Limitations of Handheld XRF Instruments as Quantitative Tools for Analyzing Heavy Metal Pesticides on Organic Art Objects

IARC Symposium "Native Collections and Pesticides: Testing, Analysis and Mediation"

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Introduction

- Handheld X-Ray Florescence instruments are used to test for heavy metal pesticides in ethnographic objects in museums. These objects are made up of organic materials varying in thickness, density, surface features, and shapes. These variables will affect the readings along with the errors inherent in the handheld analyzers.

Summary

- Brief info and history about pesticides and their detection (slides 3-11)
- X-Ray Fluorescence technique
- XRF instruments
- Limitations of the XRF instruments - experimental demonstrations (slides 22-41)
- Documentation done at the Southwest Museum

What are pesticides?

- Museums provide food (organic objects) and a suitable habitat (quite, dark, and comfortable place) for pests.
- Pesticides, fungicides, herbicides, and other substances are chemicals that have been used to prevent, destroy, or repel pests in order to preserve museum collections
- Pesticides applied in the past are now known to be toxic to humans

What are pesticides?

- Poisons or toxins are used to kill pests by entering the organisms through their:
  - Respiratory systems (inhalation)
  - Digestive systems (mouth)
  - Dermal contact (skin)
- come in many names (trade names, chemical names, synonyms)

What are these toxic pesticides applied in the past?

- Types of pesticides used in the museums:
  - Inorganic pesticides - contain heavy metals that are highly toxic to any living creature. Arsenic, lead, and mercury containing ones are common. Due to their physical and chemical nature they are persistent
  - Other type of pesticides - are usually volatile organic chemical compositions, yet poisonous by-products may not readily be decomposed
  - Sometimes the mixture of the two

The history of pesticide use

- Pesticides use by field collectors and museum personnel on natural history collections and ethnological artifacts was common from the late 19th century to the mid-20th century.
- Arsenical soaps and mercuric chloride were used in taxidermy collections, which was adapted later to natural history and ethnographic collections

The history of pesticide use

- Along with inorganic pesticides some toxic organic pesticides such as dichloro-dihpenyl-trichloroethane (DDT), dichlorvos (DDVP), and mothballs (paradichlorobenzene or naphthalene) have been used.
- Applications involved fumigation, dusting, spraying, and sometimes shoveling chemical concoctions onto artifacts

The history of pesticide use

- 1980 arsenic containing pesticides are restricted, but the utilization was ceased in the late 80s.
- Mercuric chloride restricted in the 1970s and ceased in the late 80s.

The pesticide issue

- NAGPRA objects
  - 1995 Hopi "Friends" at Harvard Peabody Museum contaminated with As
- Handling the sacred objects extensively during initial cleaning, repair, and preparation for storage, almost daily during their long-term care
- Storage places used by most family members – newborns to elders, were underground ceremonial chambers that were overcrowded and had no ventilation along with houses where dry food was kept and daily activities took place.

The pesticide issue

- NAGPRA (January 1996 addition 10.10(e) t) that gives the museums the responsibility to report on pesticides treatment histories.
- Seminars
- It was required that a proper documentation to inform tribes during repatriation process is prepared by the museums because “there was no recognition of the educational needs of tribes who would need to interpret the technical information” (Loma’omvaya).

The pesticide issue

- It was decided toxicologists and museum health professionals should be involved in to decide the levels of toxic inorganics (Pb, As, and Hg) found in these objects.
  - Nature of the pesticide
  - Place of the pesticide within the artifact
  - Amount of the pesticide in/on the artifact

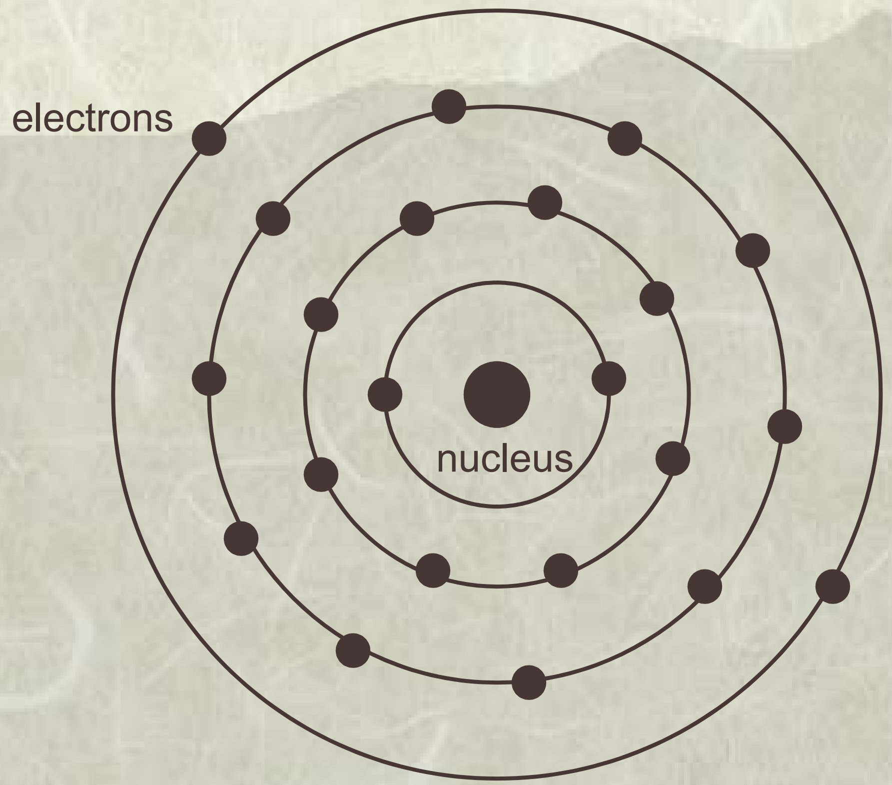
Detection and analysis of inorganic pesticides

- No sampling required
  - Visual inspection (qualitative)
  - Spot tests (qualitative)
  - Portable XRF analysis (semi-quantitative)
- Sampling required
  - ICP-AES (quantitative)
  - AAS (quantitative)

X-Ray Florescence Technique

- –Offers elemental analysis of materials
- –Elements with an atomic number of 15 (phosphorus) and higher can be identified with air path XRF instruments
- –For lighter elements a vacuum can be used.

X-Ray Florescence Technique



Bohr model showing the structure of a Titanium atom

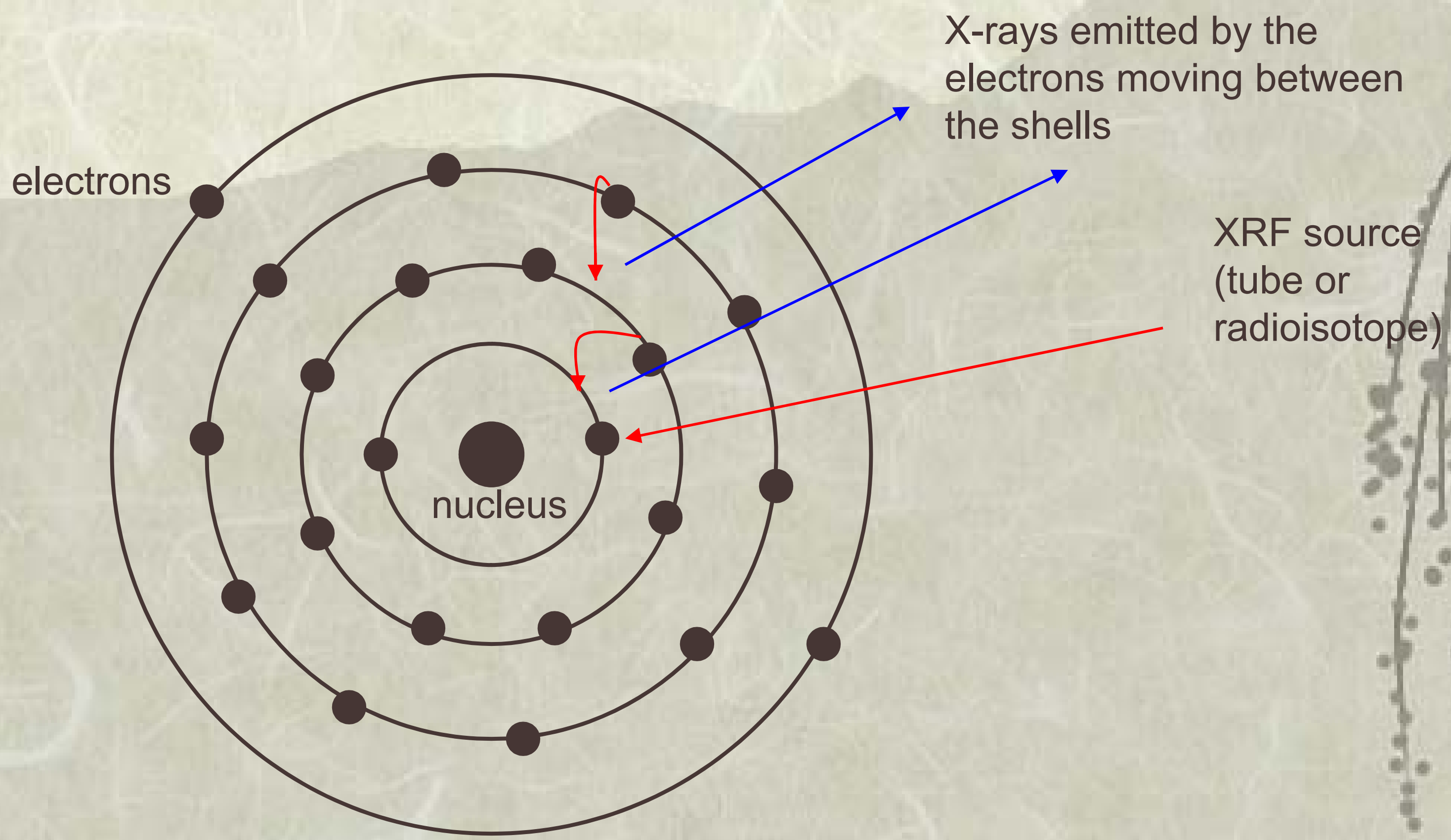
Atom: basic unit of matter consisting of:

-Nucleus

-Protons (+ charged particles) and neutrons (neutral)

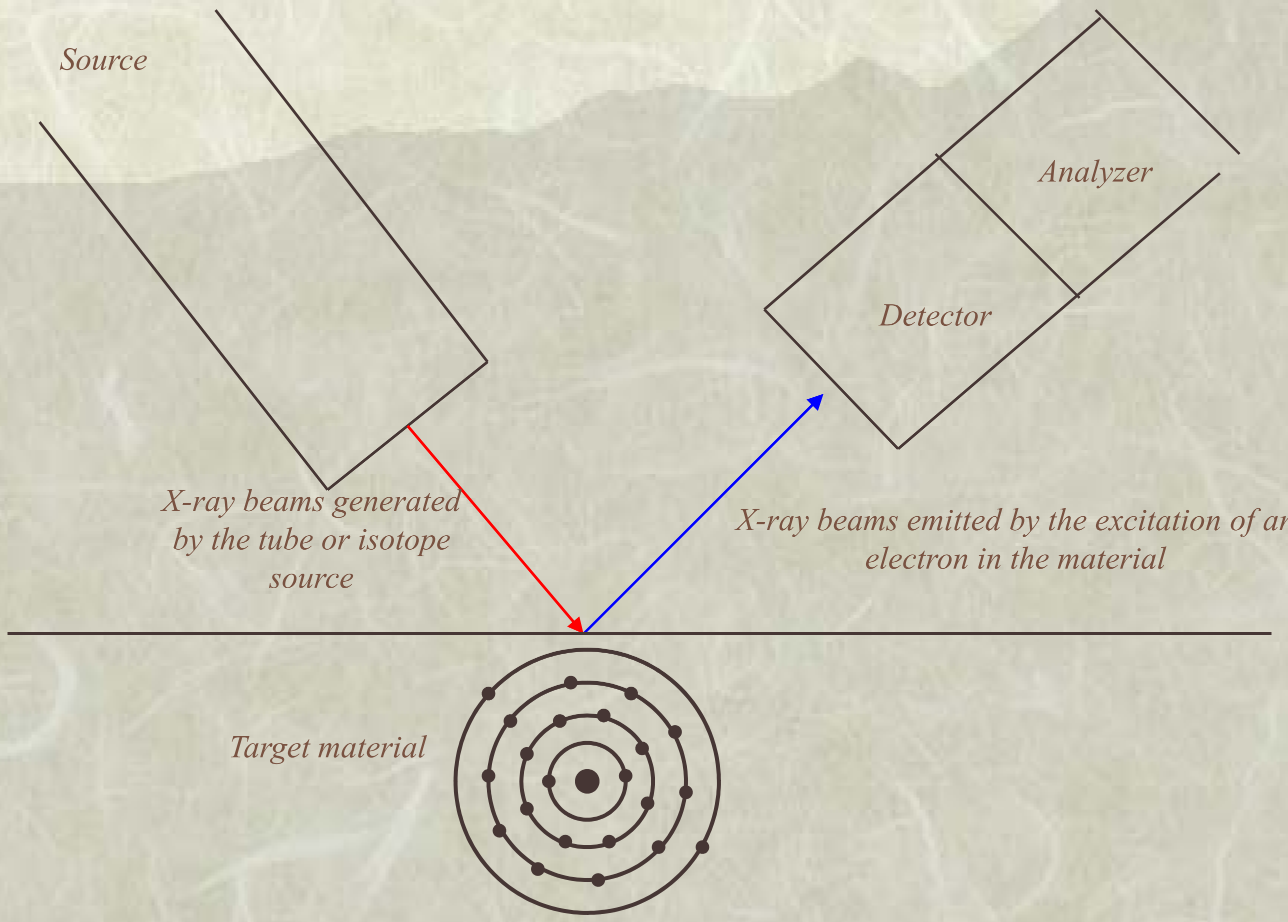
-Electron cloud (- charged particles)

X-Ray Florescence Technique



Bohr model showing the structure of a Titanium atom

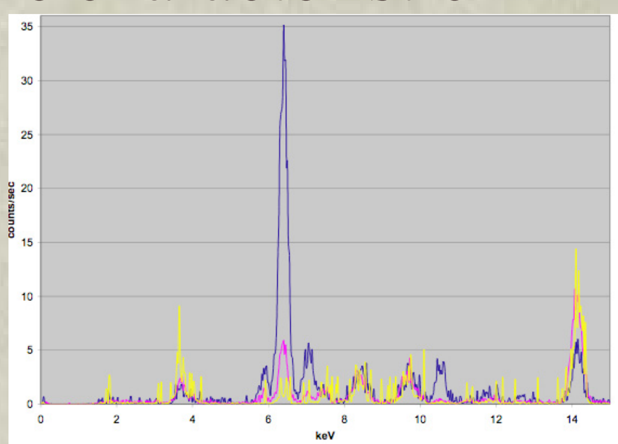
How portable XRF instruments work



How portable XRF instruments work

Results are reported as:

- Tabulated numerical results showing the amount of metals found
- Spectra showing each elements peak count of the characteristic energy levels



Handheld XRF analyzers have advantages and disadvantages

Some advantages are….

Detection and analysis with handheld XRF instruments

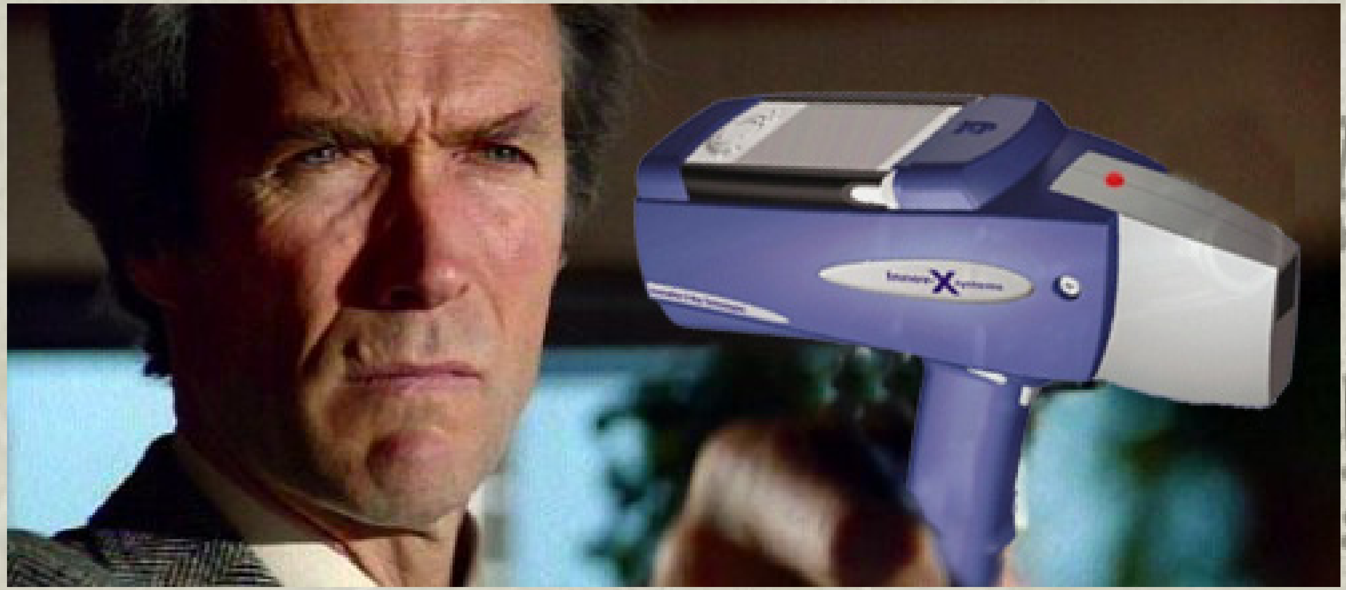
- Cost-efficient
- Fast

Detection and analysis with handheld XRF instruments

- In-situ analysis

Detection and analysis with handheld XRF instruments

- Easy to use



Limiting factors in quantitative analysis of organic objects

Some disadvantages of the portable XRF instruments are due to:

- Object
- Instrument
- Or both

Limiting factors in quantitative analysis of organic objects

Some disadvantages are:

- Relative humidity and/or temperature affect both the analyzer and the substrate
- Density and geometry of the substrate, instruments calibrated for the soil and scrap metal industry.
- Interferences caused by elements other than the metal of interest (by absorption, scattering, or enhancing the fluorescence)
- Detection limits of the element of interest
- Elements in question are not homogenously distributed in or on the artifact

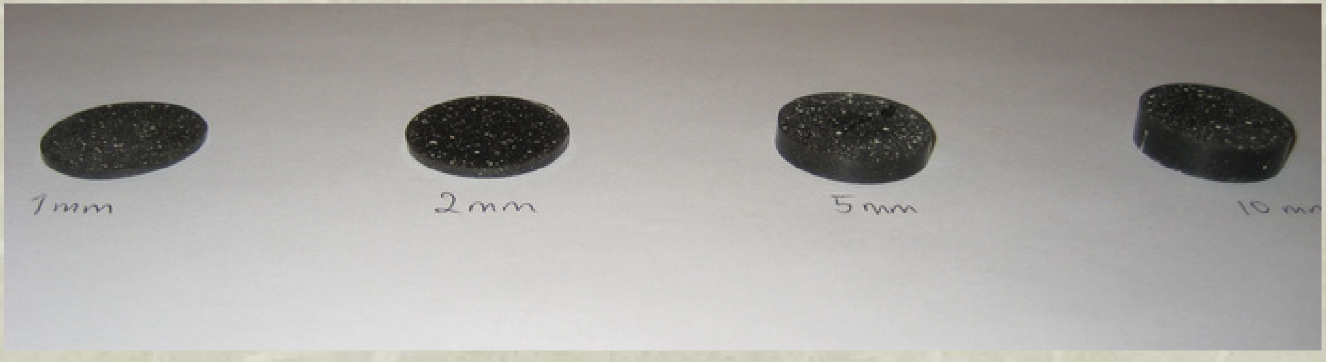
Limiting factors in quantitative analysis of organic objects

Let's investigate these limiting factors

- Density and geometry (thickness and surface geometry) of the substrate
- Interferences caused by elements other than the metal of interest (by absorption, scattering, or enhancing the fluorescence)
- Relative humidity and/or temperature

Experimental design

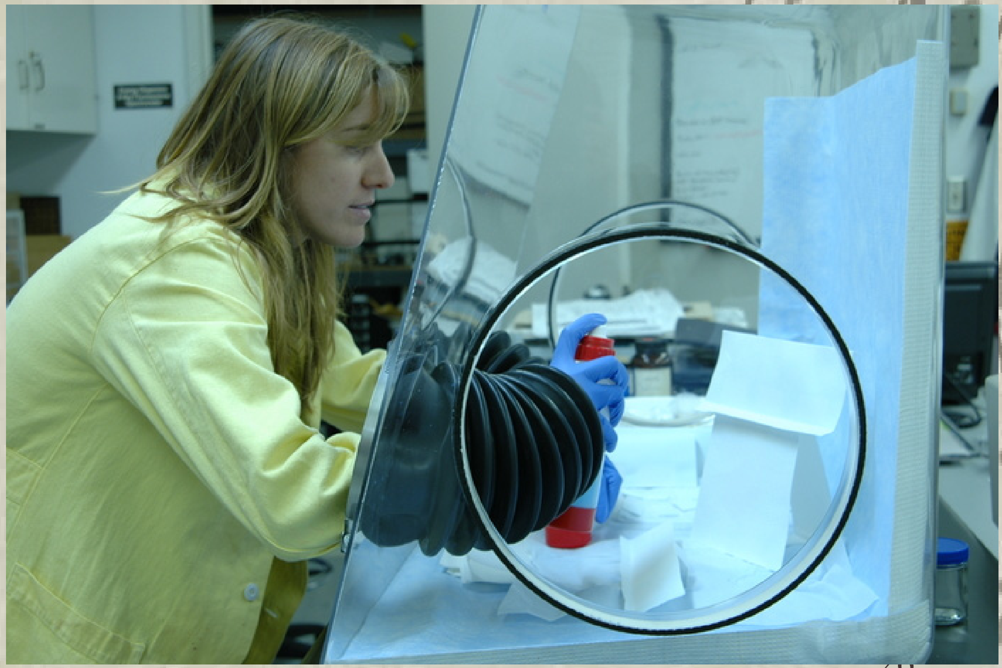
- Thickness
  - Epoxy samples
  - Paper samples
  - Wool samples



A known amount of copper oxide embedded in Devcon epoxy and cut in different thicknesses

Experimental design

- Thickness
  - Epoxy samples
  - **Paper samples**
  - Wool samples



Blotter paper sprayed with a known quantity of CuSO4 solution

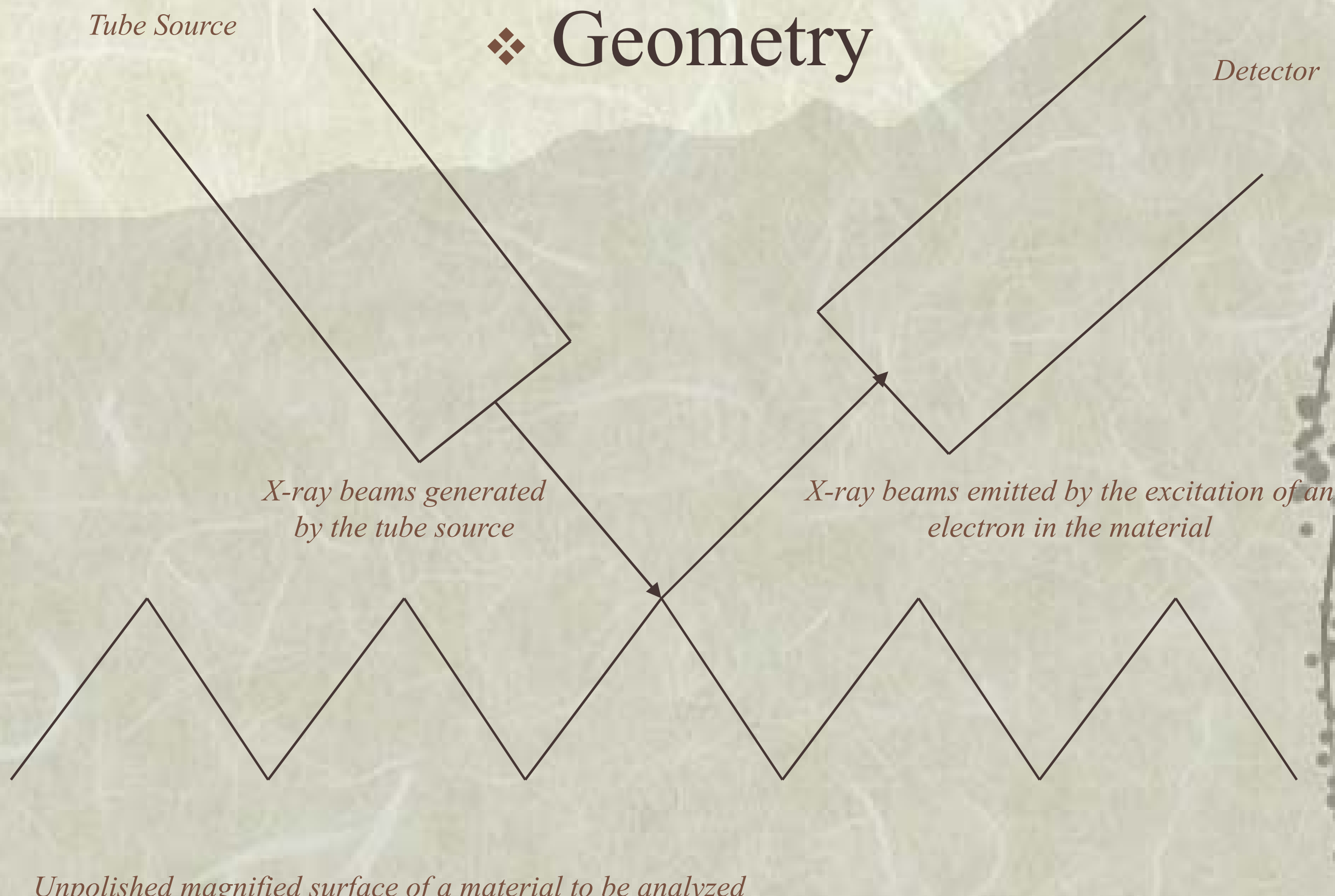
Experimental design

- Thickness
  - Epoxy samples
  - Paper samples
  - **Wool samples**

Wool fabric samples sprayed with the same amount of CuSO4 solution

Experimental design

- Geometry

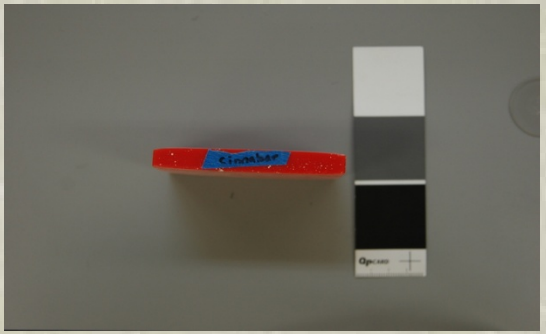


Experimental design

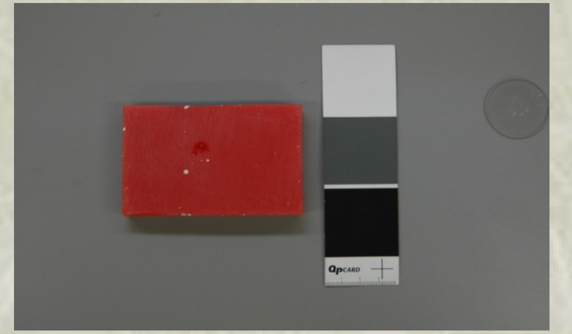
- Geometry

Cinnabar embedded in Loctite epoxy sample before it was cut into three equal pieces

a. Top surface



b. Thickness

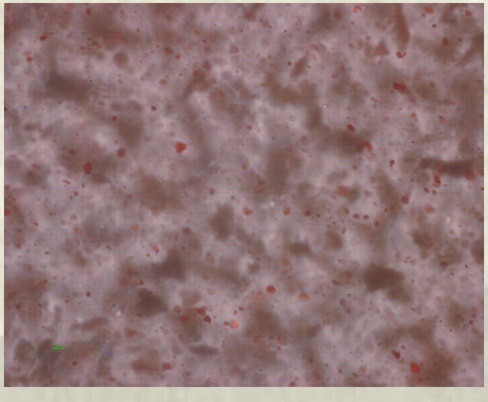


c. Polished bottom surface

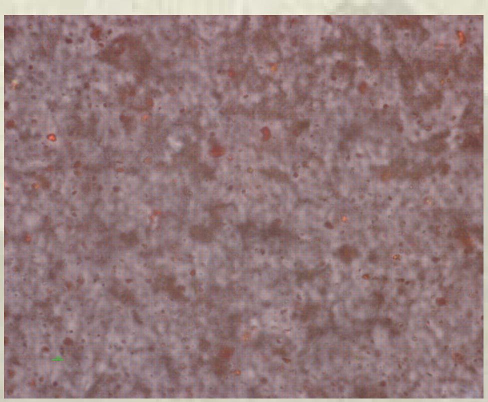
Experimental design

- Distance

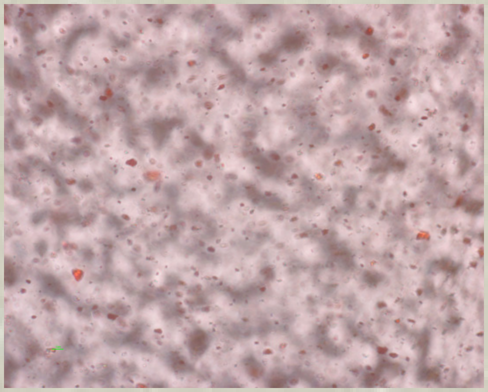
Images of cinnabar samples taken with the Nikon Microphot Polarized Light Microscope showing cinnabar distribution.



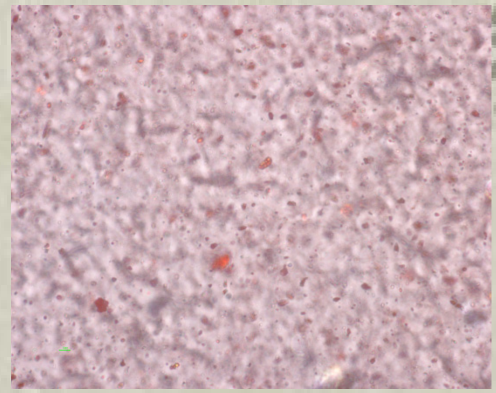
a. Sample 1. 40x, with polarizer



b. Sample 2. 40x, with polarizer

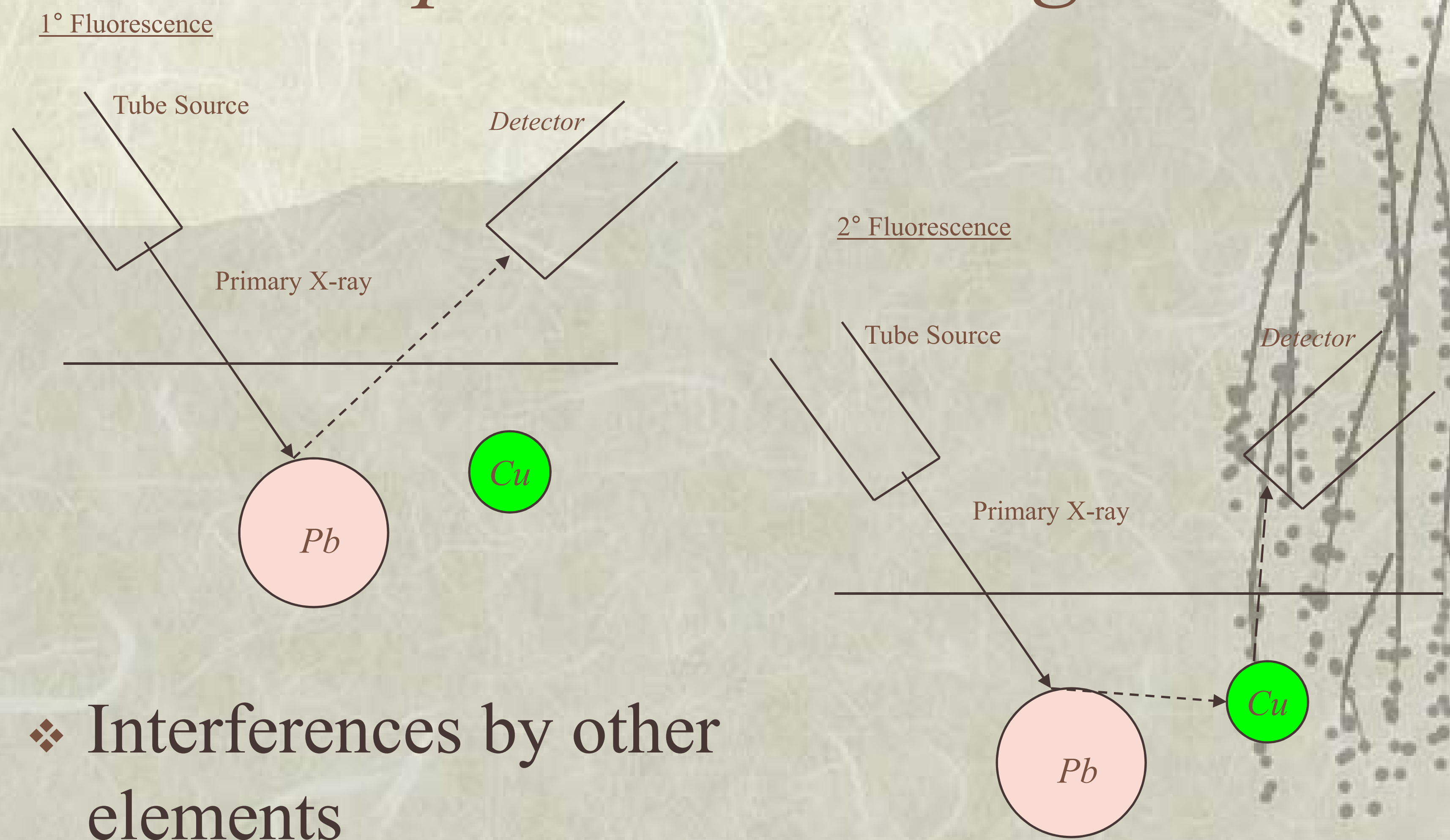


c. Sample 3. 40x, with polarizer



d. X-section of sample 2. 40x, with polarizer

Experimental design

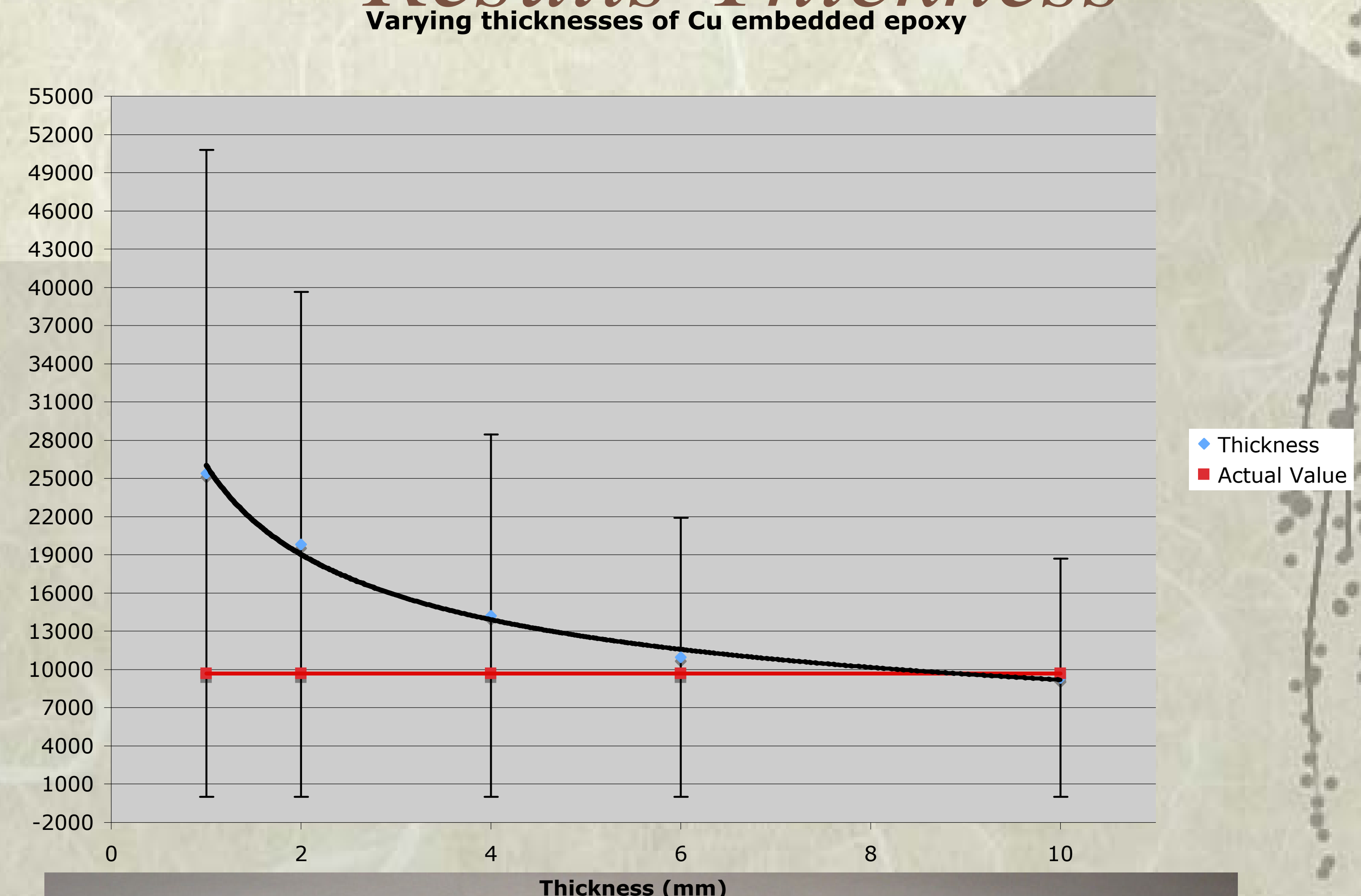


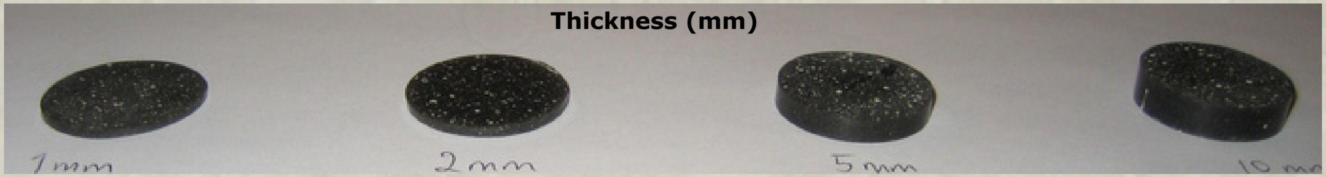
- Interferences by other elements

Experimental design

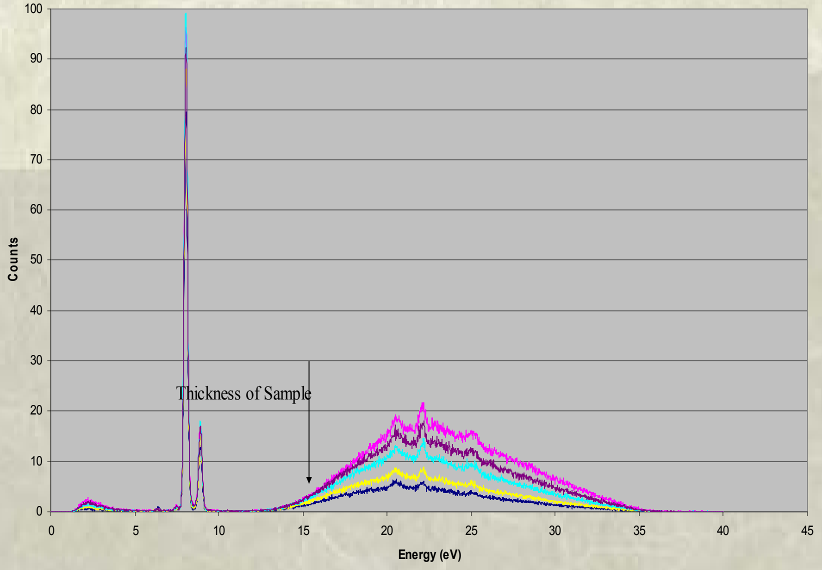
- Relative Humidity
- Samples are conditioned at 50-55% RH and then 68-70% RH
  - Paper samples
  - Wool samples

Results-Thickness

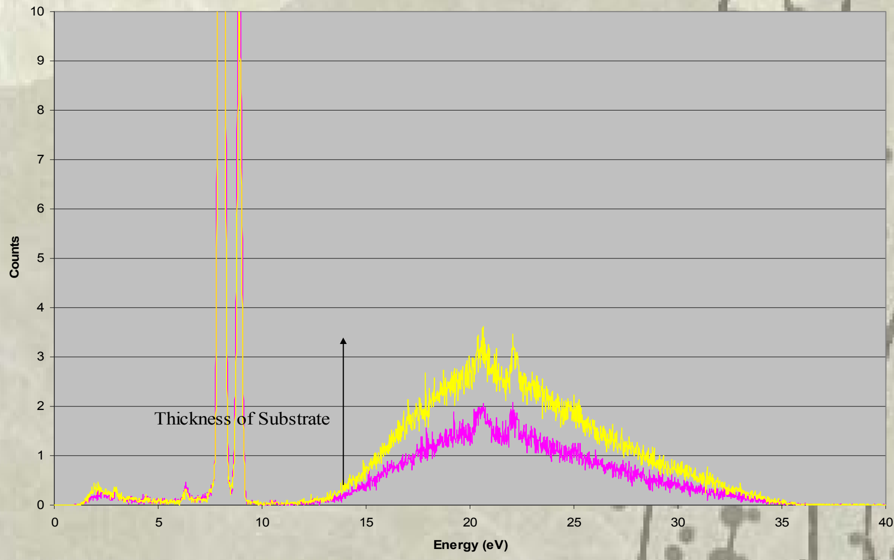




Results-Thickness



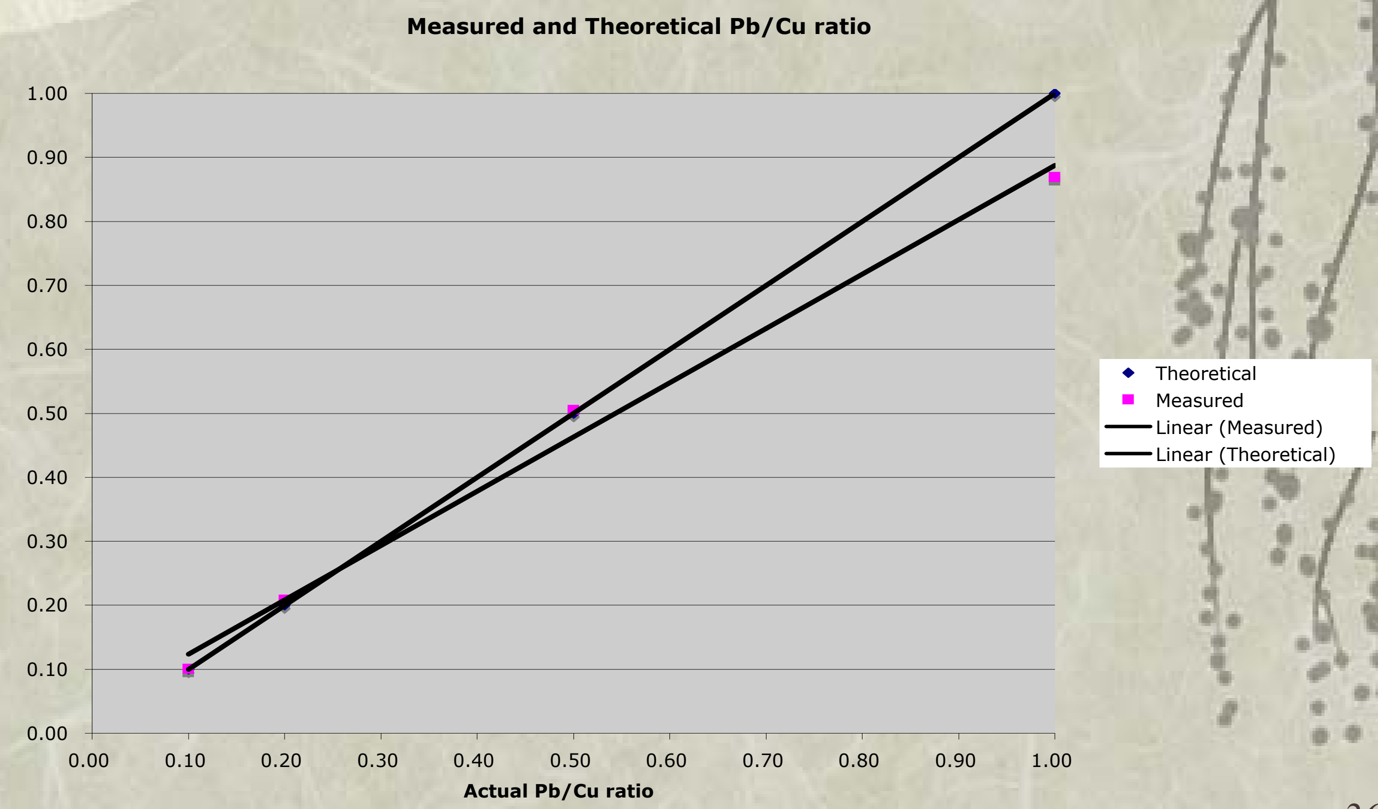
Varying thicknesses of epoxy embedded with CuO



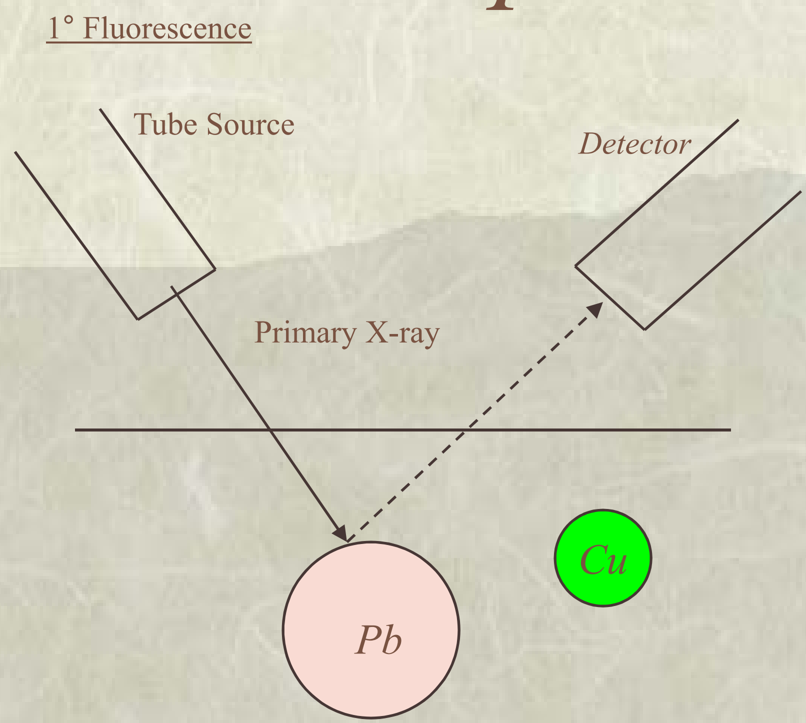
Varying thicknesses of paper embedded with $CuSO4$

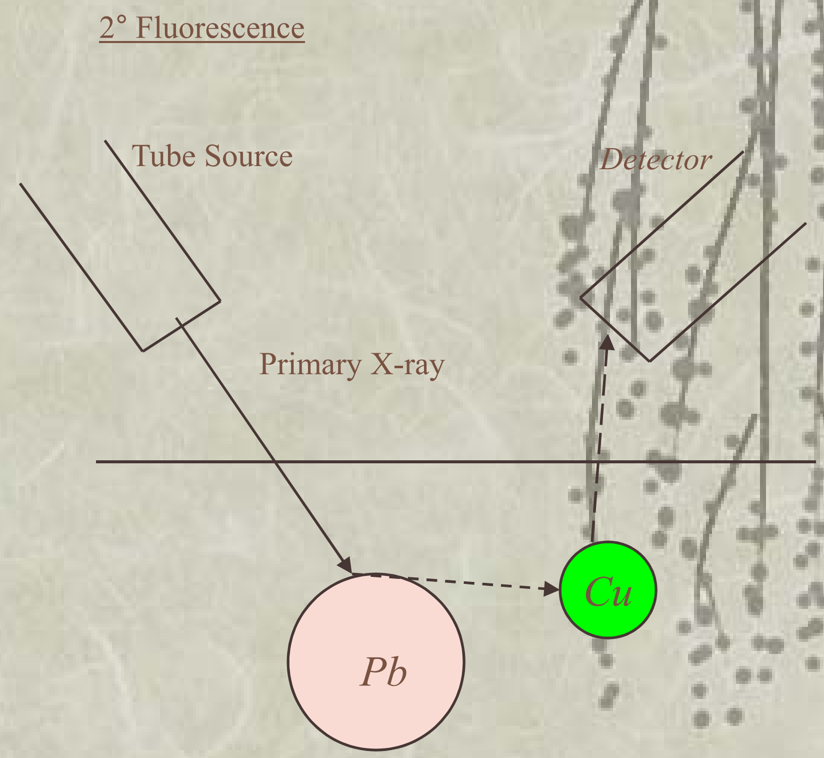
Results-Metal interference

The change in the analyzed Pb/Cu ratio due to metal interferences



Experimental design





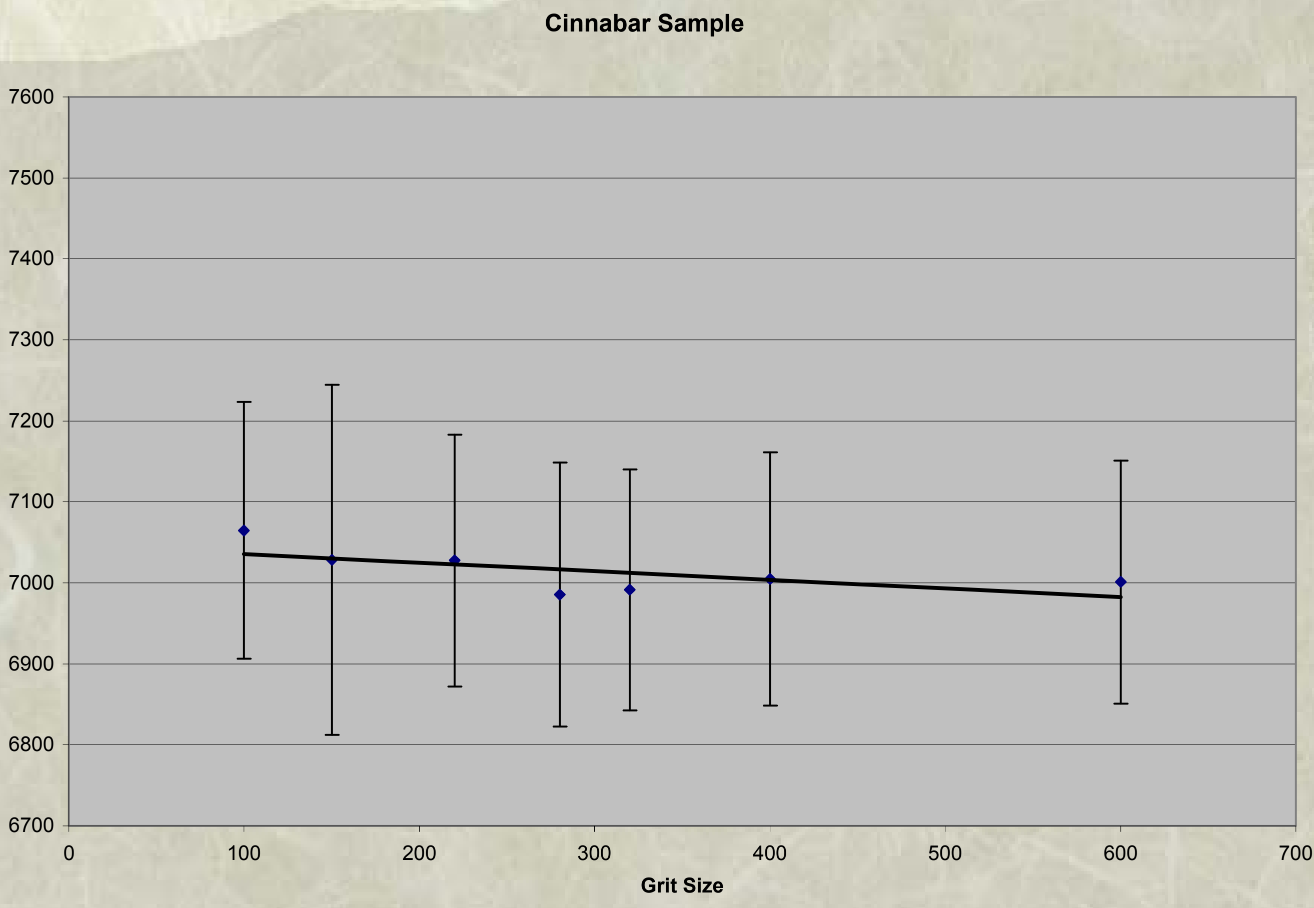
- Interferences by other elements

Results-RH

- No major change observed within the blotter paper samples
- 10-13% of error observed in the tabulated results of the wool samples between the two environmental conditions (50-55% RH and 68-70% RH)
  - More investigations

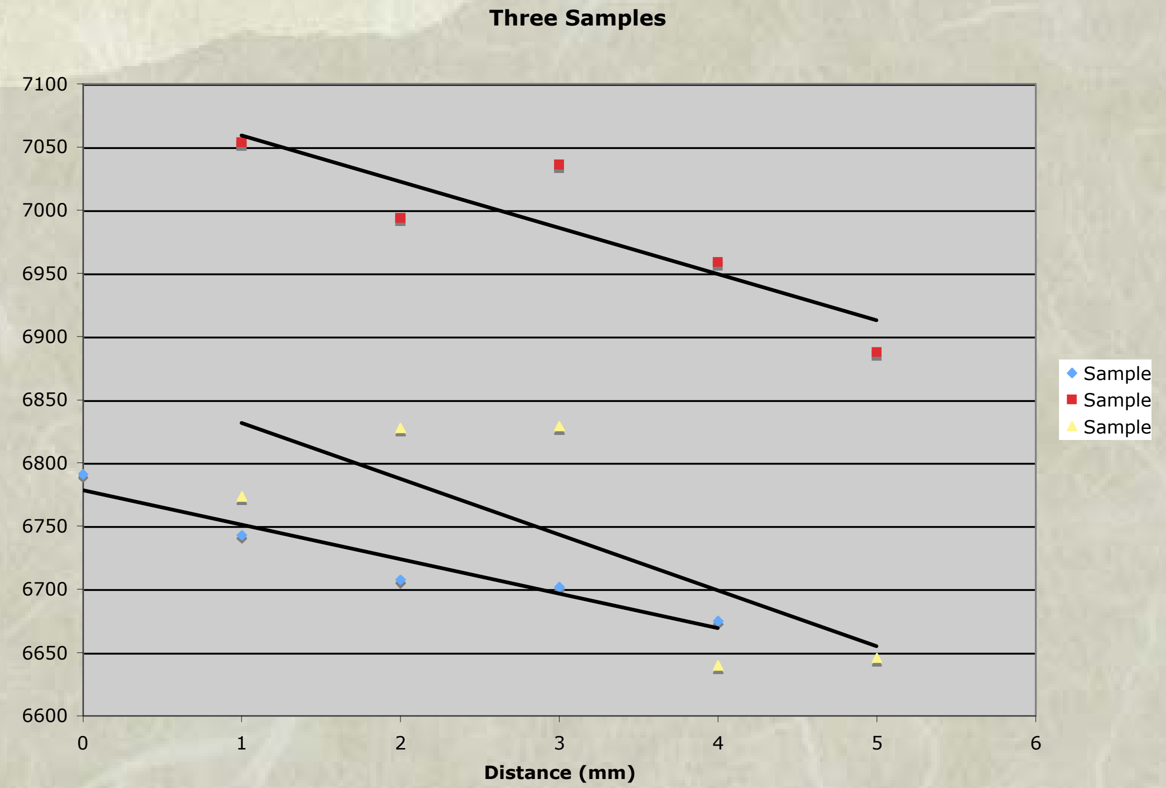
Results-Geometry

Two Trials of three cinnabar samples acquired from five spots each sample showing the quantity of Hg vs. polished surface



Results-Distance

Three cinnabar samples of three trials showing the quantity of Hg vs. distance of three trials acquired from five spots



Increasing distance

Conclusion

Software: When using handheld analyzers, one should not rely on numerical results from portable XRF instruments since SOIL mode designed for infinitely thick samples of soil matrix and not of organic matrix.

Physical: Ethnological materials to be analyzed with XRF do not always have "infinite thicknesses." They most likely resemble the scenario in which paper samples are sprayed with $CuSO_4$. This should be taken into account when preparing calibration standards. In addition RH of the environmental conditions should be taken into account.

Composition: There can be interferences between different elements on XRF results. E.g. when the relative amount of Pb is increased compared with Cu, the XRF readings are less accurate.

Conclusion

- Need proper documentation to interpret the data and report to the communities

Autry National Center

TECHNICAL ANALYSIS FOR PESTICIDE SCREENING

I. GENERAL INFORMATION

Catalogue number: 11.F.77
Object name: shell
Culture: Yokut
Collector: Walker, Mr. Edwin F.

II. HISTORY OF PESTICIDE TREATMENT

Inventory of past pesticides treatments of the museum and collectors are an ongoing research and a report can be submitted when it is completed. In order to prepare this document first the museum's old files along with the museum's former employees are consulted. So far no records of past heavy metal pesticides application have been found. However, it is known that some of the collections were fumigated in-house as well as sent outside to a company for fumigation, both of which with an unknown chemical. In addition, based on interviews it is suspected that paradichlorobenzene was used in the past. It is not known yet whether the museum used heavy metal pesticides throughout it's history.

Pesticide treatment: unknown

III. RECORD OF ANALYSIS

Reason for analysis: Repatriation
Substances tested for: lead (Pb), arsenic (As), mercury (Hg)
Analytical technique: Spot-testing with an XRF handheld analyzer

General information about the object

History of pesticide use of the museum

Record of analysis

Conclusion

- Need proper documentation to interpret the data and report to the communities

A. SUMMARY OF RESULTS

The object is a limpet shell, both sides of which were analyzed using X-ray fluorescence.

A positive level of arsenic and lead were detected outside near the hole. A closer examination of the object proves a red pigment on the surface. There are two red pigments that include lead and arsenic, i.e. minium (red lead), and orpiment. Two other areas analyzed do not show presence of heavy metal elements in question. Therefore, the positive readings are most likely due to this pigment inclusion on the object.

B. DETAILED ANALYTICAL RESULTS

1. Equipment

Instrument model no.: NITON XLp 723
Manufacturer and serial no.: Thermo Scientific Inc., 10257
Source: Cd-109 and Am-241
Instruments analytical setting/calibration mode: Bulk Mode
Summary of equipment set up: *One has to press and hold the trigger continuously for the analyzer to operate. The object laid down was tested with the analyzer facing the table. A reading of the background where necessary was also acquired and attached. In some cases the analyzer was laid on its side and the object was propped in front of the analyzer's head.*

2. Data

This object was analyzed in one or more locations. Artifact(s) other than human remain(s) have image(s). Each number on the image(s) corresponds to one analysis, or "reading", the data for which is listed below. The readings are consecutive numbers determined by the instrument. For this reason, the reading numbers for this object probably do not begin at "1". Since the pesticide contamination is not necessarily uniform, the artifact is described as one or more parts. A part may refer to a material of which the artifact is made or a location, such as a mouthpiece or interior of a mask. The amount of pesticide detected on each part is provided with the associated error, units of measurement ("Units"), length of analysis ("Duration"),

Summary of results

Detailed analytical results

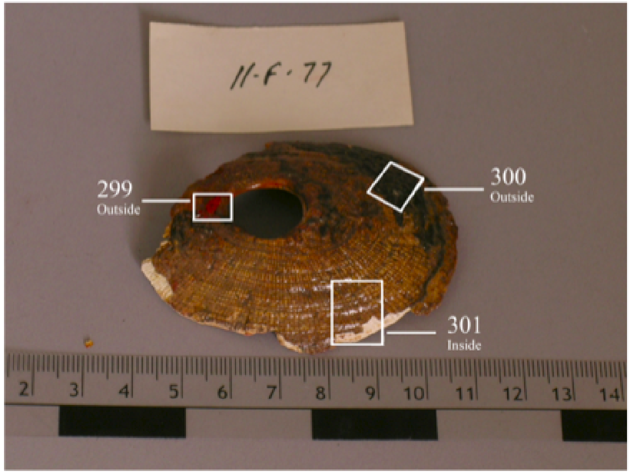
Conclusion

- Need proper documentation to interpret the data and report to the communities

and instrument's analytical setting ("Type"). The environmental conditions showing the relative humidity and temperature levels are also recorded manually during testing. For readings a dial hygro-thermometer was used.

The thickness of the areas analyzed was around eight of an inch. Three readings numbered as 299 to 301 were acquired as shown on the photos. The analysis duration for each reading was about 60 seconds. The tabulated results are attached. In addition the spectrum of each area analyzed is attached, which shows the count peaks of each heavy metal element if it is present.

Reading No	Type	Duration	Units	LOCATION	CONDITION	Pb	Pb Error	As	As Error	Hg	Hg Error
299	BULK	63.28	ppm	red pigment	39%RH 70F	282.87	57.73	750.05	73.79	5.44	44.56
300	BULK	50.24	ppm	black resin outside	39%RH 70F	41.69	28.17	21.27	21.71	12.9	34.12
301	BULK	61.73	ppm	in	39%RH 70F	25.37	31.99	25.31	24.48	3.95	40.86

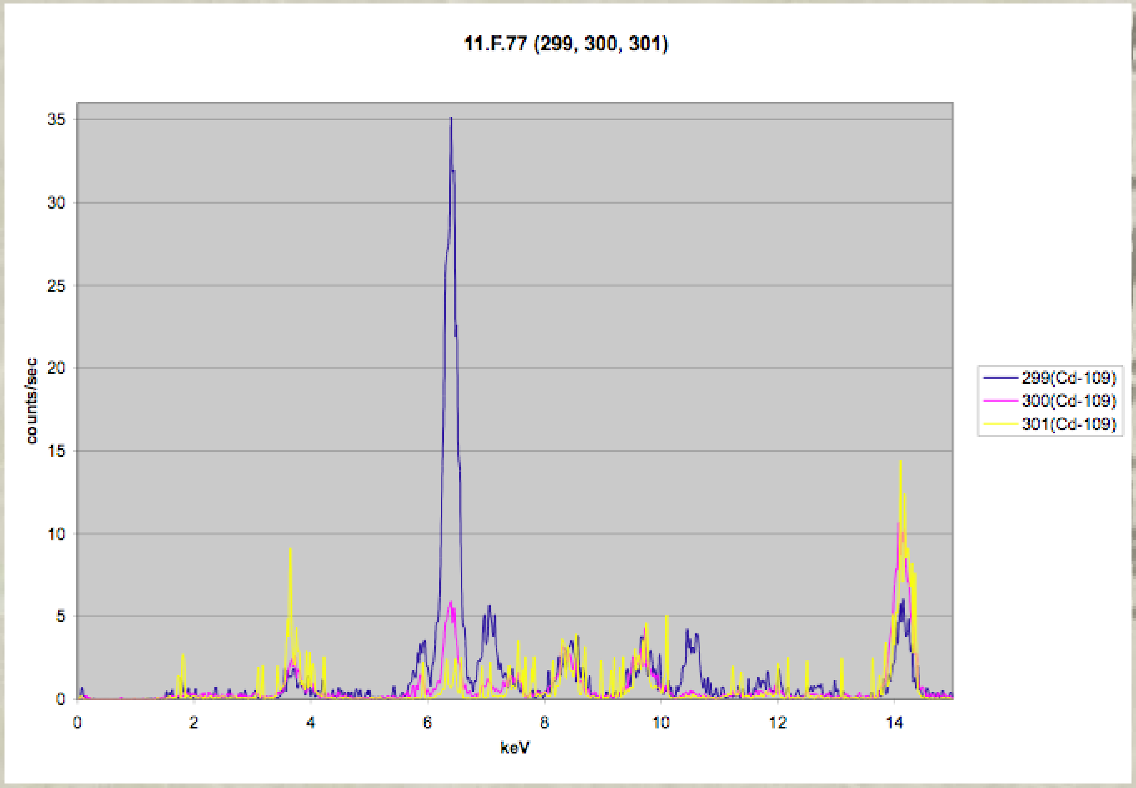


Detailed analytical results continued

Conclusion

- Need proper documentation to interpret the data and report to the communities

Spectra showing the analysis



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