Conducting a Demonstration of Method Applicability and Designing Quality Control Programs for X-Ray Fluorescence in Soil

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Stephen Dyment
U.S. EPA
Technology Innovation Field Services Division
dyment.stephen@epa.gov
Technical Session Objectives

◆ Provide an overview of the demonstration of method applicability (DMA) process used in a Triad Approach
  » Highlight activities often conducted during evaluations of field portable x-ray fluorescence (XRF) instruments

◆ Translate common DMA findings into a comprehensive quality control (QC) program for field activities involving XRF analysis of soil and sediment matrices
  » Indicate QC sample types, function, strategies for analysis, and effective use of results in real time

◆ Showcase project benefits of real time analysis and collaborative data sets
DMA History

◆ Concept founded in SW-846, performance based measurement (PBMS) initiative

  » [http://www.epa.gov/sw-846/pbms.htm](http://www.epa.gov/sw-846/pbms.htm)

◆ Initial site-specific performance evaluation

  » Analytical and direct sensing methods
  
  » Sample design, sample collection techniques, sample preparation strategies

  » Used to select information sources for field and off-site

◆ Goal is to establish that proposed technologies and strategies can provide information appropriate to meet project decision criteria
Why Do I Need a DMA?

◆ Triad usually involves real-time measurements to drive dynamic work strategies
◆ Greatest sources of uncertainty are usually sample heterogeneity and spatial variability
◆ Relationships with established laboratory methods often required – educate stakeholders
◆ Early identification of potential issues
  » Develop strategies to manage uncertainties
◆ Provides an initial look at CSM assumptions
What’s Involved?

◆ There is no template for DMAs!
  » Format, timing, documentation, etc. depend heavily on site specifics, existing information, and intended data use

◆ Perform early in program

◆ Go beyond simple technology evaluation to optimize full scale implementation
  » Method comparison, statistical analysis
  » Sample design, field based action levels
  » Sample prep, throughput, other logistics
  » Data management issues
What to Look For

◆ Effectiveness - Does it work as advertised?
◆ QA/QC issues
  » Are DLs and RLs for site matrices sufficient?
  » What is the expected variability? Precision?
  » Bias, false positives/false negatives?
  » How does sample support effect results?
  » Develop initial relationships of collaborative data sets that provide framework of preliminary QC program
◆ Matrix Issues?
◆ Do collaborative data sets lead to the same decision?
◆ Assessing alternative strategies as contingencies
More Benefits

- Augment planned data collection and CSM development activities
- Test drive decision support tools
  - Sampling and statistical tools
  - Visualization tools
- Develop relationships between visual observations and direct sensing tools
- Flexibility to change tactics based on DMA rather than full implementation
- Establish decision logic for dynamic work strategies
- Evaluate existing contract mechanisms
- Optimize sequencing, load balance, unitizing costs
Typical DMA Products – Summary Statistics

CSM of contaminant populations

High density data delineates spatial contaminant patterns

CSM guides informed evaluation of receptors, pathways & exposure units
Typical DMA Products – Statistical Evaluations/Method Comparisons

- Parametric - linear regressions
- Non-parametric - ranges or bins

![Graph showing statistical evaluations and method comparisons.](image)
Typical DMA Products – Uncertainty Evaluations

Example: Ingersoll Uncertainty Calculator

Analytical Uncertainty Calculator (PAGE 3)

Component Relative Percent Uncertainty

What is the measurement result? 56
What are the measurement units? ug/kg

If the sample measurement is 56 ug/kg, then the uncertainty interval is 41 - 71 ug/kg at the 99% Confidence Level.

For the above result, if the systematic measurement error (bias) is corrected, then the uncertainty interval is 45 - 78 ug/kg at the 99% CL.
Typical DMA Products

- QC program worksheets
The Specifics of X-ray Fluorescence

- XRF-basics and principles of operation
- Translating DMA results
- Developing a QC program
  » QC sample types
  » QC sample function, corrective action
- Developing a dynamic sampling protocol
  » Choosing collaborative samples
Principle of XRF Operation
What does an XRF Measure?

- X-ray source irradiates sample
- Elements emit characteristic x-rays in response
- Characteristic x-rays detected
- Spectrum produced (frequency and energy level of detect x-rays)
- Concentration present estimated based on sample assumptions

Figure 1: The principle of XRF and the typical XRF detection arrangement

Some Example XRF Spectra...
How is a Field Portable XRF Typically Used?

- Measurements on prepared samples
- Measurements through bagged samples (limited preparation)
- In situ measurements of exposed surfaces
What Does an XRF Typically Report?

- Measurement date
- Measurement mode
- "Live time" for measurement acquisition
- Concentration estimates
- Analytical errors associated with estimates
- User defined fields

<table>
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<tr>
<th></th>
<th>A</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>O</th>
<th>P</th>
<th>Q</th>
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<td>MN1</td>
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<td>Pass Fail Standard Pass</td>
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<td>Cr +/-</td>
<td>Mn</td>
<td>Mn +/-</td>
<td>Fe</td>
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<td>62.71</td>
<td>289.18</td>
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<td>25161</td>
<td>197.15</td>
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<td>17</td>
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<td>Soil</td>
<td>83.07</td>
<td>&lt;LOD</td>
<td>186.41</td>
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</table>
Which Elements Can An XRF Measure?

- Generally limited to elements with atomic number > 16
- Method 6200 lists 26 elements as potentially measurable
- XRF not effective for lithium, beryllium, sodium, magnesium, aluminum, silicon, or phosphorus
- In practice, interference effects among elements can make some elements “invisible” to the detector, or impossible to accurately quantify

**Standard Innov-X Factory Calibration List**

- Antimony (Sb)
- Arsenic (As)
- Barium (Ba)
- Cadmium (Cd)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Manganese (Mn)
- Mercury (Hg)
- Molybdenum (Mo)
- Nickel (Ni)
- Rubidium (Ru)
- Selenium (Se)
- Silver (Ag)
- Strontium (Sr)
- Tin (Sn)
- Titanium (Ti)
- Zinc (Zn)
- Zirconium (Zr)
How Is An XRF Calibrated?

◆ **Fundamental Parameters Calibration** – calibration based on known detector response properties, “standardless” calibration

◆ **Empirical Calibration** – calibration calculated using regression analysis and known standards, either site-specific media with known concentrations or prepared, spike standards

◆ **Compton Normalization** – incorporates elements of both empirical and FP calibration. A single, well-characterized standard, such as an SRM or a SSCS, is analyzed, and the data are normalized for the Compton peak

*In all cases, the instrument will have a dynamic range over which a linear calibration is assumed to hold.*
No analytical method is good over the entire range of concentrations potentially encountered with a single calibration.

XRF typically under-reports concentrations when calibration range has been exceeded.

Primarily an issue with risk assessments.

Figure 1: ICP vs XRF (lead - all data)

\[ y = 0.54x + 200 \]

\[ R^2 = 0.95 \]
How is XRF Performance Commonly Defined?

◆ **Bias** – does the instrument systematically under or over-estimate element concentrations?

◆ **Precision** – how much “scatter” solely attributable to analytics is present in repeated measurements of the same sample?

◆ **Detection Limits** – at what concentration can the instrument reliably identify the presence of an element?
  » 3 standard deviation rule
  » Rule of thumb: 4X increase in count time = 1/2 reduction in DL

◆ **Quantitation Limits** – at what concentration can the instrument reliably measure an element?

◆ **Representativeness** – how representative is the XRF result of information required to make a decision?

◆ **Comparability** – how do XRF results compare with results obtained using a standard laboratory technique?
Translating XRF DMA Results

◆ Comparability - usually with ICP or AA methods
  » Regression analysis is the ruler most commonly used to measure comparability
  » Standard laboratory data can be “noisy” and are not necessarily an error-free representation of reality
  » SW-846 Method 6200: “If the r2 is 0.9 or greater…the data could potentially meet definitive level data criteria.”

◆ Focus should be on decision comparability, not laboratory result comparability
  » Parametric and non-parametric techniques available
What is a Regression Line?

Image of a regression line with data points and a linear equation.

Equation: $y = 0.95x + 0.38$

$R^2 = 0.89$

Graph shows real-time vs. traditional results.
Heteroscedasticity is a Fact of Life for Environmental Data Sets

**LIBS vs Lab Beryllium**

- Equation: $y = 1.6x + 23$
- $R^2 = 0.67$
Appropriate Regression Analysis

- Based on paired analytical results, ideally from *same sub-sample*
- Paired results focus on concentration ranges pertinent to decision-making
- Non-detects are removed from data set
- Best regression results obtained when pairs are balanced at opposite ends of range of interest
- No evidence of inexplicable “outliers”
- No signs of correlated residuals
- High R2 values (close to 1)
- Constant residual variance (homoscedastic) is nice but unrealistic
Example: XRF and Lead

- Full data set:
  - Wonderful $R^2$
  - Unbalanced data
  - Correlated residuals
  - Apparently poor calibration

- Trimmed data set:
  - Balanced data
  - Correlation gone from residuals
  - Excellent calibration
  - $R^2$ drops significantly
Cautionary Tale

Small scale variability can impact data quality more than the analytical method.
A Properly Designed QC Program Will Help You Manage...

- Initial calibration problems
- Instrument drift
- Window contamination
- Interference effects
- Matrix effects
- Unacceptable detection limits
- Matrix heterogeneity effects
- Operator errors
XRF Quality Control Procedures

- Initial warm-up (30 minutes)
  - Energy calibration/standardization checks
- Blanks - silica or sand
- Calibration checks - initial and continuing
- Detection limit evaluation and monitoring
- Duplicates - instrument, sample replicates
- Monitor for inference effects, trends
- Matrix effects - variability, moisture
- Watch sample or decision unit variability
- Watch dynamic range
- Decision error rates
Basic XRF QC Requirements: Initial Calibration Check

- Energy calibration/standardization checks
- Calibration checks using NIST-traceable standard reference material (SRM), preferably in media similar to what is expected at the site
- Calibration checks using blank silica/sand
- Calibration checks using matrix spikes
- Calibration checks using well-characterized site samples
# Initial Calibration Check Example

<table>
<thead>
<tr>
<th>Sample</th>
<th># of Measurements</th>
<th>Known U</th>
<th>Moly</th>
<th>Reported U</th>
<th>Moly</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2 Blank</td>
<td>1</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td>50 ppm U</td>
<td>3</td>
<td>50</td>
<td>NA</td>
<td>&lt;LOD</td>
<td>14</td>
</tr>
<tr>
<td>150 ppm U</td>
<td>3</td>
<td>150</td>
<td>NA</td>
<td>116</td>
<td>23</td>
</tr>
<tr>
<td>50 ppm Moly</td>
<td>3</td>
<td>NA</td>
<td>50</td>
<td>55</td>
<td>42</td>
</tr>
<tr>
<td>150 ppm Moly</td>
<td>3</td>
<td>NA</td>
<td>150</td>
<td>&lt;LOD</td>
<td>134</td>
</tr>
<tr>
<td>100 ppm U/Moly</td>
<td>6</td>
<td>100</td>
<td>100</td>
<td>68</td>
<td>112</td>
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<tr>
<td>Archived Site Sample</td>
<td>10</td>
<td>100</td>
<td>NA</td>
<td>230</td>
<td>21</td>
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</table>
Basic XRF QC Requirements: Continuing Calibration

- Standardization checks: follow manufacturer recommendations (typically several times a day)
- On-going calibration checks: at least twice a day (start and end), a higher frequency is recommended
- Make sure XRF performance in relation to SRMs is well understood initially - watch for trends that indicate problems
- Typically controls set up based on initial calibration check work (i.e., a two standard deviation rule)
- Frequency of checks is a balance between sample throughput and ease of sample collection or repeating analysis
Control Charts – A Simple Continuing Calibration Check
Example of What to Watch for...

- Two checks done each day, start and finish
- 150 ppm standard with approximately +/- 9 ppm for 120 second measurement
- Observed standard deviation in calibration check data: 18 ppm
- Average of initial check: 153 ppm
- Average of ending check: 138 ppm
## Monitoring Detection Limits One Example

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Chemical Abstract Series Number</th>
<th>Innov-X¹ 120 sec acquisition (soil standard – ppm)</th>
<th>Innov-X¹ 120 sec acquisition (alluvial deposits - ppm)</th>
<th>Innov-X¹ 120 sec acquisition (elevated soil - ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb)</td>
<td>7440-36-0</td>
<td>61</td>
<td>55</td>
<td>232</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>7440-38-0</td>
<td>6</td>
<td>7</td>
<td>29,200</td>
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<tr>
<td>Barium (Ba)</td>
<td>7440-39-3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>7440-43-9</td>
<td>34</td>
<td>30</td>
<td>598</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>7440-70-2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>7440-47-3</td>
<td>89</td>
<td>100</td>
<td>188,000</td>
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<tr>
<td>Cobalt (Co)</td>
<td>7440-48-4</td>
<td>54</td>
<td>121</td>
<td>766</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>7440-50-8</td>
<td>21</td>
<td>17</td>
<td>661</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>7439-89-6</td>
<td>2,950</td>
<td>22,300</td>
<td>33,300</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>7439-92-1</td>
<td>12</td>
<td>8</td>
<td>447,000</td>
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<tr>
<td>Manganese (Mn)</td>
<td>7439-96-5</td>
<td>56</td>
<td>314</td>
<td>1,960</td>
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<tr>
<td>Mercury (Hg)</td>
<td>7439-97-6</td>
<td>10</td>
<td>8</td>
<td>481</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>7439-93-7</td>
<td>11</td>
<td>9</td>
<td>148</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>7440-02-0</td>
<td>42</td>
<td>31</td>
<td>451</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>7440-09-7</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
**Duplicates and Replicates**

Spreadsheet for recording & assessing XRF instrument duplicate measurement QC results

Calculates duplicate agreement statistically (from "error" reported by instrument), and as RPD (on the reported values of the duplicates)

This spreadsheet is designed to be used to establish statistical evaluation of duplicate agreement (RPD calculation included for information purposes)

*Note that acceptable statistical agreement does not always agree with an arbitrary RPD acceptance limit (20% in this example)*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>1st Result of Duplicate Pair</th>
<th>Error as Reported by the XRF</th>
<th>Error Type (1 - 1 SD; 2 - 2 SD) (Notes 2 &amp; 3)</th>
<th>Lower Bound of 95% Confidence Interval</th>
<th>Upper Bound of 95% Confidence Interval</th>
<th>Instrument-Reported Duplicate Result</th>
<th>Is the duplicate result within the statistical confidence interval?</th>
<th>Numerical Difference</th>
<th>Relative Difference: ( \frac{a - b}{(a+b)/2} )</th>
<th>Absolute Relative Percent Difference</th>
<th>Is the RPD &lt;20%?</th>
<th>Does the RPD check agree with the statistical check?</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW1</td>
<td>99.1</td>
<td>4.7</td>
<td>1</td>
<td>90</td>
<td>108</td>
<td>104</td>
<td>yes</td>
<td>4.7</td>
<td>-0.046</td>
<td>4.6%</td>
<td>yes</td>
<td>yes</td>
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<tr>
<td>SW2</td>
<td>28.9</td>
<td>3.9</td>
<td>1</td>
<td>21</td>
<td>37</td>
<td>26.3</td>
<td>yes</td>
<td>2.6</td>
<td>0.094</td>
<td>9.4%</td>
<td>yes</td>
<td>yes</td>
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<tr>
<td>SW3</td>
<td>18.8</td>
<td>2.3</td>
<td>1</td>
<td>23</td>
<td>43</td>
<td>143</td>
<td>yes</td>
<td>4.5</td>
<td>0.272</td>
<td>27.3%</td>
<td>no</td>
<td>no</td>
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<tr>
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<td>19.3</td>
<td>3.3</td>
<td>1</td>
<td>26</td>
<td>23.7</td>
<td>yes</td>
<td>yes</td>
<td>-4.4</td>
<td>-0.205</td>
<td>20.5%</td>
<td>no</td>
<td>no</td>
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<tr>
<td>SW26</td>
<td>26.0</td>
<td>6.9</td>
<td>1</td>
<td>246</td>
<td>295</td>
<td>239</td>
<td>no</td>
<td>-35.0</td>
<td>-0.126</td>
<td>12.6%</td>
<td>yes</td>
<td>yes</td>
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<tr>
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<td>140.6</td>
<td>18.4</td>
<td>1</td>
<td>1370</td>
<td>1442</td>
<td>1396</td>
<td>yes</td>
<td>10.0</td>
<td>0.007</td>
<td>0.7%</td>
<td>yes</td>
<td>yes</td>
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<tr>
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<td>45.9</td>
<td>11.8</td>
<td>1</td>
<td>436</td>
<td>482</td>
<td>473</td>
<td>yes</td>
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<td>-0.030</td>
<td>3.0%</td>
<td>yes</td>
<td>yes</td>
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<td>SW59</td>
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<td>90.9</td>
<td>1</td>
<td>5650</td>
<td>6006</td>
<td>5803</td>
<td>yes</td>
<td>25.0</td>
<td>0.004</td>
<td>0.4%</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

**Notes:**

1. Take back-to-back readings on a sample without moving the instrument to eliminate variability introduced by sample matrix.
2. The error type (error reported as 1 or 2 SD) is available from the instrument manufacturer.
3. Niton instruments are usually set up to report analytical "error" as 2 SD; Innov-X instruments are usually set up to report analytical "error" as 1 SD.
4. Remember that a 95% CI means that 5 out of 100 (or 1 in 20) are expected to be out of control; however, if a measurement is repeated in triplicate the probability of both
5. Example data provided above are from an actual site with measurements in 2006.
6. Acquisition time must be the same for the 1st and 2nd measurement.
7. The requirement of \( \%\text{RPD} < 20 \) is problematic for very low concentration samples because division by a low value causes the quotient to be high even when the numerical
8. New data can be added to this table by adding a row and copying formulas.
Interference Effects

- Spectra too close for detector to accurately resolve
  - As Kα=10.55 KeV
  - Pb Lα=10.54 KeV
- Result: biased estimates for one or more quantified elements
- DMA, manufacturer recommendations, scatter plots used to identify conditions when interference effects would be a concern
- “Adaptive QC”…selectively send samples for laboratory analysis when interference effects are a potential issue
Algorithm predicts lead Lα in 10.5 Kev spectral region based on the “clean” lead Lβ signal. The lead contribution is subtracted leaving the arsenic Kα.
Matrix Heterogeneity Small Scale Variability Effects

◆ In-field use of an XRF often precludes thorough sample preparation

◆ This can be overcome, to some degree, by multiple XRF measurements systematically covering “sample support” surface

◆ What level of heterogeneity is present, and how many measurements are required?

◆ “Reference point” for instrument performance and moisture check with in-situ applications
## Micro-scale Contaminant – Matrix Relationships Cause Within – Sample Heterogeneity

<table>
<thead>
<tr>
<th>Small Arms Firing Range Soil Grain Size (Std Sieve Mesh Size)</th>
<th>Pb Conc. in fraction by AA (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater than 3/8” (0.375”)</td>
<td>10</td>
</tr>
<tr>
<td>Between 3/8 and 4-mesh”</td>
<td>50</td>
</tr>
<tr>
<td>Between 4- and 10-mesh</td>
<td>108</td>
</tr>
<tr>
<td>Between 10- and 50-mesh</td>
<td>165</td>
</tr>
<tr>
<td>Between 50- and 200-mesh</td>
<td>836</td>
</tr>
<tr>
<td>Less than 200-mesh</td>
<td>1,970</td>
</tr>
<tr>
<td><strong>Totals</strong> (wt-averaged)</td>
<td><strong>927</strong></td>
</tr>
</tbody>
</table>

Adapted from ITRC (2003)

What particle fraction is “representative”? 
Collaborative Data Sets Address Analytical and Sampling Uncertainties

- **Cheaper/rapid** (lab? field? std? non-std?) analytical methods
  - Targeted high density sampling
  - Manages CSM & sampling uncertainty

- **Costlier/rigorous** (lab? field? std? non-std?) analytical methods
  - Low DL + analyte specificity
  - Manages analytical uncertainty

**Increasing Information**

Collaborative Data Sets
Dynamic Measurement Example

- Bagged samples, measurements through bag
- Need decision rule for measurement numbers for each bag
- Action level: 25 ppm
- 3 bagged samples measured systematically across bag 10 times each
- Average concentrations: 19, 22, and 32 ppm
  » 30 measurements total
Example (cont.)

Simple Decision Rule:

• If 1\textsuperscript{st} measurement less than 10 ppm, stop, no action level problems

• If 1\textsuperscript{st} measurement greater than 50 ppm, stop, action level problems

• If 1\textsuperscript{st} measurement between 10 and 50 ppm, take another three measurements from bagged sample
Lead Niton vs. ICP

59 Total pairs

\[ y = 1.0222x + 34.612 \]

\[ R^2 = 0.946 \]

10 False Positive Errors = 26%

True Positive 20 Pairs

0 False Negative Error = 0%

True Negative 29 Pairs
3 Way Decision Structure with Region of Uncertainty
Lead Niton vs. ICP

59 Total pairs

True Positive
19 Pairs

True Negative
26 Pairs

3 False Positive Errors = 7.7%

11 Samples for ICP

0 False Negative Error = 0%

y = 1.0222x + 34.612

$R^2 = 0.946$

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Communicating Uncertainty in a XRF CSM

Evergreen Berm, Plan View Probability that 1-ft Deep Volumes > 250 ppm Pb

Note: Sample locations are numbered sequentially in time. See #119 (arrow) as example of adaptive fill-in of uncertain areas to firm up contaminant boundaries.
Samples Collected from Trench, North Sidewall Extending Between Locations B7 and B9 at 2505 16th Avenue South

Notes:
1) PCR IDs in **trench samples** indicate in situ replicates of **unprepared** samples shot in plastic cups using a different orientation of the XRF window for samples collected from the same depth interval.
Resources

◆ Case studies on resources CD provided
◆ Case studies and profiles on http://www.triadcentral.org/
  » Due out this year: http://www.clu-in.org/
◆ Discussions with European and US Triad practitioners