Quantitative Analysis of Mixtures using Synchrotron XANES Spectroscopy

Canadian Light Source
Centre canadien de rayonnement synchrotron

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What is a Synchrotron?

A **synchrotron** is a source of brilliant light that can be used to view the microstructure of materials.

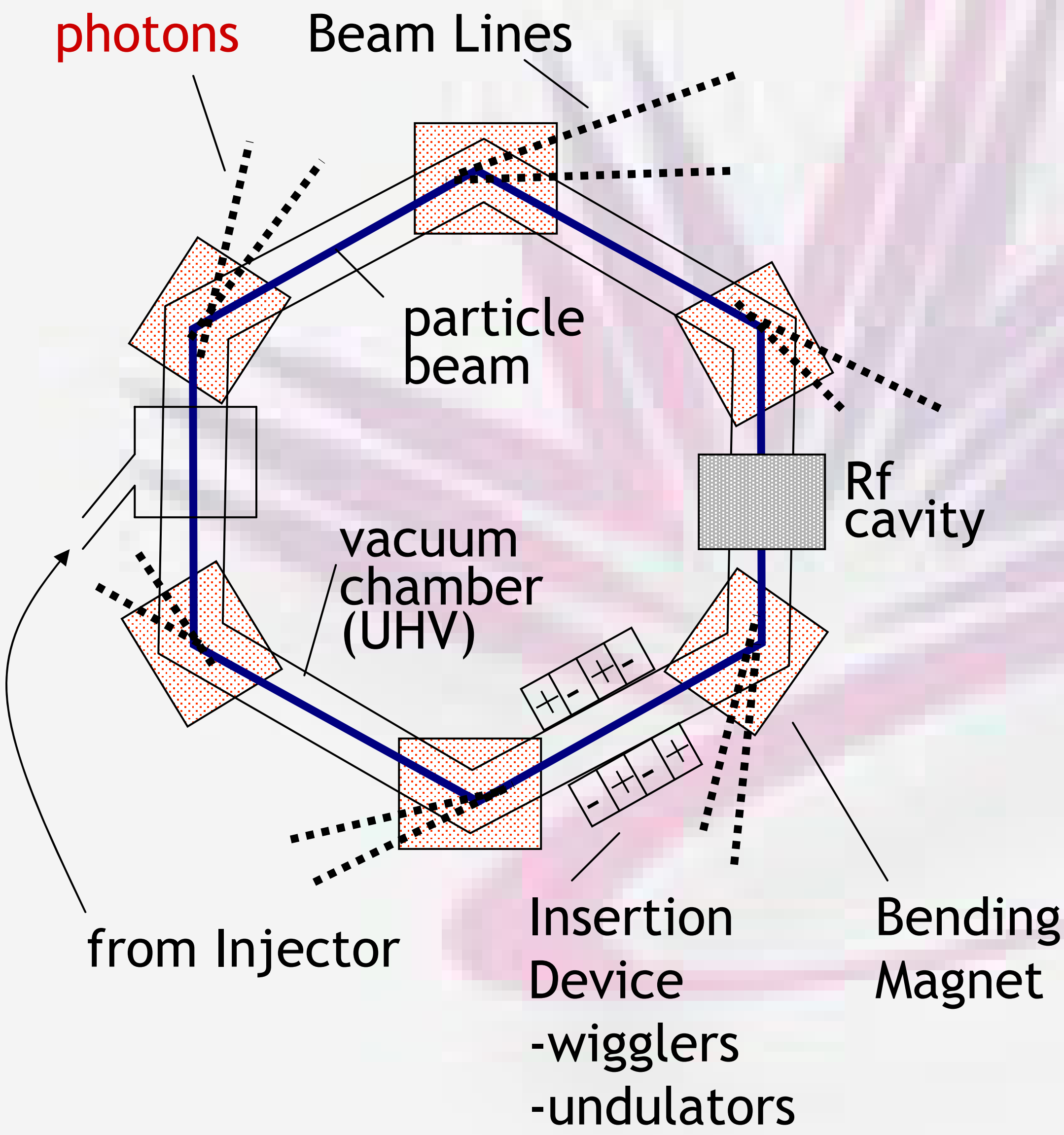
Linac ⟶ Booster ring ⟶ Electron Storage Ring

- High voltage DC (MeV) is applied to a tungsten cathode releasing electrons into an ultra high vacuum tube;
- The electrons are fed into a linac where they are accelerated by radiofrequency;
- The linac feeds the electrons into a 103 m booster ring where they receive a boost in energy (250 MeV to 2.5 GeV);
- An injection system transfers the electrons to the 171 m main ring to reach the target circulating current (200 mA).

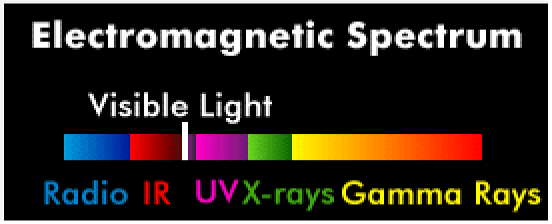
What does it do?

- emits highly collimated electromagnetic radiation from subatomic charges orbiting at ultrarelativistic energies in a storage ring with diameters of tens to several hundreds of meters.

Synchrotron schematic



- high photon flux
- broad spectral range
- high polarization
- natural collimation
- small spot size
- stability
- ring structure allows multiple users



Canadian Light Source Mission:

http://www.lightsource.ca

To advance scientific and industrial capabilities ….

Phase 1 beamlines

- XAS (3.5 – 40 keV)
- STXM (205-2000 eV)
- IR (mid, far): (450-6000/10-4000 cm^{-1})
- Soft x-rays (SGM/PGM): (5.5-250/200-1900 eV)
- PX1 (protein crystallography): (6.5-18.5 keV)

- only synchrotron in Canada
- 200 million CDN$ investment
- 2.5 to 2.9 GeV synchrotron operating at 200 mA
- 170.88 m circumference

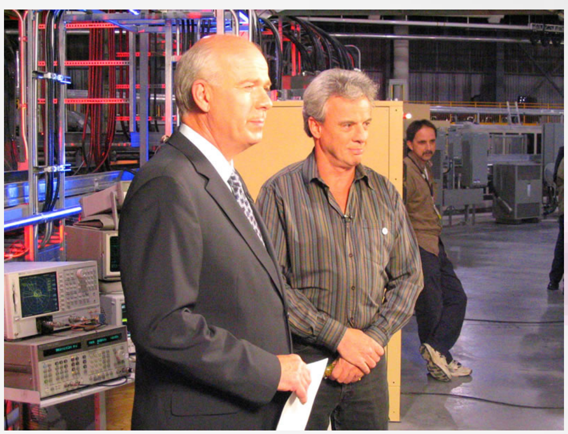
main experimental hall

CLS: 2004/2005

- Current Machine parameters
  - Stored electron current: 200 mA
  - Lifetime (1/e) @ 100 mA: **10.5** hours
  - All other design parameters met
- Two beamlines currently being commissioned
- Phase 1 operational by spring 2006

The Official Opening Ceremony – symphony at the synchrotron Oct. 22, 2004

The Prime Minister of Canada May 31, 2004



The National News from on top of the Booster ring Oct. 21, 2004

The Queen of England visits May 19, 2005

Where is Saskatoon, Saskatchewan?

Saskatchewan is characterized by prairie and rolling grassland in the south and lakes and forest in the north.

Saskatoon

- Founded 1883
- Population - 226 000
- Altitude – 482 m, 52º N
- Climate

  Precip. rain: 10 in/year

  snow: 4 in/year

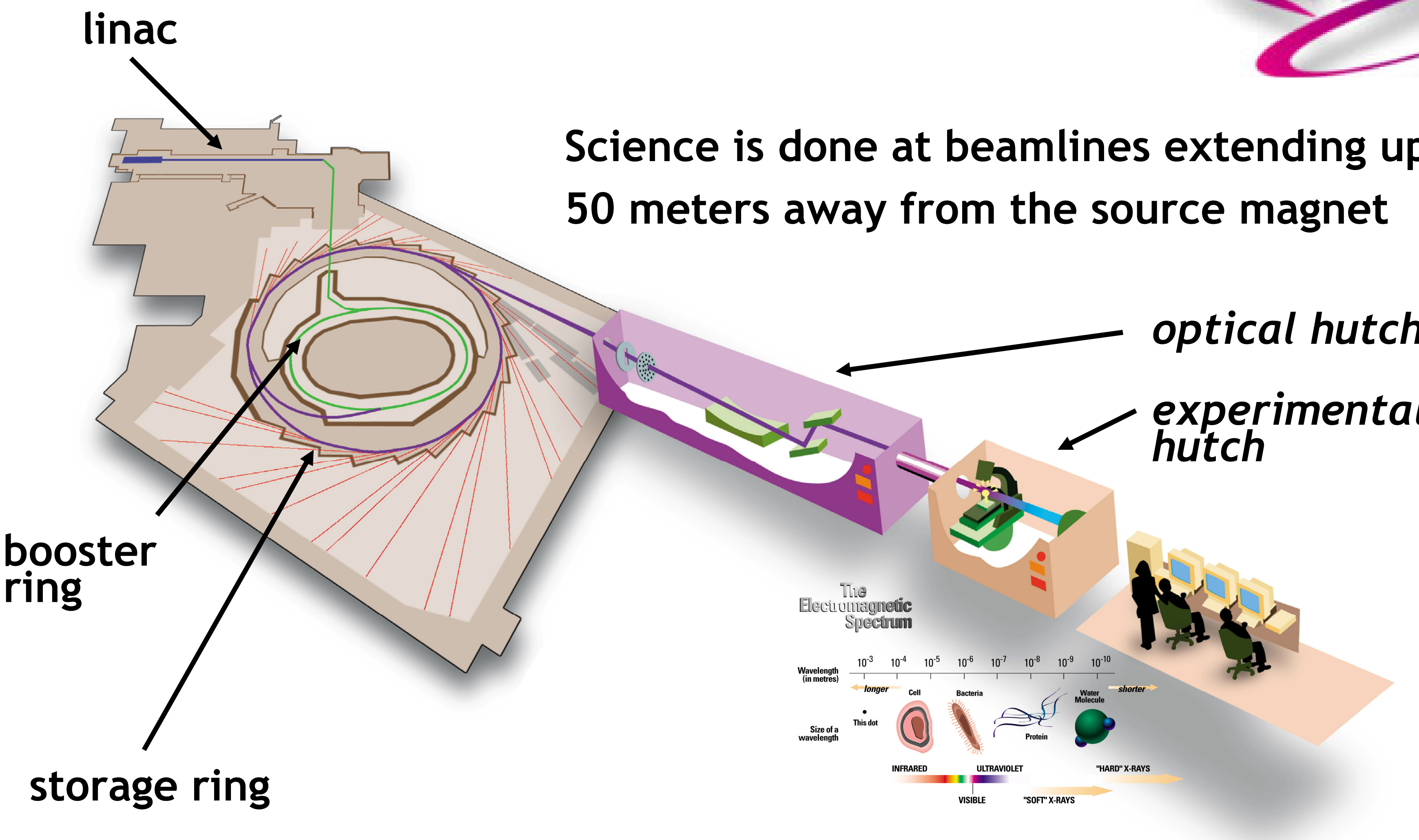
  Summer: 75 F

  Winter: -2 F

- Economy

  agriculture, mining

Beamlines



Science is done at beamlines extending up to 50 meters away from the source magnet

Synchrotrons and Environmental Science

What x-ray techniques are used for environmental science?

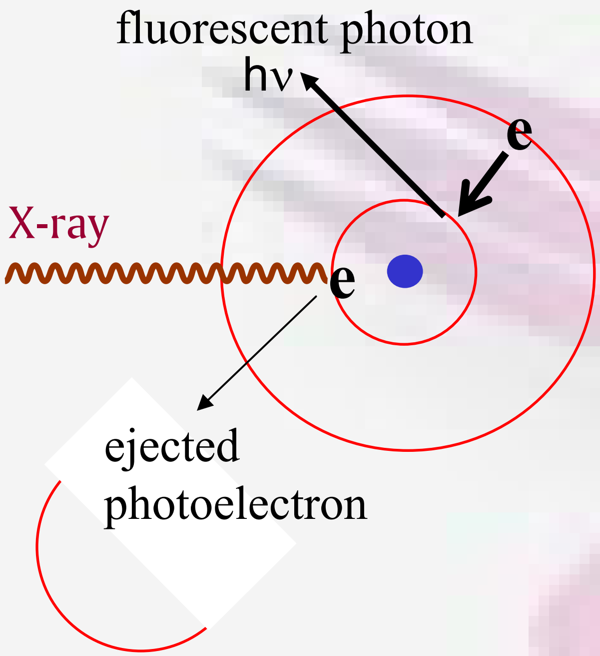
- X-Ray Fluorescence and imaging
- X-ray Absorption Spectroscopy (EXAFS, XANES)
- x-ray diffraction and scattering (including surfaces)

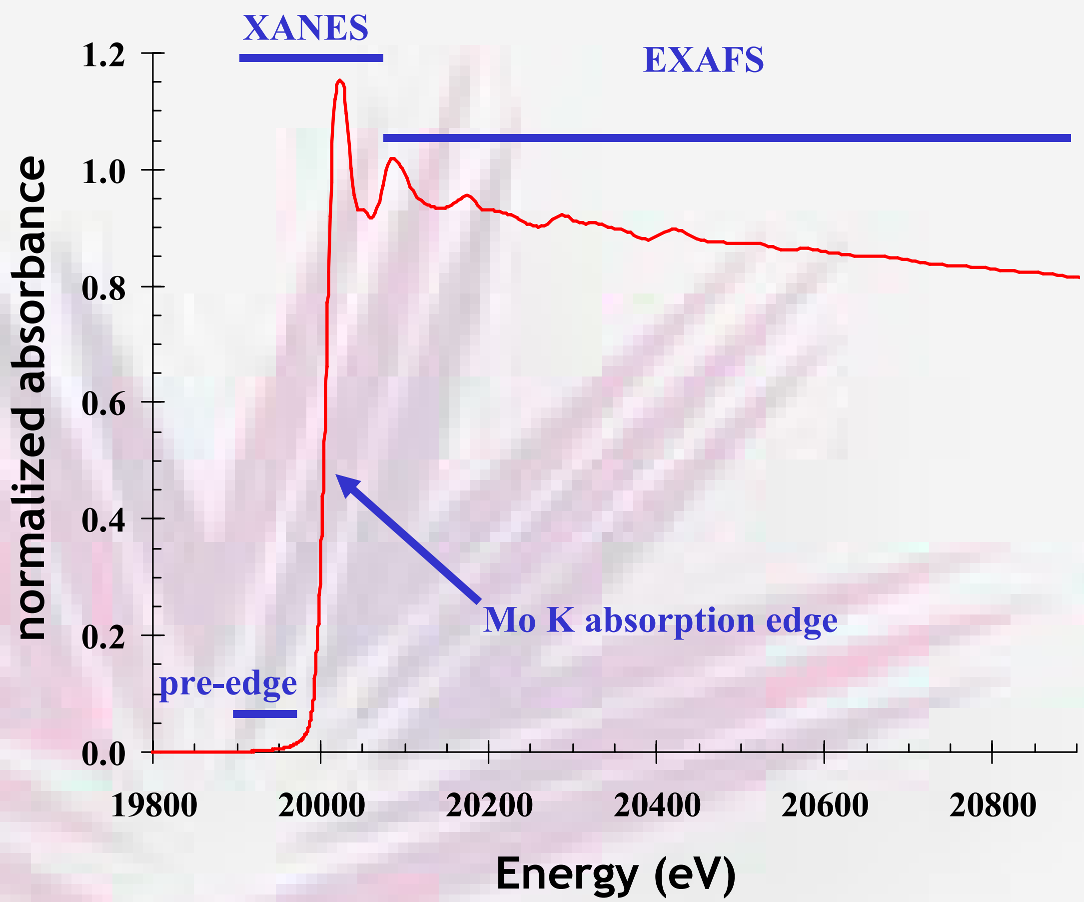
XRF (1 ppm)
XANES (1 ppm)
EXAFS (10 ppm)

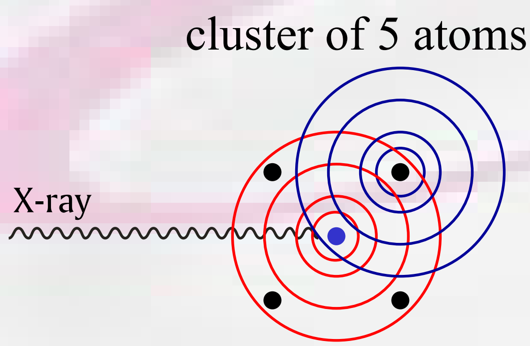
What questions are we trying to answer?

- Will the contaminant bind with soil constituents or is it mobile?
    - will it get into the groundwater
- Is the species stable or labile?
- What is the compounds toxicity? bioavailability?

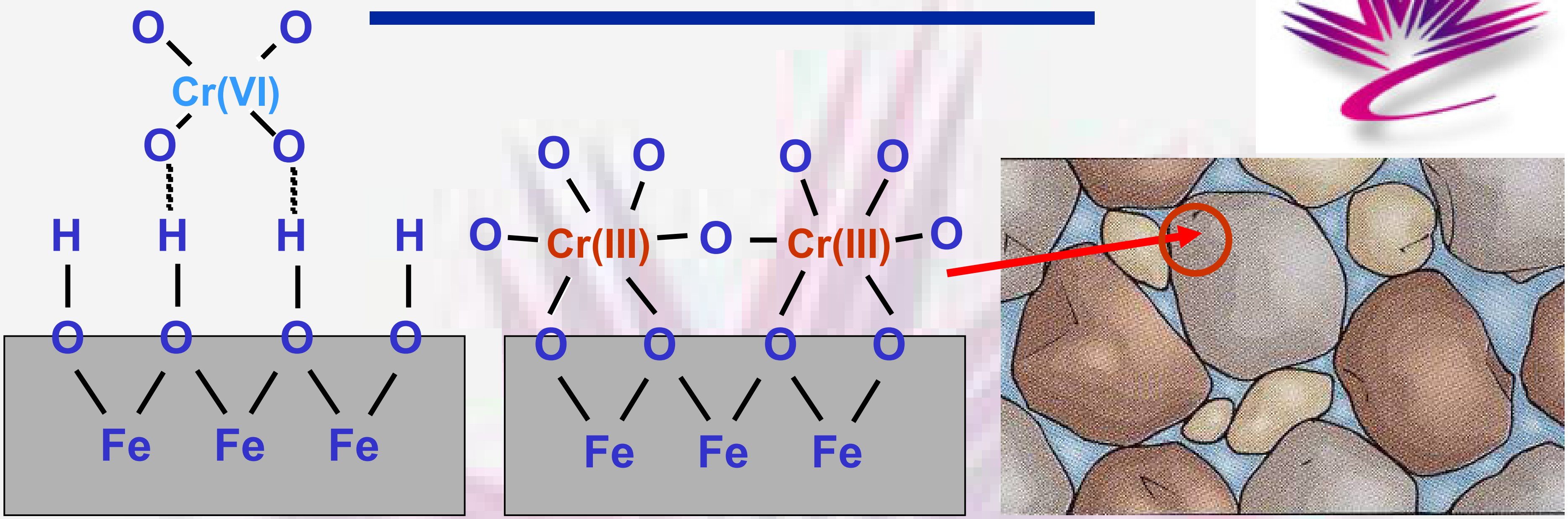
XAS: Origin


fluorescent photon
hν
e
X-ray
e
ejected
photoelectron


XANES
EXAFS
normalized absorbance
1.2
1.0
0.8
0.6
0.4
0.2
0.0
pre-edge
Mo K absorption edge
19800
20000
20200
20400
20600
20800
Energy (eV)


cluster of 5 atoms
X-ray

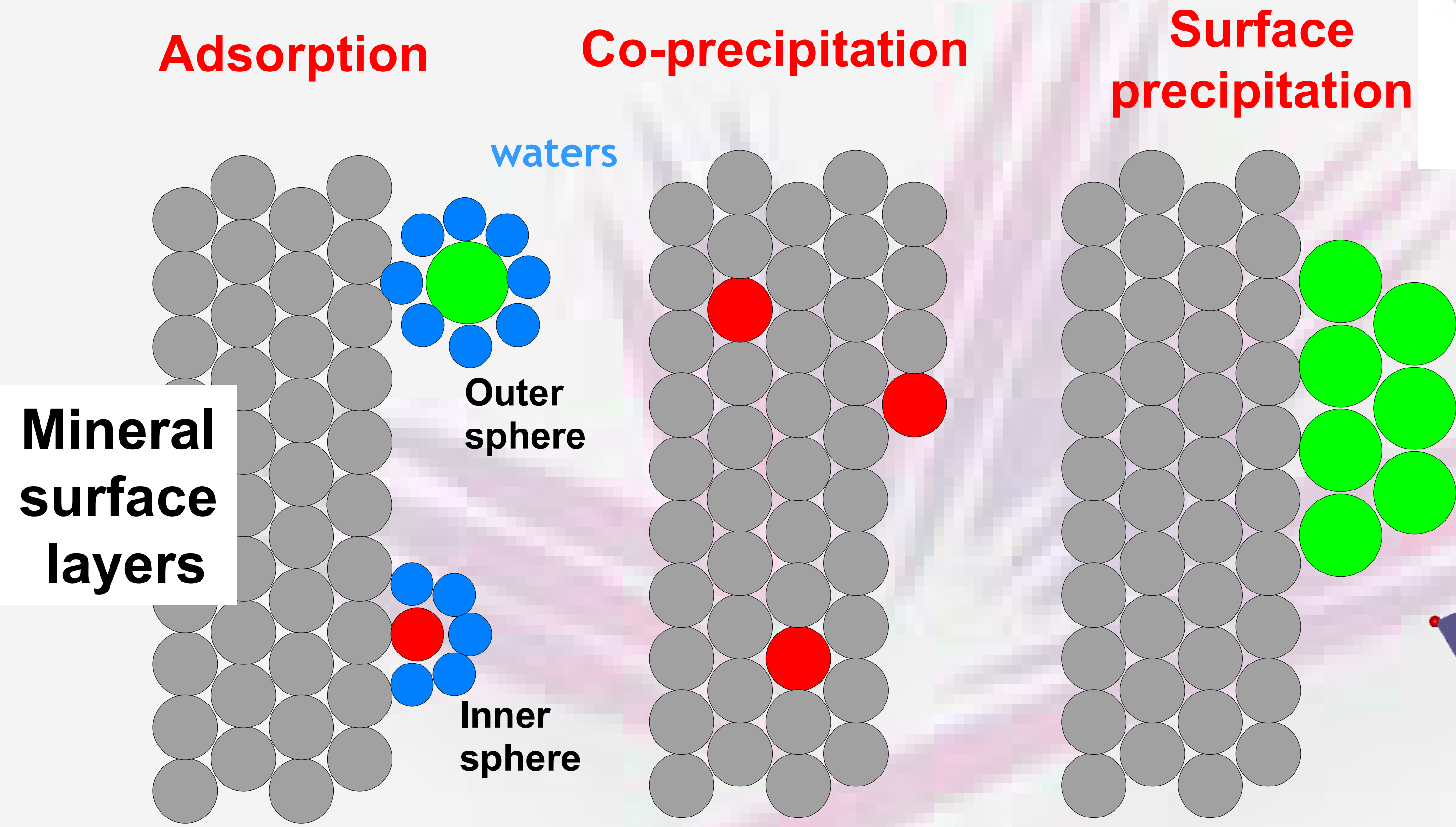
Soils and Sediments

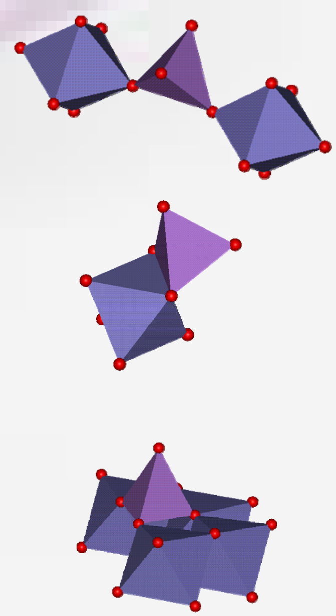


XAS spectroscopy has become a powerful tool in environmental chemistry because of these characteristics,

- any state of matter, almost any sample - wet, dry, amorphous, etc.;
- element and oxidation state selective detection;
- minimal sample preparation
    - *in-situ* studies (no chemical artifacts from extraction);
- can be bulk or surface sensitive
- low concentrations (~ppm and up)

Metal Interactions at Interfaces



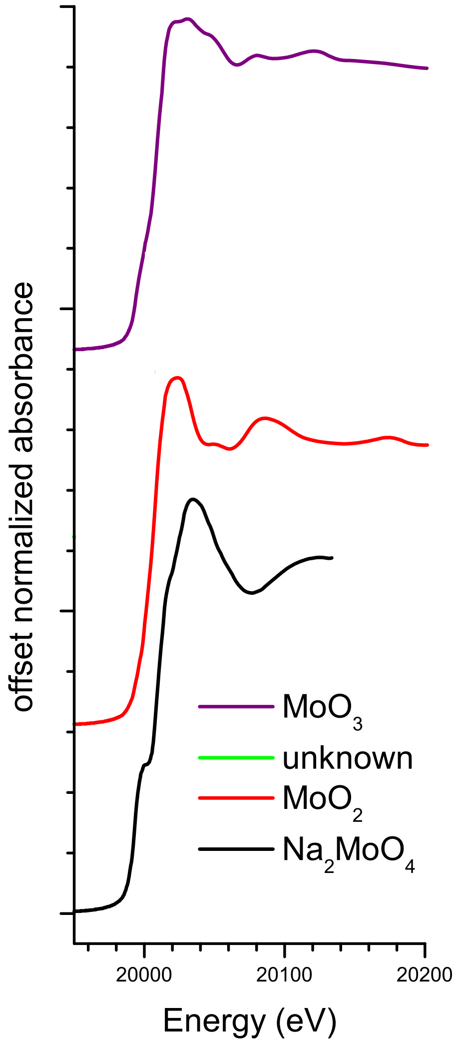


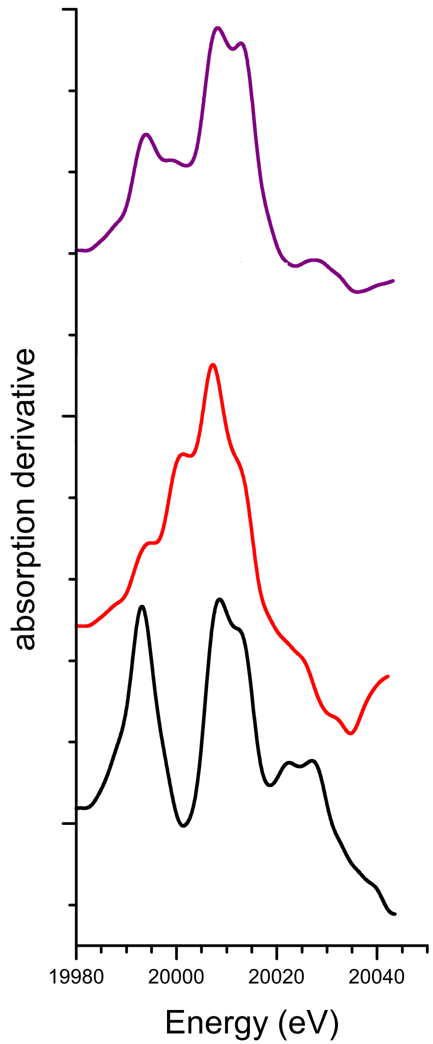
EXAFS can distinguish different types of bonding and these suggest different chemical stabilities.

It is also possible to distinguish between different adsorption modes - monodentate, bidentate, etc.

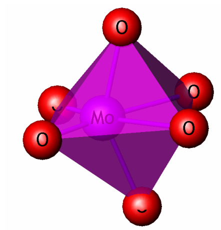
Mo XANES: a local probe

Differentiating between Mo oxides

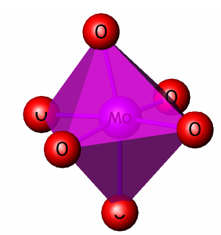




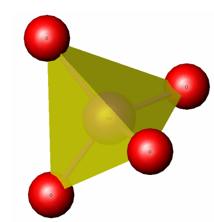
Mo K-edge [20000 eV, [Kr]$4d^5 5s^1$]



MoO_3 distorted octahedron



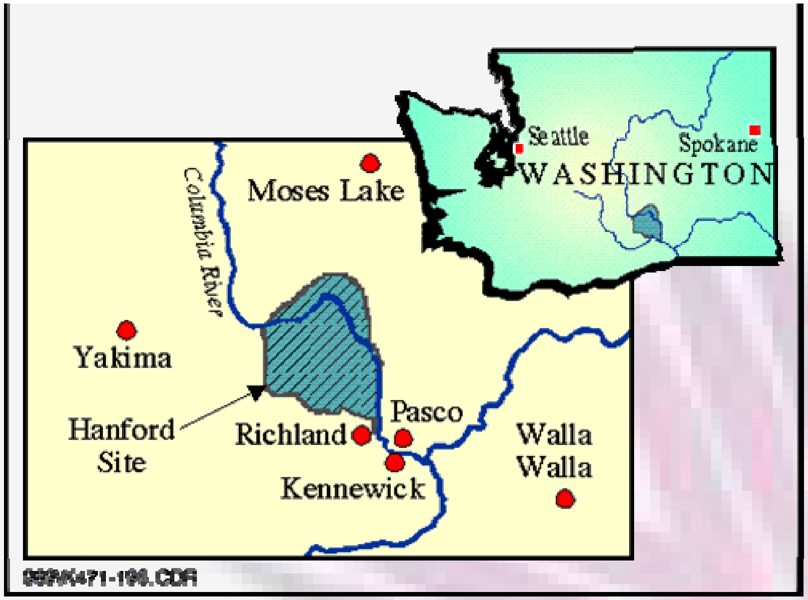
MoO_2 regular octahedron

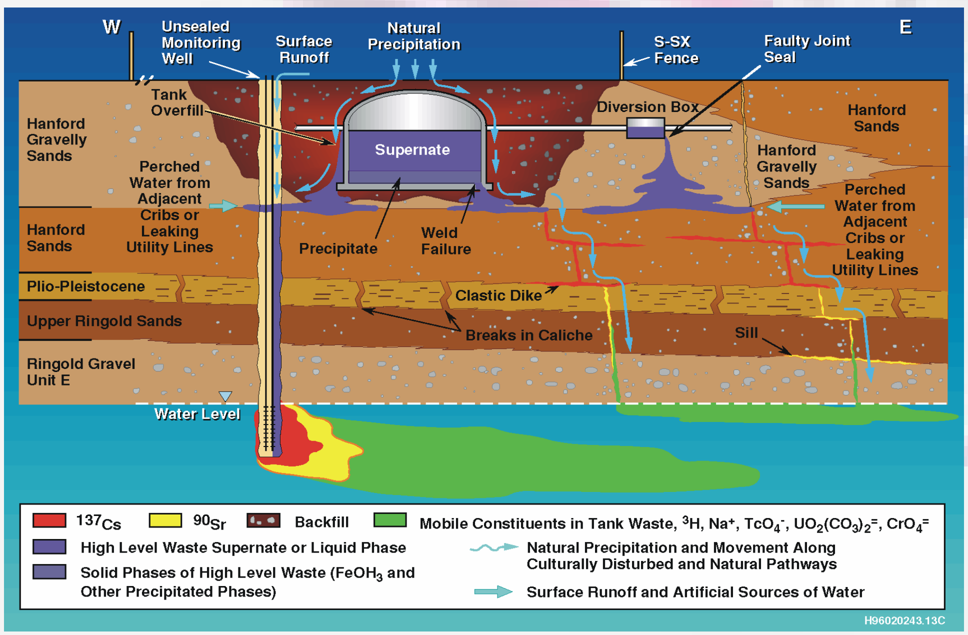


MoO_4 tetrahedron

spectra are distinct due to differing amounts of *p*/*d* orbital mixing

Speciation and Mapping of Cr in Hanford Sediments

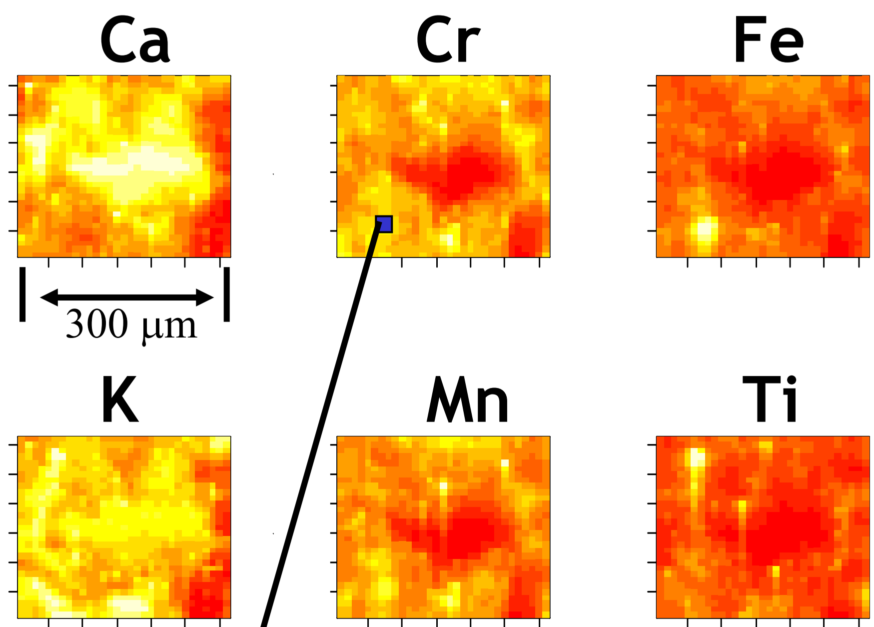


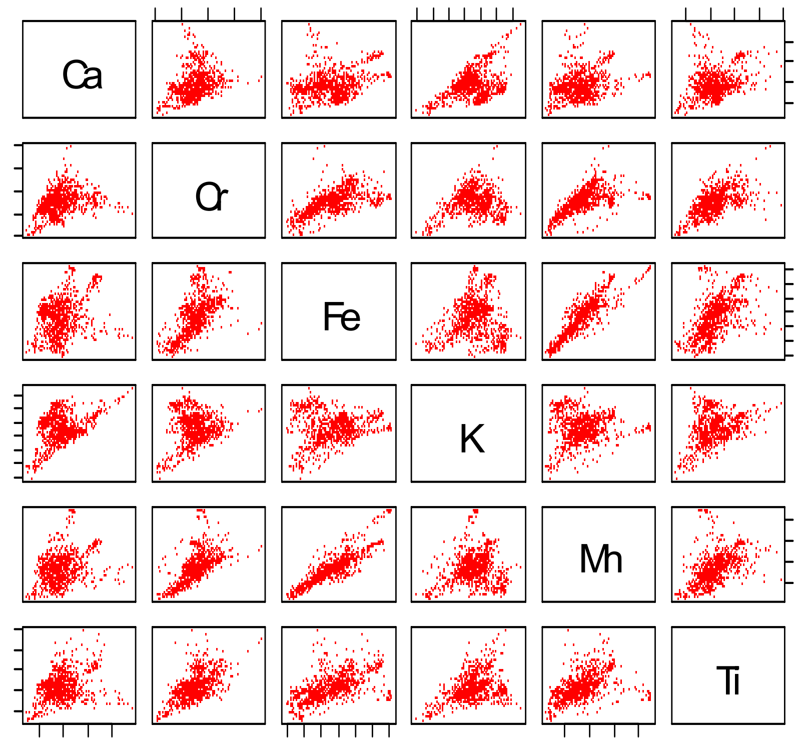


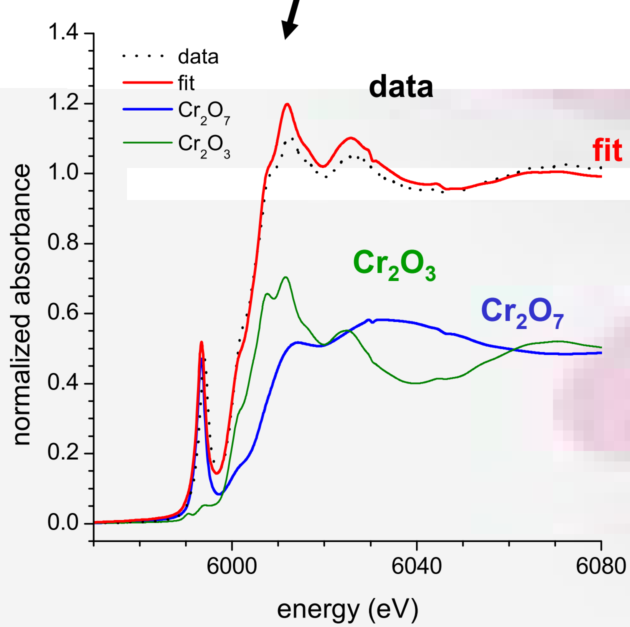
- 340 million Ci of radionuclides in tank waste.
- 1 million curies have leaked to the soil and groundwater.
- estimated cost of cleanup of the entire US weapons complex is between 189 and 265 billion dollars.

- Cr(III) can be oxidized in the field by
  Mn solids in soils.
- Cr(VI) can be reduced in the field by soil organic matter, sulfides, ferrous iron - biotite, magnetite, etc.

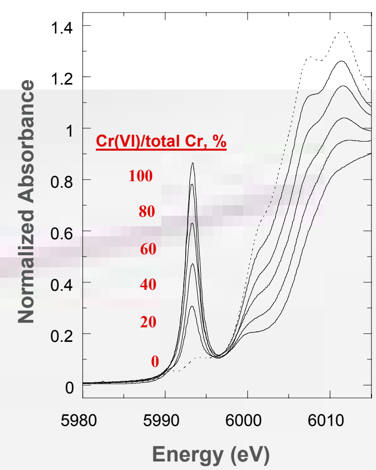
Elemental Mapping - Sample SX-108-8A

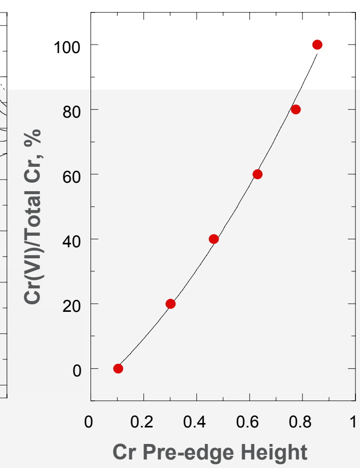






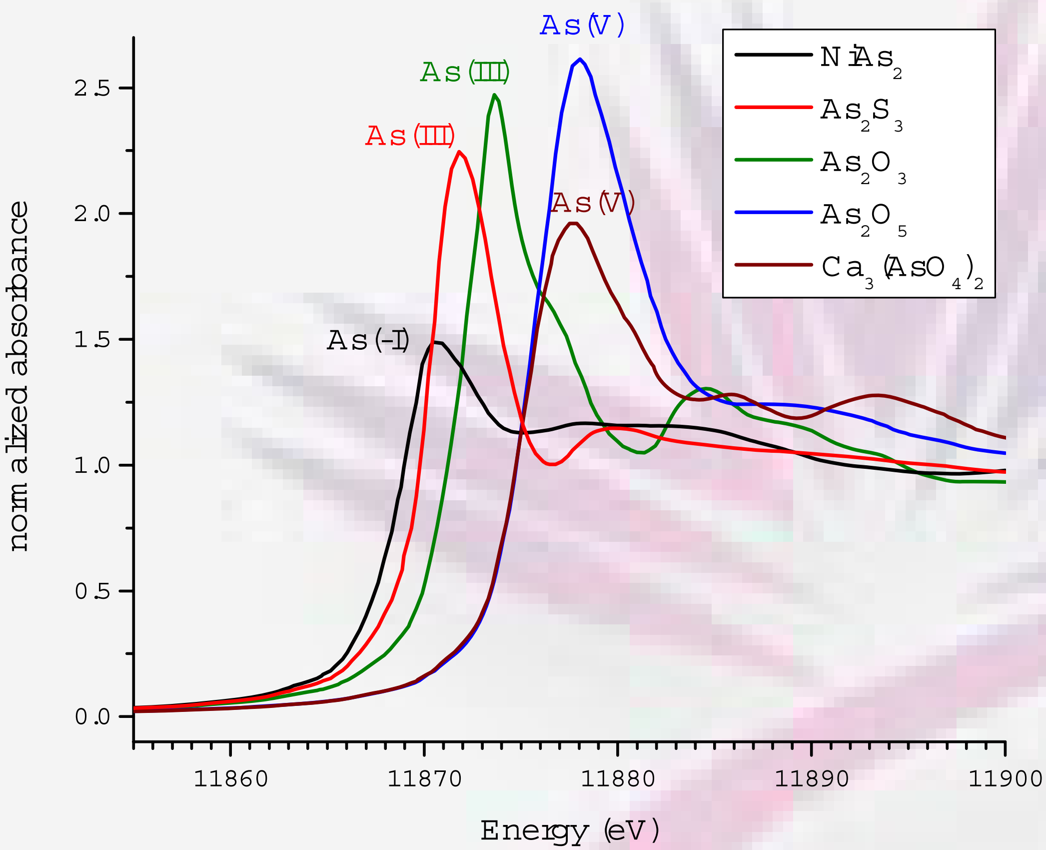
Sample	Cr(VI) (%)
41-09-39-6AB	58
41-09-39-7ABC	69
SX-108-8A	63
SX-108-7A	27



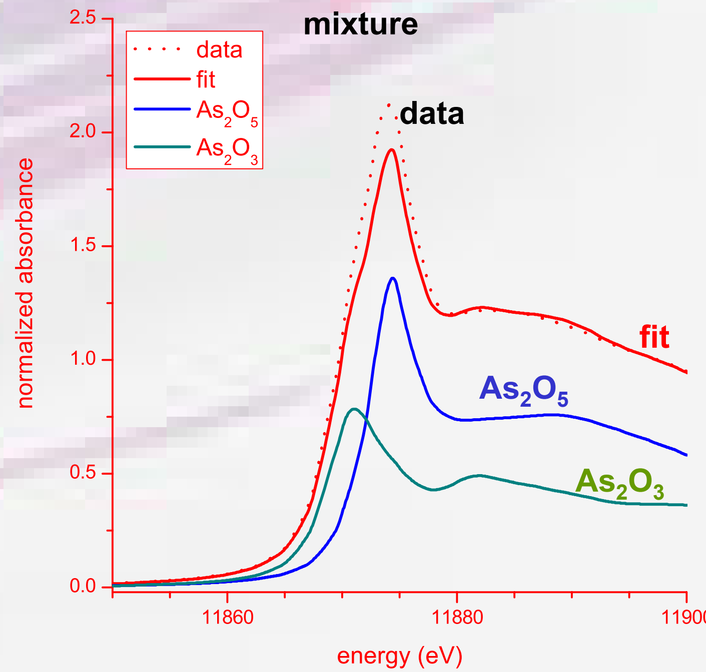


XANES

(X-ray Absorption Near-edge Structure)



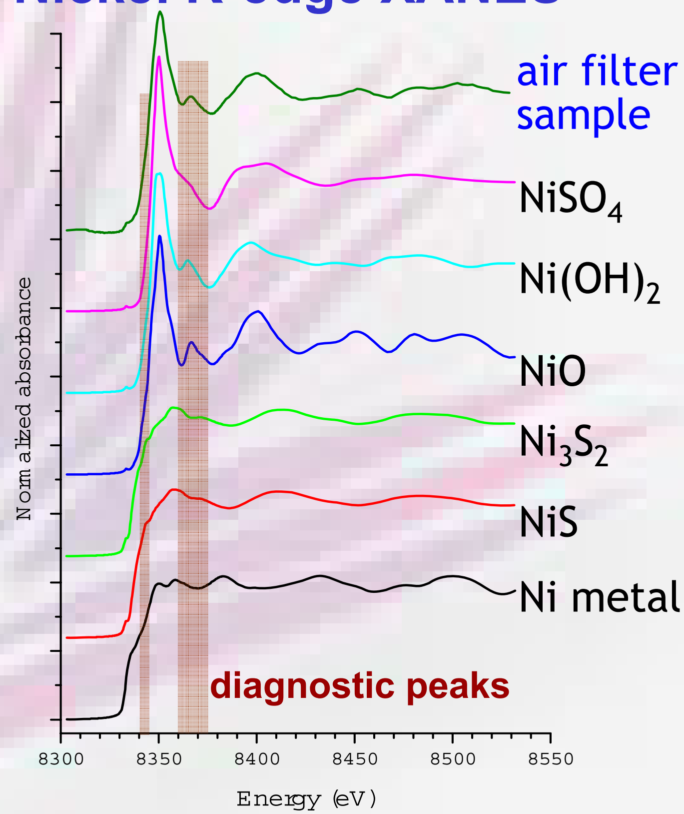
Oxidation state fit to a mixture



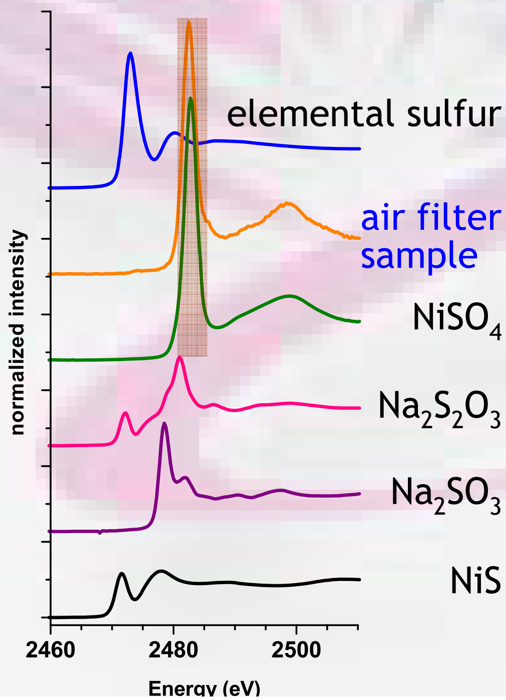
As K-edge [11867 eV, [Ar]$3d^{10}4s^{2}4p^{3}$]

Nickel and Sulfur Speciation in Aerosols

Nickel K-edge XANES



Sulfur K-edge XANES

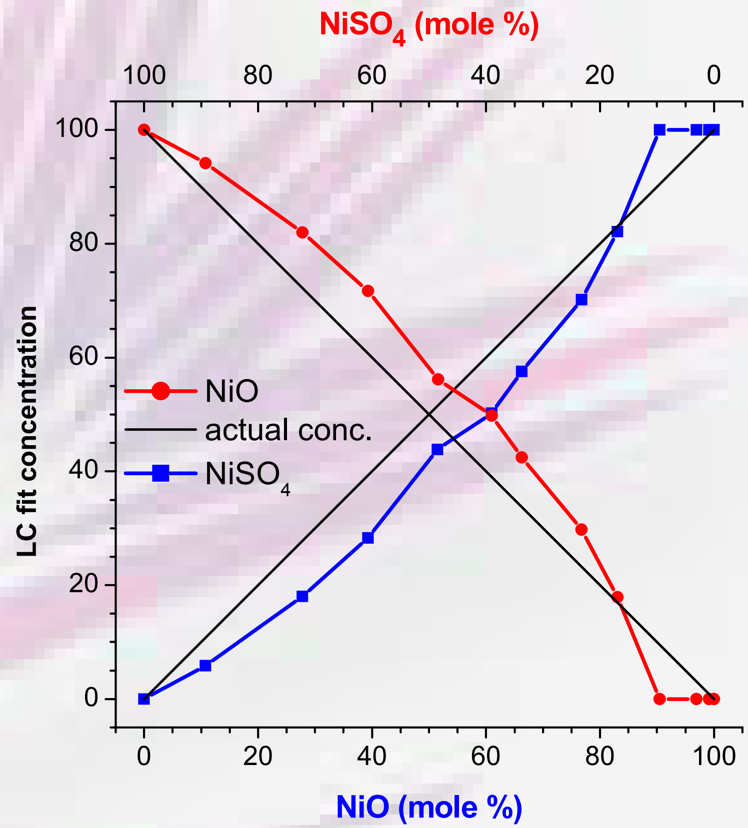


- S K-edge XANES indicates that sulfate is the dominant sulfur species in the air sample.

- Linear combination fitting of the Ni K-edge XANES indicates a NiO/$NiSO_4$ mixture

LC fit results from NiO/$NiSO_4$ mechanical mixtures

conc. (mole %)		LC Fits (mole %)	
NiO	$NiSO_4$	NiO	$NiSO_4$
10.8	89.2	5.8	94.2
27.8	72.2	18.0	82.0
39.3	60.7	28.3	71.7
51.6	48.4	43.8	56.2
61.0	39.0	50.2	49.7
66.3	33.7	57.6	42.4
76.8	23.2	70.2	29.8
83.1	16.9	82.1	17.9
90.5	9.5	100	0
96.9	31	100	0
99.1	0.9	100	0



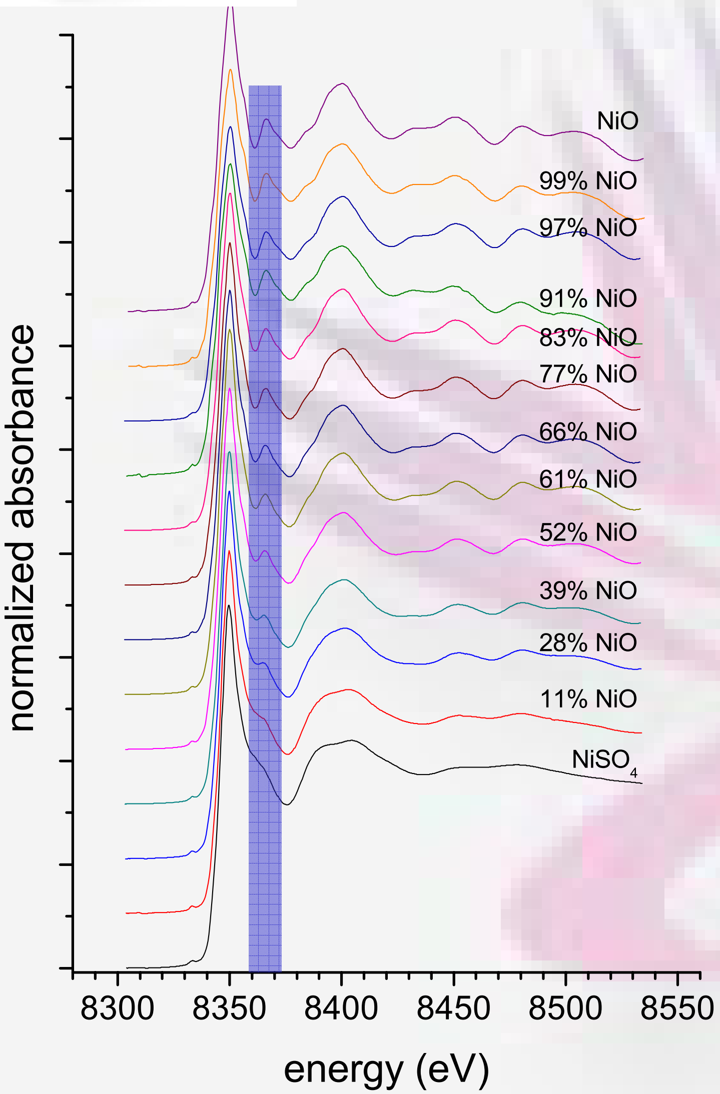
LC fitting: XANES

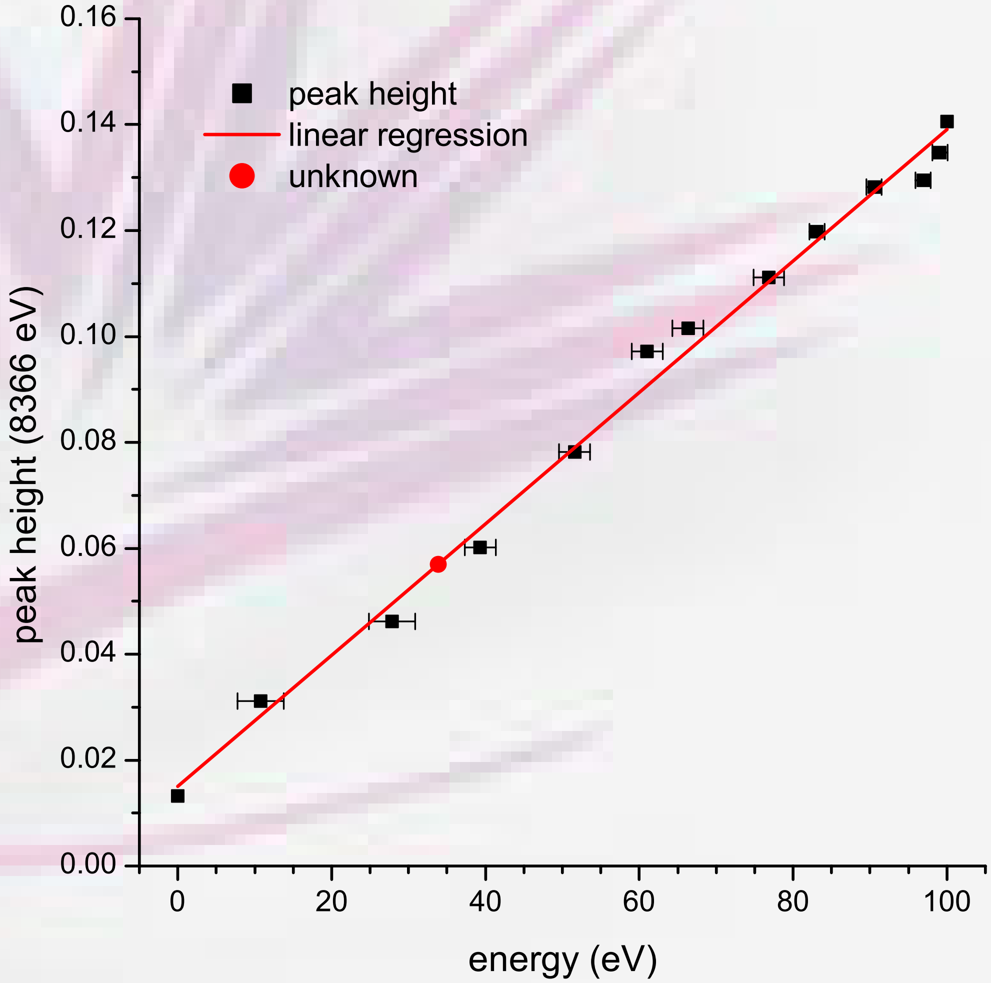
3 component mixtures

Actual composition (mole %)			XANES LC Fits (mole %)		
NiO	NiS	$NiSO_4.6H_2O$	NiO	NiS	$NiSO_4.6H_2O$
88.1	8.4	3.5	86.8	9.3	3.9
71.9	21.0	7.0	74.7	17.5	7.8
56.9	26.3	16.7	58.9	23.8	17.3
41.3	47.5	11.2	41.1	47.7	11.2
37.5	29.8	32.7	38.1	27.3	34.6
27.0	19.6	53.3	26.6	20.7	52.7
12.6	84.0	3.4	11.3	85.1	3.6

- LC fits performed on mechanical mixtures;
- Linear regression may offer better results in certain cases but applications are limited and real samples may cause difficulties.

Linear Regression from specific peak features





Quantification - Strategies

- XANES in energy space, EXAFS in k-space, first-derivative absorption spectra,
- typical approach,
  - principal component analysis (PCA) to determine the number of components in the sample
    - » IND function developed to indicate confidence
  - least squares linear combination fitting
    - » uses spectra of pure reference compounds which are combined to give the compositional fractions of these components.
- pre-edge subtraction, normalization, matrix effects ?
- method to quantify the likely fitting quality
  - Important for K-edge versus L-edge fitting;
- How reliable are these techniques?


Thanks for your Attention