Calibration and Use of XRF for Hg Analysis of Bank Soils

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Experimental Question

Can hand-held XRF analysis provide a low-cost real-time measure of Hg with sufficient accuracy and precision?

Why propose an alternative method?

- Sample Frequency
  - Nearly 5000 soil and sediment samples analyzed for Hg as a part of EcoStudy
  - Nearly 500 Hg soil samples already analyzed in 2015
- Cost
  - $20/sample for Method 7471A
  - $83/sample for Method 1631
  - Not including labor and shipping costs
- Time
  - Turnaround time on the order of weeks

Experimental Design

- Method Comparison Study

EPA Method 7471A

- 51 bank soil samples
- Lancaster Labs
- Routine QA

Hand-held XRF

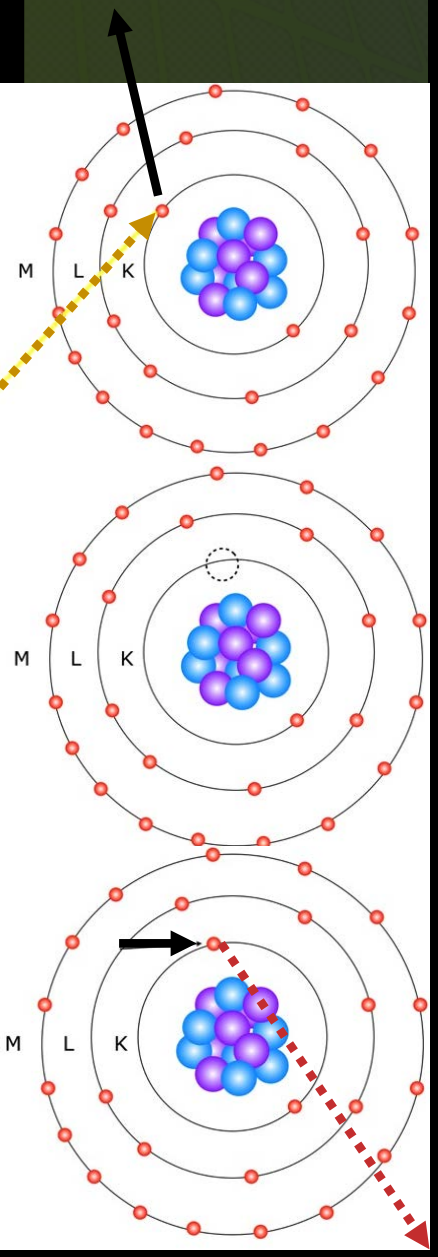
- 51 bank soil samples
- JMU ISAT Lab
- Calibration curve development; MDL determination; Triplicate analysis; precision and accuracy evaluation

Instrument Setup

Parameter	Value
Model	Bruker Tracer III Handheld XRF Spectrometer
Voltage	0-40 kV
Current	30 uA
Analysis Time	60 s and 100 s
Filter	Ti/Al/Cu

Instrument parameters were selected to optimize detection of Hg

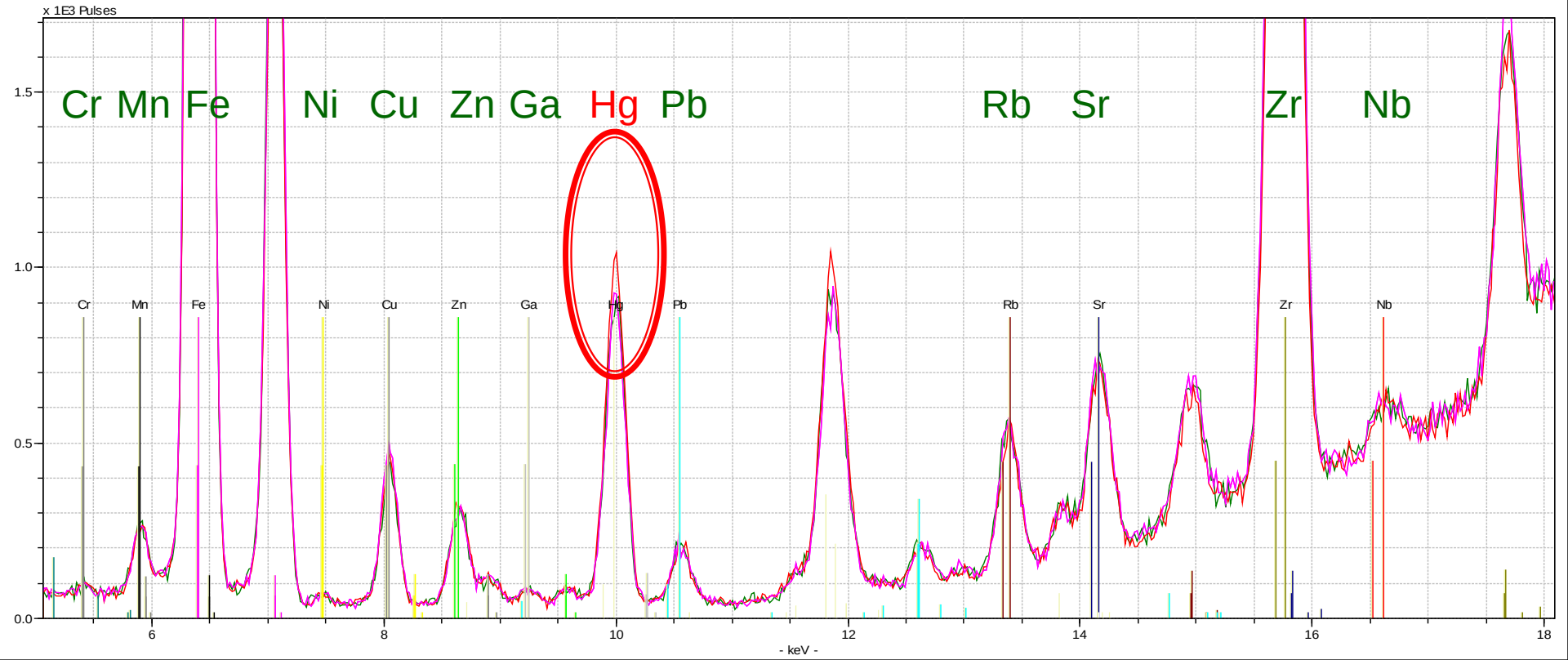
Instrument Principles



- Instrument produces x-rays that hit elements in the sample and expel inner shell electrons
- Outer shell electrons fill the void in the inner shell
- Drop in energy level releases a photon of energy in the x-ray spectrum
- Each element has a characteristic energy level of photons released

Post Processing

- Artax software used to analyze spectra
  - Bayesian deconvolution method modeled peaks and quantified electron counts for each element



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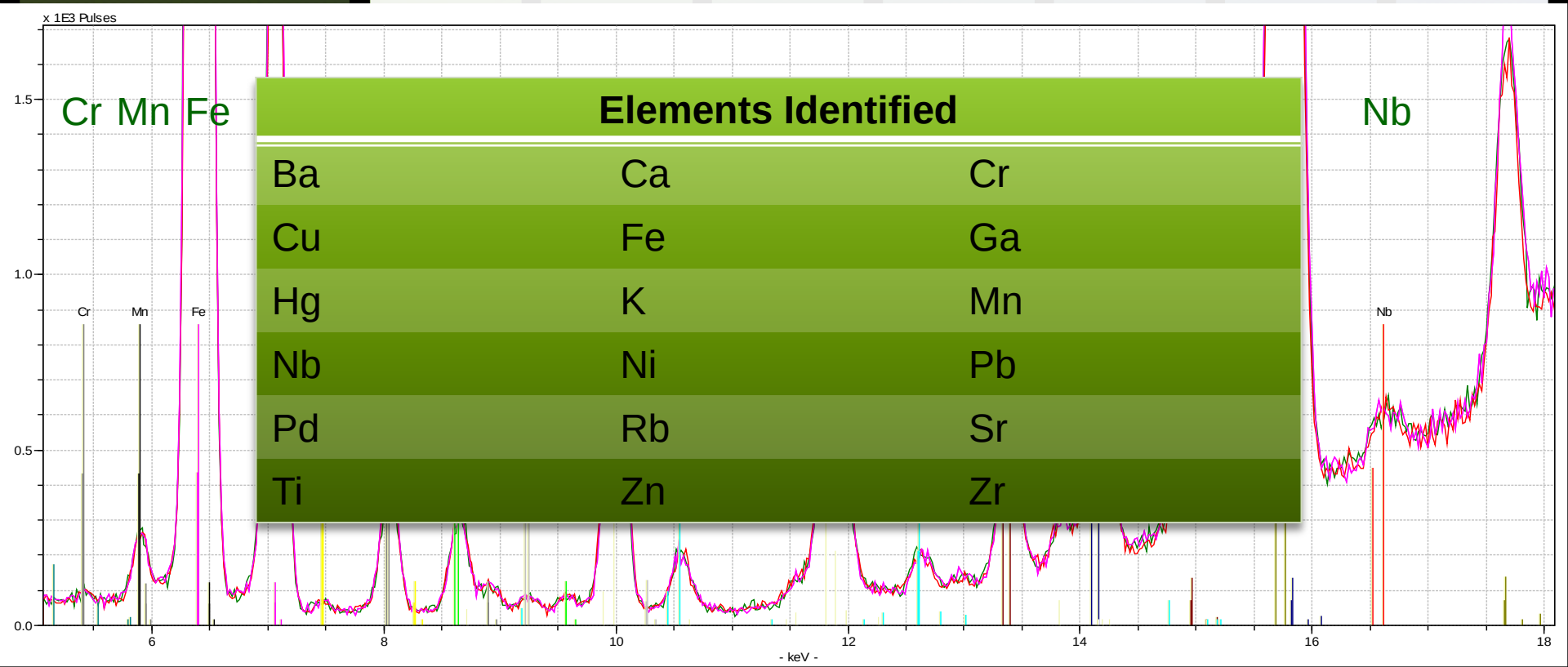
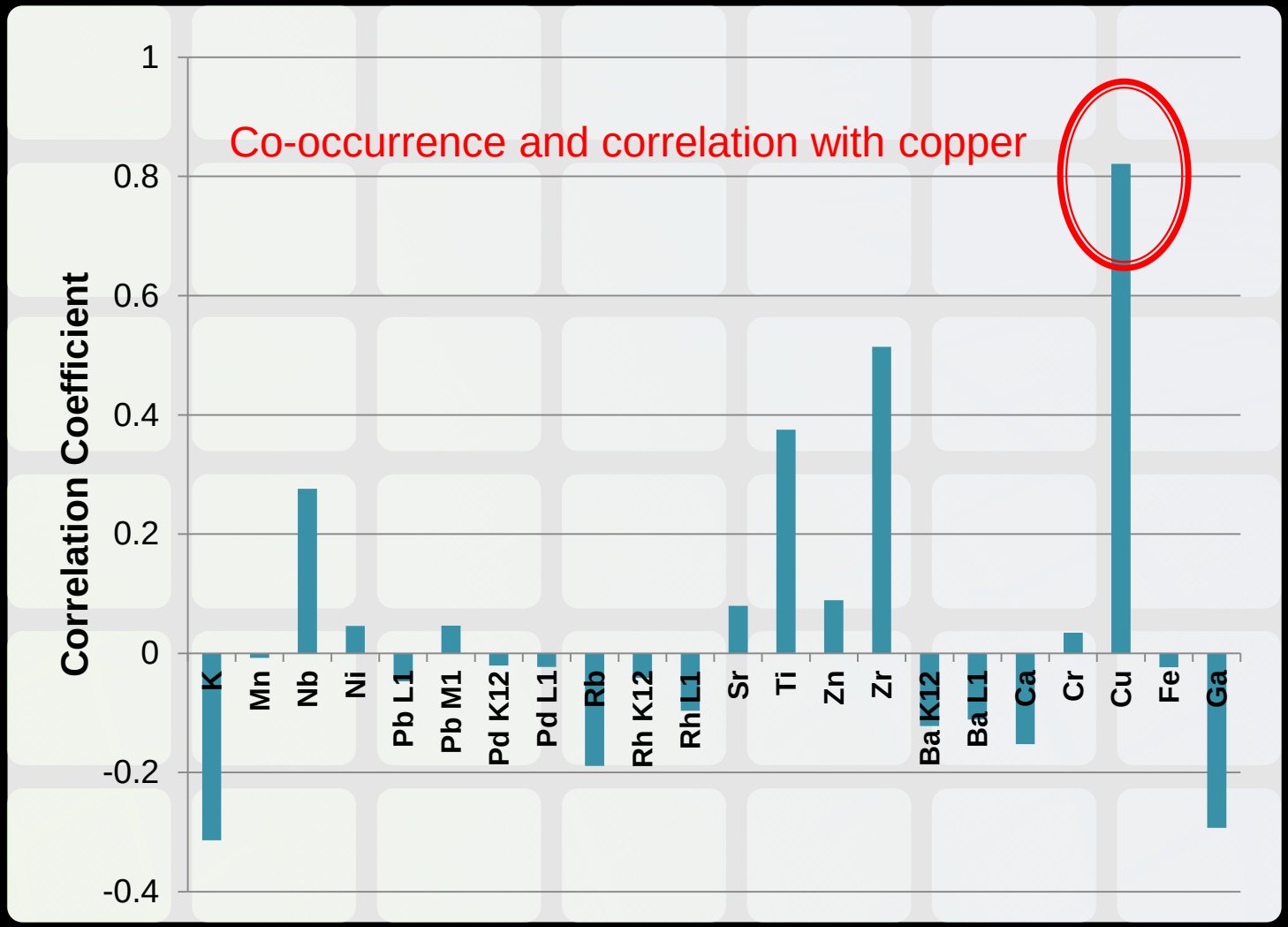


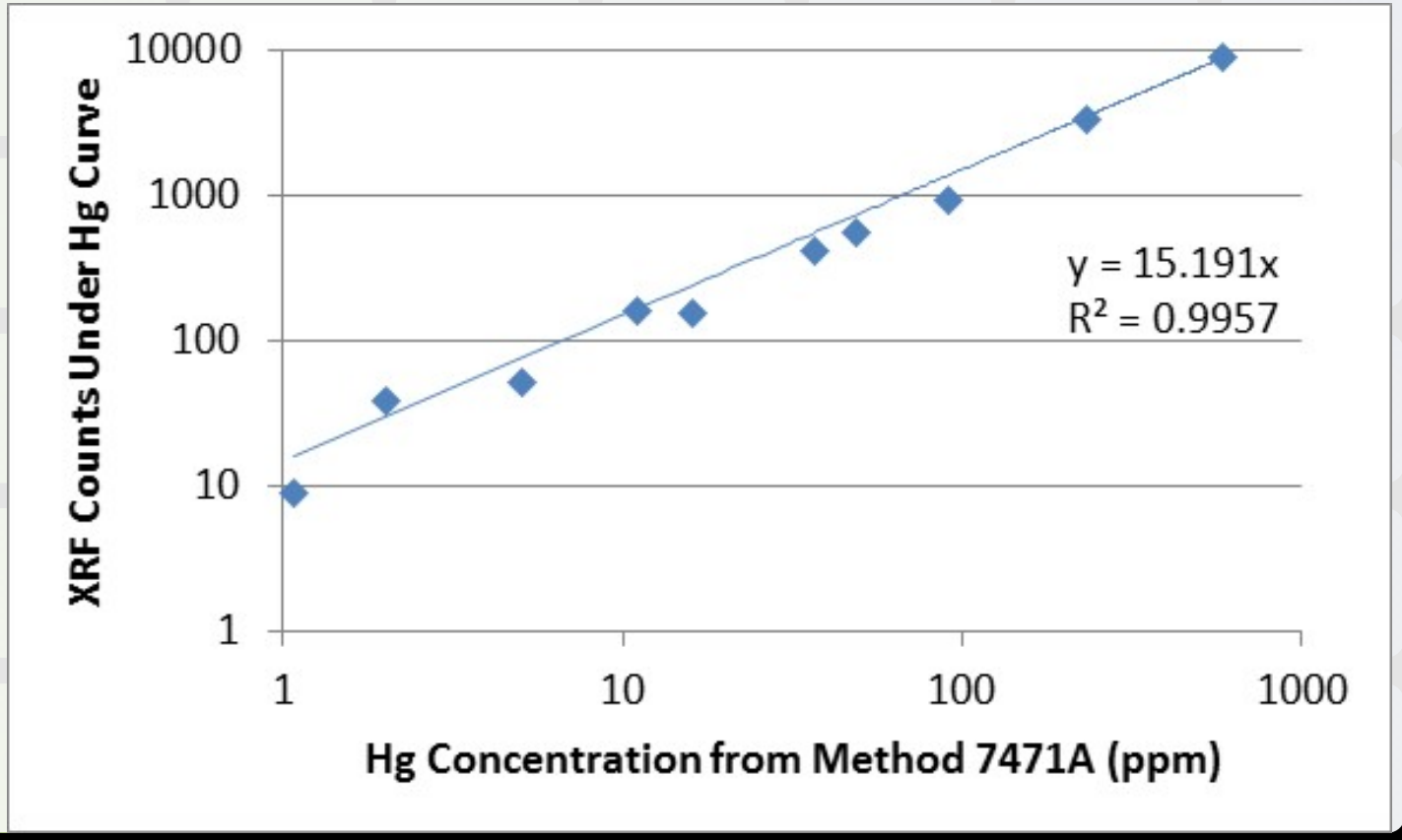
Elements Identified		
Ba	Ca	Cr
Cu	Fe	Ga
Hg	K	Mn
Nb	Ni	Pb
Pd	Rb	Sr
Ti	Zn	Zr

Element Comparisons



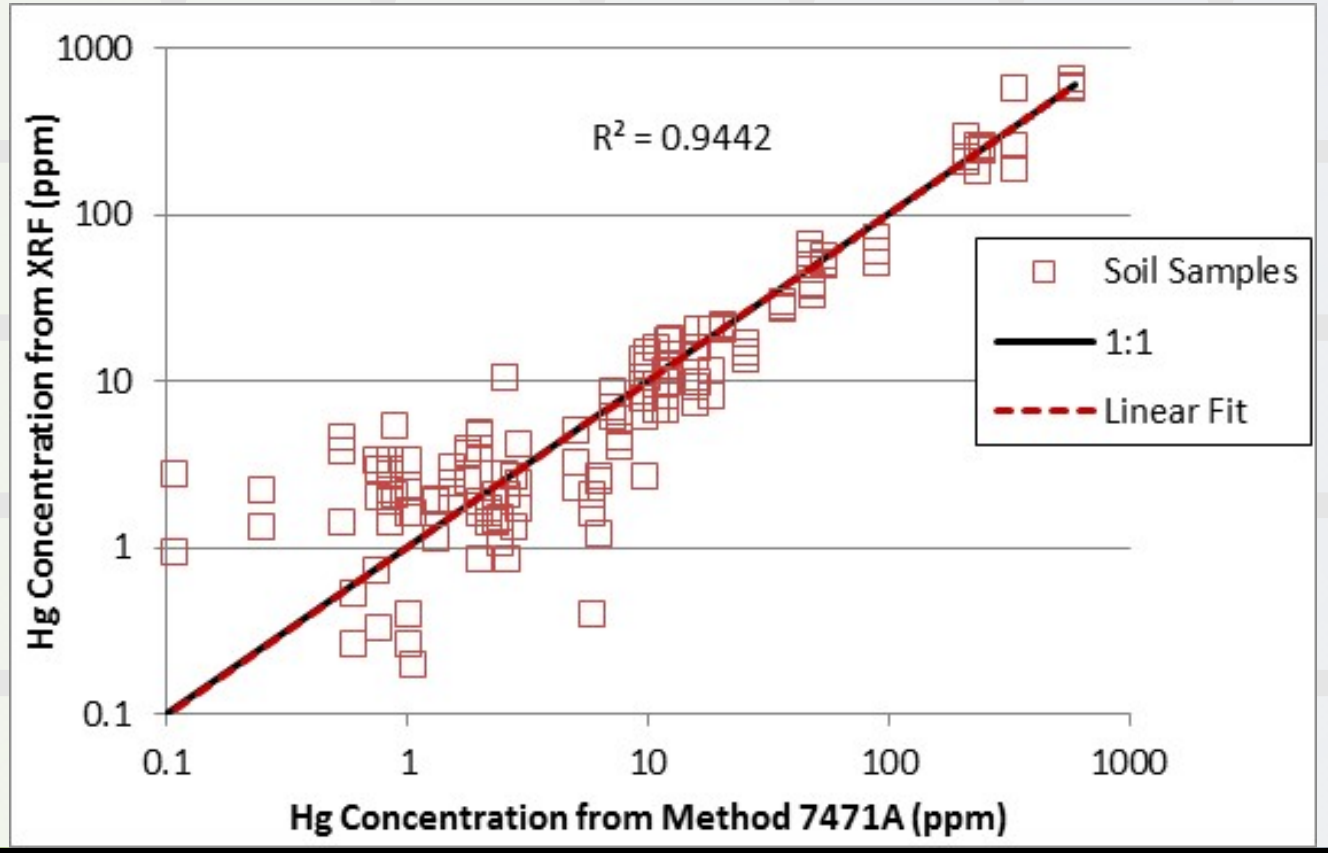
Calibration

- 10 samples of known Hg conc. ranging from 1.07 to 587 ppm



Analysis Results

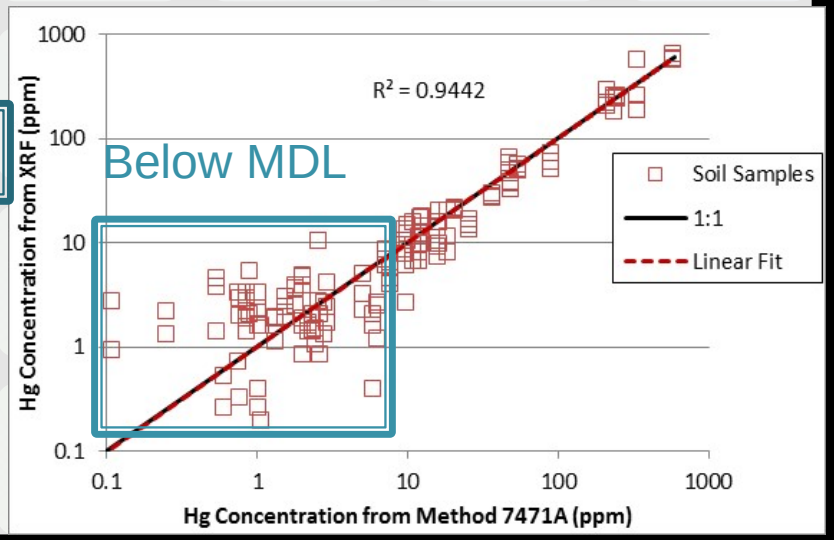
- All samples, all replicates analyzed according to calibration.



Method Detection Limit

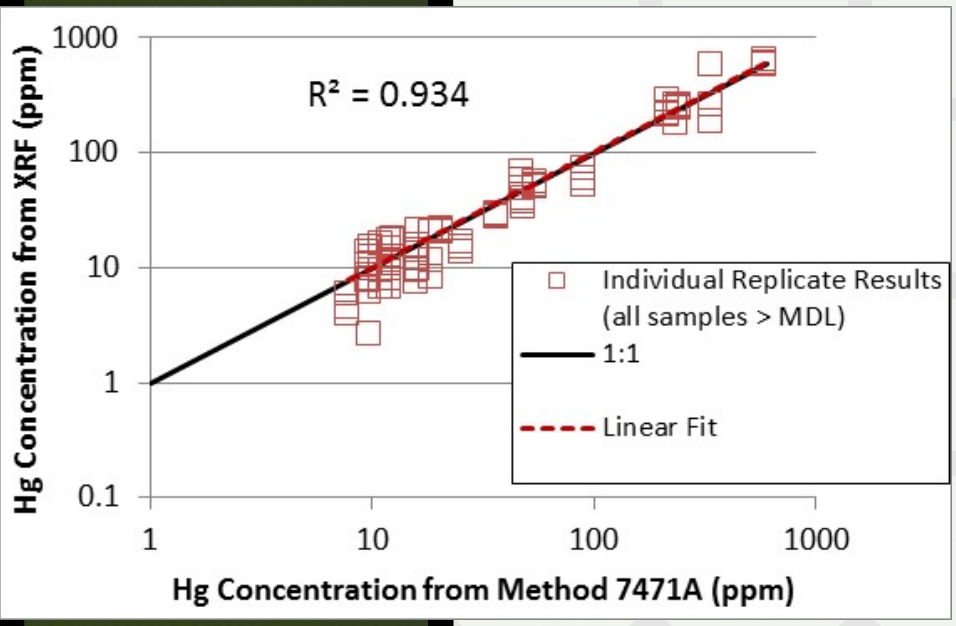
- Sample containing 10 ppm Hg
- 10 duplicate analyses conducted
- Calculated MDL as concentration that can be distinguished from zero with 95% confidence
- At 60 sec
  - MDL = 7.4 ppm
- At 100 sec
  - MDL = 3.4 ppm

Method 7471A
MDL ~ 0.11

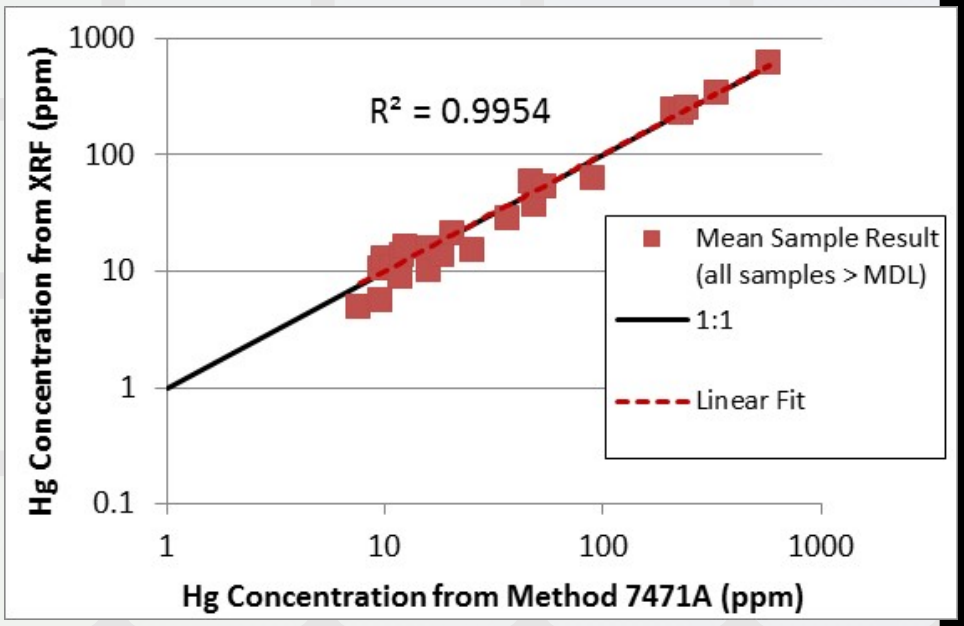


Results >MDL

All Replicates

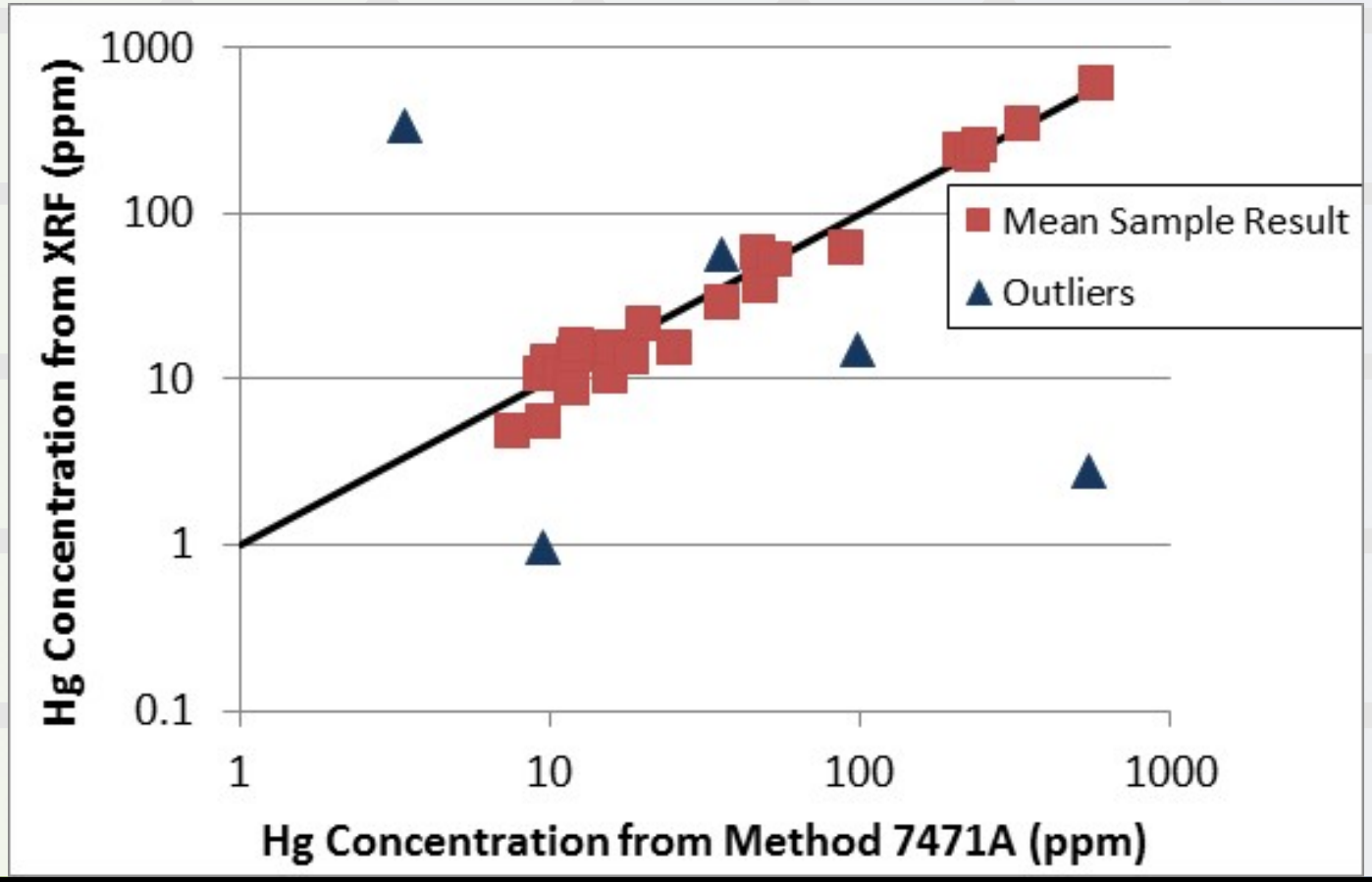


Mean Results



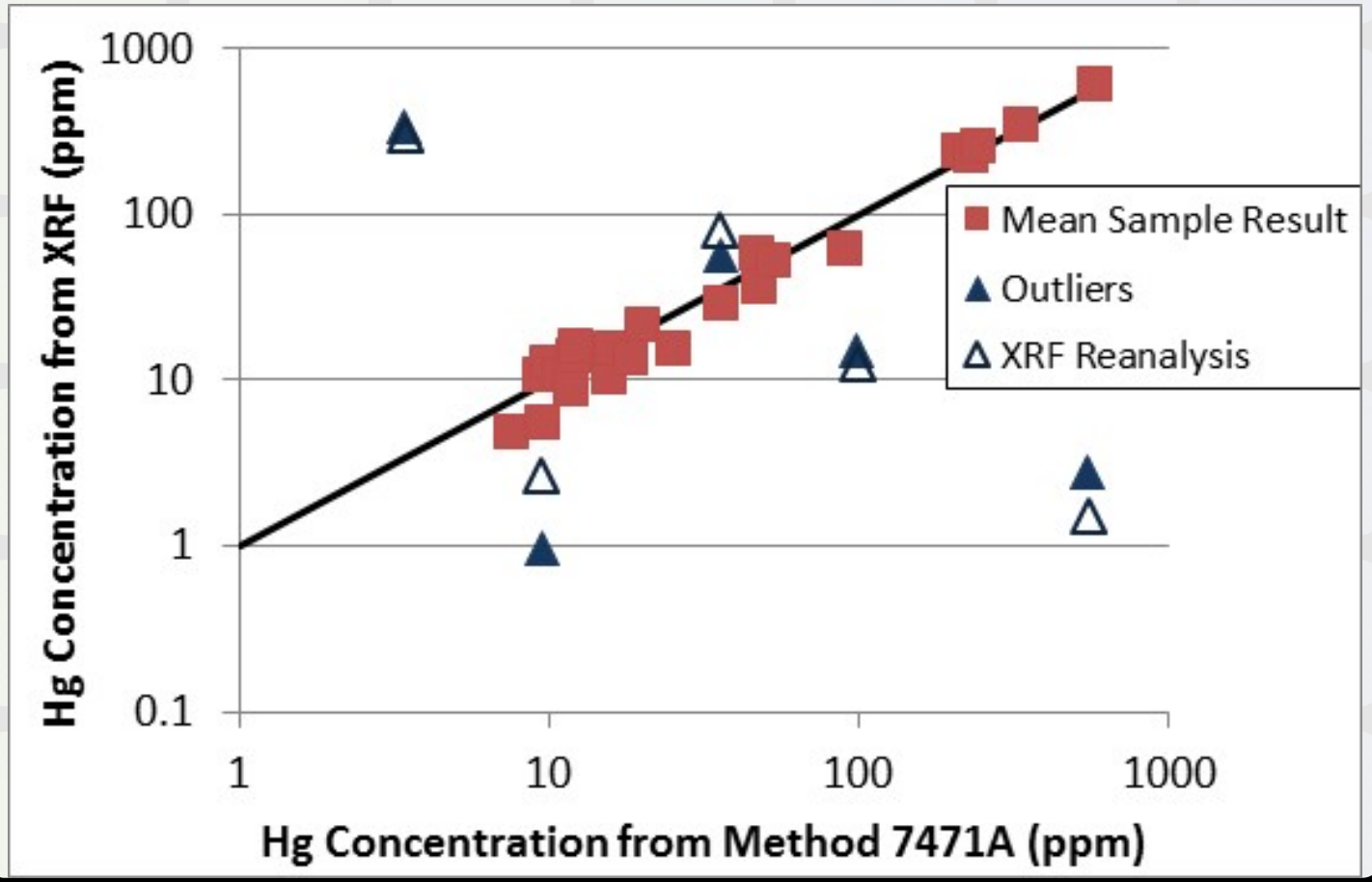
Outliers

- Outliers identified?



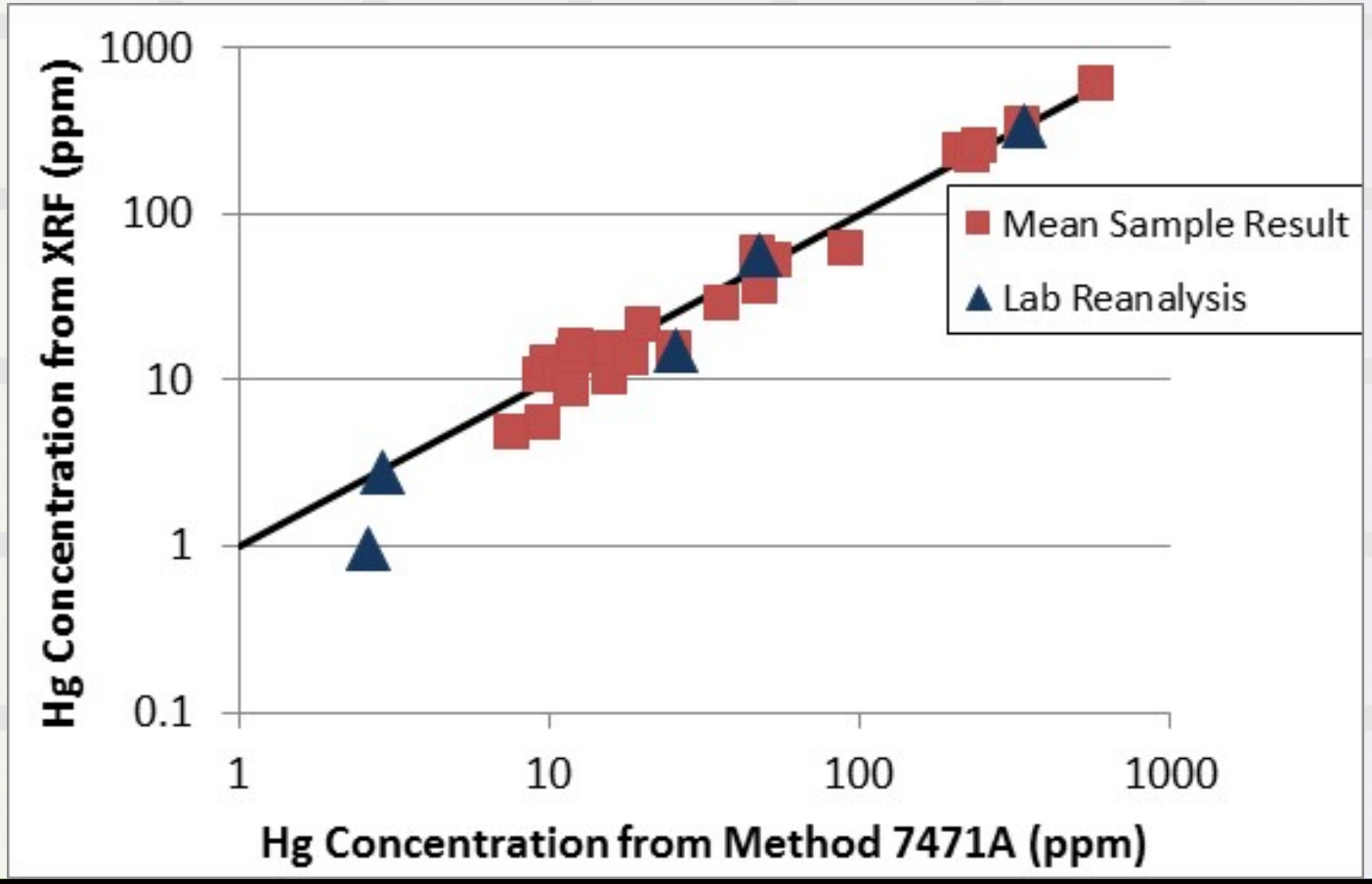
Outliers

- XRF Reanalysis



Outliers

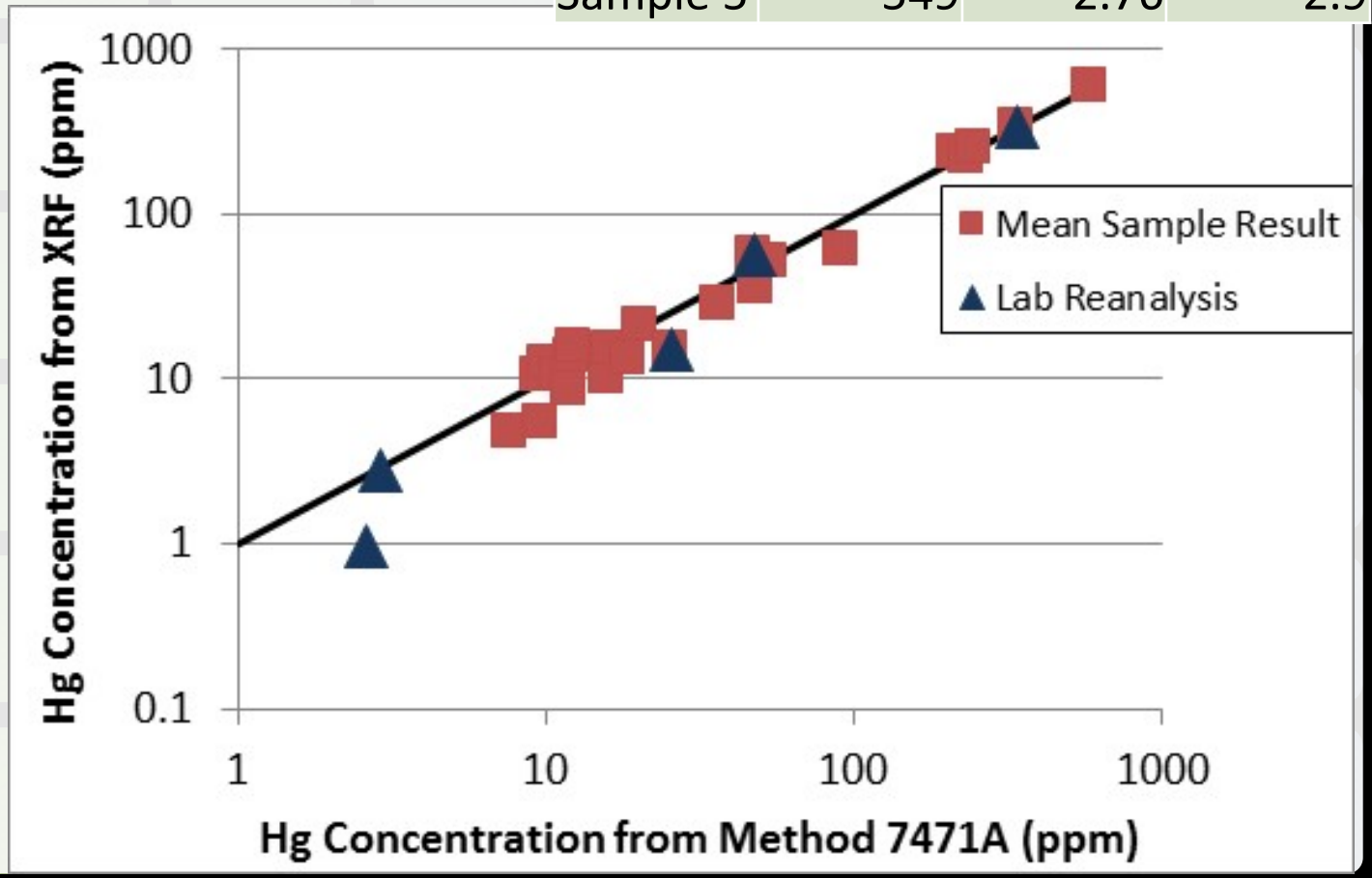
- Lab Reanalysis



Outliers

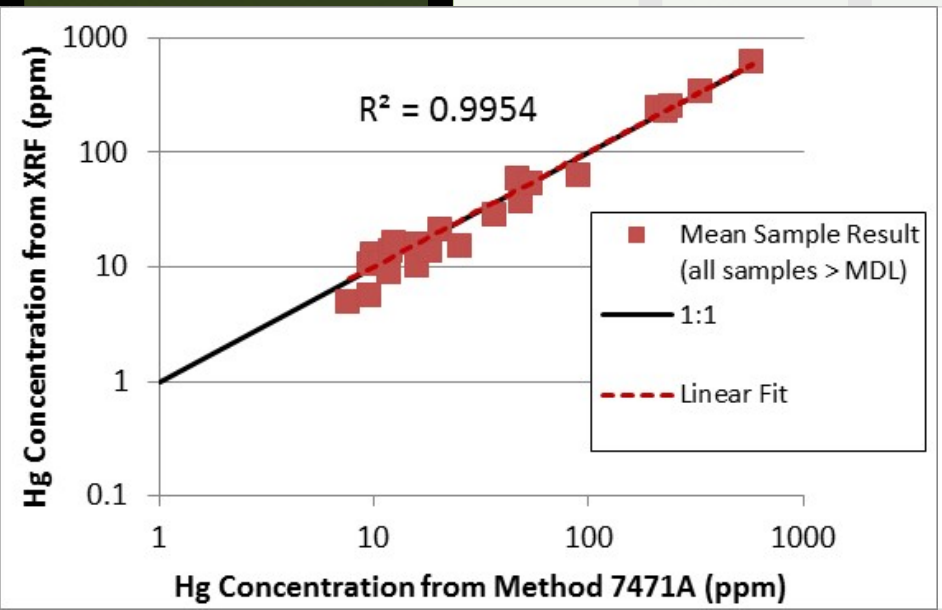
	Lab Result	XRF Result	Lab Re-analysis
Sample 1	3.42	338	336
Sample 2	9.48	0.965	2.62
Sample 3	35.8	57.4	47.5
Sample 4	98.2	14.9	25.5
Sample 5	549	2.76	2.9

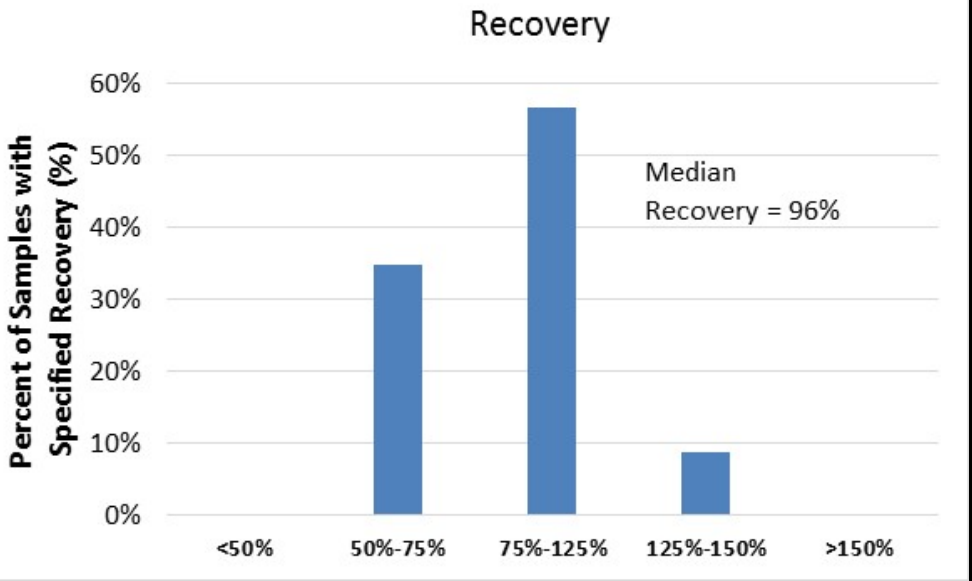
- Lab Reanalysis



Accuracy – Comparison with Known

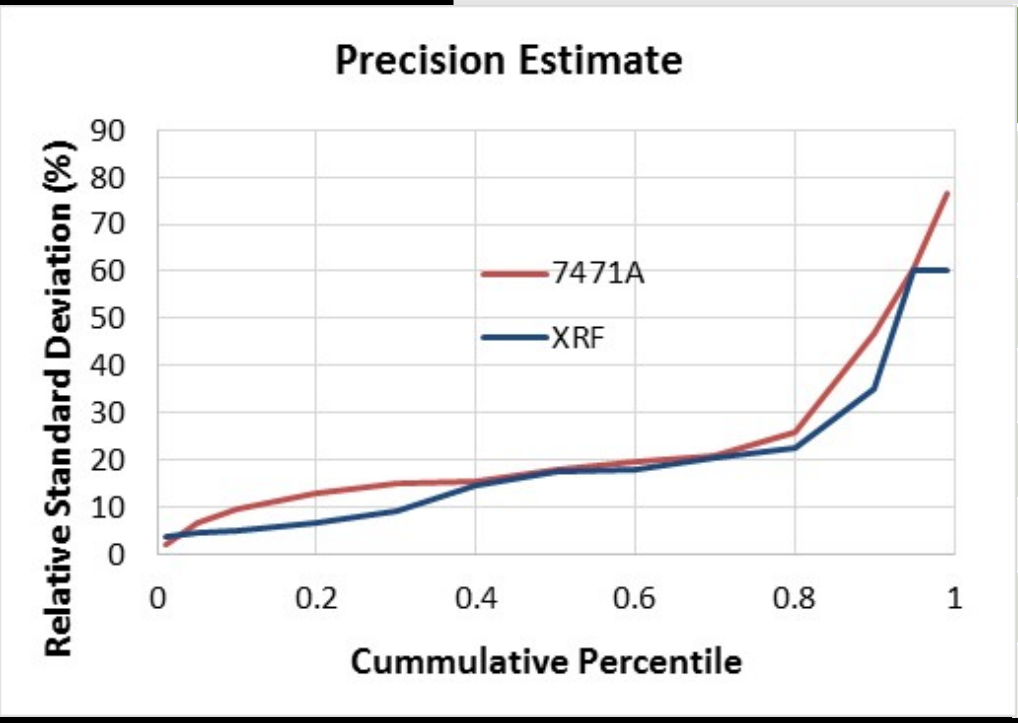
- R^2 of known vs measured regression
- Recovery = measured/known * 100
  - Includes both XRF measurement variability and Method 7471A measurement variability





Precision – Duplicate Analysis

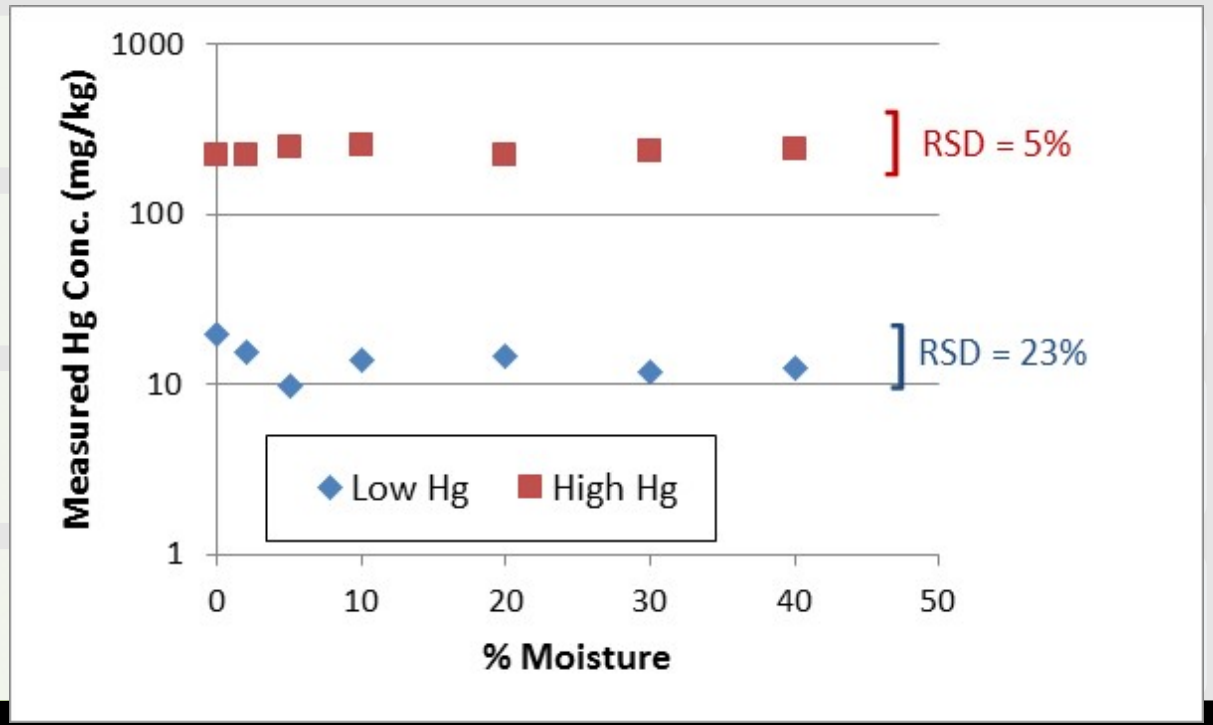
- Relative Standard Deviation (RSD or CV)
  - Duplicate standard deviation / duplicate mean * 100
- Relative Percent Difference (RPD)
  - Duplicate range / duplicate mean *100



		Method 7471A	XRF Method
RSD	N	28	23
	Mean	23	23
	Median	18	18
	Range	1-81	3-60
RPD	N	28	23
	Mean	33	44
	Median	25	35
	Range	1-115	6-113

Moisture Investigation

- XRF measurements tested on samples adjusted to varying moisture levels
  - Low Hg = 18.6 mg/kg; High Hg = 214 mg/kg
  - Moisture Levels = 0, 2, 5, 10, 20, 30, 40%



Conclusions

	Criteria	Description
✓	Cost	Only labor cost; no lab or shipping costs
✓	Turnaround Time	60 sec (or 100 sec)
✓	Detection Limit	7.4 ppm (@ 60 sec); 3.4 (@ 100 sec); below thresholds for determining bank management areas
✓	Accuracy	Acceptable accuracy; Median recovery = 96%; avoids errors from sample handling
✓	Precision	Acceptable precision; Mean RSD = 23%; precision identical to Method 7471A
✓	Interference	Moisture not a significant interference

Future Work

- Additional Lab Validation
  - Spiked samples
- Field Validation
  - Comparison of:
    - In situ XRF field measurement before sampling
    - XRF field measurement on collected sample
    - XRF lab measurement on collected sample
    - Method 7471A lab measurement on collected sample
- Analysis of banks in next 2 miles of river (2-4 miles)
  - Hg measurement and mapping using XRF and GPS