EVALUATION OF AN X-RAY FLUORIMETER
FOR MEASURING LEAD IN PAINT

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Background

A laboratory analysis of key performance features of the Warrington Microlead I XRF Analyzer was conducted. This analysis included the determination of instrument accuracy and precision as measured against standard reference materials as well as the instrument's ability to provide information for multiple layers of a lead-based paint.

Materials and Methods

Instrument Description and Specifications

The Warrington Microlead I (revision 4.0) is a portable X-ray fluorescence analyzer used for the detection of lead in paint. It consists of a micro-processor controlled analyzer unit and a hand-held probe. The probe contains a shielded source of ^{57}Co , a trigger-activated "shutter" for producing a beam of gamma rays from the source, and an X-ray fluorescence detector. High abundance gamma rays from the ^{57}Co (122 & 136 keV) are used to excite outer k-shell electrons in lead atoms. These electrons, in turn, emit (fluoresce) lower energy (72-88 keV) X-rays which are measured by the detector. The X-ray signal is subsequently converted to a reading that indicates the mass of lead per unit area (i.e., mg/cm²). The instrument can store and average a limited number of measurements and has data logging capabilities.

Accuracy and Precision

Instrument accuracy and precision were determined by collecting multiple measurements from surface lead standards issued by the National Institute of Standards & Technology (NIST)¹; a summary of their properties appears in Table 1. After zeroing the instrument according to manufacturer's recommendations, 30 independent measurements were taken from each surface standard. Substrates analyzed included the wood, gypsum, and concrete blocks provided with the instrument as well as a formica-covered particle board. Data were analyzed for normality by inspection of frequency distributions (histograms) for each unique standard and substrate combination and summarized statistically with the mean and standard deviation.

Analysis of Multiple Layers of Paint

A lead-based paint was applied by hand brushing to thin (0.18 mm thickness) acetate sheets. Each layer was air-dried overnight and sheets containing up to 5 layers of paint were prepared. To measure thicker layers of paint, multiple sheets were stacked together. To determine the effect of increased source-to-detector distances, varying thicknesses of sheeting were positioned above a lead standard and measurements made as above. To further extend the range of area lead concentrations studied, additional measurements were made with thin lead foils. The average thickness of a paint layer was calculated from the weight of a known area of paint and its density; manual measurements of thickness were also made with a micrometer.

¹Model SRM 2579, NIST, Gaithersburg, MD 20899

Results and Discussion

For the range of surface standards available from NIST, the Microlead I analyzer provided highly accurate measurements of the area concentration of lead (Figure 1). However, as shown in Figures 2-6, measurements varied considerably about their mean. In all cases, measurements approximated a normal distribution, indicating that the standard deviation is a suitable estimate of precision. For the standards sampled, standard deviation ranged from 0.23-0.36, while the coefficient of variation (standard deviation/average x 100) ranged from 6-78%.

As initial measurements were made with the concrete substrate, the relatively high standard deviation was believed to be due to the high density of the concrete substrate. However, subsequent measurements of the same standards on other properly zeroed substrates produced similar levels of variability. The consistency of the standard deviation across all of the standard and substrate combinations suggests that instrument imprecision may not be a function of the analytical system but instead the result of confounding mechanical error. For example, the shutter consists of a heavily shielded bar that mechanically slides over the detector iris. If measurement commences with shutter movement, then any variability in the shutter's travel time will systematically affect the readings. Imprecision in the detection cycle timer will also systematically bias results. No attempt was made to evaluate this possible source of error.

Collecting measurements from surfaces with substrates different from the one against which the instrument has been zeroed can also systematically bias results (e.g., after zeroing on the concrete substrate, blank measurements on either the gypsum or wood substrate gave readings of approximately -1.1 mg/cm^2). Given this potential, the importance of good instrument zeroing technique and collection of multiple readings during field inspections cannot be over-emphasized, especially for surfaces that are within the HUD's "ambiguous" range of $1.0 \pm 0.5 \text{ mg/cm}^2$.

The instrument provided area lead concentrations for surfaces coated with up to 50 layers of paint. Instrument response (Figure 7) was linear over the first approximately 10 layers of paint but produced increasingly non-linear measurements over an additional 40 layers. Although multiple paint layers were prepared by stacking painted acetate sheets, the increasing source-to-detector distance could, at most, account for about 10% of the loss of signal (Figure 8). Instead, most of this error is probably associated with a self-absorption effect within increasing amounts of lead. For example, when the range of area lead concentrations was extended with thin lead foils, the data showed the inverse exponential function that is typical for radiation shielding curves (Figure 9). The non-linearity should not, however, pose a problem during field investigations with this X-ray fluorimeter since it becomes most pronounced at about two orders of magnitude above the HUD limit.

Conclusions

The Microlead I XRF lead analyzer is an accurate but, as also reported by the manufacturer, potentially imprecise instrument for measuring area lead concentrations on painted surfaces. The imprecision may be a function of a mechanical or procedural component(s) of the instrument and not the analytical method of X-ray fluorimetry. As noted by HUD for this and other commercially-available X-ray fluorimeters used in the field analysis of lead paint, methodological imprecision led to the establishment of the wide $\pm$ value associated with the current standard of 1.0 mg/cm². As recommended by HUD and Warrington, Inc., the practical implications of this imprecision are that field inspectors must collect multiple readings from the same location to minimize variability and ensure that the mean is truly representative of the area lead concentration.

Due to the differential densities of various building materials, proper instrument zeroing is also essential. This operation must be performed on representative substrates, preferably actual building construction material(s) found in the field that are identical to the surface(s) to be sampled but which are devoid of lead paint. Unusually high or low readings from a surface should be interpreted with care and only with reference to other readings taken from the same homogenous sampling area.

Recommendations for Additional Work

1. Sequentially evaluate the source(s) of instrument imprecision by testing the shutter, detector, and timer operating sequences.
2. Establish the correlation, if any, between area, mass, and TCLP lead concentrations of paint by measuring a large number of field surfaces and collecting bulk samples for laboratory analysis. If statistically significant, this correlation could find use as a rapid indicator of hazardous waste characteristics of abatement debris.

References

U.S. Department of Housing and Urban Development (HUD). 1990. Lead-Based Paint: Interim Guidelines for Hazard Identification and Abatement in Public and Indian Housing. *Federal Register* 55(75):14556-14716.

Table 1. Reference standard specifications (NIST Model SRM 2579).

Level	Lead Concentration	Estimated Uncertainty ^a
I	3.53 mg/cm ²	0.24 mg/cm ²
II	1.63	0.08
III	1.02	0.04
IV	0.29	0.01
Blank	<0.0001	

^a95% confidence intervals

Figure Legends

Figure 1. The MicroLead I instrument provided highly accurate area lead measurements of the NIST reference standards (see Table 1). Data points represent the mean $\pm$ standard deviation of 30 replicate samples taken on the (zeroed) concrete substrate.

Figures 2-6. Frequency distributions for measurements taken from the (zeroed) concrete substrate with the NIST reference standards (Table 1). Thirty replicate measurements were collected for each standard. The data approximate normal distributions, with standard deviations ranging from 0.23-0.36.

Figure 7. Area lead measurements for multiple layers of paint. Instrument response was essentially linear over the first 10 layers of paint (inset) but became increasingly non-linear as the number of paint layers approached 50. Data points represent the mean $\pm$ standard deviation of 5 replicate measurements. Each layer of paint averaged 38-46 μm in thickness, and contained 1.58 (± 0.18) mg/cm^2 of lead.

Figure 8. Effect of increased source-to-detector distance on area lead measurements. Blank acetate sheets were placed over the NIST Level I reference standard to estimate the worst-case signal loss due to the stacking geometry of multiple layers of paint (see Figure 7). Data points represent the mean $\pm$ standard deviation of 5 replicate measurements. Under the maximum source-to-detector distance condition (i.e., total thickness of 10 acetate sheets and 10 layers of paint), area lead measurements could be reduced by about 10%.

Figure 9. Self-shielding due to increasing area concentrations of lead. The upper range of the area lead measurement curve for multiple paint layers (Figure 7) was extended with measurements taken from sheets of lead foil (0.2 mm thick or 225 mg/cm^2). Data show an inverse exponential function, a relationship that is typical for radiation shielding curves. Data points represent the mean $\pm$ standard deviation of 5 replicate measurements.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

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