Looking Into the Past: Using XRF Technology to Test Medieval Ink

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Topics

- Niton XLp300A General Information
- Campus applications
- Radiation Safety
- Unusual request
- Results
- Conclusions
Nitron XLp 300A

- Lead paint analyzer
- Source: Cd-109 40 mCi
- Energies: 22.5 and 88.1 keV
- Intensity: 315 mREM/hr
- Sampling modes: Standard and K&L
- Unit of measurement: mg/cm²
Campus Applications

- OSHA compliance (1910.1025, 1926.62)
  - General and Construction Lead Standards
  - Applies if any detectable lead
  - Prior to scraping, demolition, repair
  - Determine lead concentration in paint
  - Ensure there is air monitoring data indicating acceptable exposure
Campus Applications

Previous air monitoring results performed in the past 12 months for similar work activities:

- Type of material (i.e., concrete, drywall, plaster)
- Lead concentration in material
- Task (i.e., wet scraping of paint or demolition)
- Environmental conditions (i.e., indoor or outdoor)
Personal Protective Equipment

- Coveralls
- work shoes
- gloves
- respirator
Campus Applications

- **EPA Compliance**
  - Lead-based paint regulations
    - Definition: 1.0 mg/cm²
  - Target Housing and Child-Occupied Facilities
    - Built prior to 1978
    - Rental housing and FPG Child Development Center
  - Protect kids under the age of six
  - Work practice requirements
  - Clearance requirements
Radiation Safety: Sealed Source

Weld
SS Shell
Shielding
Substrate
Radioactive Material
Window

Source: Niton XRF Analyzers
Radiation Safety

Know beam location

Source: Niton XRF Analyzers
Radiation Safety

Know beam location

Source: Niton XRF Analyzers
Radiation Safety

Know when the primary beam is open

“Shutter Open” LED indicators

Proximity Switch

Release Trigger

Source: Niton XRF Analyzers
Leak Tests
Sampling modes

- **Standard mode**
  - Provides fast readings
  - Beeps twice when the 95% confidence level is reached, then terminates reading
Sampling Modes

- **Depth Index**
  - Indication of the amount of non-leaded paint covering the lead
  - \( DI \leq 1.5 \)
    - Lead near the surface
  - \( 1.6 \leq DI \leq 4.0 \)
    - Lead at moderate depth
  - \( DI \geq 4.0 \)
    - Lead deeply buried
Sampling modes

- **K&L mode**
  - Beeps twice when 95% confidence level is reached
  - Flexibility of continuing test up to user-defined maximum test time
    - Default: 20 secs
Unusual Request

- Contacted by Conservators for the Rare Book Collection
- Test the ink in a illuminated medieval manuscript
- XLp 300A provides qualitative data on other elements
Illuminated Medieval Manuscript

Authored by a monk from a French monastery. Includes a calendar and books from the Bible.
Illuminated Medieval Manuscript

- Illumination: the embellishment of a manuscript with luminous colors (especially gold)
- Calendars: most often precede devotional texts; identify feast days pertinent to the patron and the region

Source: www.leavesofgold.org
What caused the discoloration of the ink? Is there a difference in the ink?
Illuminated Ink

What caused the discoloration?
Testing
Results

Most peaks in "Low Energy Spectra":
0-40 keV
Results
Spectra: X-Ray Line

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Spectra: X-Ray Line

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Ce-Ka

Ce-Kb

35.00

42.50
Results

Rhodium (Rh)

Palladium (Pd)
Results

- Titanium (Ti)
- Potassium (K)
- Calcium (Ca)

Graph showing counts per second and energy levels for different elements.
Results

Copper (Cu)

Zinc (Zn)
Results
Results
Results

#328 has more Au and Pb
Results

#328

#330
#330 has slightly more Au but less Pb
Medieval Ink

- Sources included animals, plants and natural minerals
- Early scribes prepared own pigments
  - Recipes differed
- Early 13th century scribes began purchasing ingredients
  - Standard colorants began to emerge
Cause of Discoloration

- Incompatible colors?
  - Orpiment
    - Naturally occurring
    - Yellow
  - Darkens Lead and Copper
  - In Europe used to mix with azurite to make green
Nitron XLp 300A Limitations

- Designed specifically as a lead paint analyzer
- “Likely present” elements are not well defined
- Cd-109 emits gamma rays
  - Perfect for seeing all of the XRF lines of lead
  - Too much signal for other elements
- Detector specific for lead
  - Trade off is higher resolution
  - Hard to discern elements at low levels
Nitron XLp 300A Limitations

- Readings taken in Standard Mode
  - All at 1.4 seconds
  - Short duration to see low levels of elements
  - Longer the reading = more signal = more defined peaks
XL3t Niton XRF Analyzers

- Equipped with a 50 keV x-ray tube
- Lower detection limits for higher-Z elements
- Shorter measurement times
GOLDD Technology

- **Geometric Advantage**
  - Detector closer to sample
  - Higher count rate

- **Optimized Excitation**
  - Higher voltage = Higher excitation
  - Produce more X-rays

- **Large Drift Detector**
  - Use largest area drift detectors commercially available
  - Collect more X-rays
GOLDD Technology

- **Metal and Alloy Analysis**
  - Scrap metal sorting
  - Jewelry analysis & precious metal identification

- **Mining and Exploration**
  - Exploration
  - Mine mapping
  - Ore grade control

- **Environmental Analysis**
  - Soil testing
# Lead Paint Testing: Isotope vs. X-Ray Tube

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy Level</th>
<th>Analysis</th>
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<tr>
<td>Cd-109</td>
<td>22.5 and 88.1 keV</td>
<td>K and L shells</td>
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<tr>
<td>X-Ray Tube</td>
<td>50 keV</td>
<td>L shell only</td>
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Lead Paint Testing: Isotope vs. X-ray Tube

- **22.5 keV (isotope) and 50 keV (X-ray tube)**
  - Produce fluorescent L shell Pb X-rays
    - 10.55 and 12.61 keV
  - Too weak to escape layers of paint
    - Chance of missing deeply buried lead
    - False negative result

- **88.1 keV (isotope)**
  - Produces fluorescent K shell Pb X-rays
  - Enough energy to penetrate paint layers
Lead Paint Testing: Isotope vs. X-ray Tube

- X-ray Tube instruments have inconclusive range near 1.0 mg/cm² (lead-based paint)
  - Cannot determine reading + or -
  - Have to collect paint chips for lab analysis
  - Provide inconclusive results 16% of all samples
  - Provide false-positive results 2.5% of all samples
  - Provide false-negative results 1.9% of all samples
Conclusions

- XLp 300A is designed for lead paint analysis
- Other XRF analyzers are more suited for detecting other elements