

Comparison Between XRF and Atomic Absorption Spectroscopy for the Determination of Total Arsenic in Soil

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Abstract

Studies have shown that arsenic leaches from pressure treated wood into the surrounding soil. For decades chromated copper arsenate (CCA), applied during pressure-treatment of lumber, was used as wood preservative. The EPA banned the use of pressure-treated wood containing CCA for residential applications on December 31, 2003. However, studies showed that existing CCA-treated structures pose a risk of arsenic exposure especially to small children from hand-to-mouth contact with CCA-treated structures and accidental ingestion of contaminated soil. The goal of this study is to compare two different spectroscopic methods for the determination of total arsenic in soil samples collected from a local playground: X-ray fluorescence and atomic absorption. A total of 51 subsurface soil samples were oven-dried at 40 °C and sieved prior to spectroscopic and XRF analysis. For GFAA analysis, the soil samples were analyzed using a Perkin-Elmer AAnalyst600 graphite furnace atomic absorption (GFAA) spectrometer following EPA method 3050B. No further sample preparation was used for XRF analysis using Innov-X Systems Alpha Series portable XRF spectrometer. Results from the two methods showed a linear correlation (Pearson correlation), but XRF results were consistently higher than those from GFAA.

Background

- ❖ Chromated copper arsenate (CCA)
 - Preservative used to treat lumber since 1940s
 - In playground equipment, fences, decks
- ❖ Arsenic is a known human carcinogen
 - Presents the highest risk of exposure (vs. Cu, Cr)
- ❖ Voluntary phase out of CCA for residential use by manufacturers - Dec. 31, 2003¹
- ❖ Studies: As, Cu and Cr leach from CCA-treated wood
 - Elevates levels of these metals, especially As, in soil
- ❖ Ingestion of As-contaminated soil; direct contact with CCA-treated wood
 - Health risk to small children (frequent hand to mouth activity)

Image available at <http://babyblog.org>



Objectives

The goal of this study is to compare two different spectroscopic methods for the determination of total arsenic in soil samples collected from a local playground: **portable x-ray fluorescence** and **atomic absorption**. This will allow us to determine if XRF can be a fast and reliable substitute for GFAA in the quantitation of arsenic in soil samples.

Atomic absorption vs. x-ray fluorescence for arsenic analysis in soil

X-ray fluorescence (XRF) for elemental analysis²

- ❖ Commonly used for elemental analysis in solid matrix
- ❖ Easy and fast ID and quantitation of elements over a wide dynamic concentration range
- ❖ Non-destructive
- ❖ For soil testing, requires little or no sample preparation
- ❖ Portable XRF ideal for field testing
- ❖ Sensitivity and LOD not as good as AA methods



Alpha handheld XRF analyzer. Image available at INNOV-X Environmental Brochure "Handheld XRF Revolutionizes Environmental Testing"

Perkin-Elmer AAnalyst600 GFAA spectrometer with AS-80 autosampler



Graphite furnace atomic absorption (GFAA) spectroscopy

- ❖ Highly sensitive; very low detection limit
- ❖ Ideal for analysis of trace levels of metals in water, soil and sludge
- ❖ Established EPA methods
- ❖ For analysis of soil and sludge, sample preparation is long and tedious

Methodology

Soil sampling and processing

- Soil samples were taken ~ 0-10 cm from surface
- Variable distance from base of wooden structure; also underneath picnic tables
- Total collected: 51 samples and control
- Sample and control dried at 40 °C and sieved

GFAA analysis: Total As

- One gram of dried sample was digested at 95 °C on a Modblock digester following EPA method 3050B³
- Digested sample was diluted to 100 mL after cooling and centrifuged prior to GFAA analysis
- Perkin-Elmer AAnalyst600 graphite furnace atomic absorption spectrometer (EPA Method 7060A⁴)
- Extraction efficiency: Reference soil, SRM 2710 (NIST, Montana soil)
- QC: Sample spikes, duplicates and reagent blanks

XRF Analysis: Total As

- No further sample preparation was used
- Dried and sieved sample placed on a Ziploc bag
- Total arsenic was measured against reference standards using Innov-X Systems Alpha Series portable XRF spectrometer

Results

- ❖ XRF data for arsenic in soil were consistently higher than GFAA data by an average of 34 % ± 22 % (Figure 1)
- ❖ A very strong correlation ($r^2 = 0.95$) was observed between XRF data and GFAA data (Figure 2)

NOTE: Method detection limits (MDL) for total arsenic

- ❖ XRF = 7-10 ppm
- ❖ GFAA using EPA Methods 3050B and 7060A = 0.0023 ppm

Figure 1: XRF vs. GFAA data for arsenic in soil near wooden fence

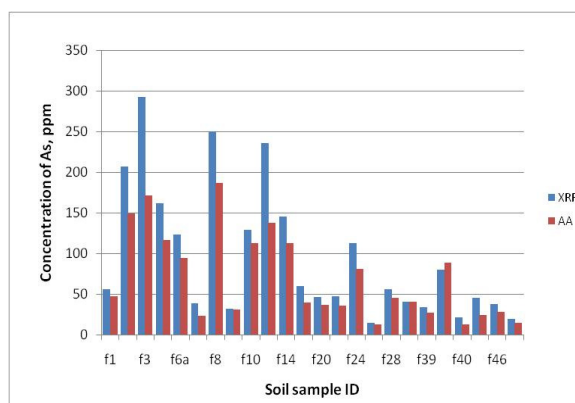
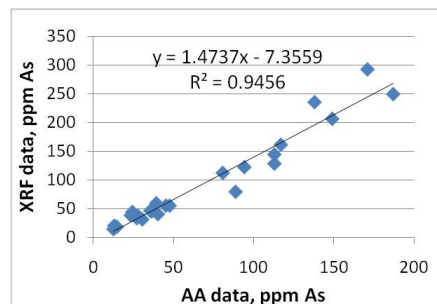


Figure 2: Correlation between XRF and GFAA data for arsenic in soil near wooden fence



Conclusion

For the determination of total arsenic in minimally processed (oven-dried, sieved) homogeneous soil samples, handheld XRF analyzer yields data comparable to those obtained from graphite furnace atomic absorption (GFAA) spectroscopy. Results are not consistent in the field with heterogeneous soil samples.

Arsenic data from XRF were consistently higher than data from GFAA. This discrepancy can be due to the limitation of the sample digestion procedure based on Method 3050B for organic-bound arsenic. Thus, arsenic bound to silicate materials in soil cannot be extracted by the digestion procedure. XRF, however, yields data based on all electronically excitable forms of arsenic, including silica-bound.

A very good correlation ($r^2 = 0.95$) between XRF data and GFAA data for arsenic in homogeneous soil samples indicate that handheld XRF analyzer can be used as an alternative to atomic absorption techniques, thus cutting down on tremendous amount of time required for sample digestion characteristic of AA techniques. However, AA techniques are still superior to XRF when sensitivity and low detection limits (ppb levels) are desired.

Works Cited

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BSU CHEM 499 (Directed Study in Chemistry) students using the XRF to test for arsenic in a local playground