Overview of X-Ray Fluorescence Analysis
What is X-Ray Fluorescence (XRF)?

– A physical process:
  Emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by high-energy X-rays or gamma rays.

– A technique in analytical chemistry:
  Method to identify elements in a sample and measure their concentrations

  Non-destructive, quick, and simple to carry out.
Physical Process

- Incoming radiation hits an atom
- Ejects an electron from an inner shell, creating a vacancy
- An electron from an outer shell “drops down” to fill the vacancy.
- The excited atom emits an X-ray with energy equal to the difference between the levels

\[ E_{X\text{ray}} = \Delta E = E_K - E_L \]
- Since each element has a unique set of levels, it produces a unique set of “characteristic” X-rays
Physical Process

- XRF is similar to optical spectroscopy but at higher energy
- Independent of chemical state → **Elemental analysis**
- Intensity of X-ray line proportional to number of atoms → **Quantitative**
- X-rays pass through surface into sample
  → **Nondestructive** and no sample preparation is necessary
    
    Best accuracy requires sample preparation
  
  → **Bulk measurement** rather than only surface
    
    Notion of “bulk” vs “surface” depends on the X-ray energy
- Presence of Cu and Zn K lines → Elements are in sample (qualitative)
- Intensity of the lines → How much is in sample (quantitative)
Typical spectrum and results

- Photopeak intensity varies with concentration
- Final result is quantitative concentration

### Table: Certified vs XRF

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified</th>
<th>XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1000 ± 20</td>
<td>895 ± 198</td>
</tr>
<tr>
<td>Br</td>
<td>1100 ± 22</td>
<td>1089 ± 23</td>
</tr>
<tr>
<td>Cd</td>
<td>300 ± 6</td>
<td>264 ± 26</td>
</tr>
<tr>
<td>Hg</td>
<td>1100 ± 22</td>
<td>1050 ± 53</td>
</tr>
<tr>
<td>Pb</td>
<td>1200 ± 24</td>
<td>1194 ± 39</td>
</tr>
<tr>
<td>Cr</td>
<td>401 ± 8</td>
<td>388 ± 167</td>
</tr>
<tr>
<td>Br</td>
<td>500 ± 10</td>
<td>487 ± 13</td>
</tr>
<tr>
<td>Cd</td>
<td>100 ± 5</td>
<td>68 ± 13</td>
</tr>
<tr>
<td>Hg</td>
<td>200 ± 5</td>
<td>183 ± 27</td>
</tr>
<tr>
<td>Pb</td>
<td>400 ± 8</td>
<td>398 ± 23</td>
</tr>
<tr>
<td>Cr</td>
<td>0 ± 5</td>
<td>7 ± 40</td>
</tr>
<tr>
<td>Br</td>
<td>0 ± 5</td>
<td>1 ± 2</td>
</tr>
<tr>
<td>Cd</td>
<td>0 ± 5</td>
<td>9 ± 10</td>
</tr>
<tr>
<td>Hg</td>
<td>0 ± 5</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>Pb</td>
<td>0 ± 5</td>
<td>10 ± 9</td>
</tr>
</tbody>
</table>
What are the main factors limiting XRF?

- **Counting variance**
  - The measurement is based on count discrete X-rays
  - Arise from random processes → Inherent statistical variation in number of X-rays
  - Percent uncertainty = 1/√N
    - 100 X-rays detected → 10% precision
    - 1,000 X-rays detected → 3% precision
    - 1,000,000 X-rays → 1000 ppm precision
  - Good precision means many X-rays which means high count rates or long times

- **Detector response**
  - Photopeak has some width
  - There is always spectral background and overlapping peaks
  - Ability to remove these depends on counting variance, energy resolution, and accuracy of software algorithms
  - Better energy resolution helps but there are physical and practical limits
What are the main factors limiting XRF?

- **Attenuation lengths**
  - Penetration depth depends on energy & therefore element
    - In silica, Al X-rays go 3 µm while Sn go 3 mm
  - Response depends on energy/element
  - Sample condition & homogeneity are critical

![Graph showing XRF energy vs. attenuation length for different elements.](image)
• **How accurate is EDXRF?**
  - In the best case, relative accuracy ~ 0.2% (1.00% ± 20 ppm).
    Requires sample prep, a known matrix, good statistics, etc
  - Nondestructive screening, relative accuracy ~ 2% (1.00 ± 0.02%)
    Requires careful optimize and setup, known sample type
  - Quick check on unknown, relative accuracy ~20% (1.0 ± 0.2 %)

• **What is the detection limit for EDXRF?**
  - <1 ppm for prepared samples in a known matrix under good conditions
  - 10 ppm in nondestructive screening with no interfering elements
  - When elements interference or overlap, 1% of other element

• **What elements can be analyzed with EDXRF?**
  - Na to U (down to Be with EDS)
  - Low Z elements (below S) are a challenge
  - Need multiple measurements to cover a wide range of elements
XRF is one of many methods used in material analysis.

**Advantages of XRF**
- Non-destructive
- No sample preparation
- Fast (seconds to minutes)
- Good precision and accuracy
- Measure Na to U
- Suitable for portable equipment and field use

**Disadvantages of XRF**
- Limits of detection modest (10 ppm typical)
- Accuracy usually modest (few % relative)
- Difficult to use for lower Z elements

**Best results require**
- Sample preparation (damaging)
- System optimization
- Matched calibration standards
XRF Applications

How is XRF used?
Hazardous Material Screening

- Is there cadmium on this toy?
- Is there lead in this paint?
- Does this circuit board contain Pb, Cd, or Cr?
- Nondestructive critical for screening products!

![Graphs showing energy and counts for different materials: Amptek SDD Pb free circuit board, Lead paint on wood, Cd painted PVC](image)
Metal Alloy Analysis

- Are these bolts stainless steel 316?
- Is there Ni in this scrap metal?
- Is there Cd plating on this MILSPEC connector?
- How much Au is in a white gold ring?
- **Speed critical, accuracy moderate**
Art and Archeology

- How did the artist make their paints?
- Is this an ancient or a modern pigment?
- What is the effect of cleaning on the surface of a statue?
- Nondestructive testing is vital for art!

XRF Overview
• Is there any change in spectrum?
• Absolute composition not needed but quick, real-time, non-destructive vital.
Field Measurements

Measuring ores in mines.

Identifying minerals on Mars.

Measuring soil contamination.

Amptek Inc.
14 Deangelo Drive
Bedford, MA 01730 USA
www.amptek.com
Related Analytical Methods
Energy Dispersive X-ray Spectroscopy

- a.k.a. EDS, EDX, XEDS, EDXA

- Uses electron beam in vacuum chamber to excite the atoms
- Electrons have short range in matter → Only way to measure lightest elements, down to Be (Z of 4)
- High spatial resolution (75 um spatial, 1 um in depth)
Wavelength Dispersive X-ray Spectroscopy (WDXRF)

- Crystal diffractometer disperses the X-ray wavelengths much like a prism disperses visible light.
- X-rays at a particular wavelength (energy) are recorded by a detector.
- It measures only one energy at a time; it obtains a spectrum by sweeping the wavelength over time.

- Advantages of WDXRF
  - Much better energy resolution
  - Leads to much better accuracy and detection limits

- Disadvantage of WDXRF
  - Very long time to acquire whole spectrum
  - Requires destructive sample preparation

- Uses similar detectors and signal processors