Poisoned Pages

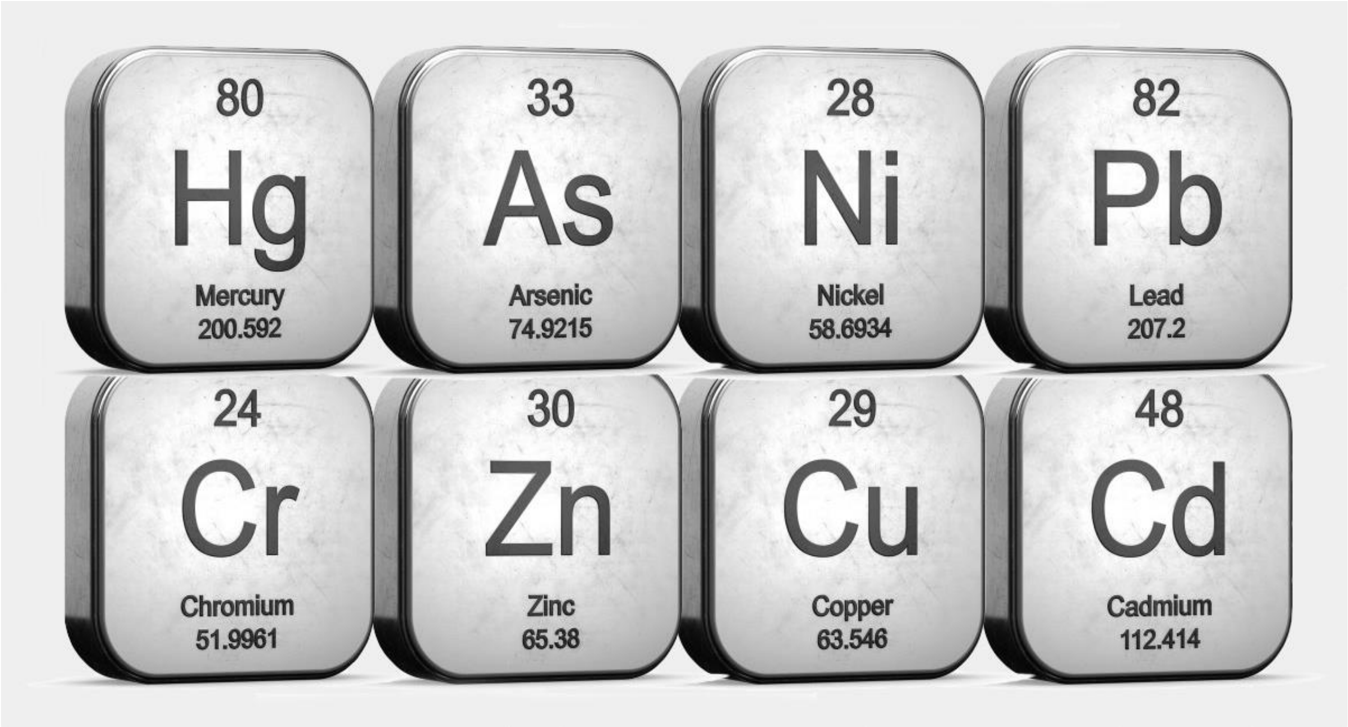
Testing For Toxic Elements in 19th Century Book Bindings

Brantley Harriman and Ethan Coyle

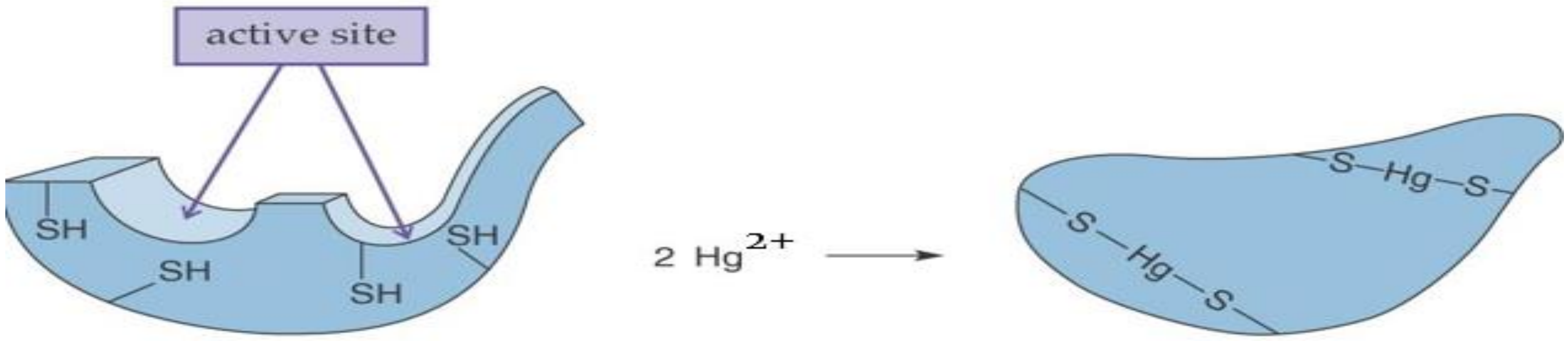

YAMAHA

Heavy Metals as Toxicants

- Heavy metals are a unique class of toxicant that occur and persist in nature.
- Typically defined as high density, atomic weight, or atomic number.
- Mercury (Hg),
  Lead (Pb), Copper(Cu), Arsenic (As), Chromium (Cr), and Iron (Fe)



Https://allamericanenviro.com/heavy-metals-effects-of-soil-contamination-on-the-ecosystem-human-health/



Active Enzyme

Inactive Enzyme

Mercury acts as an inhibitor, bonding with sulfur in enzymes to block activation sites. Inactive enzymes are unable to contribute to crucial metabolic processes.

Buell, P.; Girard, J. *Chemistry Fundamentals 2e*; Jones & Bartlett Learning, 2002.

Historical Use of Heavy Metals

- Heavy metal-based pigments and paint grew in popularity through the 19th century.
- Used to dye book cloths, tending to be more of an expensive process.
- Mixing pigments was also common due to produce other colors.

Arsenic

- Arsine gas likely killed Napoleon.
- Use in cosmetics and clothing.
- Used by the Romans as a poison
- Used as a food dye in sweets like green blancmange
- Scheele's green was known to be poisonous.

Lead

- Lead white can be seen in many famous paintings of the 19th century.
- Venetian ceruse was a popular makeup that contained lead white, used by Queen Elizbeth I.
- Lead was also used as a pewter plate. Problem when eating tomatoes.

Lead pipes have been around for centuries.

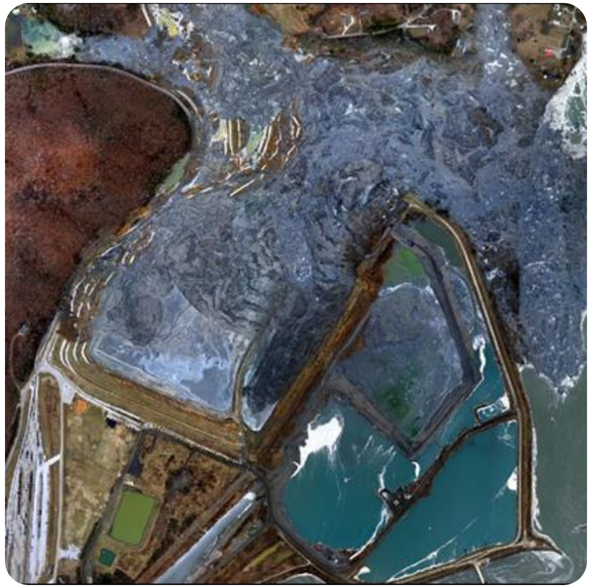
Mercury

Mad as a hatter.

Qin Shi Huang 's death is often attributed to mercury poisoning in his pursuit for eternal life.

Coffins in a Bottle

Dr. Karen Wetterhahn



Chromium

- Erin Brockovich

Chromium in art

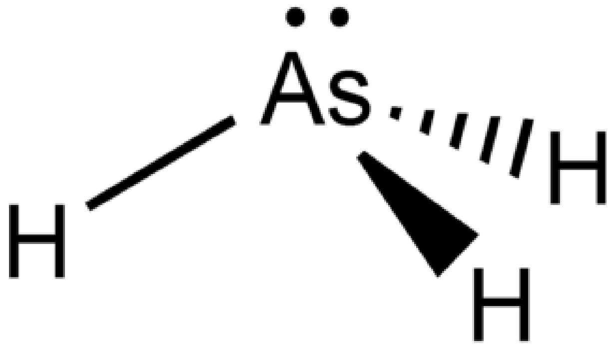
Tennessee Coal Ash Spill

Breathalyzers (BAC)

Pigment Name	**Chemical Compound**	**Chemical Formula**	**Color**
Chrome Yellow	Lead Chromate	$PbCrO_4$	
Paris Green	Copper Acetoarsenite	$Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$	
Scheele's Green	Copper Arsenate	$CuHAsO_3$	
Lead White	Lead (II) Carbonate	$2PbCO_3 \cdot Pb(OH)_2$	
Vermillion	Mercury Sulfide	HgS	
Prussian Blue	Iron (II) Hexacyanoferrate (II)	$Fe_4[Fe(CN)_6]_3$	
Orpiment	Arsenic (III) sulfide	As_2S_3	
Lead Red	Lead (II,IV) Oxide	Pb_3O_4	

Risks

- Over time, heavy metal-based pigments become friable.
- Pigments are susceptible to rubbing off when touched and contributing to dust.
- Inhalation of heavy metals can result in a variety of major health risks.
- Arsenic-based pigments can react with water to release arsine gas (AsH_3).



Hypothesis

We believe that a sizable portion of mid-19th century books in the Special Collections of the Walker Library contain heavy metal-based pigments such as lead, arsenic, mercury, and chromium, which can be tested through non-destructive X-ray fluorescence analysis. The identification of these toxicants will confirm the need for implementing revised safety protocols for the handling and storage of these historical materials to mitigate health risks to library staff and students.

Experimental Setup

Resistant lead (Pb) apron-->

Experimental Book in use-->

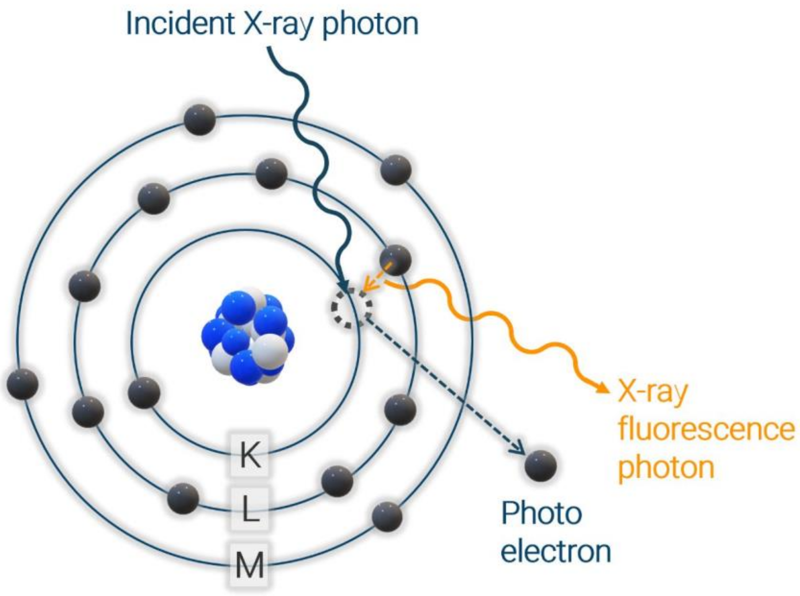
Thick Sheet of solid lead
(Underneath) -->

<--Ring stands

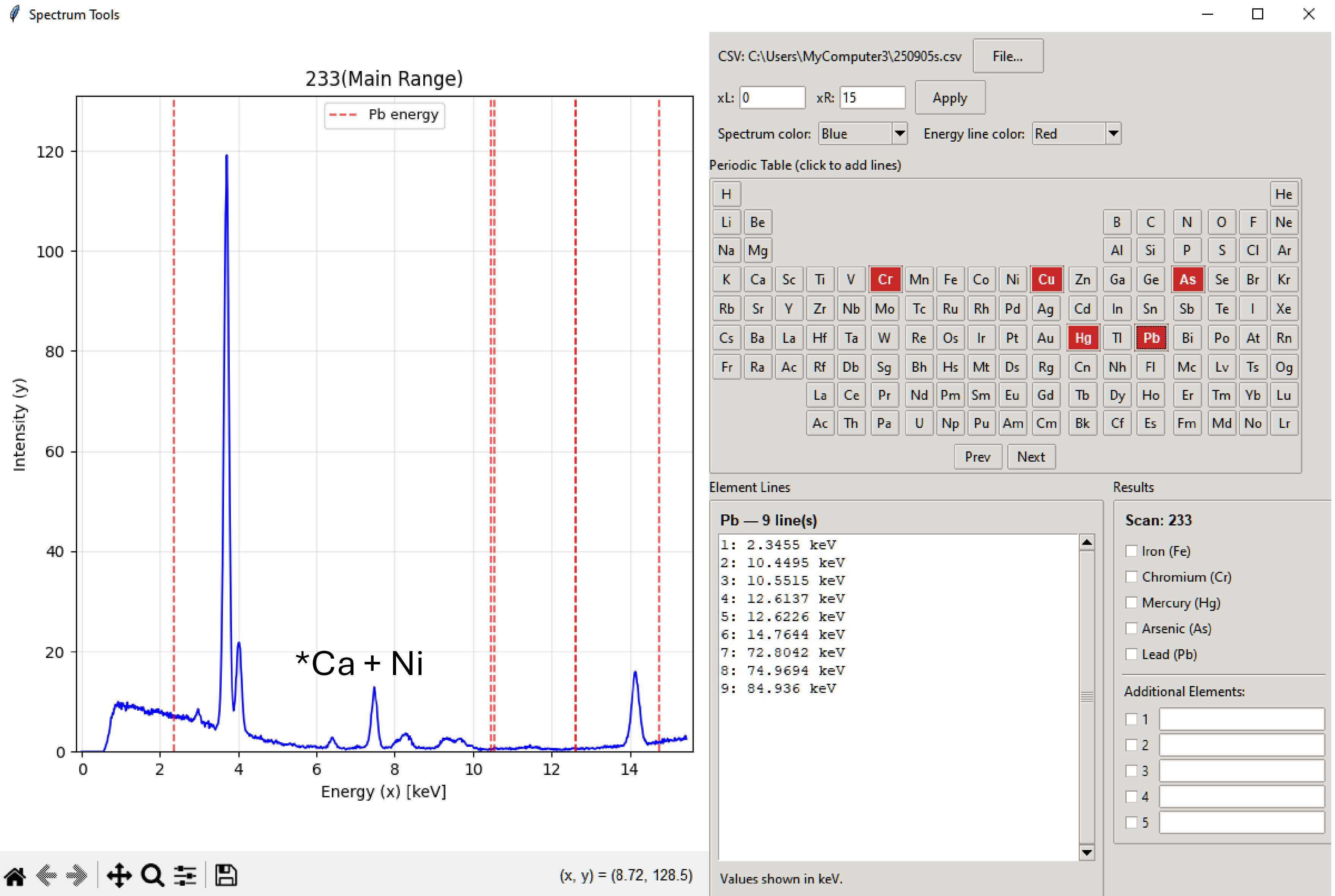
[Niton™ XL3t X-Ray Fluorescence (XRF) Analyzer]

Methods

- Portable XRF instrument was held in place for 180 seconds while taking scans at 3 different energy levels.
- The XRF was used in the "Soil" mode, which allowed for high, main, and low energy levels.
- Low energy levels were utilized to detect Cr, which displayed more distinct peaks at lower energy levels.
- Raw data files were then exported to a group developed python code to ensure no false positives were present.



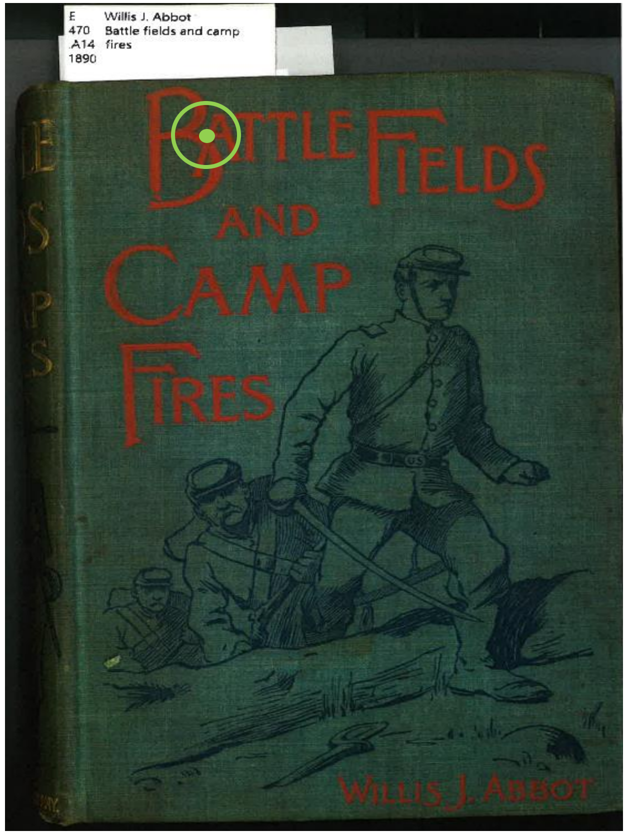
Python Interface of Blank Scan



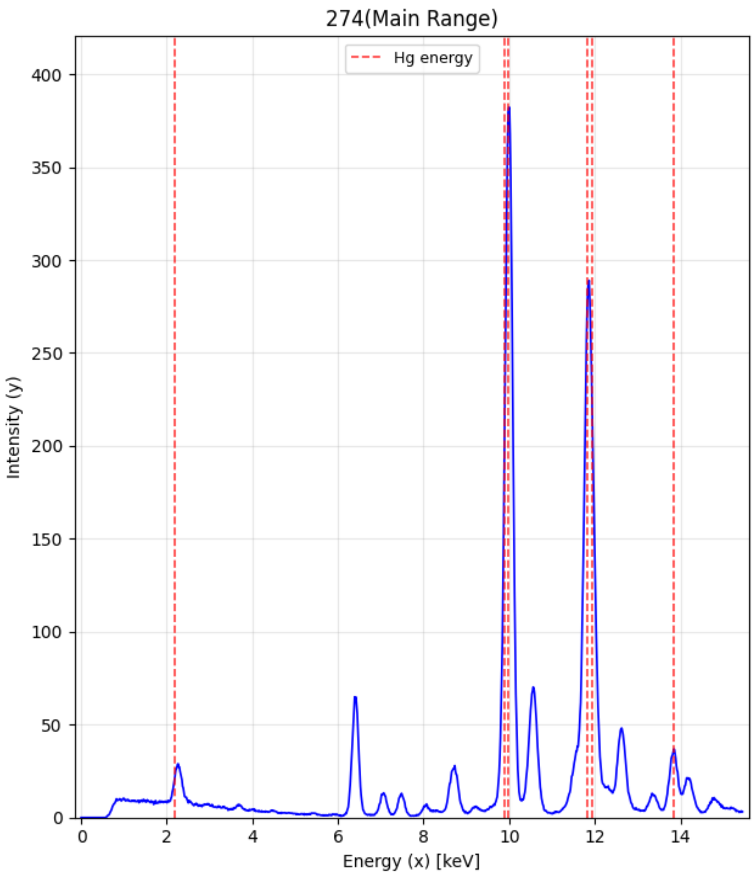
Analysis

- Spectra interpreted by the Python code allowed for the identification of heavy metals in the book cloth.
- The peaks were compared with reference energy levels.
- The Python code also determined a list of possible pigments by comparing the known metals present with a list of pigments and their chemical formula
- Because the exact concentrations of heavy metals cannot be determined, we are only able to make a tentative identification of pigments

Collecting and Interpreting Data



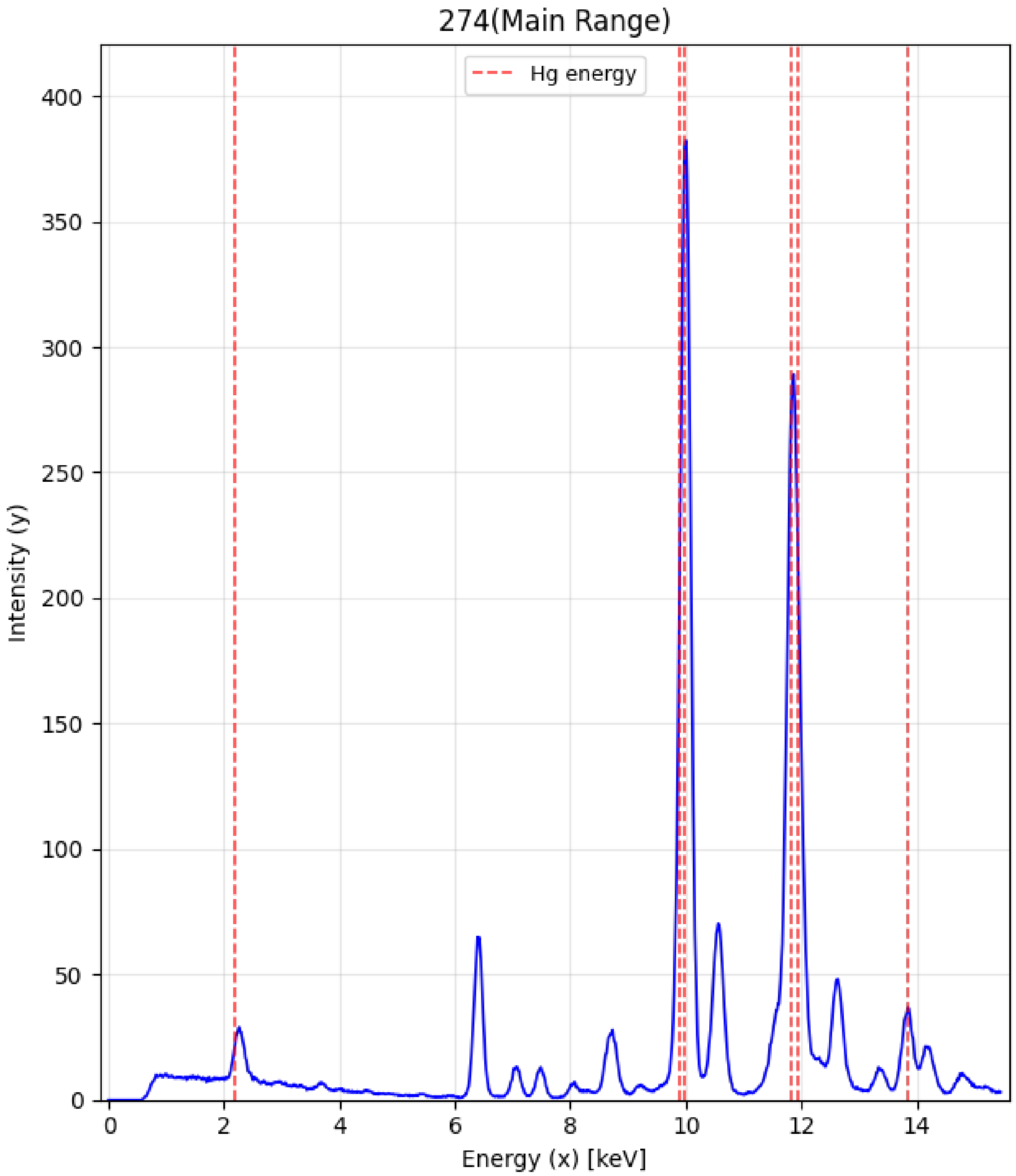
Sample Selection



Spectral Data

Vermillion Pigment

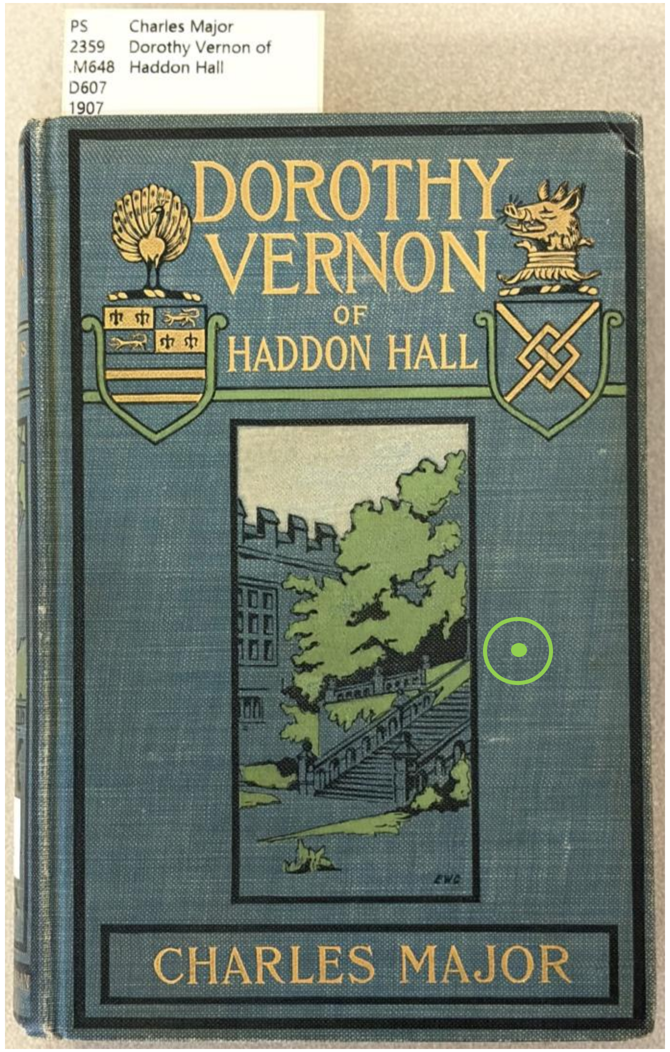
Make Conclusions



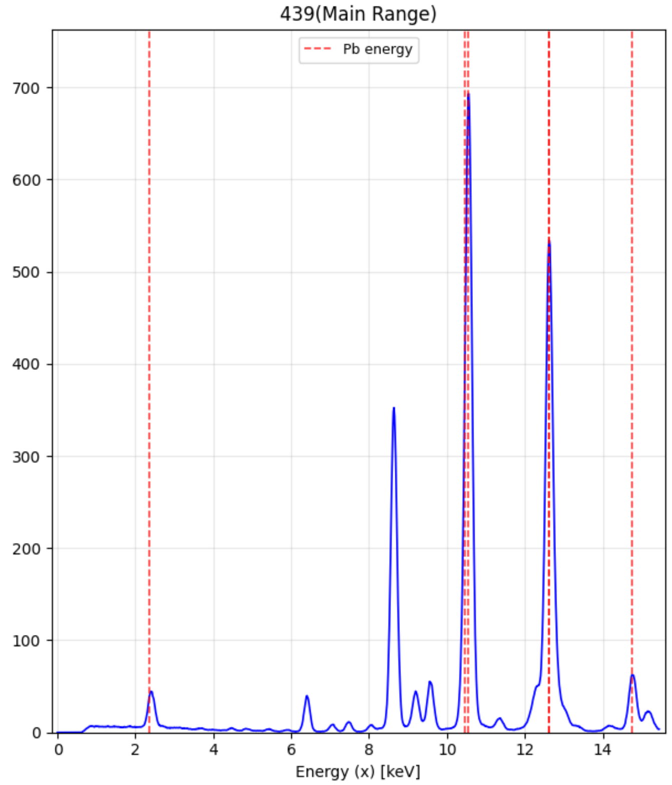
- The spectrum shows high relative concentration of mercury

- Lesser peaks show Fe + Pb

Collecting and Interpreting Data

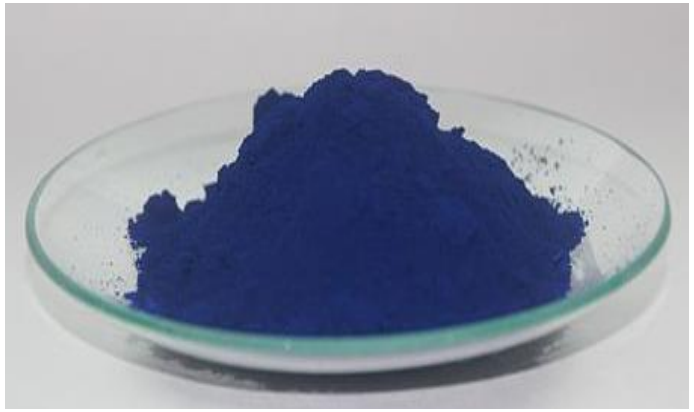


Sample Selection



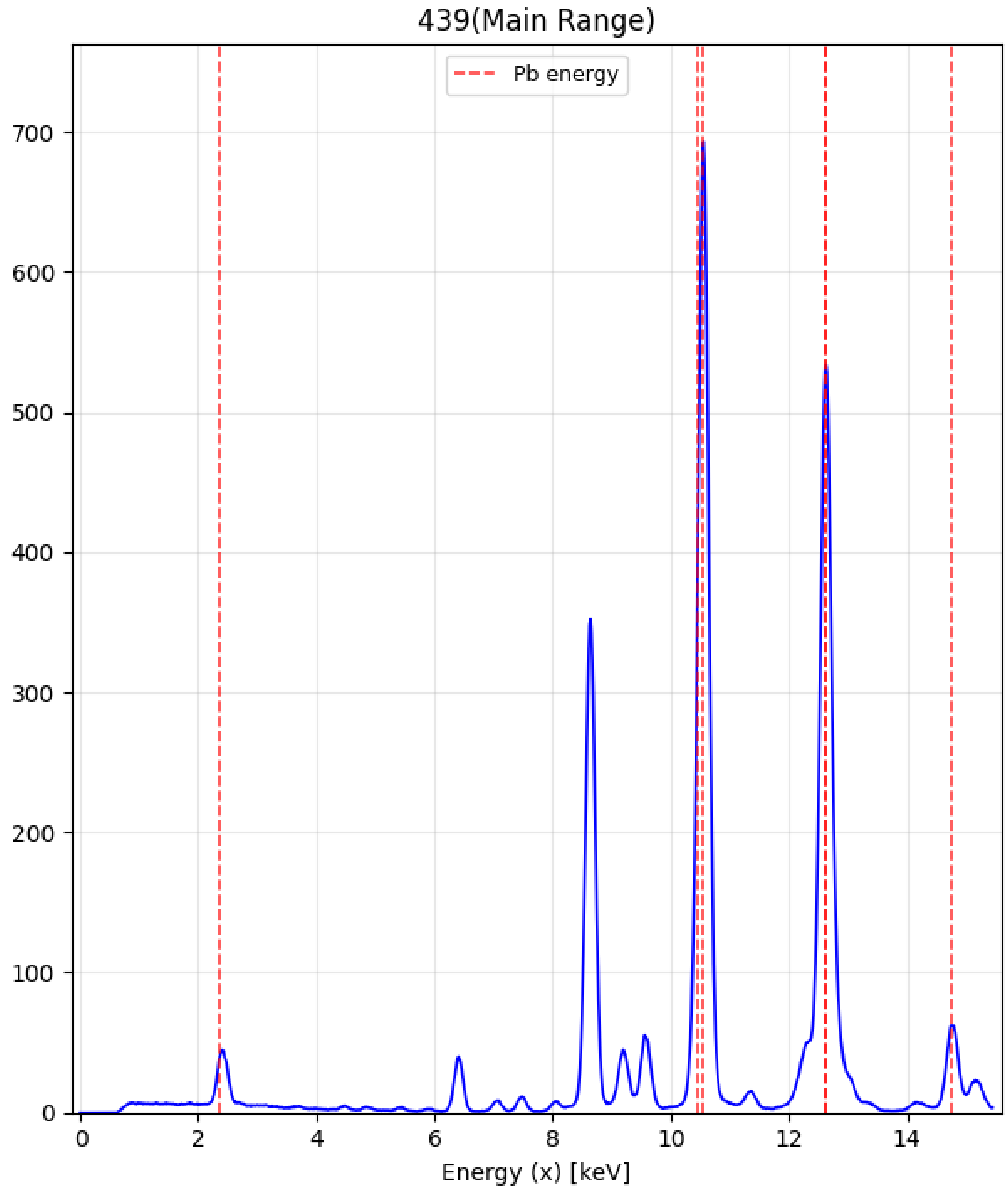
Spectral Data

Prussian Blue Pigment



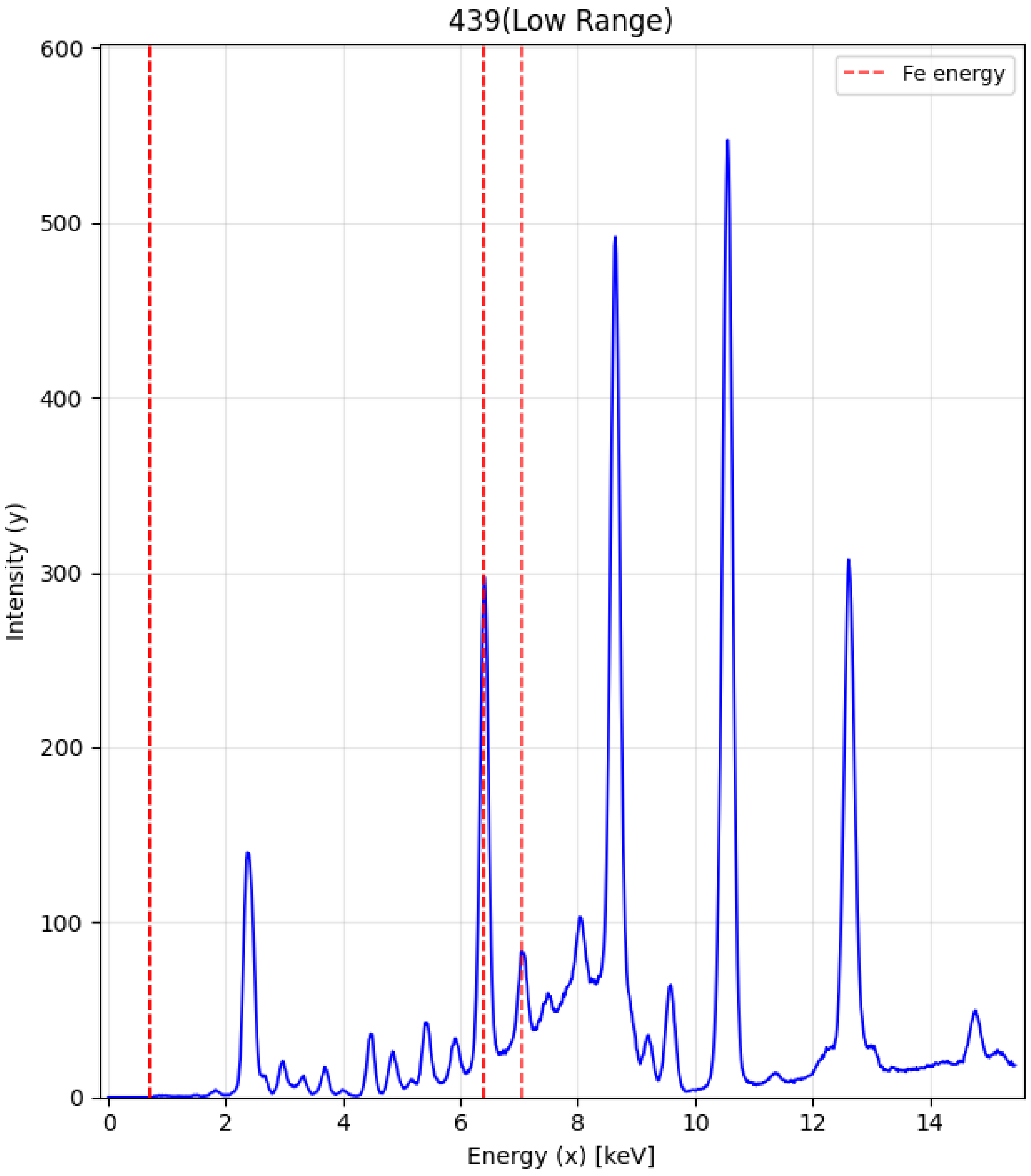
Make Conclusions

-Lead (Pb)

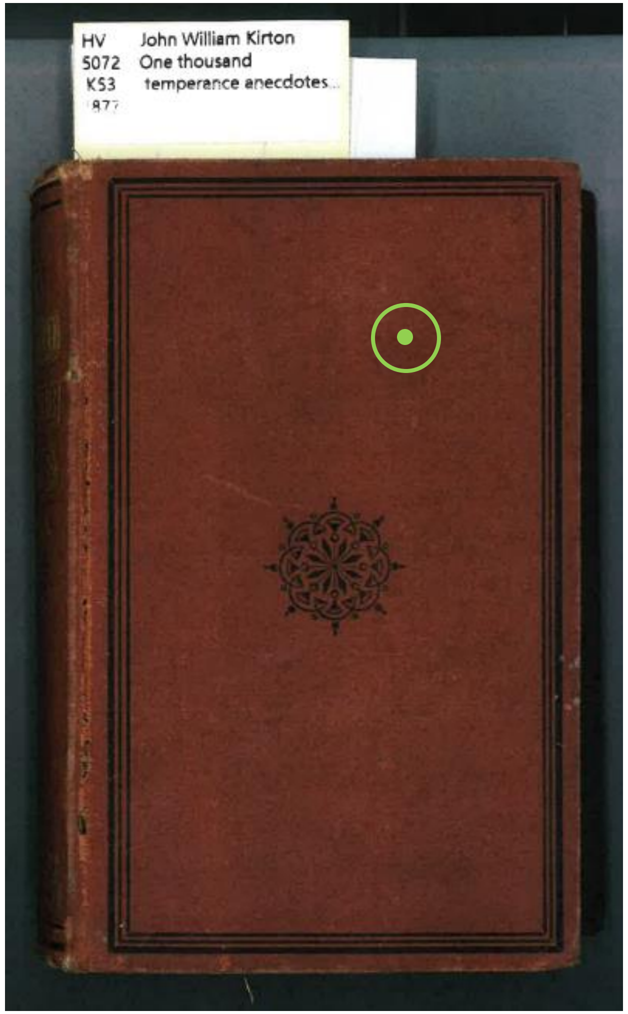


+

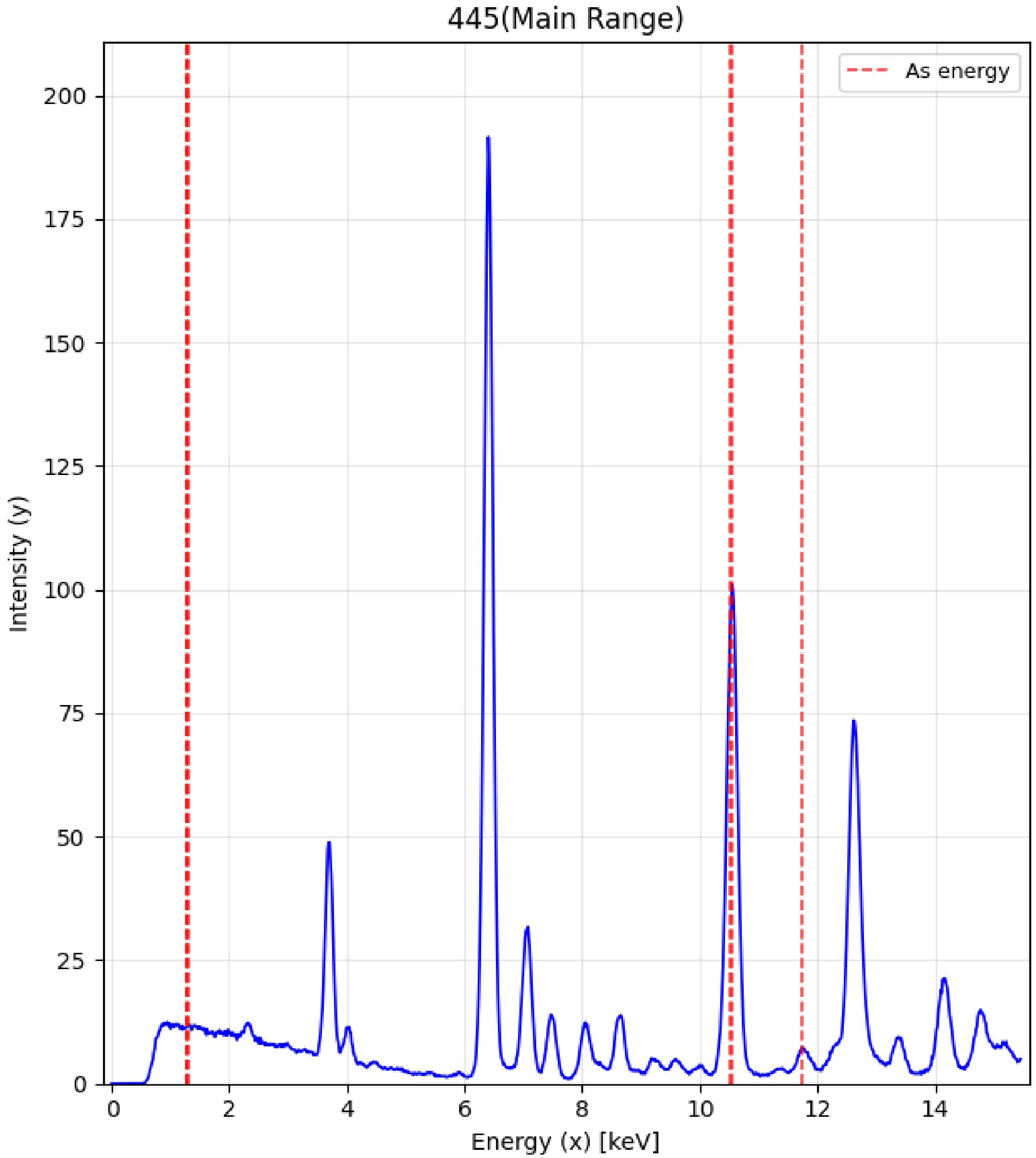
-Iron (Low Range Mode)



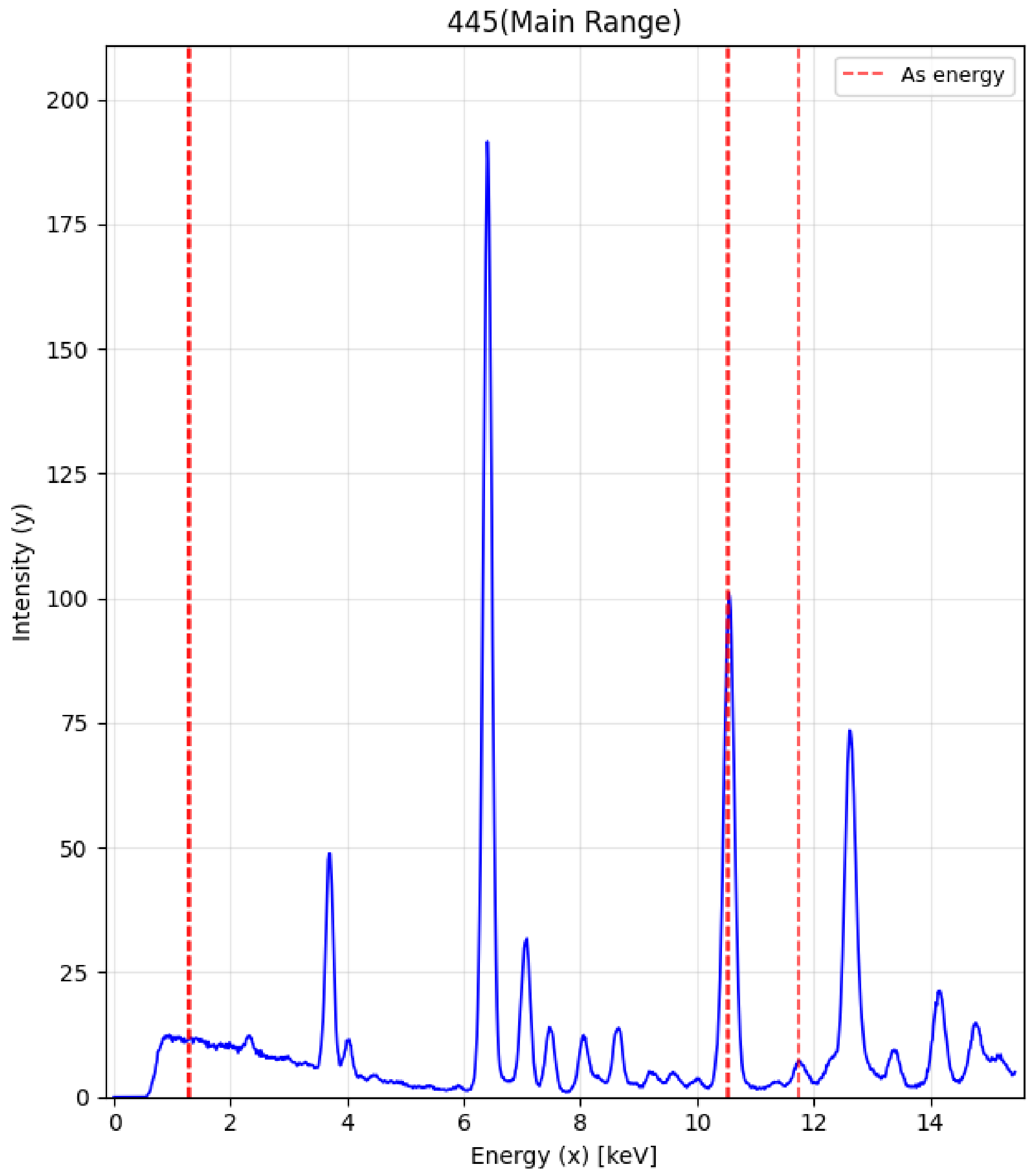
Arsenic Example



Sample Selection



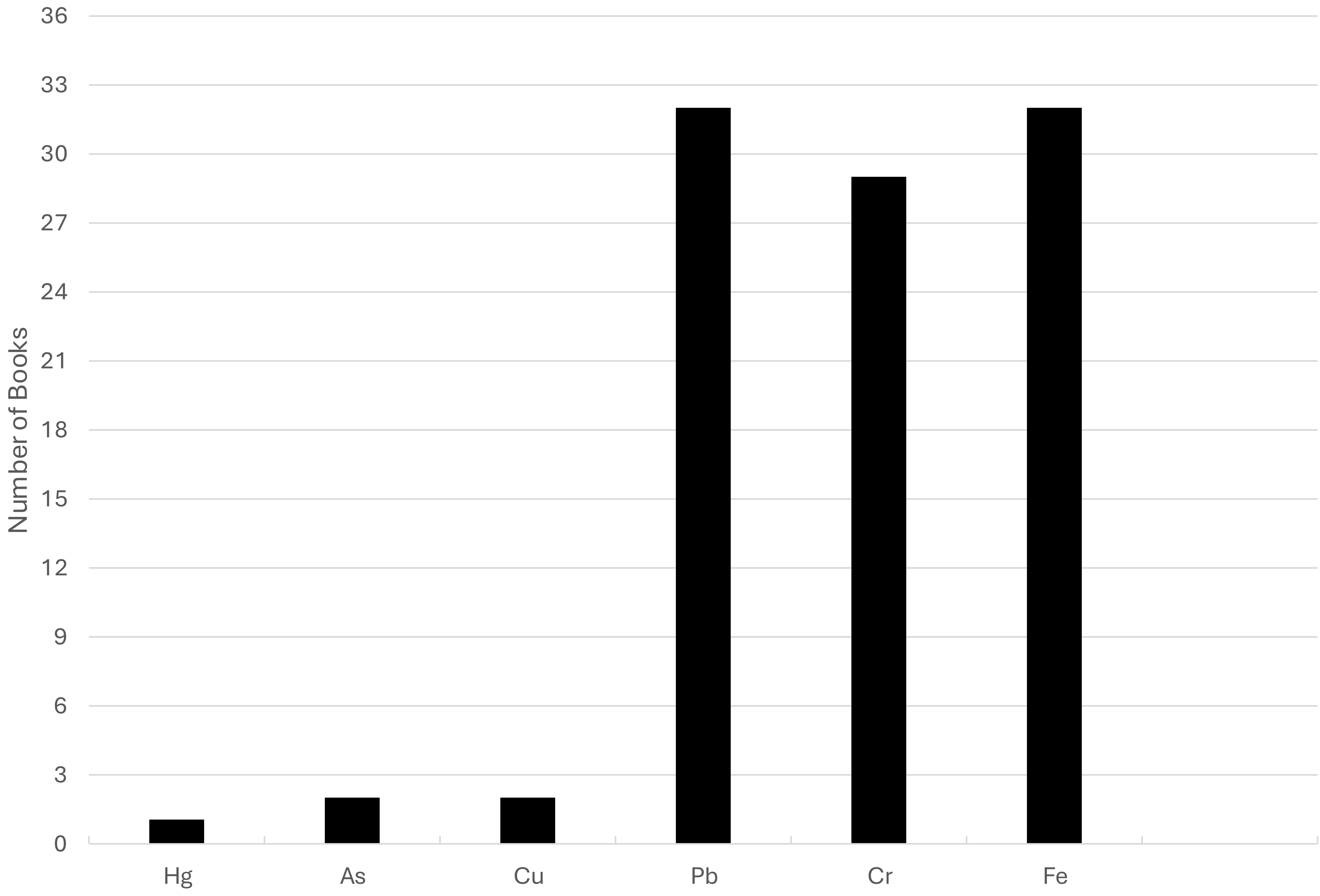
Spectral Data



- Very small, yet defined peak at ~10.5 *KeV*.
- The XRF instrument displays elemental "hits" in real time post scanning.
- The Software is used to confirm and catalog positive matches.

Results

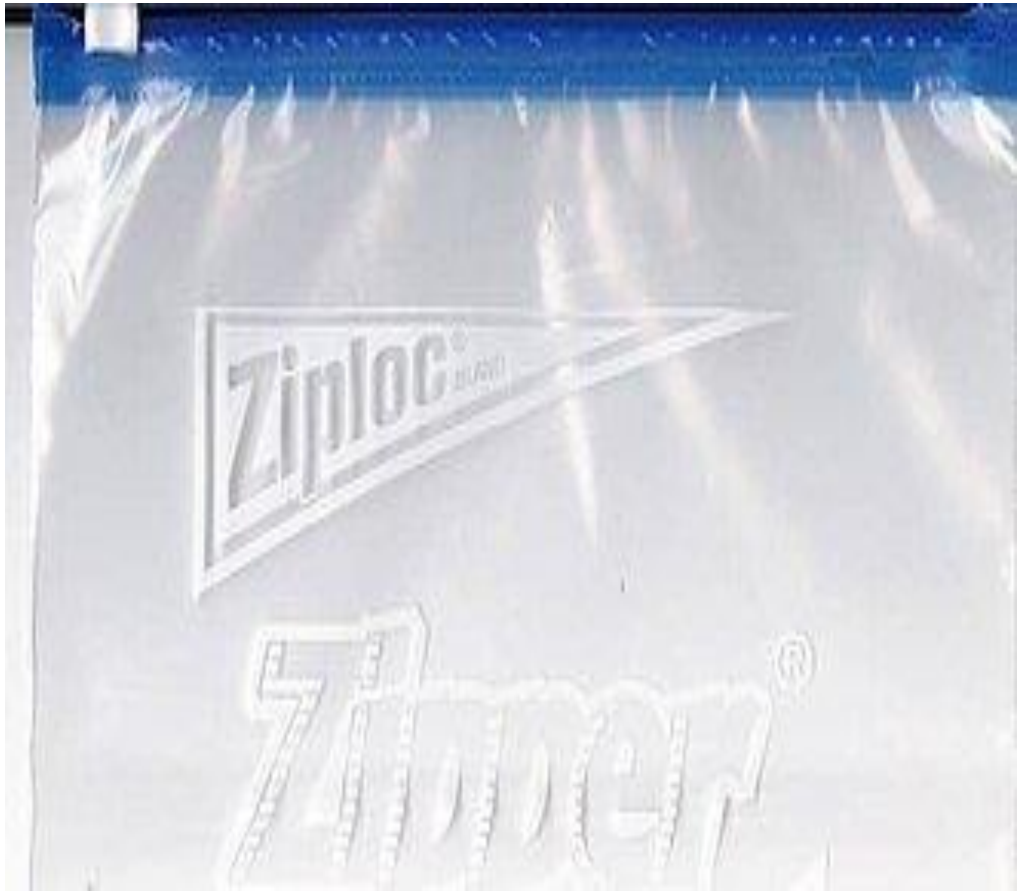
- 34 books scanned this semester
- 33 of these books had at least one heavy metal (97.1%)
- Pb and Fe were most common amongst the samples



Research Importance

- Biblio-toxicological research at MTSU highlights the need for safe handling procedures and long-term storage solutions of the books.

Proposed Solution

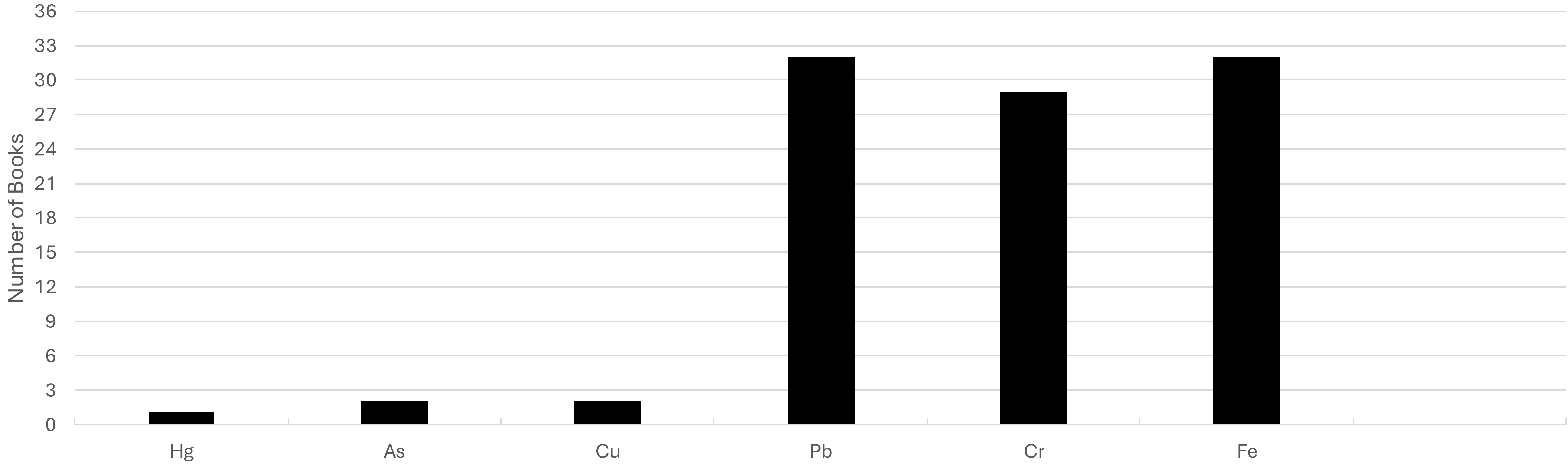


- Some toxic book researchers suggest storing old books in polyethylene bags.
- Mold growth is a concern with this method.
- Use of silica packets could prevent mold growth.

Tedone, M.; Grayburn, R.; Wittine, J. Handling "Poison Books": Dry *Versus* Wet Scenarios. *Studies in Conservation* **2025**, 1–8.

Conclusions

- Of the 34 books scanned this semester, 33 were found to contain toxic pigments (97.1%).



- Future MTSU researchers will continue to scan books as part of ongoing efforts

Acknowledgements

Organizational Support

- URECA
- James E. Walker Library
- Department of Chemistry

Additional Support

- Dr. John DiVincenzo
- Mr. Clay Trainum

Project Team

- Ms. Brittney Cupp
- Ms. Susan Hanson
- Ms. Susan Martin
- Dr. Sarah Pierce
- Mr. Jessie Weatherly

MTSU
UNDERGRADUATE RESEARCH CENTER

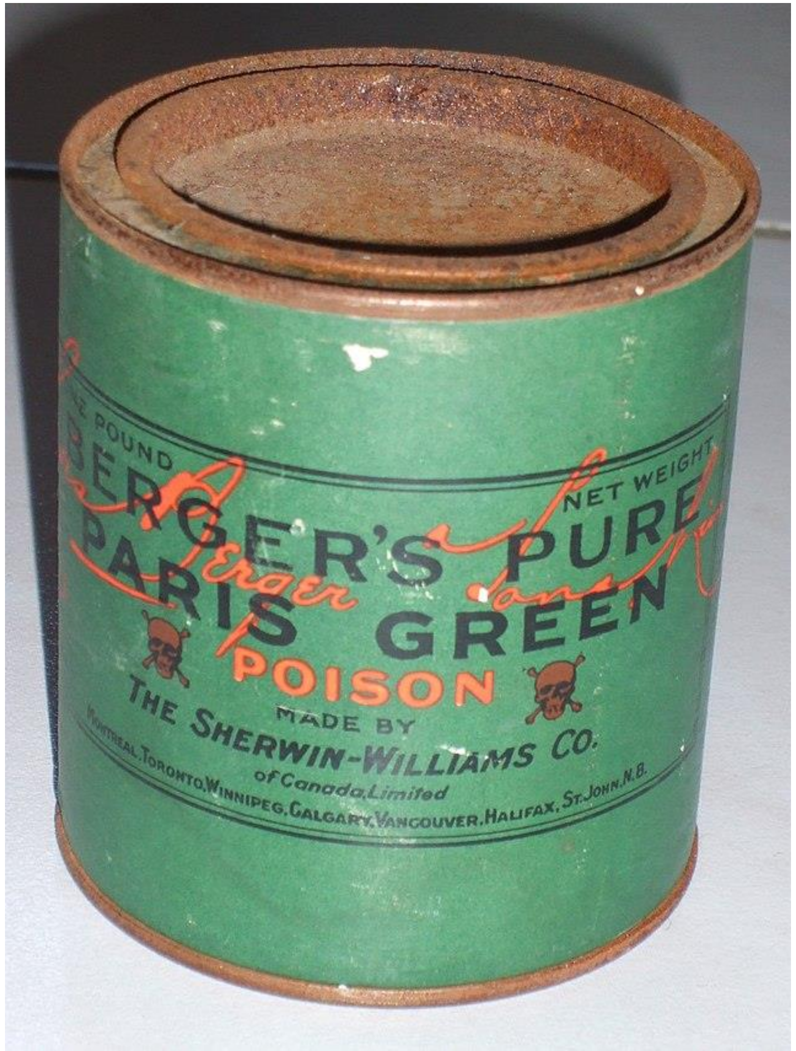
MIDDLE TENNESSEE
STATE UNIVERSITY

Questions ?

UNDERGRADUATE RESEARCH EXPERIENCE AND CREATIVE ACTIVITY
URECA

MTSU

UNDERGRADUATE RESEARCH CENTER



MIDDLE TENNESSEE STATE UNIVERSITY

UNDERGRADUATE RESEARCH EXPERIENCE AND CREATIVE ACTIVITY

MT

URECA