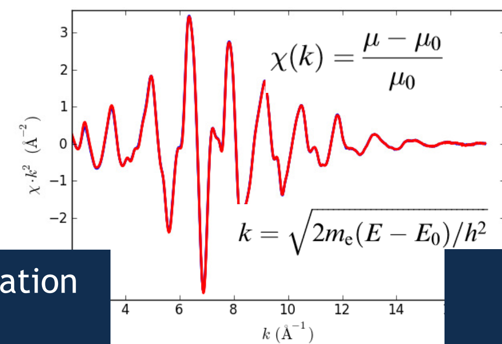
1. What is X-ray absorption spectroscopy?

EXAFS (Extended X-ray Absorption Fine Structure)

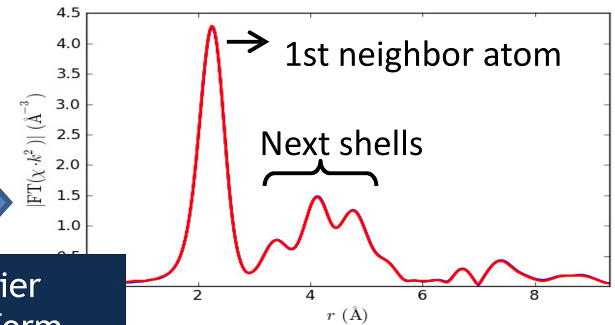
- The data treatment is a “little bit” more complex than in XANES.



Normalization + Extraction

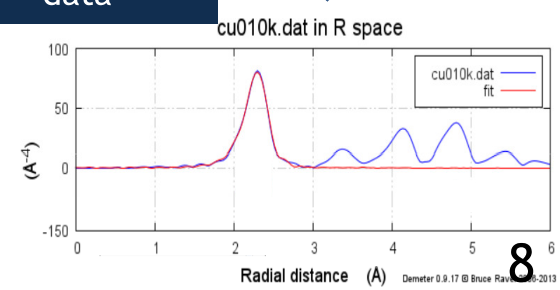


Fourier Transform



Some more steps…

Fitting the data



- More information can be extracted

Bond distances

Coordination number

Static and dynamic disorder

2. What is XAS used for?

- The wiggles in the XAS data tell us something about the **atomic** and **electronic structure** of the material measured.

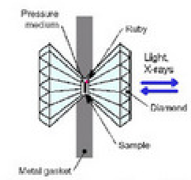
Valence	the charge state of the absorber
Species	what kinds of atoms surround the absorber
Number	how many of those atoms there are
Distance	how far away they are
Disorder	thermal and structural disorder

Almost anything can go on the sample stage

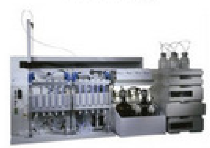
XAS is usually capable of measuring your sample very close to the "proper" state → in-situ

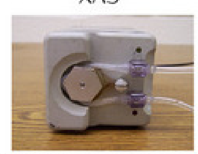

Gas flow reactor for redox chemistry


Tube furnace for high-T XAS


Diamond anvil cell for high-P XAS


Cryostat (ARS Displex)

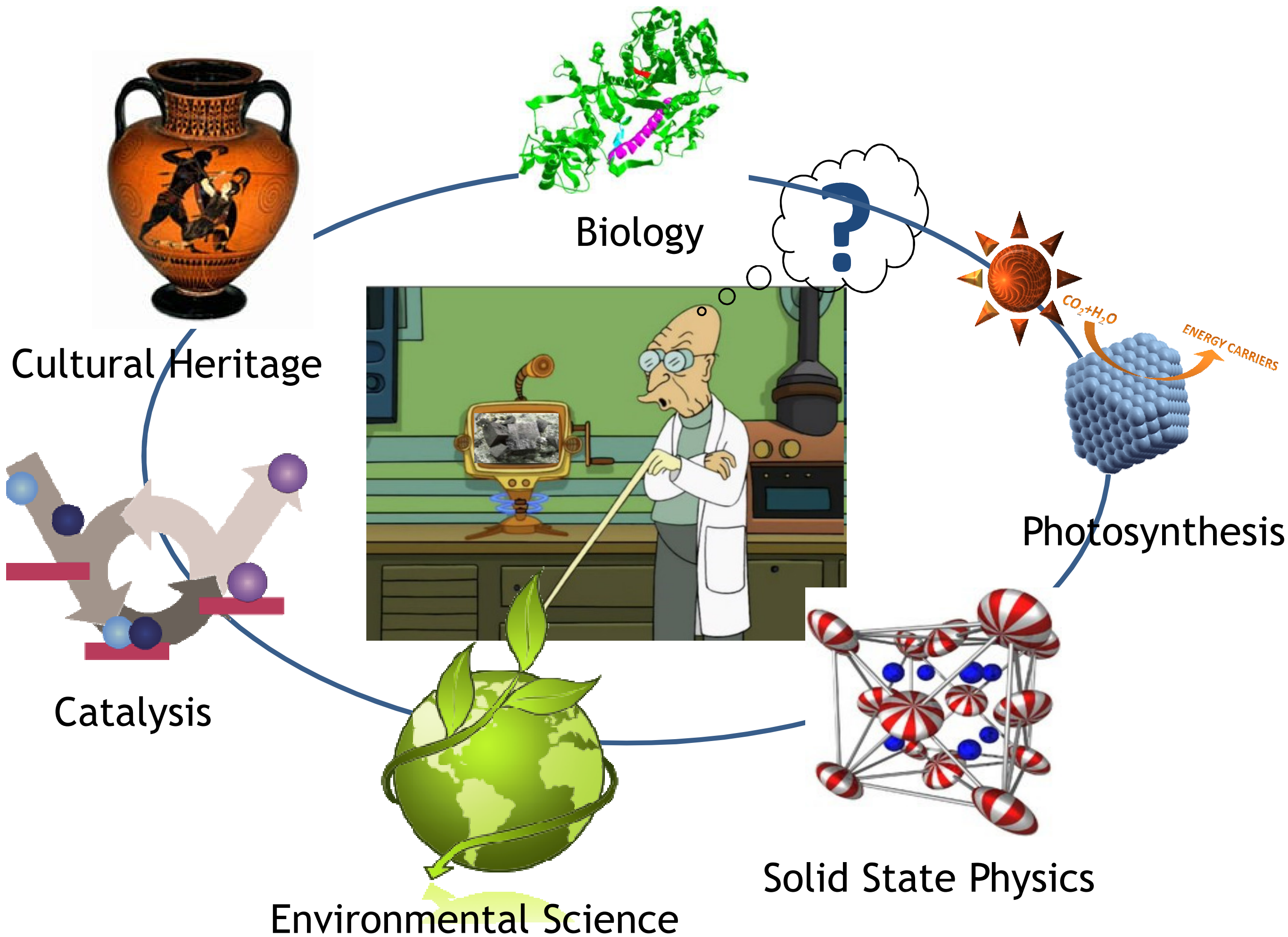

Combinatorial chemistry (Argonaut Technologies Surveyor)


Peristaltic pump for fluid flow


Cryostream, bio samples (Oxford Cryosystems Cobra)


Tilt stage for grazing incidence

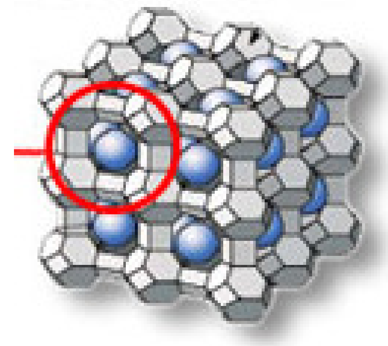
2. What is XAS used for?



3. Applications

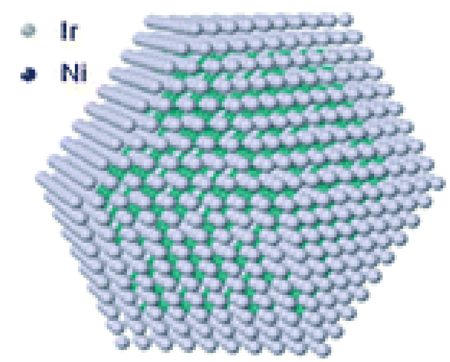
Catalysis Controls 80 % world´s chemical manufacturing processes

Reproduce real catalytic reaction conditions (car´s exhaust pipe) to develop new catalytic converters



Structure of metal particles in a zeolite matrix in function of the pretreatment/reaction

Determination the metal particle structure of catalysts during process



To study the alloy formation and structure

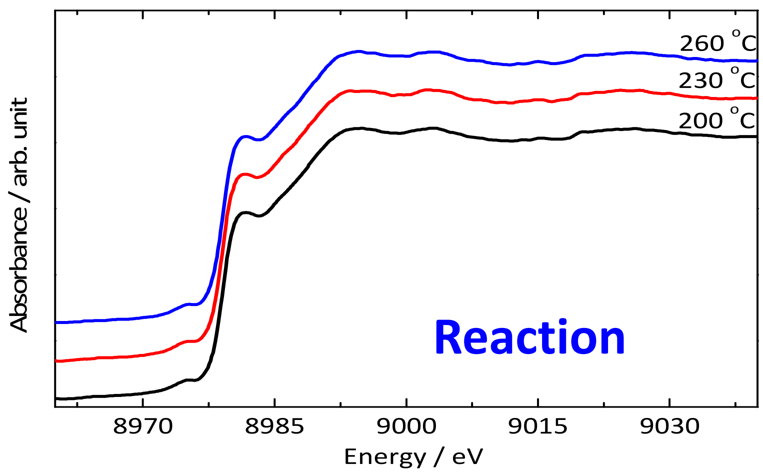
3. Applications

Catalysis at CLÆSS

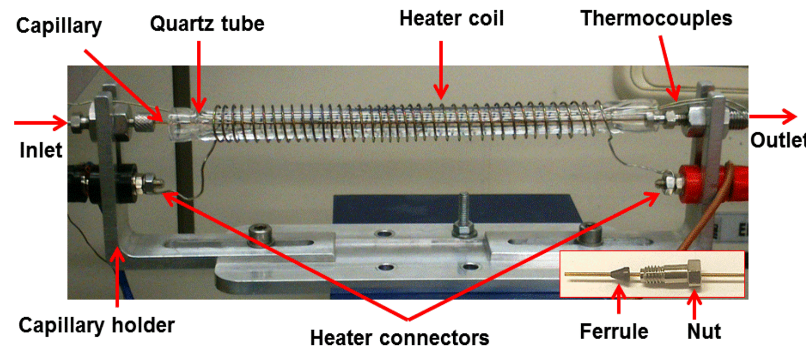
$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

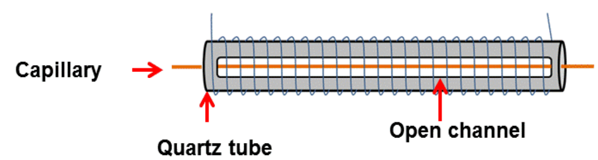
High relevance in C recycling

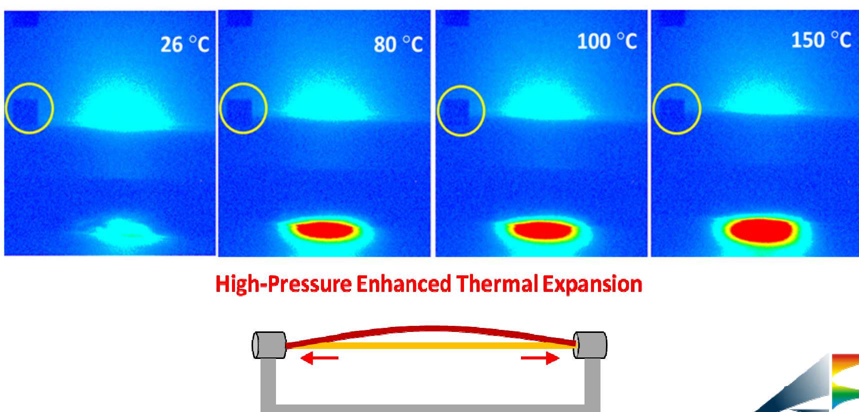
- Catalyst: Cu/Al_2O_3 (Cu k-edge)
- Gases: 5% H_2/He
- **Pressure: 200 bar**
- Temperature: 250 ºC
- Continuous scan
- Each EXAFS scan (1200 eV) took 10 min



Cu remained at Cu(0) oxidation state under all examined conditions







A. Bansode, G. Guilera, V. Cuartero, L. Simonelli, M. Avila and A. Urakawa, Submitted to Rev. Sci. Instrum.

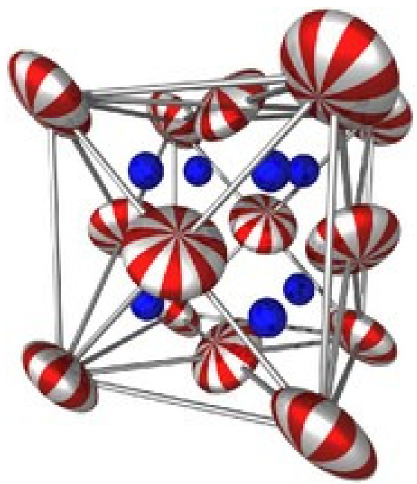
3. Applications

Solid State Physics

Structural changes due to phase transitions

- ❑ Temperature
- ❑ Pressure
- ❑ Magnetic Fields,…

Study of structure of batteries to extend its life and performance

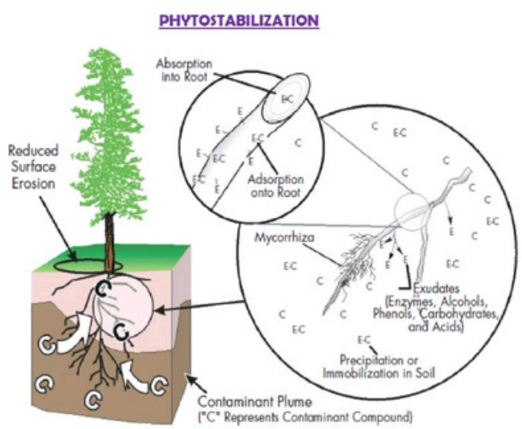


3. Applications

Environmental sciences

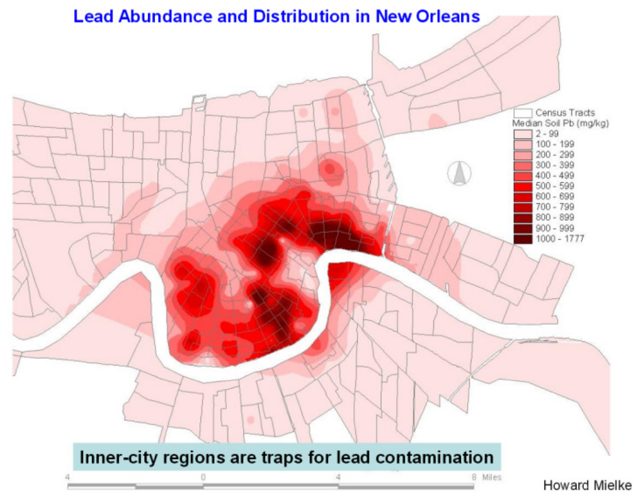
Why speciation is so important?

Cr^{3+} is good
Cr^{6+} is very toxic



To study the mechanisms of absorption of pollutants on plants or absorbents

- Chemical speciation controls mobility, toxicity, and bioavailability



Assess the real toxicity of polluted soils

Study of the chemical species of metals (As, Cu, Zn, …) in food

3. Applications

Cultural heritage

Non-destructive technique

Anal. Chem. **2006**, *78*, 7484–7492

Blackening of Pompeian Cinnabar Paintings: X-ray Microspectroscopy Analysis

Marine Cotte,*,† Jean Susini,† Nicole Metrich,‡ Alessandra Moscato,§ Corrado Gratziu,§ Antonella Bertagnini,|| and Mario Pagano⊥

Mario Pagana

Turning black. A wall painted red in the remains of Pompeii.

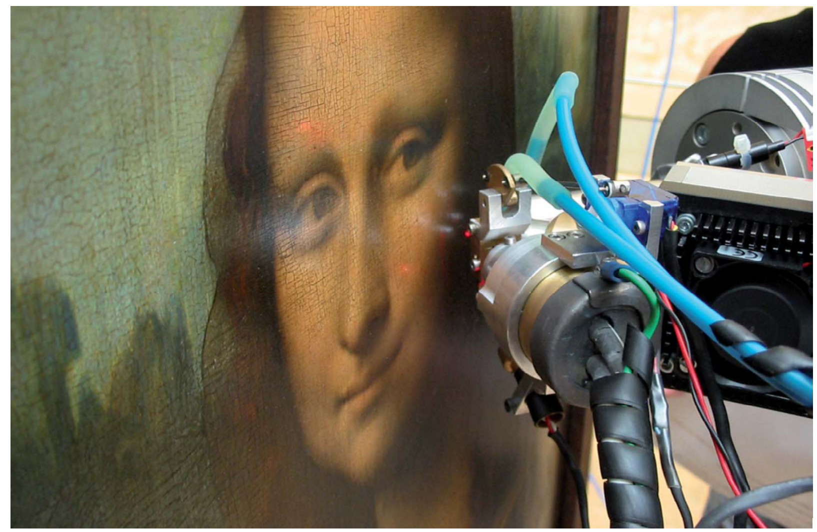
Why do the red walls of Pompei go black?

Analyzing Works of Art

DOI: 10.1002/anie.201001116

Revealing the *sfumato* Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy**

Laurence de Viguerie, Philippe Walter, Eric Laval, Bruno Mottin, and V. Armando Solé*



4. How can we make XAS experiments?

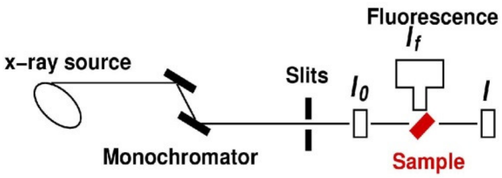
CLÆSS beamline

- Hard x-rays beamline
  E= 4-68 keV
- $\Delta E/E=1.4\cdot10^{-4}$
- 10^{13} ph/s

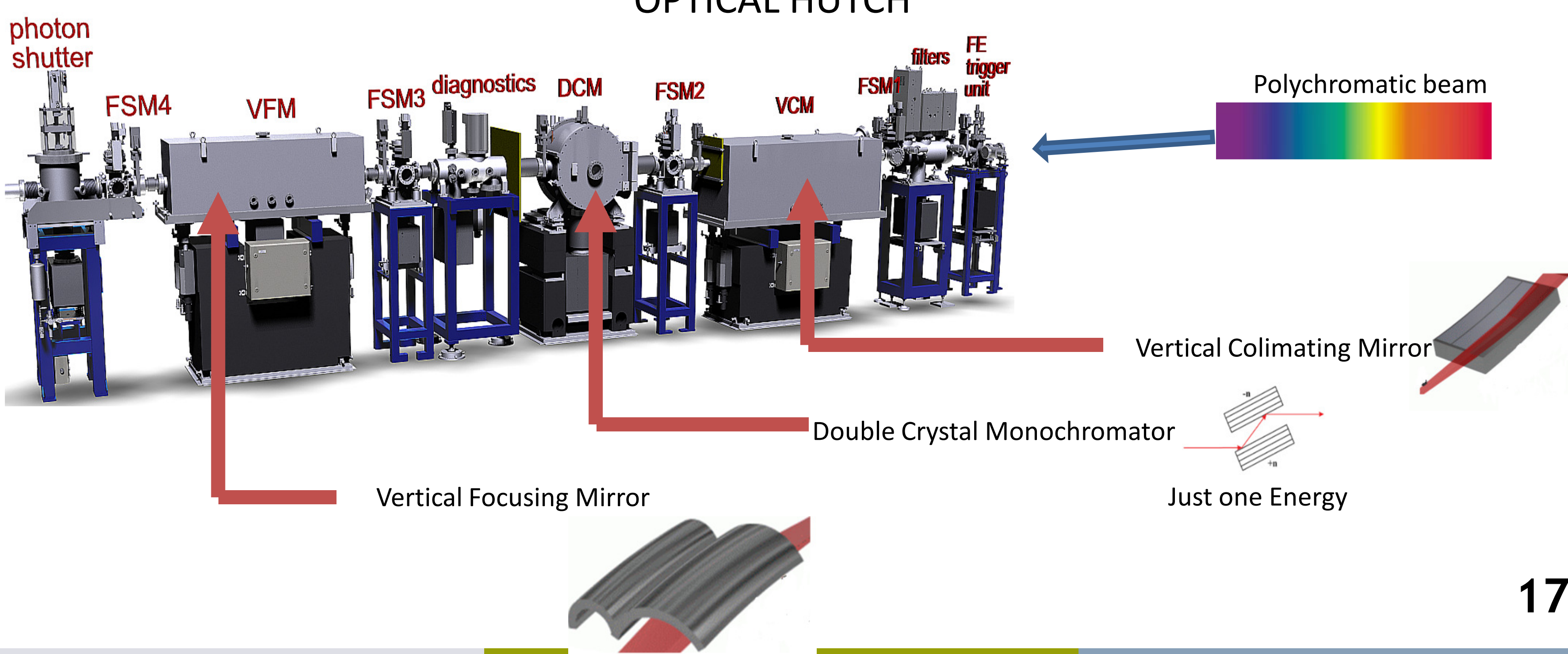
OPTICAL HUTCH

EXPERIMENTAL HUTCH

4. How can we make XAS experiments?



OPTICAL HUTCH



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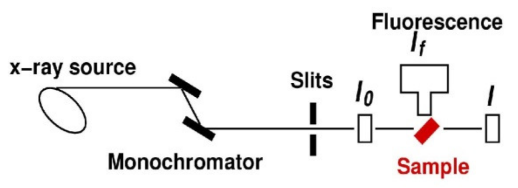
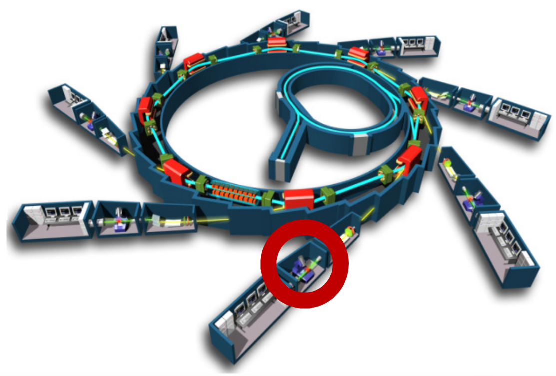
4. How can we make XAS experiments?





EXPERIMENTAL HUTCH

- Detection:

Transmission (Ion Chambers)

Fluorescence (SDD, CdTe, PD),

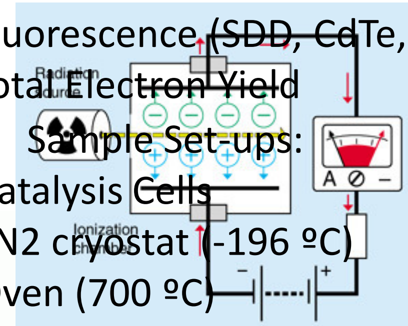
Total Electron Yield

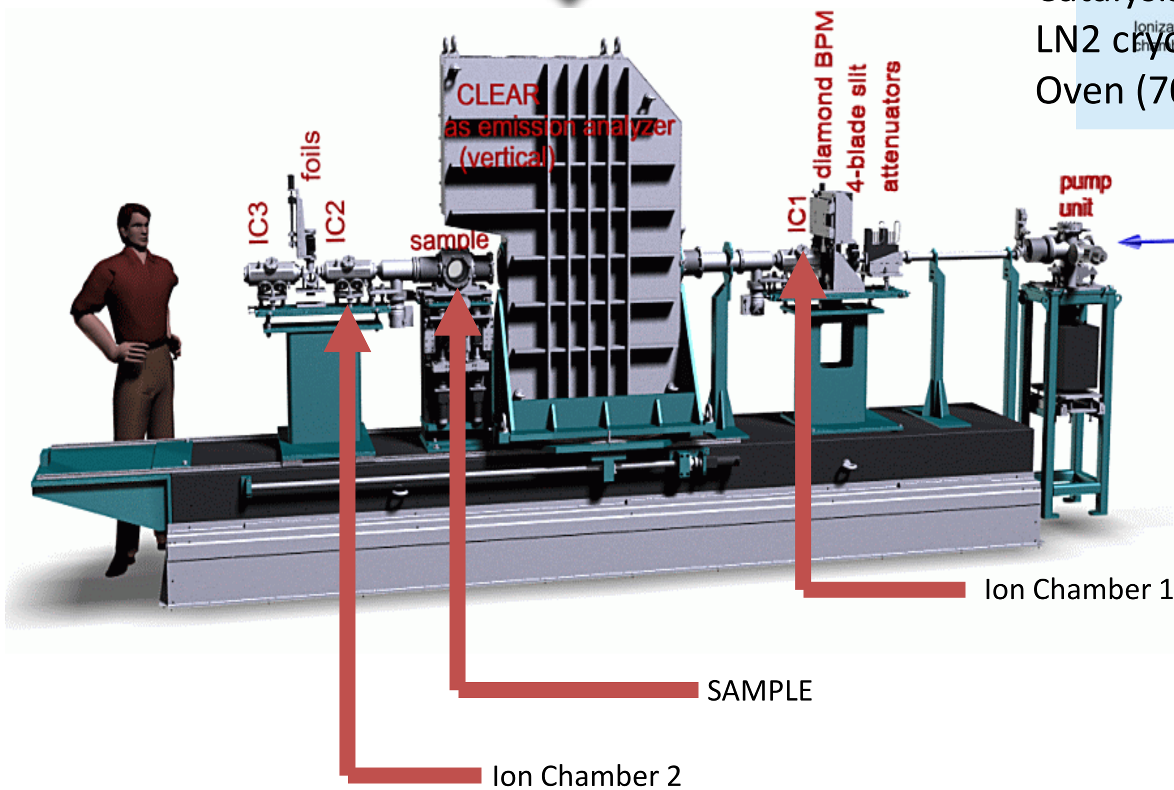
- Sample Set-ups:

Catalysis Cells

LN2 cryostat (-196 ºC)

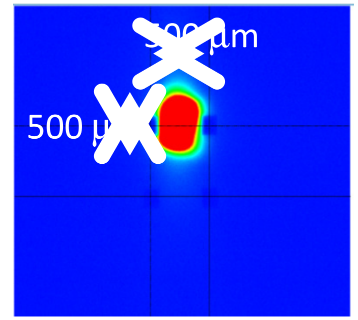
Oven (700 ºC)



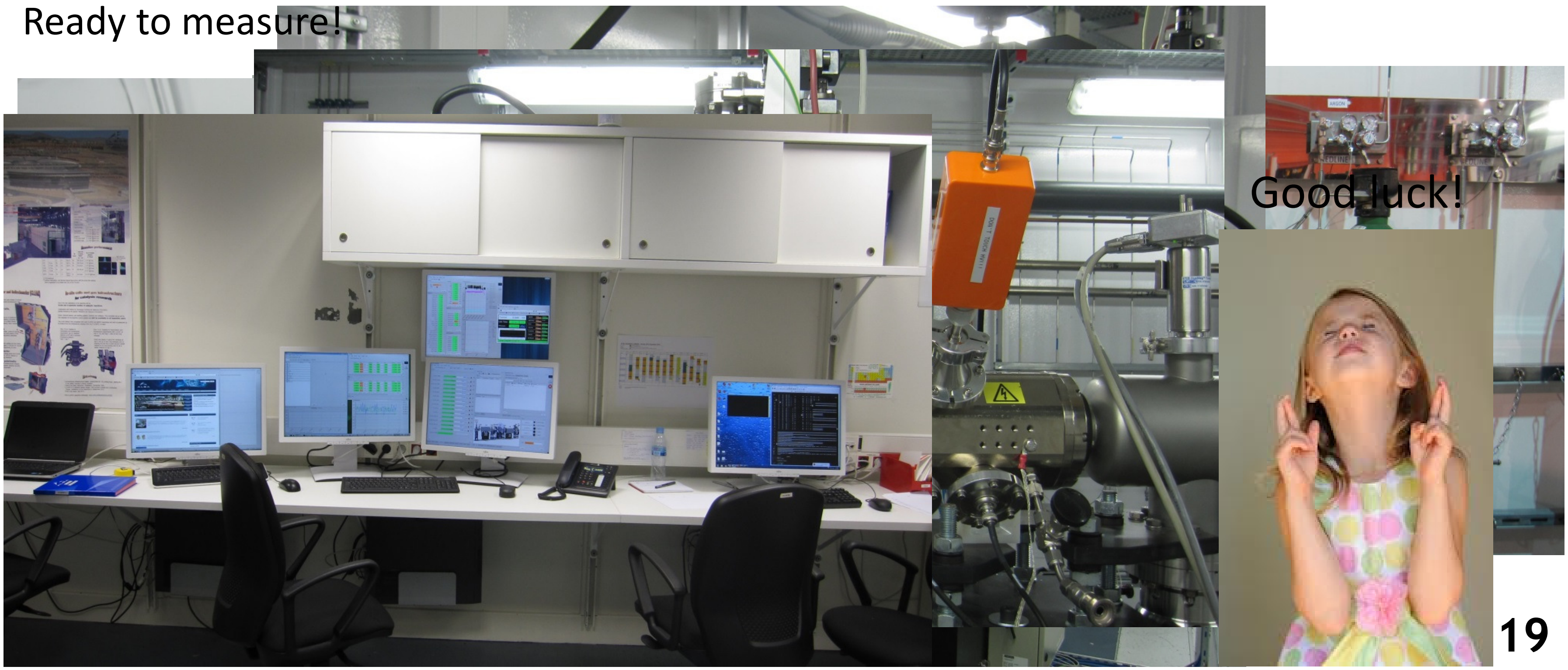


4. How can we make XAS experiments?

1. Align the optics to the required Energy
2. Focus the beam at the sample position
3. Refill the Ion Chambers
4. Put the sample and select your detector
5. Put a reference foil



Ready to measure!



Good luck!

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Controls Engineer: Roberto Homs

Electronic Engineer: José Ávila

Mechanical Engineer: Llibert Ribó

Technician: José Prieto

CLÆSS beamline

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THANKS FOR YOUR ATTENTION!