The NSLS’s X-ray Microprobes, Imaging the Chemistry of Our Natural World with Pinpoint High Intensity X-ray Beams

Tony Lanzilotti
University of Chicago
Center for Advanced Radiation Sources
Synchrotron X-ray Microprobes

- These beamlines focus these bright beams to very small size (<10 µm ...f.y.i human hair is ~100 µm diameter) to:
  - Examine the distribution of elements at micron scale
  - Evaluate the molecular form of these elements
  - Determine the mineralogy of a sample at micron scale
Synchrotron X-ray Microprobes

- Elemental analysis done through detecting fluorescent X-rays emitted from a material after excitation.
- In-situ chemical characterization allows us to analyze elements at the femtogram level (0.000000000000001 or 1x10^-15 grams).
- We can produce “images” of the elemental distribution by scanning the sample through the X-ray beam in small steps.
What is X-Ray Fluorescence?

- X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been “excited”.
- In general, when we refer to XRF, the implication is that the excitation source is a high energy x-ray or gamma ray source.
- However, a variety of source types can be employed to excite materials and generate x-ray fluorescence:
  - X-Ray Tubes
  - Radioisotopes
  - Scanning Electron Microscopes
  - Synchrotrons
  - Positron and other particle beams
XRF as a chemical analysis tool

- Widely used for elemental analysis of geologic materials, forensic analysis, archeological materials, ceramics, steel, glass manufacturing industry.
- Commercial instruments utilize anode x-ray tubes and are capable of analyzing elements between beryllium (Z = 4) and uranium (Z=92).
- Due to low x-ray yields for the light elements, difficult to quantify elements lighter than sodium (Z = 11).
- Multiple elements can be detected simultaneously.
- Detection limits generally in the 10-100 ppm range for heavy elements.
- For rocks and metals, major elements can be measured with an accuracy of ~0.1% using standards calibration (alpha coefficients). Fundamental Parameters can estimate the elemental composition of unknowns without standards.
The X-Ray Fluorescence Process

• A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected it from the atom.

• Higher energy electrons cascade to fill vacancy.

• Giving off characteristic fluorescent X-rays.

• These are detected using very sensitive X-ray detectors.
Energy Dispersive X-ray Detectors

• XRF from sample detected using either Energy Dispersive Spectrometers (EDS) or Wavelength Dispersive Spectrometers (WDS).

• Most XRF instruments employ EDS detection systems. EDS systems are also the norm on SEM and PIXE instruments. EMPA instruments typically employ WDS detectors.

• An EDS detector is composed of a non-conducting or semi-conducting material between two charged electrodes.

• When X-rays ionize the detector material, it becomes momentarily conductive, generating an output pulse.

\[
E_n = \frac{E}{e}
\]

where:  
\( n \) = number of electron-hole pairs produced  
\( E \) = X-ray photon energy  
\( e \) = 3.8 ev for Si at LN\(_2\) temperatures
X-ray Energy Dispersive Spectra

- Energy of the peak is element specific
- Intensity of the peak is proportional to concentration
We can then “Raster” the sample through the beam to make a map.
X-ray Absorption Spectroscopy

• We can also measure the absorption of the incident radiation as a function of energy due to its interaction with a sample

• X-ray absorptions are associated with the excitation of inner shell electrons in atoms

• The shape and intensity of features in an absorption spectra can be used to determine:
  ◆ the formal valence of an element
  ◆ the coordination environment (e.g., octahedral, tetrahedral coordination)
  ◆ and subtle geometrical distortions of the coordination
X-ray Absorption Spectroscopy

Chromium
Unique Scientific problems Addressed using X-ray Fluorescence Microprobes

- X-rays are penetrative and the power deposited to a sample from the beam is very low
Unique Scientific problems Addressed using X-ray Fluorescence Microprobes

- X-rays are penetrative and the power deposited to a sample from the beam is very low
- Samples can be analyzed in a wet or moist state (in-situ)
- Large samples can be analyzed and the analysis generally requires only the most minimal of sample preparation
Unique Scientific problems Addressed using X-ray Fluorescence Microprobes

• X-rays are penetrative and the power deposited to a sample from the beam is very low
• Samples can be analyzed in a wet or moist state (in-situ)
• Large samples can be analyzed and the analysis generally requires only the most minimal of sample preparation
• In its simplest form experiments are done as an “imaging” technique where image “intensity” directly correlates to element concentration
• You get a broad range of elements simultaneously
Mercury is a naturally occurring element that is found in air, water and food.

Most people are exposed to mercury via food. Fish take up mercury as they feed. This mercury is in the more toxic, methylmercury form.

Pregnant women - or, rather, their unborn babies - are at the greatest risk. Babies developing in the uterus (womb) seem to be most vulnerable to the effects of mercury on their nervous systems.

Tony Lanzilotti and Keith Jones (BNL), NSLS
Human Health Risks From Methyl Mercury In Fish

- Mercury is a naturally occurring element that is found in air, water and food.
- Most people are exposed to mercury via food. Fish take up mercury as they feed. This mercury is in the more toxic, methylmercury form.
- Pregnant women - or, rather, their unborn babies - are at the greatest risk. Babies developing in the uterus (womb) seem to be most vulnerable to the effects of mercury on their nervous systems.
Tree Rings

Tree cores of black willows growing at the Savannah River DOE site record contamination from contaminated pond

Tracy Punshon (Dartmouth) and Tony Lanzirotti, NSLS
Salix negra L., Steed Pond, Section 2

Tree age = 8 years

Beaver dam dismantled; increased rainfall

Ni (mg kg⁻¹ DW)


Fe

log (Fe)

Mn

Y (mm)

0 5 10 15 20 25

0 5 10 15 20 25

0 5 10 15 20 25

0 5 10 15 20 25

0 5 10 15 20 25
Environmental Hazards of Pressure Treated Lumber

- Most woods are susceptible to attack by fungus and insects. To make wood more resistant to attack, the lumber industry embedded insecticides and anti-fungal agents.

- The wood is injected with an aqueous solution of Copper, Chromate and Arsenic (CCA) under pressure.

- A 12 foot 2 x 6 contains enough arsenic, if released, to kill about 250 adults.

- The EPA announced a transitional ban on the production of CCA wood for residential use in 2002.
Environmental Hazards of Pressure Treated Lumber

Cabbage grown near degrading CCA lumber

Satish Myneni and Matthew Cooper (Princeton) and Tony Lanzirotti, NSLS
**Thermopolis Archaeopteryx**
The image is a composite blend of scans of the elements phosphorus, silicon, sulfur, and iron. The bright colors in the wing areas show how part of the feather chemistry has been preserved.

---

*Fossil of an ancient squid, X-rays image chemical traces of the animal's soft tissue left behind in the limestone; at right, the tentacles are clearly visible*
Stardust – NASA’s Cometary Sample Return Mission

- The Stardust spacecraft was launched on February 7, 1999
- On January 2, 2004 Stardust successfully encountered comet Wild 2, collecting samples of cometary dust
- On January 15 2006, Stardust successfully returned to Earth by parachuting a reentry capsule weighing approximately 125 pounds.
- Comets are made up of material left over from the solar nebula after the planets were formed. Unlike the planets, most comets have not changed very much since the formation of the solar system. Therefore, comets may hold the key to understanding the early development of the solar system.
- Wild-2: only 5 solar passes; right place at right time

Tony Lanzirotti, Steve Sutton (U. Chicago) and George Flynn (Plattsburgh), NSLS & APS
Comet Wild 2 dust capture at 6.1 km/s

The biggest particles travel the furthest

< coarse grained fraction >

< fine-grained fraction >

Probably, finer-grained materials have been preferentially abraded away during capture, and are sitting along the tracks, leaving the largest grains at the end
Synchrotron µXRF Mapping in-situ in aerogel

Similar primitive chemistry to what we’ve observed from IDP’s
Surprising number of high T minerals observed
OK, teachers and students likely won’t have access to space dust
But...

Americans spend more than 80% of their time indoors
Understanding and managing risk requires understanding metal sources and species
Analyzing Dust Bunnies

Analysis of Dust from homes in Ottawa, Canada
Identified particles:
- calcite, vaterite, gypsum (wall boards)
- halite (table salt)
- portlandite (concrete)
- metallic Fe and Cu (electrical, appliances)
- Fe and Cu oxides (oxidized metals)
- wood cellulose, some high in Cu, Cr, As (CCA lumber)
- Pb carbonates and sulfates (paint and solder)

Coupled X-ray fluorescence (chemistry), diffraction (mineralogy), and absorption spectroscopy (speciation) used to characterize variable components in house dust

Heather Jamieson (Queen’s U.), Steve Walker (Queen’s U.), Tony Lanzìrottì, Health Canada, NSLS
**K & L Spectral Lines**

- **K - alpha lines:** $L$ shell e- transition to fill vacancy in $K$ shell. Most frequent transition, hence most intense peak.

- **K - beta lines:** $M$ shell e-transitions to fill vacancy in $K$ shell.

- **L - alpha lines:** $M$ shell e-transition to fill vacancy in $L$ shell.

- **L - beta lines:** $N$ shell e-transition to fill vacancy in $L$ shell.
Evaluating Energy Dispersive Spectra

What types of peaks do we need to watch out for?

- K & L Spectral Peaks (maybe M)
- Rayleigh Scatter Peaks
- Compton Scatter Peaks
- Escape Peaks
- Sum or Pileup Peaks
- Spectral Overlaps
Sample Preparation

For SXRF samples in any form can be analyzed

Third dimension (depth) is important
- Sampling depth is relatively large (compared to EMPA, for example) and element dependent
- Optimum thickness for highest sensitivity
- Need to know thickness for absorption corrections
- Buried objects (e.g., inclusions) can be analyzed
- Clean substrates need to be used

Typical sample mounts
- Thin sections on pure silica slides
- Dispersed particles on plastic film or silica
- Individual particles on fibers or film
- Contained liquids
Sample Preparation

- Large samples feasible, but best to stick to 35mm format or microscope slides
- Thick samples OK, but beware analysis of buried materials
- Avoid substrates that are trace element impure
- Be aware of higher scatter and background from dense substrates such as glass
- Standard microscope slides are very dirty.
- Scotch tape actually very clean, as are mylar and polypropylene films.
Detection Sensitivity

- XRF detection at NSLS typically between 2-20 keV
- XAS analysis generally between 5-20 keV
### Approach 1: First Principles

Compute concentration from incident beam intensity $I_o$ and measured fluorescence intensity $I$, taking into account all intermediate processes...this is a major challenge to do with high precision/accuracy!

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_o$</td>
<td>Incident Energy</td>
<td>keV</td>
<td>20</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fluorescence Energy</td>
<td>keV</td>
<td>14.1</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Incident and Detection Angles</td>
<td>deg</td>
<td>45</td>
</tr>
<tr>
<td>$z$</td>
<td>Sample to detector distance</td>
<td>cm</td>
<td>10</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Detector efficiency</td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Detector filter attenuation</td>
<td></td>
<td>0.96</td>
</tr>
<tr>
<td>$w$</td>
<td>Fluorescence yield</td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>Strontium Concentration</td>
<td>wt fraction</td>
<td>1.00E-04</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Detector Subtension</td>
<td></td>
<td>0.000625</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Photoelectric cross section</td>
<td>1/cm</td>
<td>180.0253</td>
</tr>
<tr>
<td>$\mu_o$</td>
<td>Attenuation coefficient for incident energy</td>
<td>1/cm</td>
<td>68.0752</td>
</tr>
<tr>
<td>$\mu_f$</td>
<td>Attenuation coefficient for fluorescence energy</td>
<td>1/cm</td>
<td>182.5727</td>
</tr>
<tr>
<td>S</td>
<td>Sample thickness</td>
<td>cm</td>
<td>0.01</td>
</tr>
<tr>
<td>$I/I_o$</td>
<td>Ratio of Measured Fluorescence to Incident Intensity</td>
<td></td>
<td>2.87E-08</td>
</tr>
</tbody>
</table>
Approach 2: Standards

If a standard for the element of interest is available of identical matrix as the unknown, then

\[ C_{\text{unk}} = C_{\text{stand}} \times \frac{I_{\text{unk}}}{I_{\text{stand}}} \]

where
- \( C_{\text{unk}} \) = concentration in the unknown
- \( C_{\text{stand}} \) = concentration in the standard
- \( I_{\text{unk}} \) = measured fluorescence from unknown
- \( I_{\text{stand}} \) = measured fluorescence from standard

This approach is straightforward but often impractical
- Matrices of standards are significantly different from unknowns
- Limited element coverage
- Lack of homogeneity at the microscale
Avoiding sample inhomogeneities

- In XRF analysis, the standards based approach works best when standards are “matrix matched” to the unknowns and where both standards and unknowns are ideally homogenous and isotropic.
- Mixtures of multiple crystalline components powders can result in absorption effects that deviate from those calculable from theory.
- So in bulk XRF analysis considerable effort is made to approach the ideal of homogeneity and isotropy.
Approach 3: Internal Reference

Similar to the Standards approach but in this case the standard is a single element of known concentration within the unknown

\[ C_{\text{unk}} = C_{\text{stand}} \times \left( \frac{I_{\text{unk}}}{I_{\text{stand}}} \right) \times \left( \frac{S_{\text{stand}}}{S_{\text{unk}}} \right) \]

where \( \frac{S_{\text{stand}}}{S_{\text{unk}}} \) is the relative sensitivity (counts/second/mg kg\(^{-1}\)) for the standard element compared to the unknown element.

• No external standard required

• Compute the sensitivity ratios theoretically

• Can be done with sufficiently high precision/accuracy because some factors cancel out (e.g., incident flux, detector efficiency and solid angle)

• NRLXRF (Criss et al. 1978), a package developed by the Naval Research Laboratory for conventional XRF

• Focused spot size ~ 5µm x 9µm (VxH)
• Visible field of view ~ 1mm (microscope-type view)
• Scan range ~ 100 mm
• Detection sensitivity variable (S Kα requires wt.%, Sr Kα can be detected at a few ppm)