# The limitations of handheld XRF analyzers as a quantitative tool for measuring heavy metal pesticides on art objects

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## Introduction

Handheld XRF instruments are being 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. The aim is to demonstrate the relationship between the thickness, shape, and surface features of organic substrates and XRF readings.

Handheld XRF analyzers have advantages and disadvantages. Some are:

**Advantages**

- Cost-efficient
- In-situ analysis
- Easy in use

**Disadvantages**

- Relative humidity and/or temperature affect both the analyzer and the substrate
- Density and geometry of the substrate
- Interferences caused by elements other than the metal of interest (by absorption, scattering, or enhancing the fluorescence)
- Detection limits of the metal of interest

## Technical specification of the handheld XRF unit:

Innov-X Alpha 2500 Series with Ta anode excitation source. Thermoelectrically cooled SiPiN diode detector (Resolution <280 eV). The tube operates with 40 kV and 20 µA current. The analysis type was standard SOIL mode. Handheld instruments use fundamental parameter to calculate concentrations (ppm). According to the formula the intensity of the counts is inversely proportional to the matrix value, which is dependent on the composition of the substrate. In addition, the machine is setup to do 6 iterations.

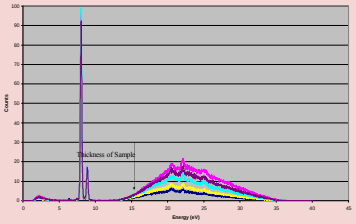
## Materials for samples

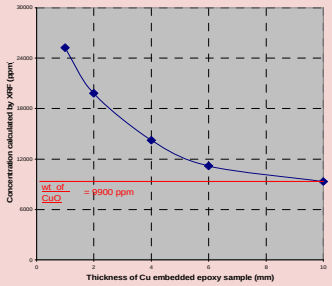
Epoxy samples: Commercial 5 minute epoxy, CuO and PbO powder, ground using a mortar

Paper samples: 2.54 mm and 0.508 mm thick blotter paper, thin wool samples impregnated by spraying four times with 0.05618 g/ml of $CuSO_4$ in deionized $H_2O$

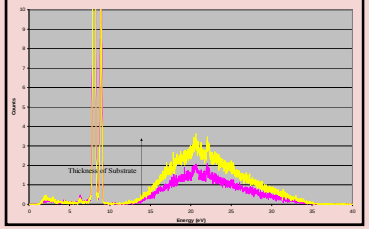
## Results and Discussion

Varying thicknesses of epoxy embedded with CuO



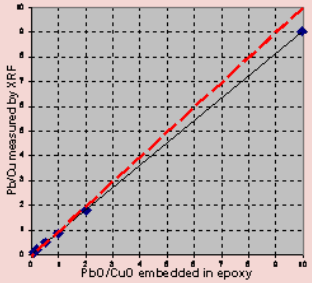

Varying thicknesses of paper sprayed with $CuSO_4$



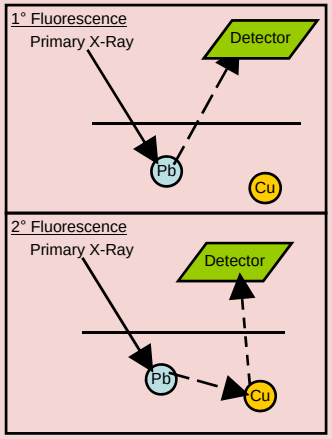

It was observed that the back-scattering decreased from the thin to the thick epoxy samples (left), whereas the back-scattering increased from the thin paper to the thick paper (right).

- The Cu is dispersed throughout the epoxy substrate, but only on the surface of the paper. Thus, as thickness increases for the epoxy, the x-rays can interact with more Cu. As thickness increases for the paper, the x-rays can only interact with more paper.
- For both substrates, the calculated concentration increased as the thickness decreased. This is due to the calculations and error inherit within the software of the machine.

Varying Cu:Pb ratios embedded in epoxy




Secondary Excitation of copper by lead causes an apparent decrease in lead/copper ratio.




## 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.

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.

## Future studies

Our research is being carried out for the effect of XRF readings on varying surface topographies and geometrical shapes of organic substrates

The effect of RH on XRF readings is also being conducted.

## References

Criss, J. 1982 "Using Fundamental Parameters in XRF Analysis" *SUNYA*

Gianoncelli, Kourousias 2007 "Limitations of portable XRF implementations in evaluating depth information: An archaeometric perspective" Appl. Phys. A 89, 857–863

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