INTRODUCTORY COURSE:

Synchrotron EXAFS & XANES for Chemical Speciation on Environmental Systems

ALBA 6-9th October 2014

DESIGNING AN EXPERIMENT FOR XAS

Part I

Marta Avila

CLÆSS - Core Level Absorption and emission spectroscopies

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Design of a good experiment

XAS is a fairly easy experiment

However, requires PLANNING

- Good SAMPLE PREPARATION
- Choice of the DETECTION MODE
- Choice of SAMPLE CONDITIONS
- Adequate STATISTICS

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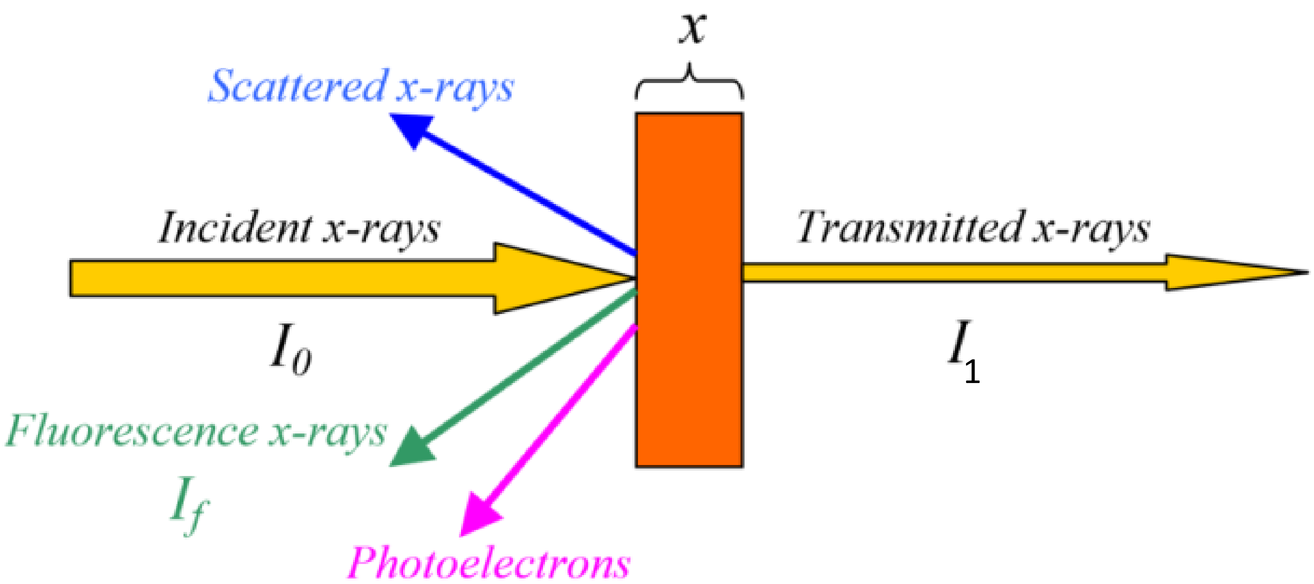
Outline

- Part I
  - What do we need to run a XAS experiment?
  - Detection modes: Transmission and Fluorescence
  - Sampling regions
  - Scan repetitions
  - Beam size
  - Radiation damage
  - Take away message

- Part II
  - Sample setups
  - Sample preparation techniques
  - Bibliography

What do we need to do a XAS experiment?

XAS measures the energy dependence of the X-ray absorption coefficient μ(E)



- High intensity → Synchrotron source
- Tunable energy → Monochromator
- Variable beam size → Slits and mirrors
- Incident, transmitted, and/or fluorescence intensity → Detectors

What do we need to do a XAFS experiment?

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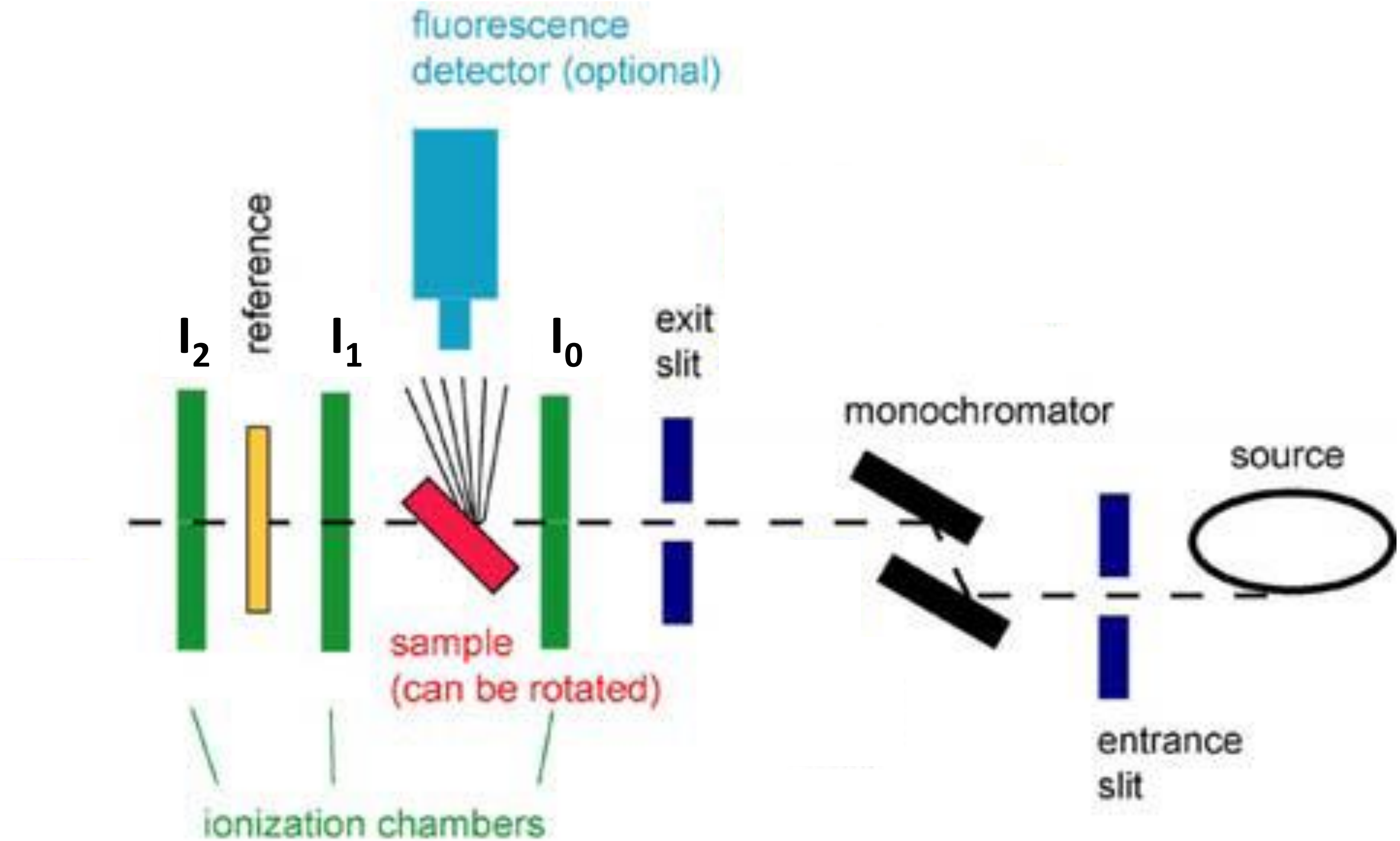
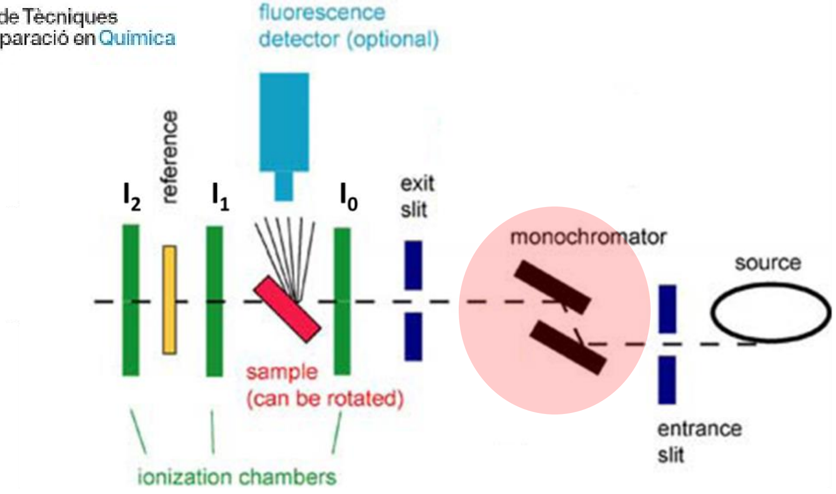
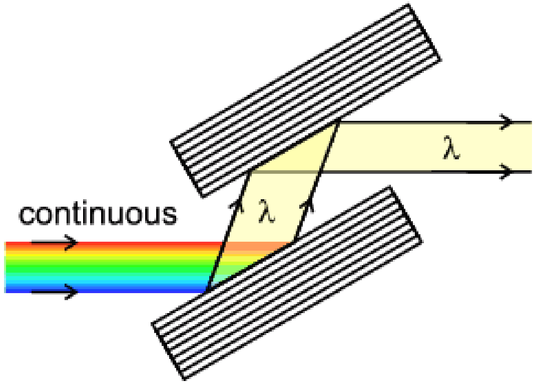
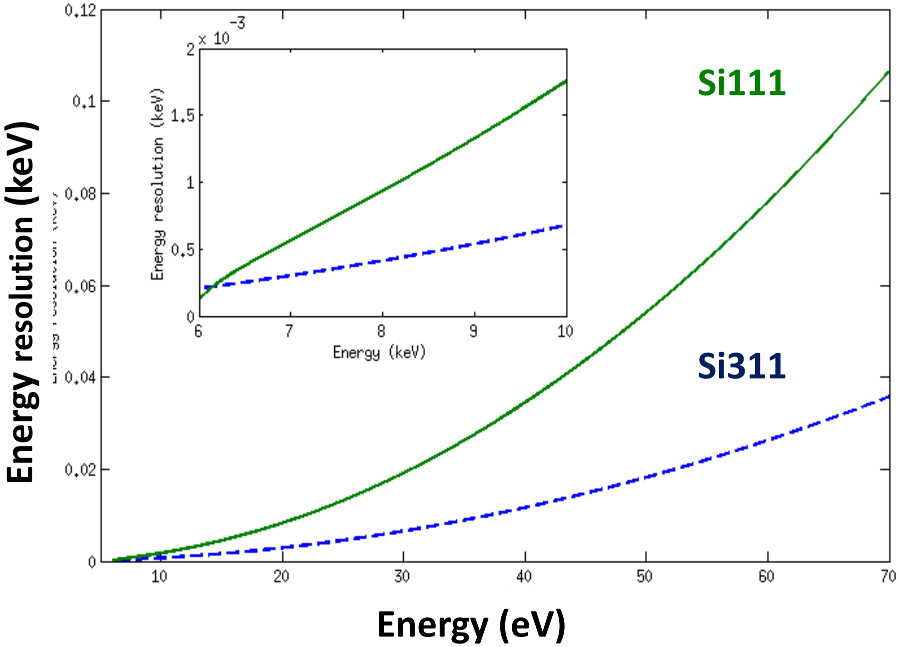


The monochromator: the energy resolution





a monochromator selects a single energy



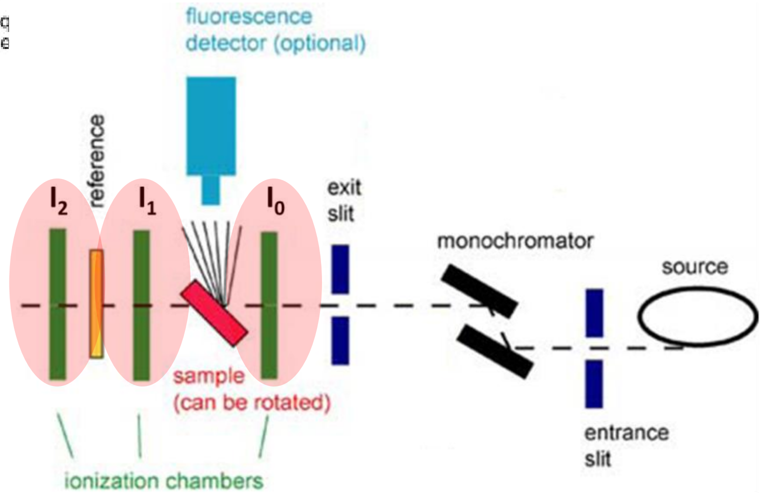
Different monochromator cuts give access to different energy ranges with different energy resolutions

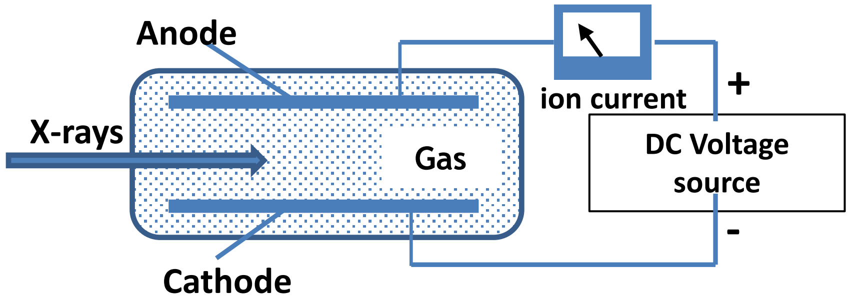
Si(111)

Si(311)

CLÆSS beamline

Ion chamber: measure x-ray intensity



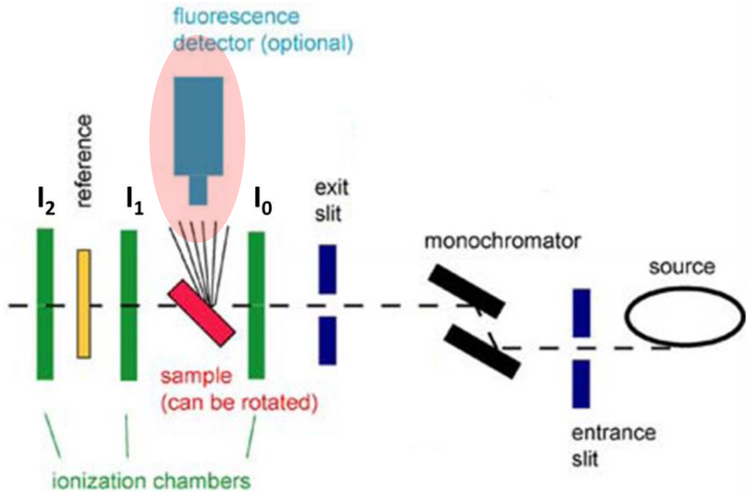


Inert gas mixture is chosen depending on the photon beam incoming energy

I_0 : incident x-ray intensity (10-15%)
I_1 : transmitted x-ray intensity after the sample (75-80%)
I_2 : transmitted x-ray intensity after the reference (100%)

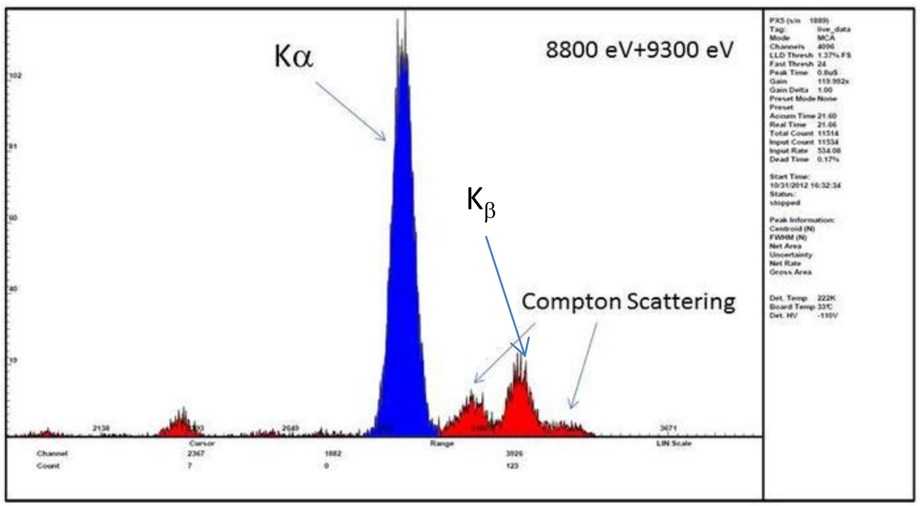
Values for the mixture of gases to absorb the desire amount of x-rays can be calculated (for example by Hephaestus)

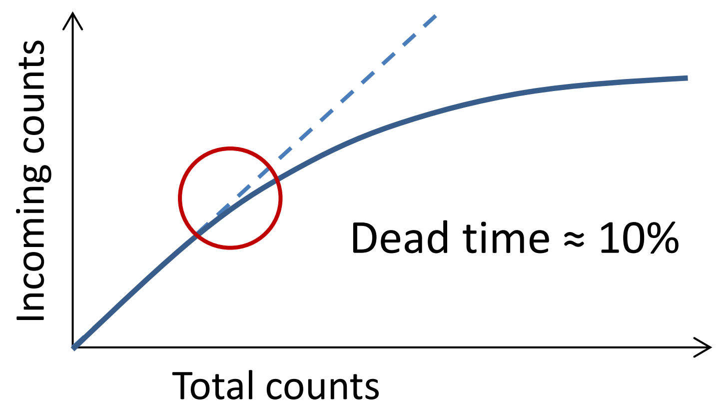
Fluorescence detectors



Fluorescence detector is set at 90 degrees respect to the incoming beam to minimize the scattering peak.

The electronic energy discrimination takes a finite amount of time, which limits the total amount of signal that can be processed.





X-rays emitted spectrum contains lines characteristic of the elements present in the sample, as well as scattered x-rays.

We need to select a region if interest (ROI) around the right emission line

Sampling regions

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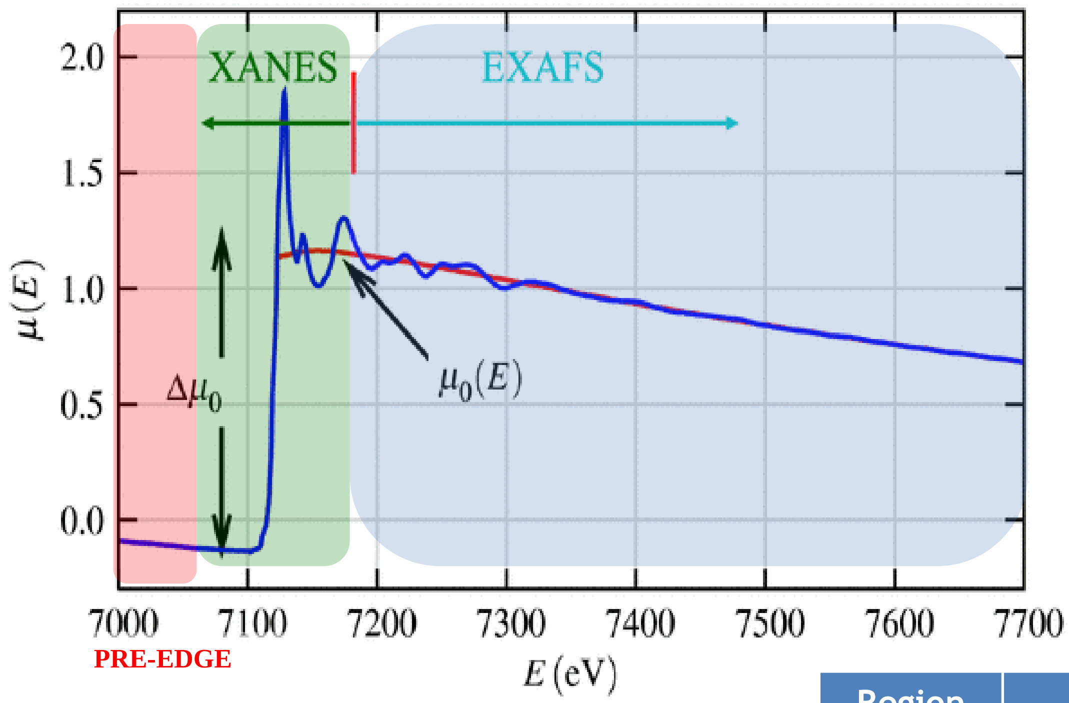


The measurement grid change as a function of the XAS spectral region:

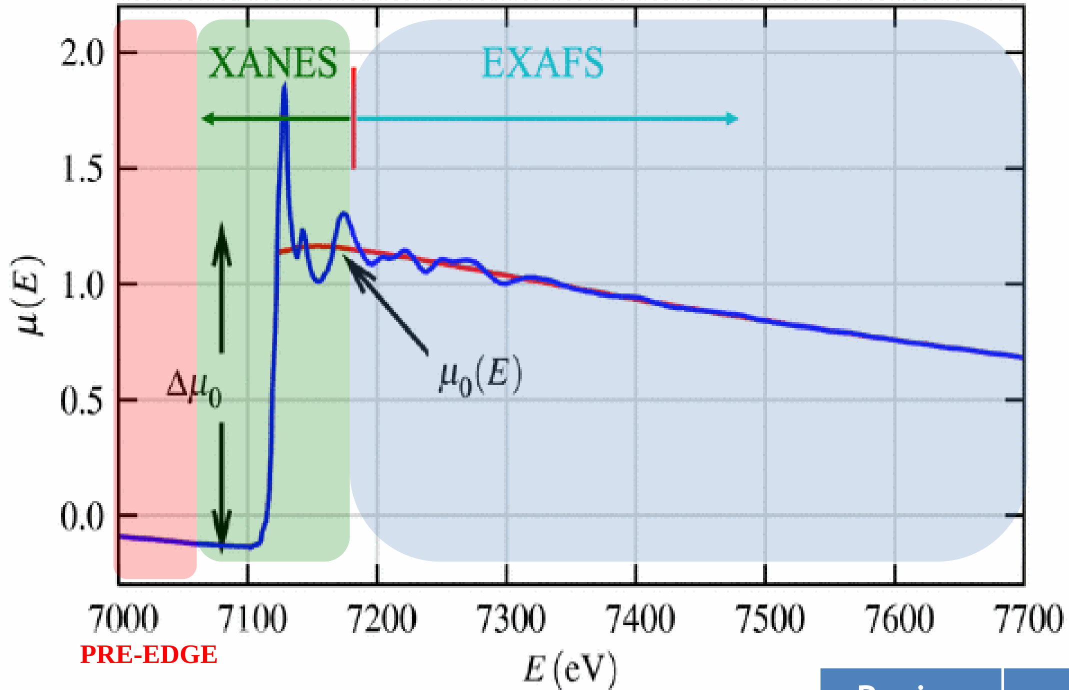
Pre-edge: large grid – only for back ground subtraction
XANES: fine grid – depends from the incoming energy resolution and the sharpness of the electronic transition (core-hole broadening)
EXAFS: intermediate grid – the oscillation are broad, it's common to step in wavenumber rather than in energy.

The integration time when possible is increased during the scan as the signal becomes smaller.

Region	Starting energy (eV)	Ending energy (eV)	Step size (eV)
Pre-edge	E_0 - 200	E_0 - 20	5.0 - 10
XANES	E_0 - 20	E_0 + 30	0.2 - 0.5
EXAFS	E_0 + 30	E_0 + ~1000	~1 eV (~0.05 A $^{-1}$)

Sampling regions

XAS measures the energy dependence of the X-ray absorption coefficient μ(E)



Two modes to measure the data:

Transmission	Fluorescence
High signal to noise ratio	Low signal to noise ratio

Typical count times are 0.3 to 15 sec per point depending on the energy region, the measurement mode, and the sample. A spectrum can take minutes or several hours. Very fast measurements can be made at specialized beamlines.

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When to choose transmission or fluorescence?

The choice depends only on the SAMPLE → CHARACTERIZE YOUR SAMPLE!!!

Transmission

- Concentrated samples (element of interest is above ~10 wt. %)
- Thin enough sample

ADVANTAGE

- high signal to noise ratio
- fast scan

DRAWBACK

- More stringent sample preparation

Fluorescence

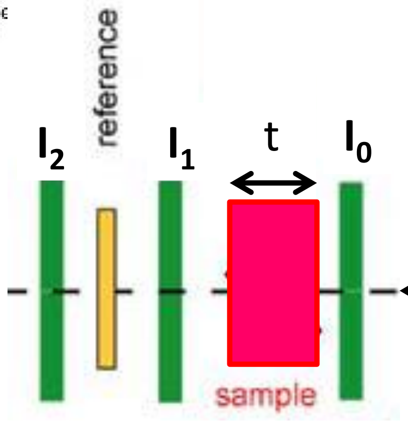
- Dilute samples - element of interest is below ~ 10 wt. %.
- Concentrated samples that cannot be made thin enough for transmission

DRAWBACKS

- Possible self-absorption effects
- Low signal to noise ratio
- Dead time effects
- Maintenance, setting up, operation…

Do transmission (when possible) as it usually yields superior data quality and is easier

XAFS measurements: Transmission



Lambert-Beer: $I=I_0\, e^{-\mu(E)t}$

$\mu(E)t= -\ln(I/I_0)$

$\mu(E)$ = x-ray absorption coefficient at energy E,
t=thickness of the sample

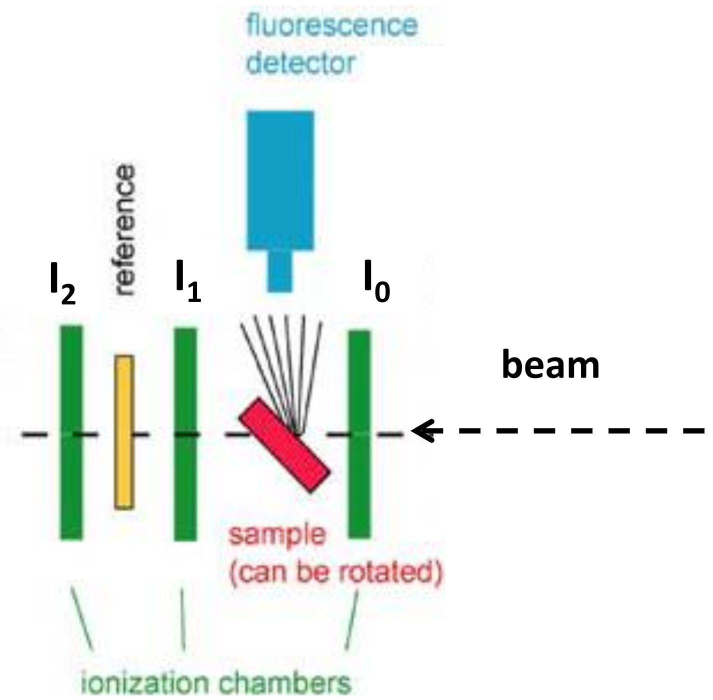
1) t should be chosen so that the jump $(\mu^+ - \mu^-)$ t = $\Delta\mu\,(E)\,t \approx 1$ and/or the total absorption $\mu^+(E)t<2.5$

2) The sample must be uniform, homogeneous and free of pinholes

3) The particles forming the sample should be smaller compared to the absorption length $(1/\mu)$ and smaller than the beam size

Optimal sample thickness can be calculated using several programs, i.e. XAFSmass (K. Klementiev) → Tomorrow!

XAFS measurements: Fluorescence



Measure the fluorescence X-rays I_f that are emitted following the X-ray absorption event.

Fluorescence: $\mu \propto (I_F / I_0)$

(total absorbance << 1 $e^{-\mu x} \rightarrow 1-\mu x$)

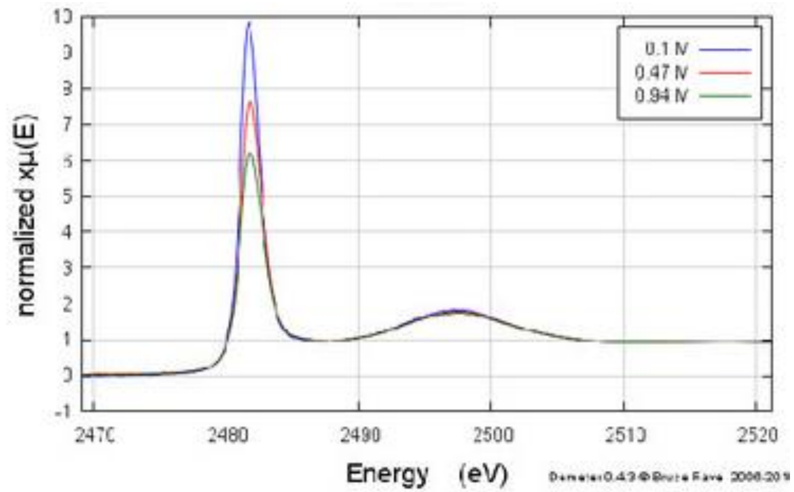
Like for transmission: small particle size, homogeneous distribution

Concentrated or thick samples require numeral corrections due to self-absorption

Fluorescence: Self-absorption

XAS oscillation measured on a thick or concentrated sample in fluorescence mode can be damped due to self-absorption.

0.1M (blue), 0.47 M (red) and 0.94 M (green)



Consequences of self-absorption

- Incorrect XANES peak intensity
- Dumping EXAFS oscillations

SELF-ABSORPTION CORRECTIONS:

By acquiring spectra at different angle is possible to collect the information necessary to empirically correct the self-absorption.

Applying mathematical corrections during data treatment, however these corrections are tricky and requires advanced knowledge

How many scans per sample?

At least 3! If one of them is presenting artifacts, the reproducibility is checked by the other 2.

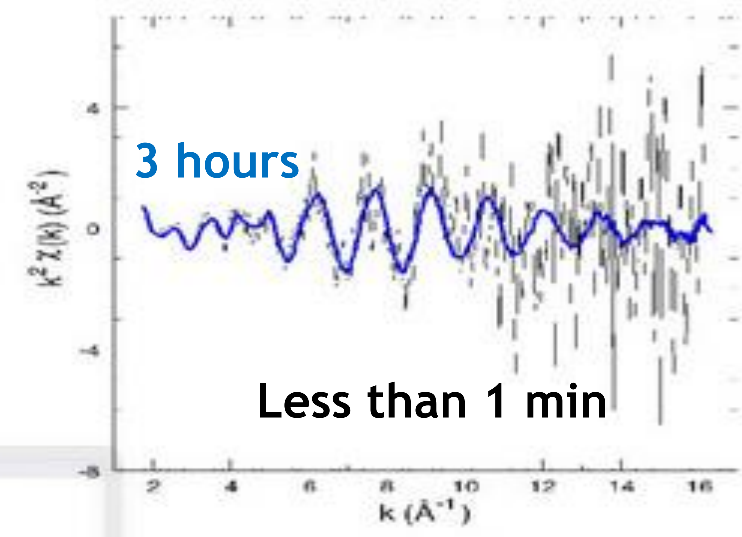
Time per scan at CLÆSS (min)		
Detection mode	**XANES region**	**EXAFS region**
Transmission	5-10	10-15
Fluorescence	7-15	45-60

The data signal you intend to analyze should be large compared to the level of noise

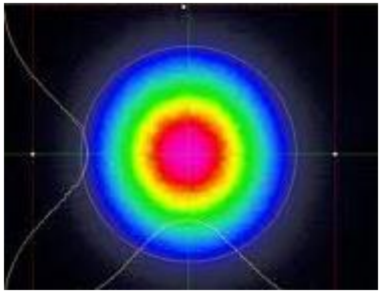
It is necessary a compromise between acquisition time, and number of repeats, to reach the necessary statistic; the error is decreasing following $1/\sqrt{n}$; *n*= number of repetition

Remember then the number parameter in an EXAFS fit should be less then the number of independent point:

$$N_{ind} \sim (2\Delta k\Delta R)/\pi$$



Beam size



The beam size can be adjusted depending on:

Sample size

Sample homogeneity

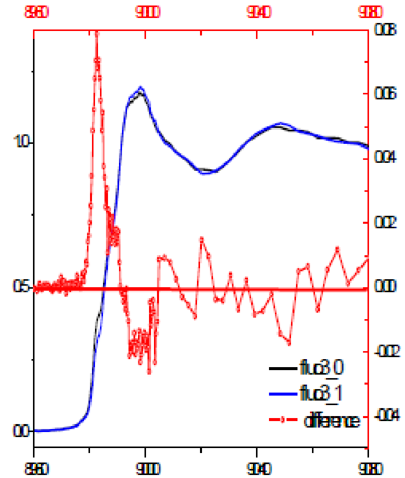
Sample concentration

Radiation damage

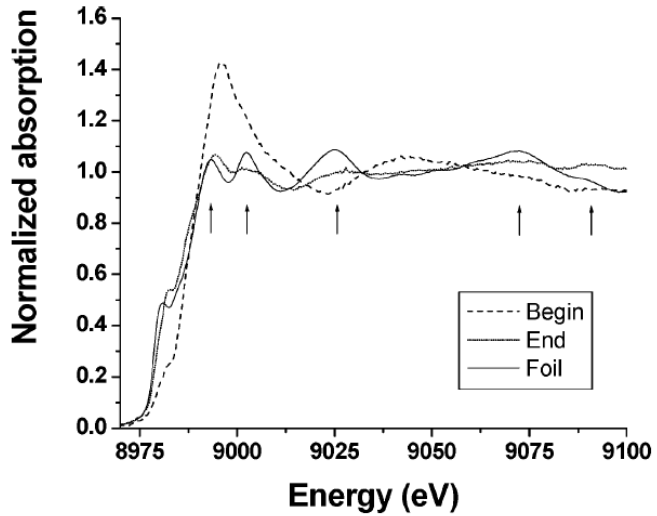
The high photon flux of synchrotron can damage your samples!

Photoreduction, precipitation (e.g. protein solutions), create bubbles due to photolysis in solution samples, etc…

Biological samples



Photoreduction



from J. G. Mesu et al, J. Phys. Chem. B 109 (2005) 4042

unfocus the beam

chopper

Cooling down

moving the sample respect to the beam

Two more advices…

Be careful to the chemical composition of the sample environment: it could contain the same elements that you are investigating

In few cases it can be useful to measure a blank sample (matrix without the element of interest) under the same conditions as your real sample

Take away message:

Choose the appropriated detection method (transmission or fluorescence) depending solely on the sample

If possible use transmission (is simpler and provides better results)

Try to do your samples as homogeneous as possible

For transmission prepare the sample to have a jump around 1
(or however with $\mu^{+} < 2.5$)

Acquire at least 3 repeats

THANKS FOR YOUR ATTENTION!

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