La superficie, el elemento clave en la interacción con el medio

C. Escudero
BL24 – CIRCE BEAMLINE

Metalurgia y tratamiento de superficies

ALBA Synchrotron Light Source

1 de Junio, 2018

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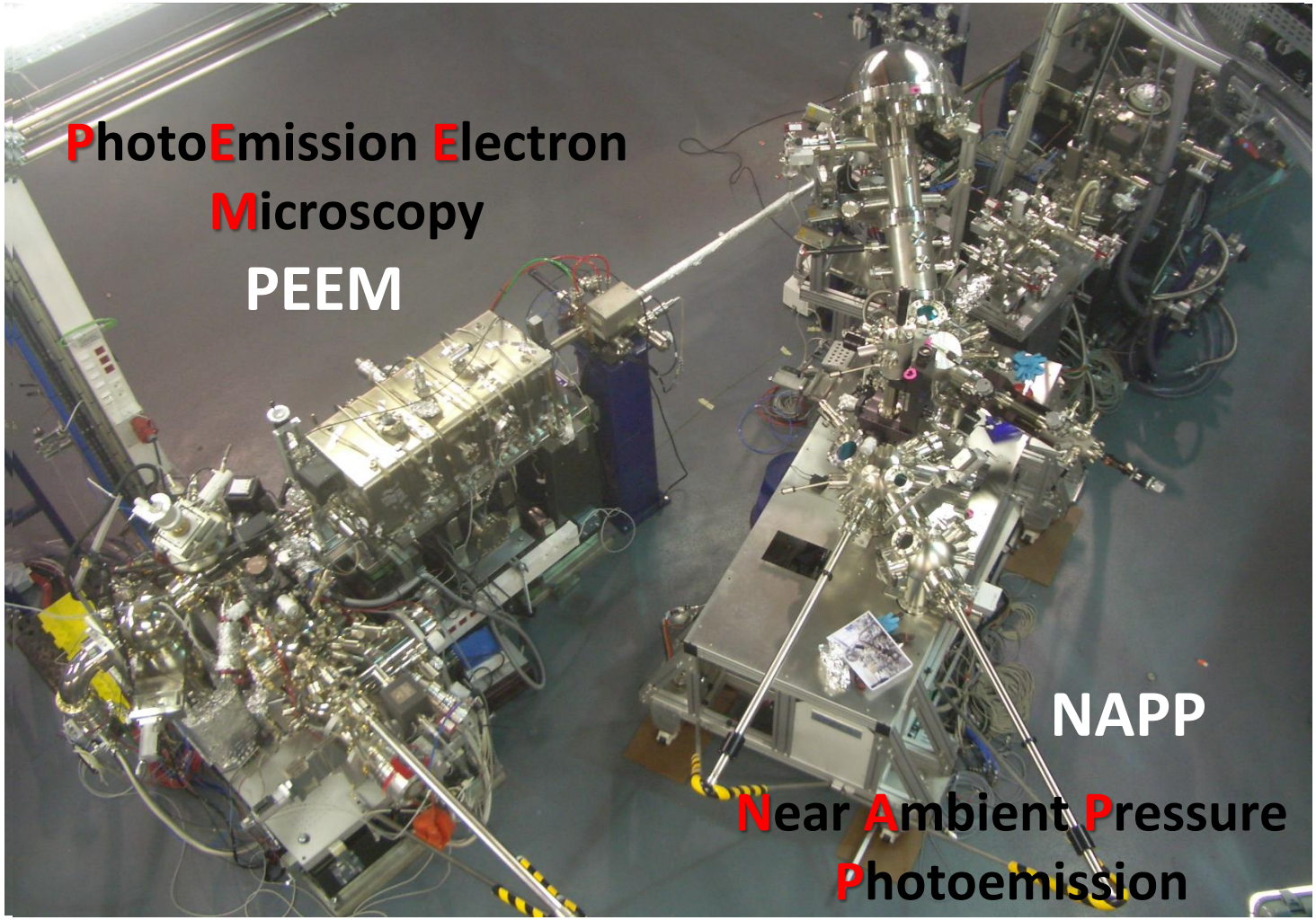
Outline

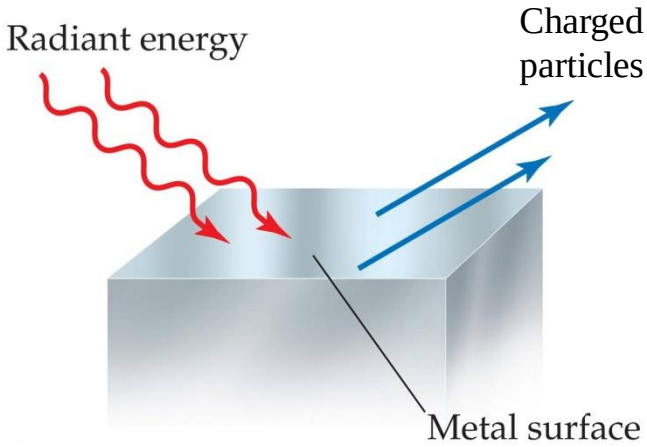
- **BL24- CIRCE @ ALBA synchrotron**
  - Introduction to BL24-CIRCE
  - Photoelectric effect
- **PhotoEmission Electron Microscopy (PEEM)**
  - Overview and main capabilities
  - Applications
- **Near Ambient Pressure Photoemission (NAPP)**
  - Overview and main capabilities
  - Applications

CIRCE - BL24 @ ALBA Synchrotron

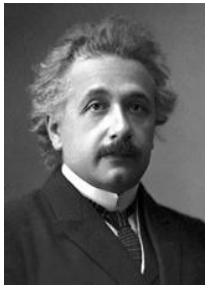


Photoelectric effect

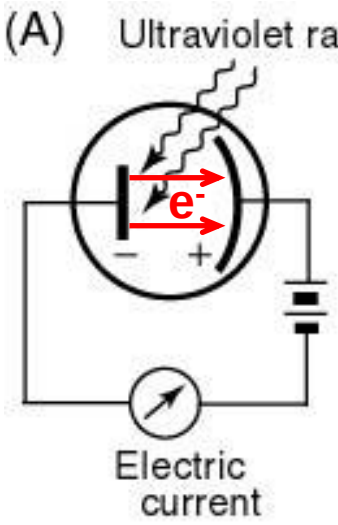
Heinrich Hertz

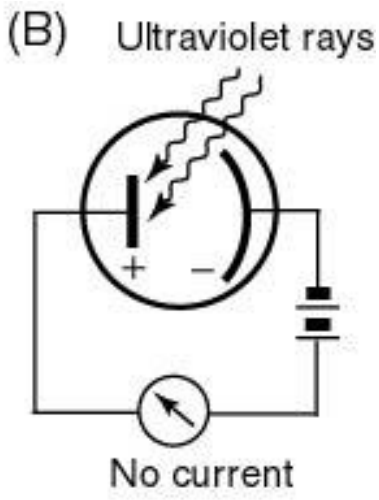


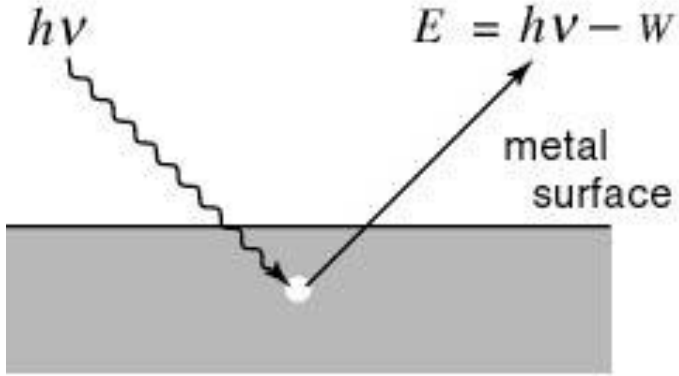
Albert Einstein



Nobel Prize in Physics 1921

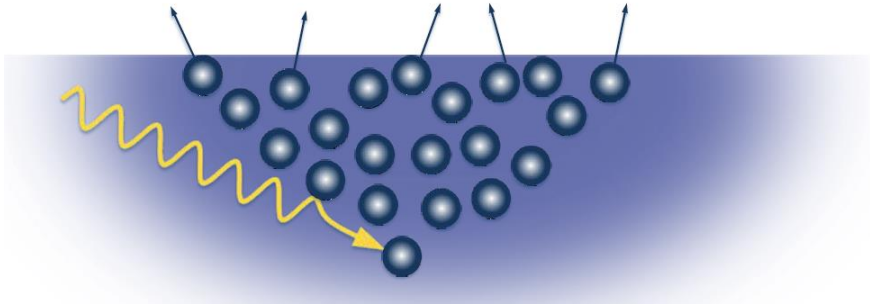


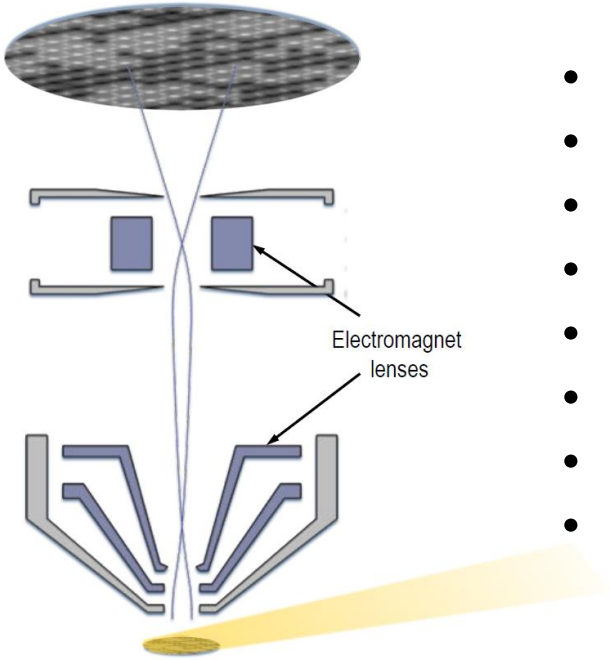




PEEM: PhotoEmission Electron Microscopy

An electron microscope where the electrons are obtained from the sample surface by photoelectric effect (illumination by photons)



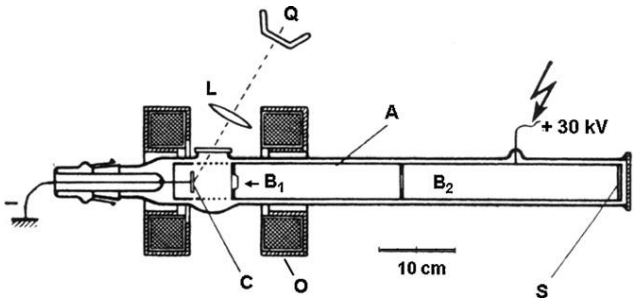


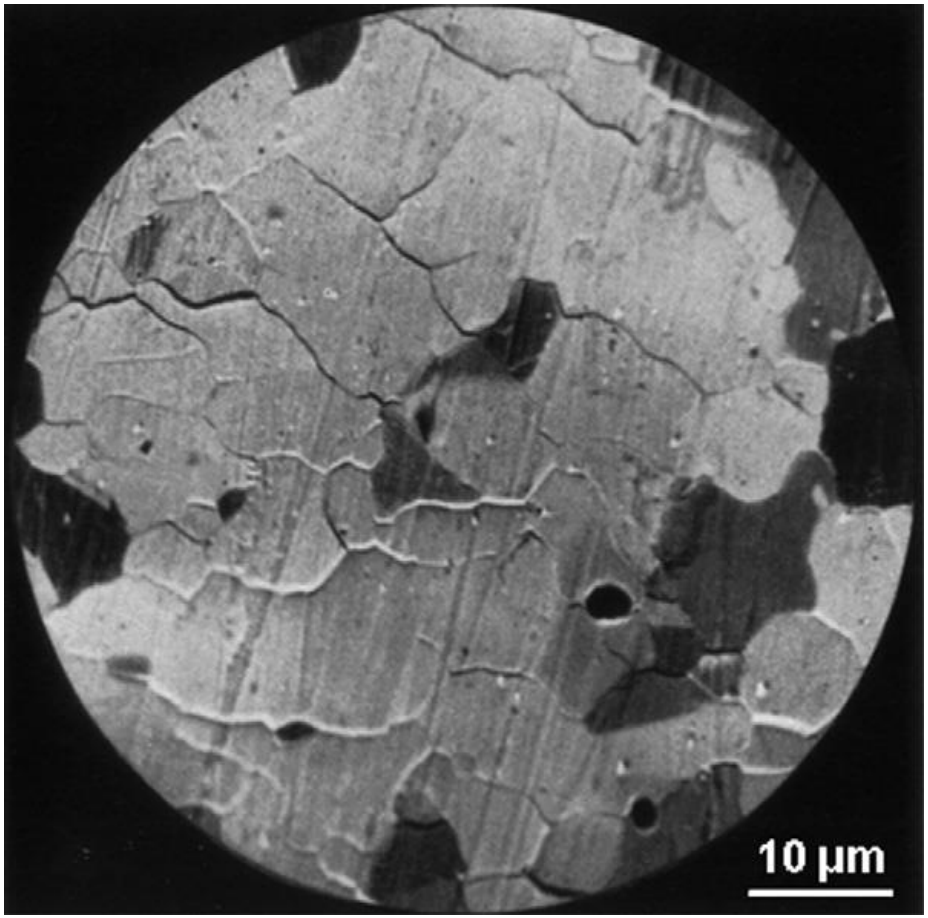
- Very high surface sensitivity (< 10 nm)
- Samples must be conductive and relatively flat.
- Down to 20 nm lateral resolution
- Variable temperatures (0 to 1500 °C)
- Application of electric and weak magnetic fields
- Application of electric currents
- Exposure to gases at low pressures
- Possible to follow sample evolution under some treatments.

PEEM Applications (I)

With laboratory UV-Source:

- **work function contrast**
- **fast (video rate) imaging**





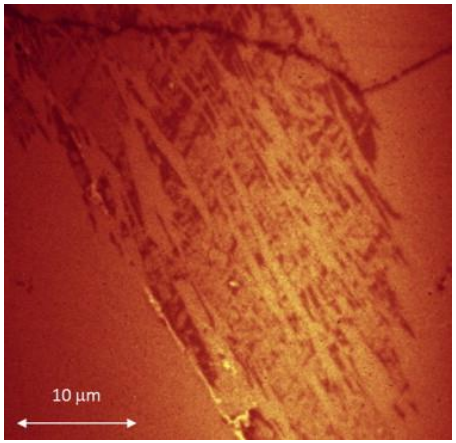
PEEM image of a polycrystalline Pt foil after annealing at high temperature showing work function contrast and grain boundary grooving

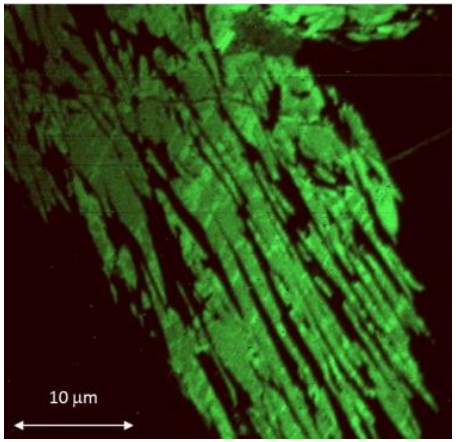
J. Pohl, *Z. Tech. Phys.* 15 (**1934**) 579–581

PEEM Applications (II)

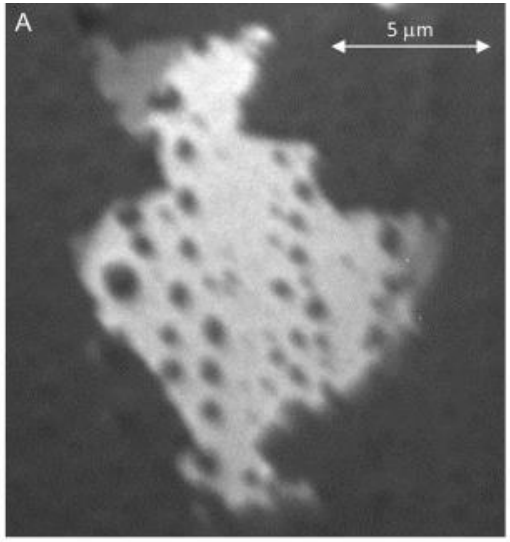
With synchrotron X-rays:

- **chemical contrast**
- **full XPS or XANES spectra from submicron regions**
- **magnetic contrast**
- **images in seconds**





XPEEM chemical images across the **Fe (red) and Ni (green)** L_3 edges showing an exsolution intergrowth between pentlandite, **$(Fe,Ni)_9S_8$**, and pyrrhotite, $Fe_{1-x}S$. [Schofield et al, Coordination Chemistry Reviews **2014**]

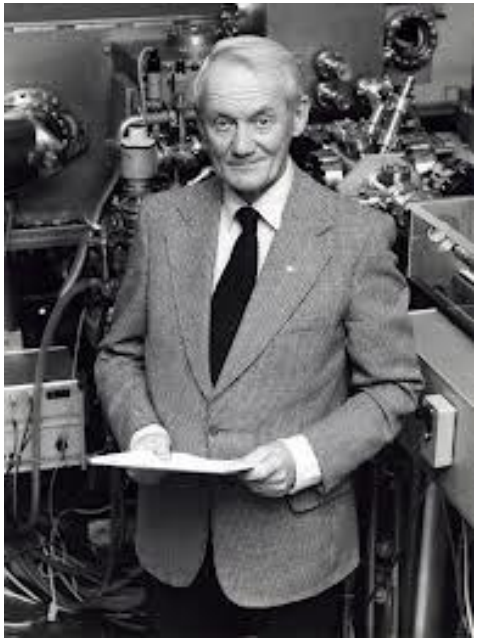


XPEEM **oxidation state** image at the Cr^{3+} edge for a chromite grain surrounded by a matrix of plagioclase and maskelynite.

NAPP: Near Ambient Pressure Photoemission

XPS or ESCA

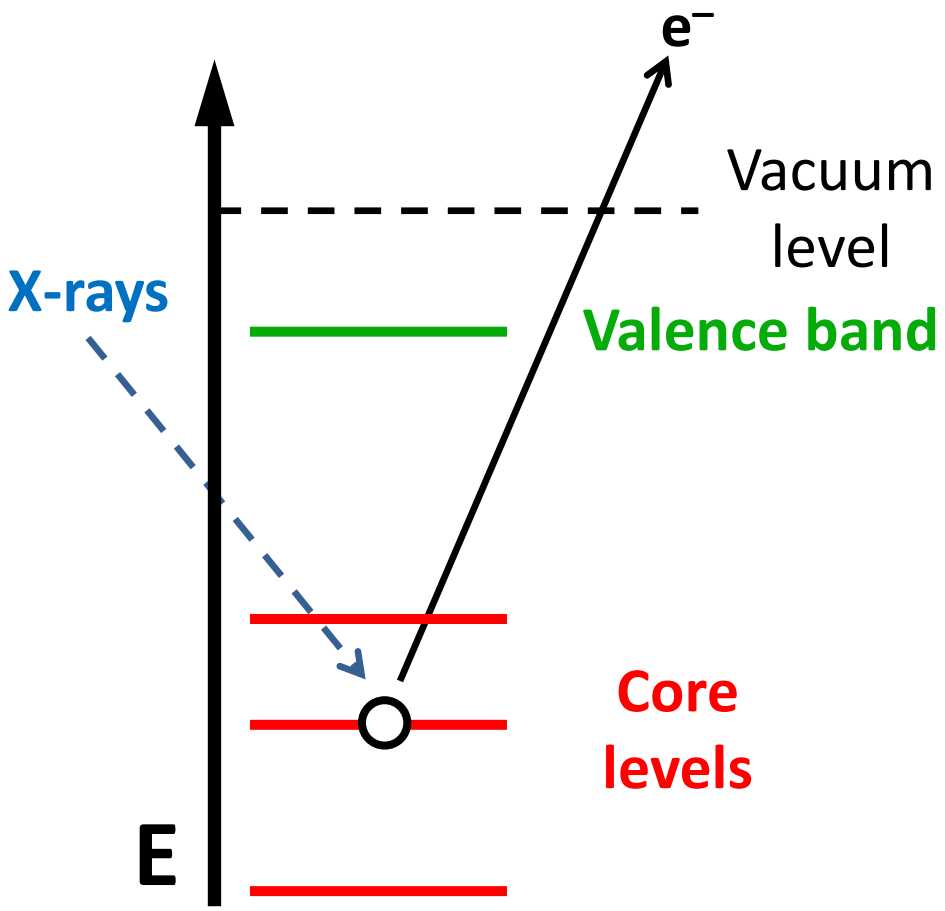
Kai M. Siegbahn



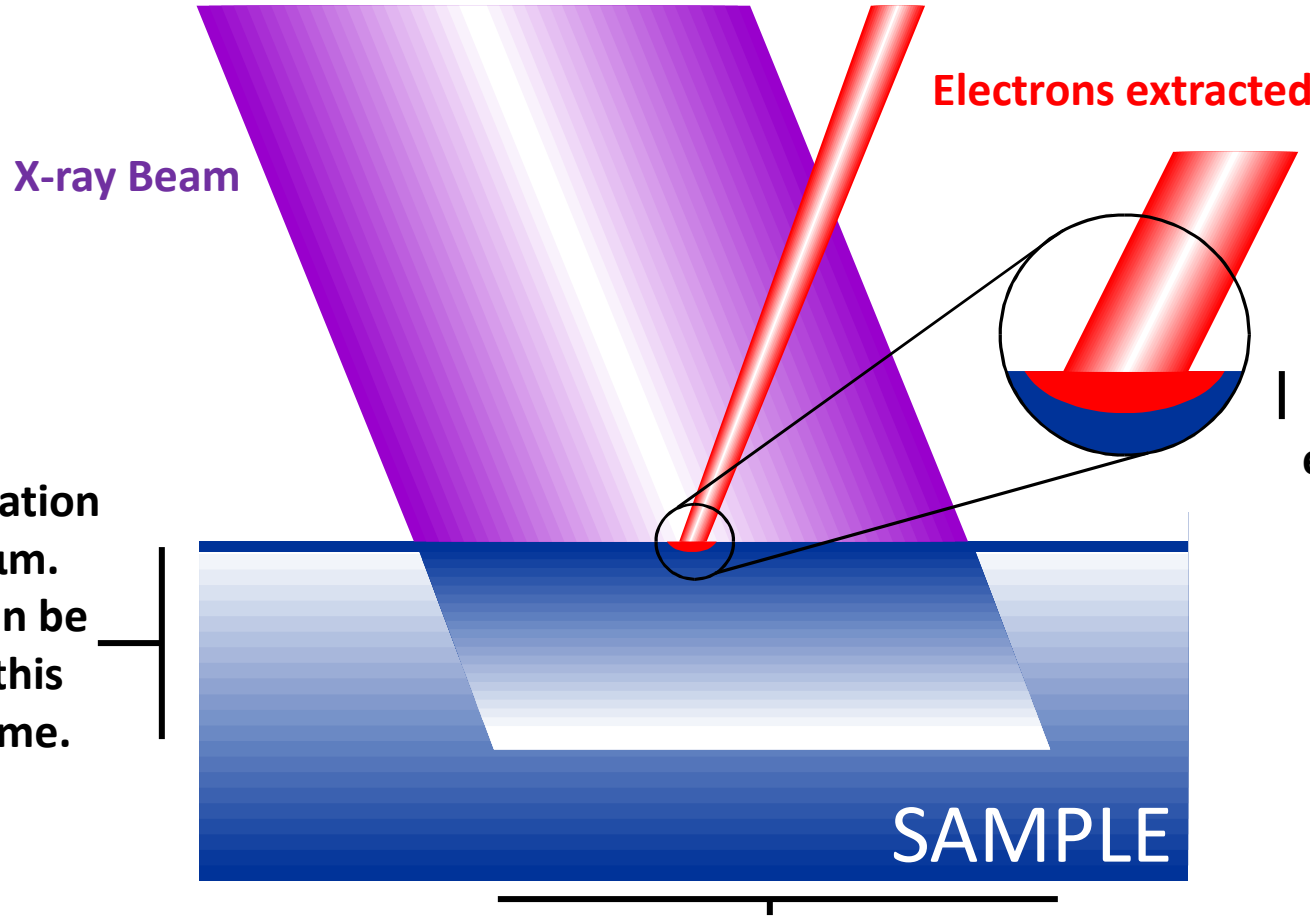
Nobel Prize in Physics 1981

XPS provides quantitative information about the elemental composition and chemical specificity (e.g., oxidation state) of the surface

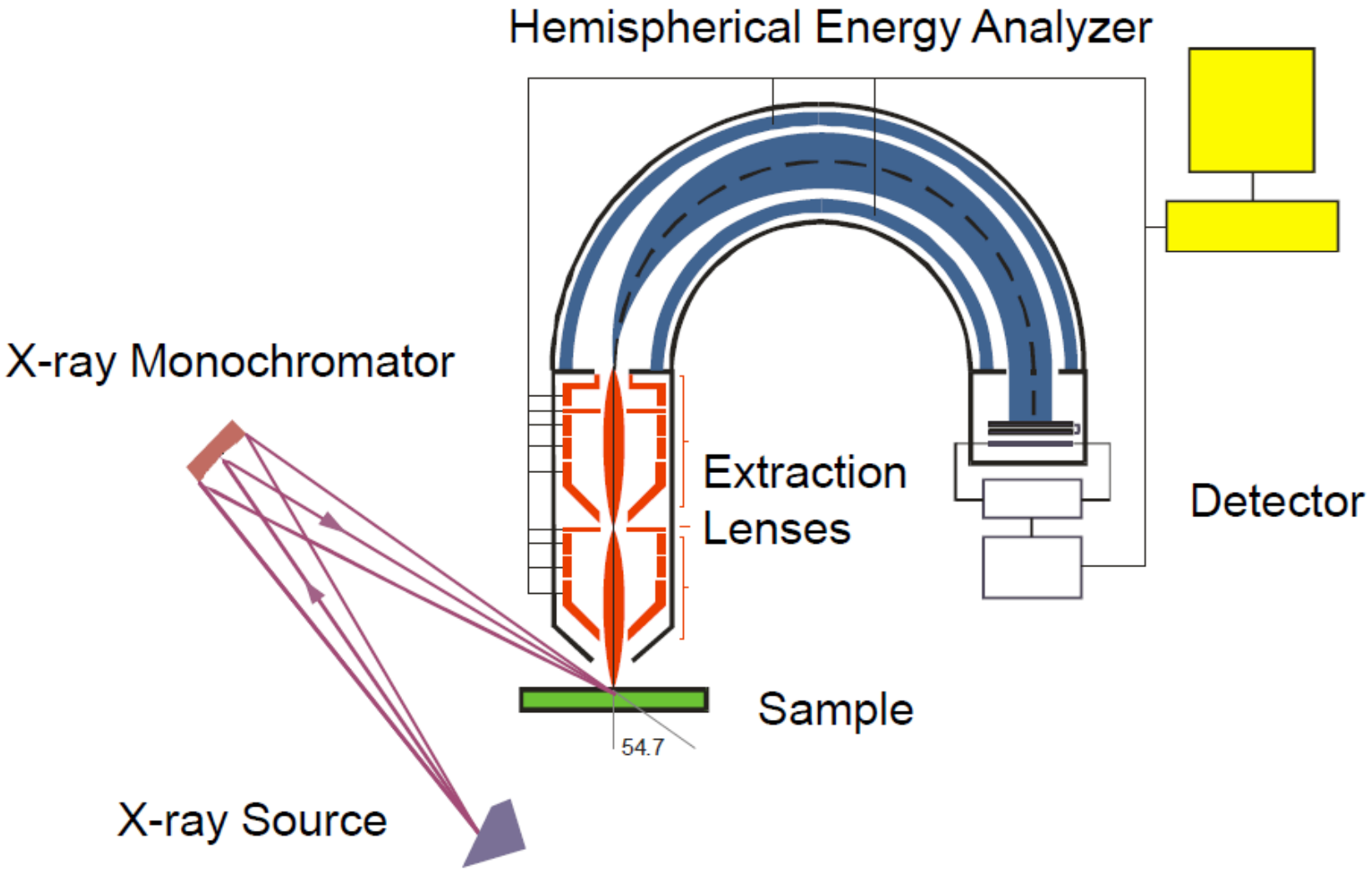
$$E_{binding} = E_{photon} - (E_{kinetic} + \varphi)$$



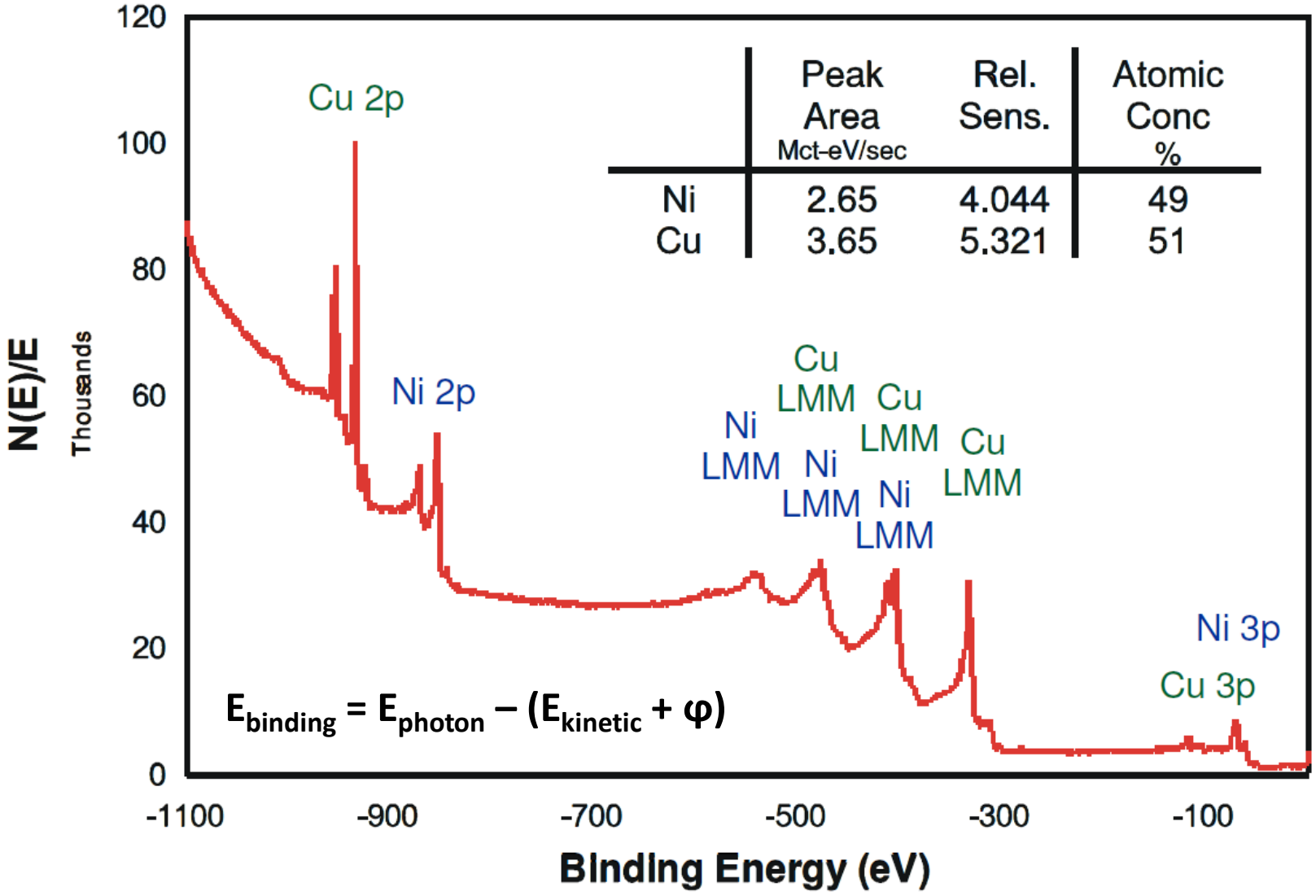
XPS, a traditional surface science technique, UHV!



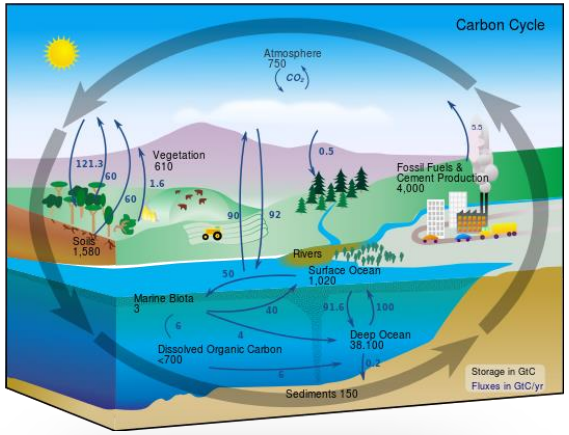
XPS… UHV


Hemispherical Energy Analyzer
X-ray Monochromator
Extraction
Lenses
Detector
Sample
54.7
X-ray Source

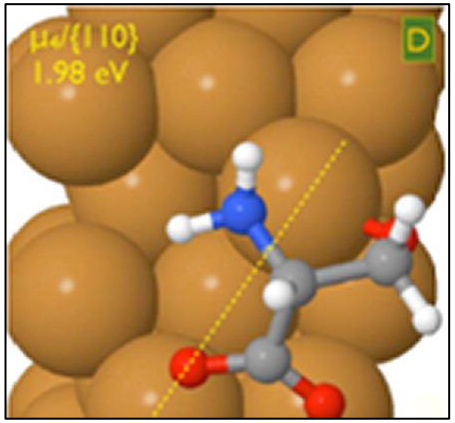
XPS spectrum



Why is it important to study surfaces in equilibrium with gases and liquids at ambient pressures ?



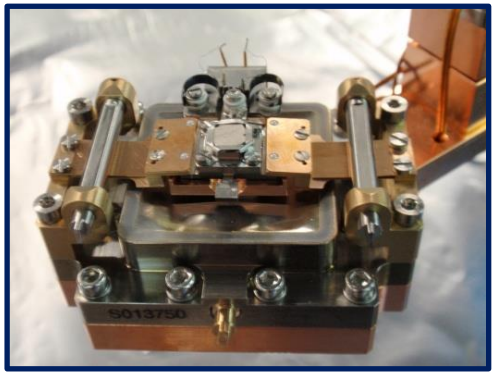
Environmental science
Corrosion
Catalysis
Biological surfaces



We need to develop spectroscopy and microscopy techniques that can operate in relevant environments !

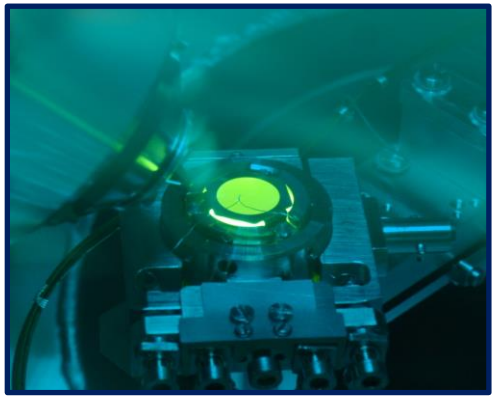
NAPP, main capabilities

- XPS measurements under gas mixtures: O_2, H_2, CO, inert gases, hydrocarbons and vapors (*e.g.* MeOH, EtOH, H_2O)
  - *up to ≈ 20 mbar, with and without flow control*
  - *Gas monitoring by RGA spectrometer*



- Peltier manipulator for sample cooling
  - *down to – 22.3°C (UHV) in 10 min*
  - *down to – 13°C (1 mbar H_2O_v) in 10 min*

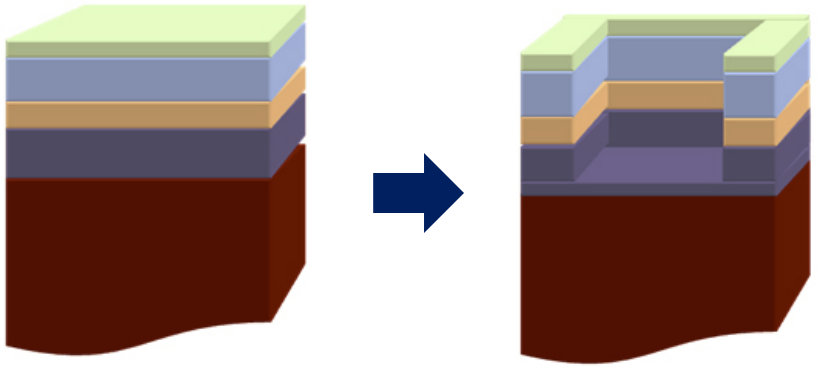
- Sample heating by resistive heater or IR laser
  - *With button resistive heater up to 900°C in UHV) and 700°C (20 mbar N_2)*
  - *With IR laser heater up to 1200°C in UHV) and 900°C (20 mbar N_2)*

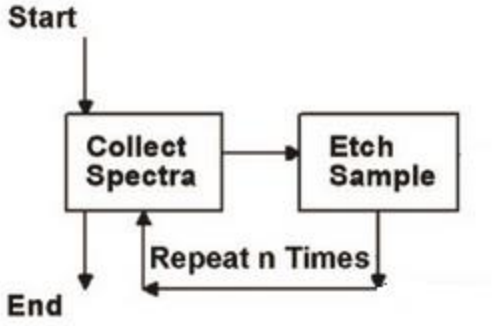


NAPP Applications (I)

XPS: Depth profiling

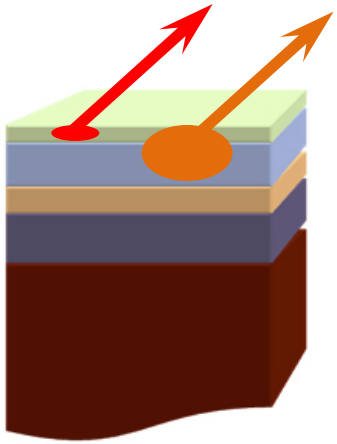
Destructive depth profile analysis





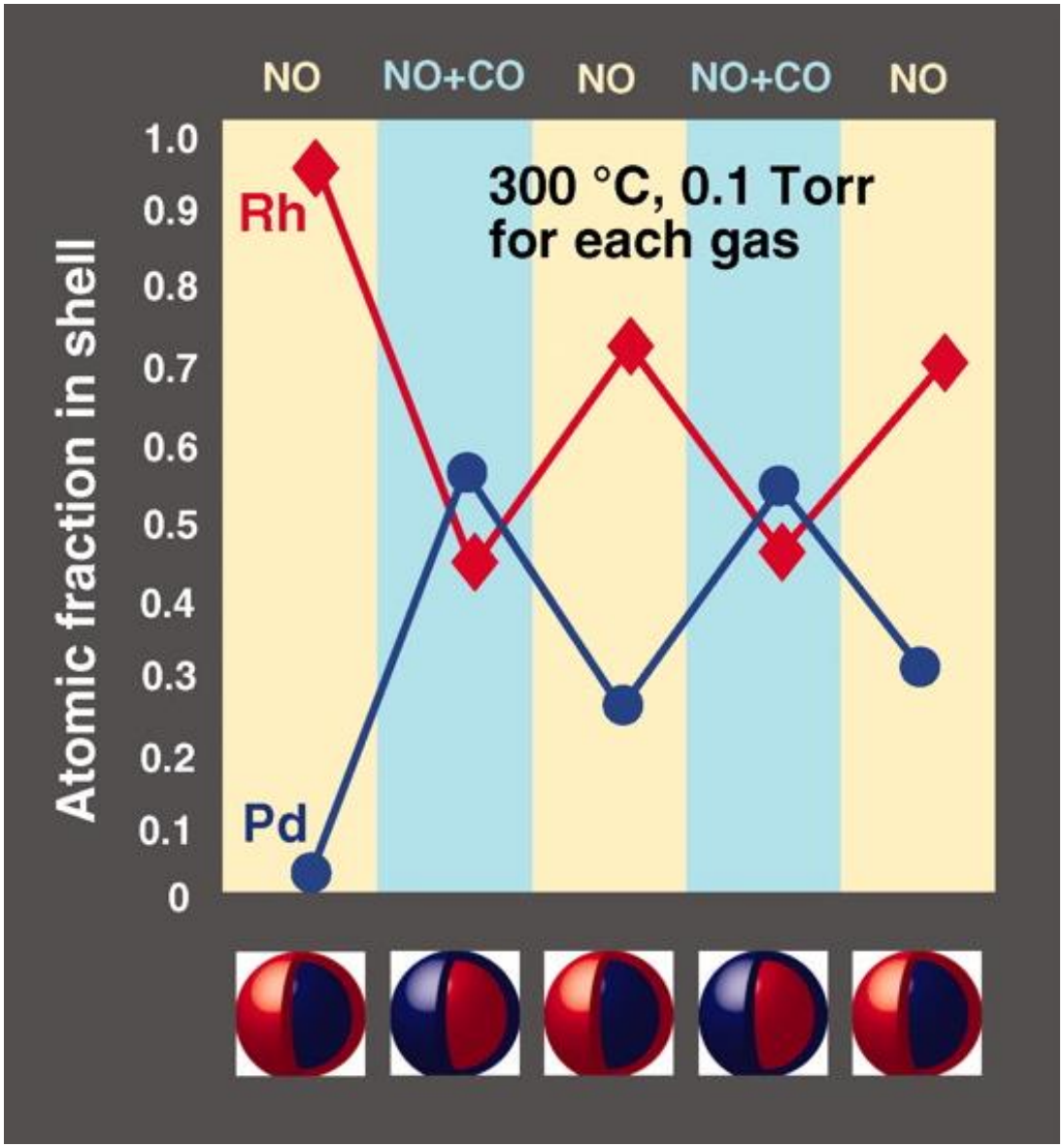
Non destructive depth profile analysis

….by varying photon energy and thus photoelectron kinetic energies



E_{ph}

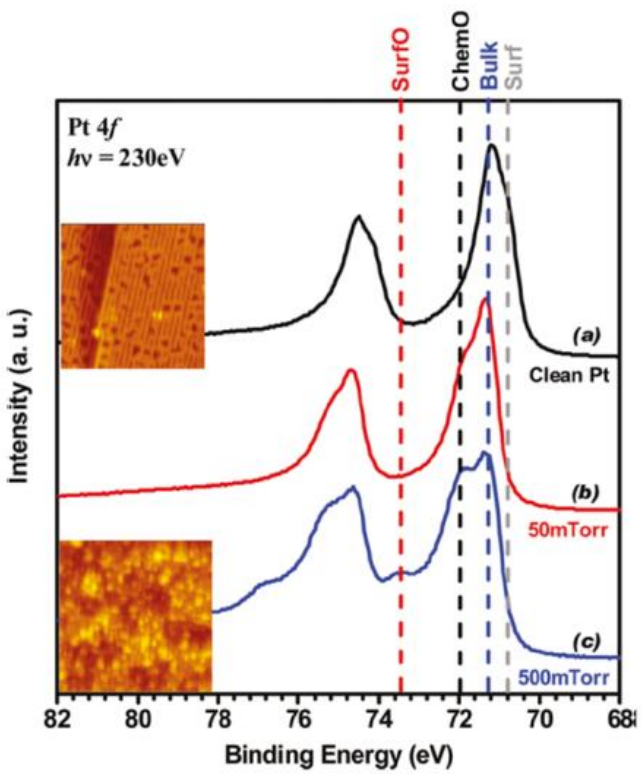
E_{kin}

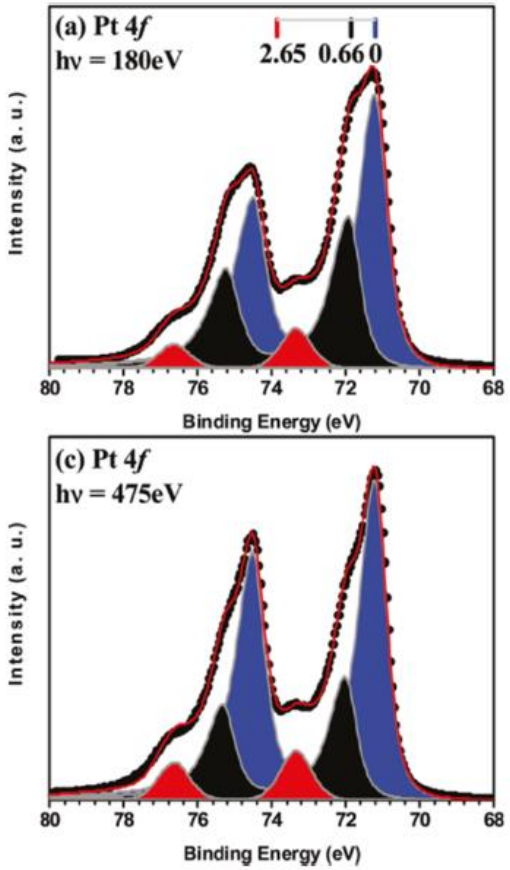


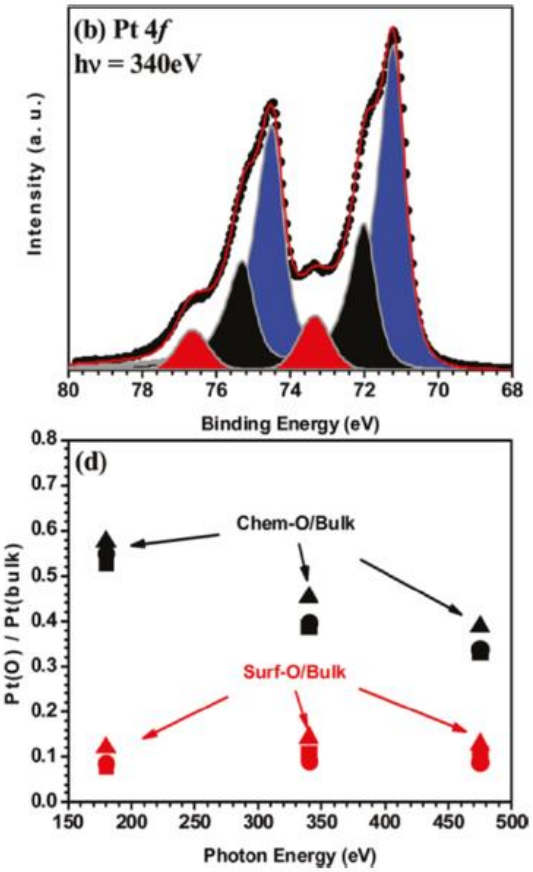
F. Tao et al, ***Science*** *322, p.932 (2008)*

NAPP Applications (II)

In Situ Oxidation Study of Pt







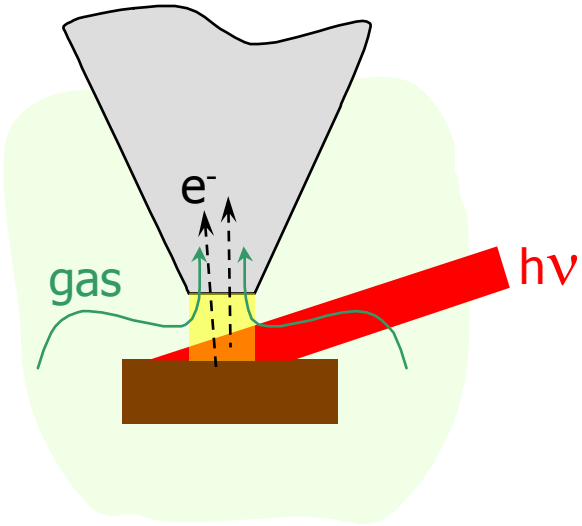
J. Am. Chem. Soc. 2011, 133, 20319–20325


Generalitat
de Catalunya
Departament
d'Economia
i Coneixement
Thanks to all ALBA staff
GOBIERNO
DE ESPAÑA
MINISTERIO
DE ECONOMIA
Y COMPETITIVIDAD
... And thank you for your attention!

Supplementary Material

Problem:

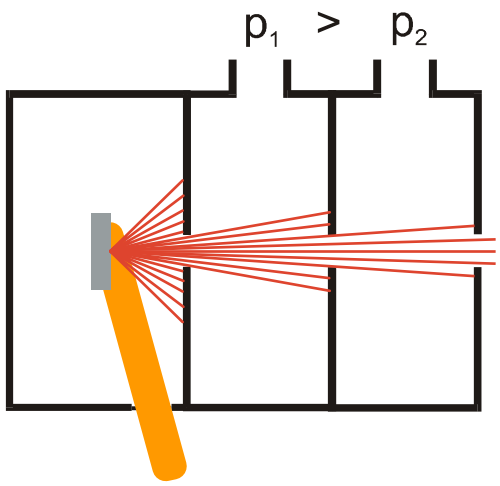
Scattering of electrons by gas or liquid phase molecules



Solution:

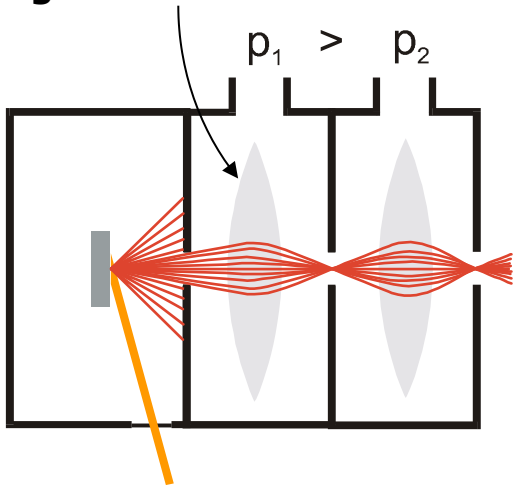
Capture the electrons before they collide with gas molecules by means of differential pumping

previous designs:



conventional X-ray source

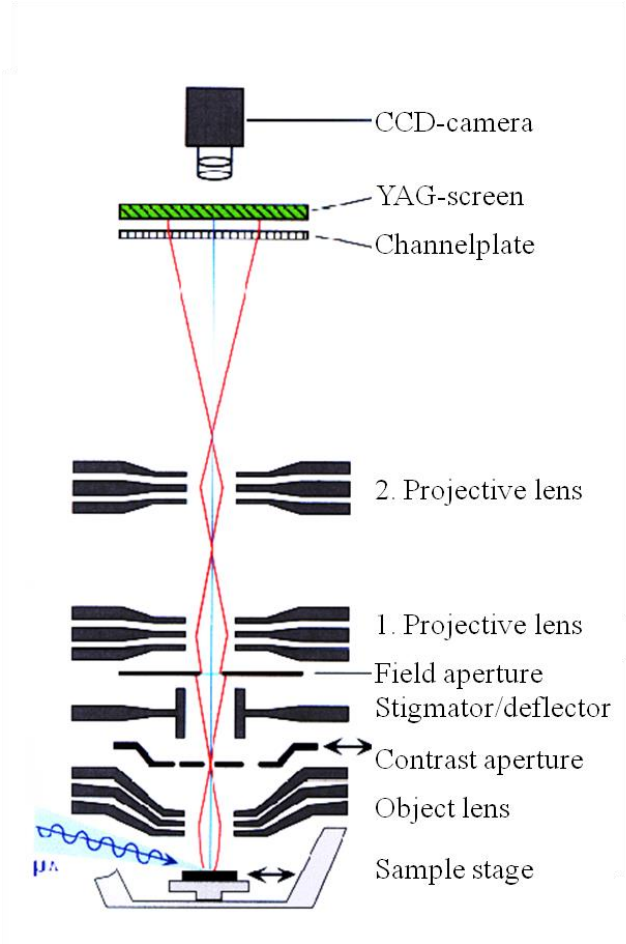
our design: **electrostatic focusing !**

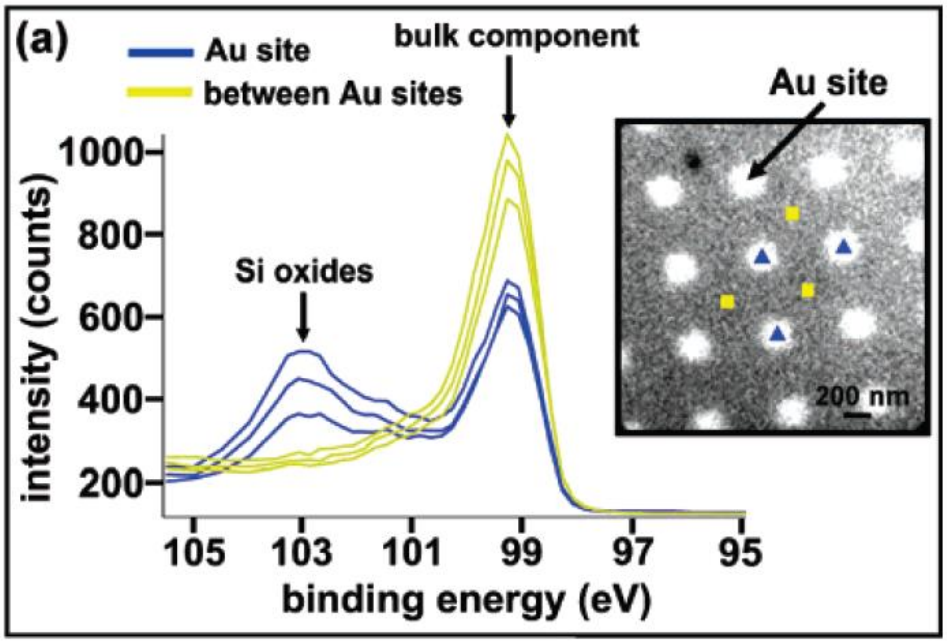


X-rays from synchrotron

BL24 - CIRCE

PEEM: PhotoEmission Electron Microscopy



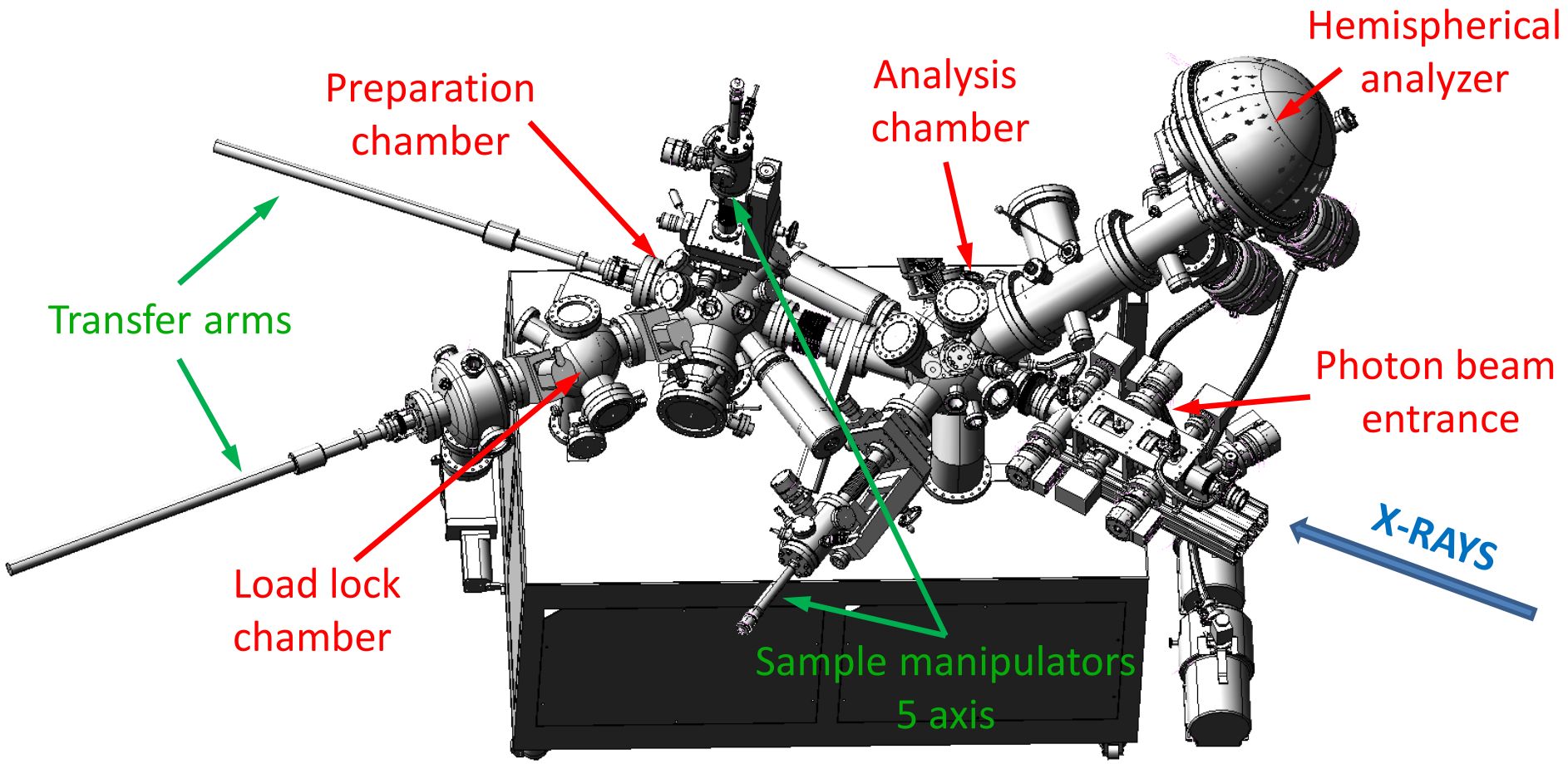


J. T. Robinson et al. Nanoletters vol 7 (2007)

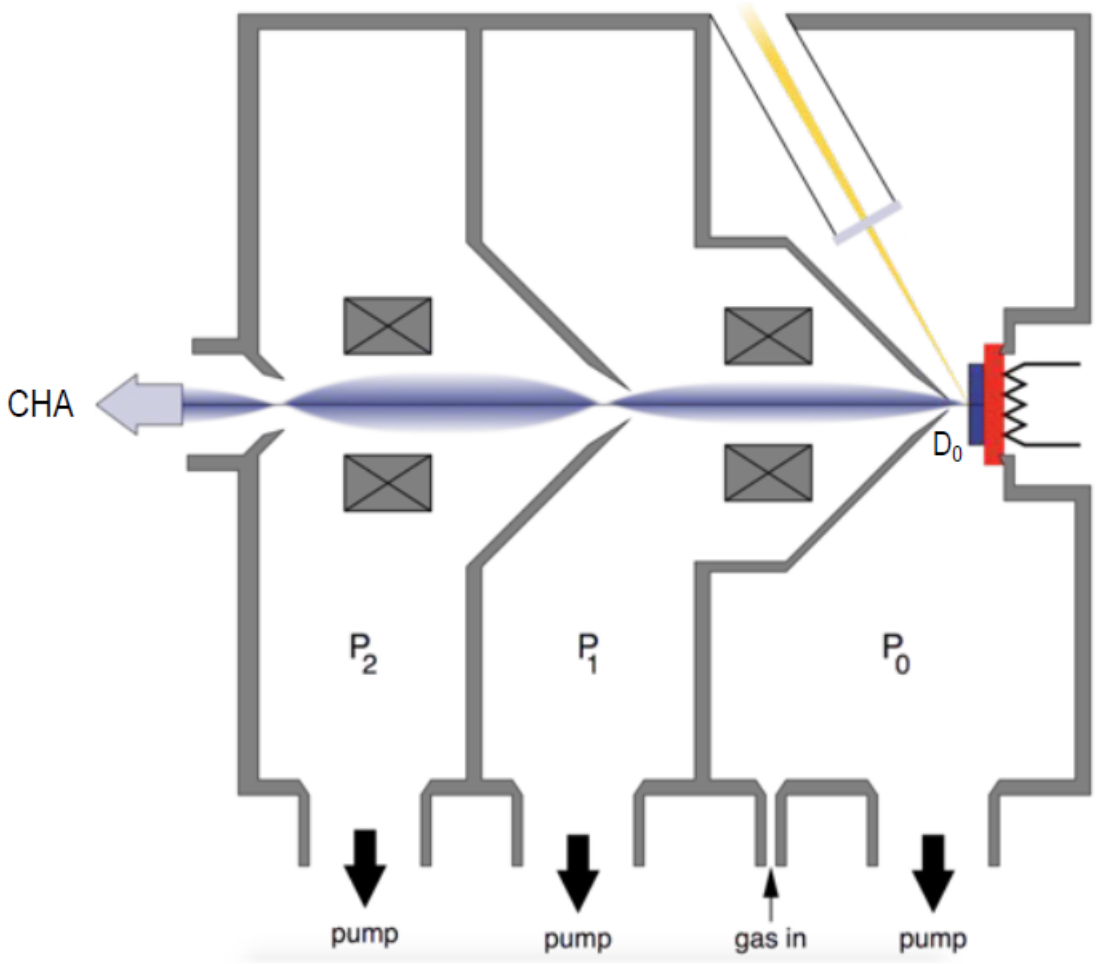
Silicon is oxidized only at the Au sites

NAPP

Near Ambient Pressure Photoemission



Our analyzer: Phoibos 150 NAP with a multichanneltron detector (MCD9)


CHA
D_0
P_2
P_1
P_0
pump
pump
gas in
pump

Archaeometallurgical studies