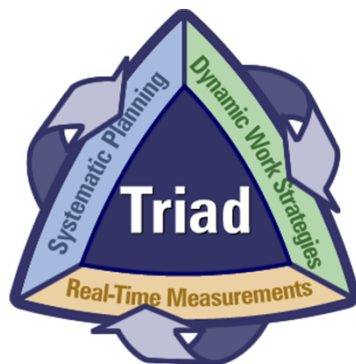Module 9

X-Ray Fluorescence (XRF)

Basic Concepts/Applications

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)
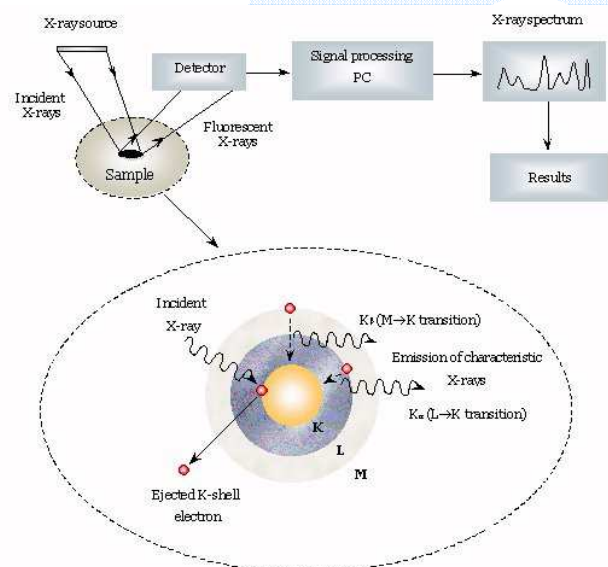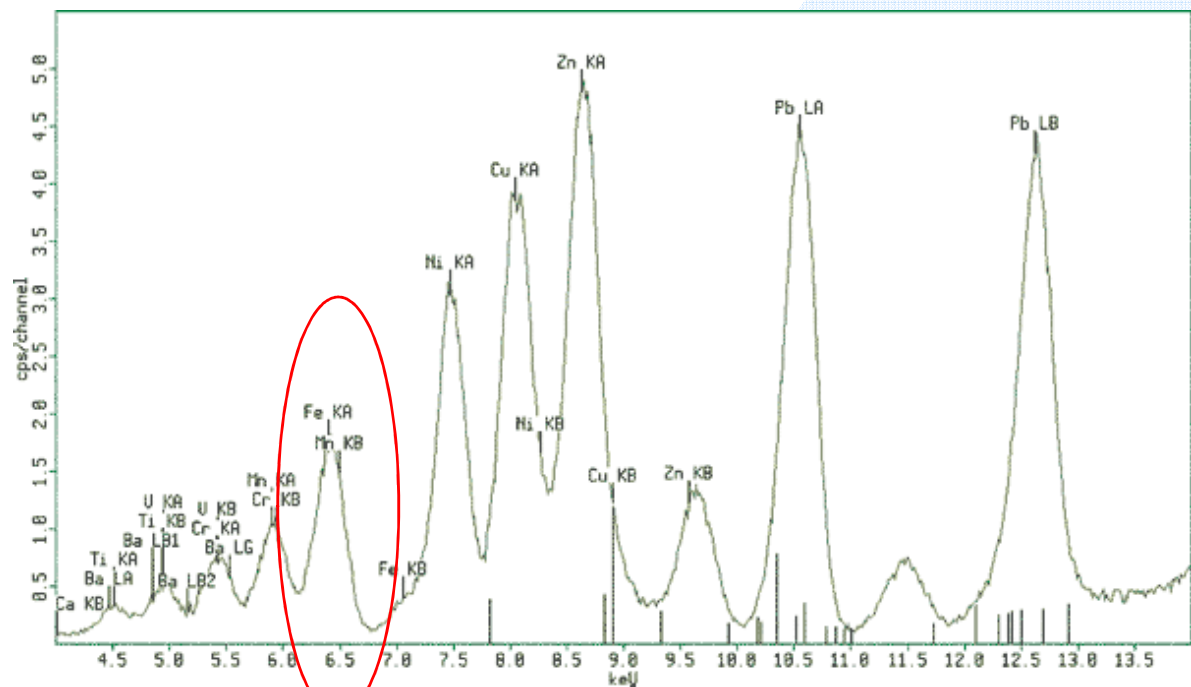- Concentration present estimated based on sample assumptions

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

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An Example XRF Spectrum…

How is an XRF Typically Used?

- Measurements on prepared samples

- Measurements through bagged samples (limited preparation)

- In situ measurements of exposed surfaces

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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

	A	C	D	E	F	G	H	O	P	Q	R	S	T
1	Date	Mode	LiveTime	Match1	MN1	Pass/Fail	Pass Fail Standard	Cr	Cr +/-	Mn	Mn +/-	Fe	Fe +/-
2	6-Dec-04	Standardization	53.46	0.0208	240	-0.0256	PASS						
13	6-Dec-04	Soil	76.53					<LOD	170.85	249.86	41.7	24698.13	184.68
14	6-Dec-04	Soil	80.24					196.44	60.31	263.28	43.37	25348.6	192.79
15	6-Dec-04	Soil	76					<LOD	175.72	373.11	43.1	21279.25	168.1
16	6-Dec-04	Soil	83.61					226.5	62.71	289.18	45.05	25161	197.15
17	6-Dec-04	Soil	83.07					<LOD	186.41	477.87	48.01	26620.96	205.4

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
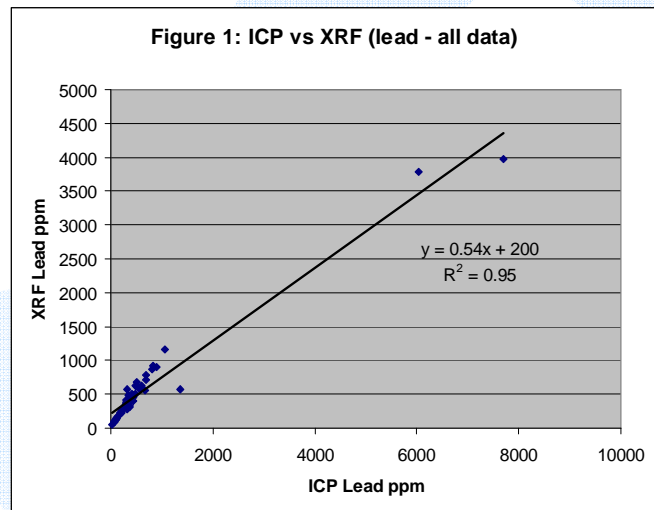
How Is An XRF Calibrated?

- **Fundamental Parameters Calibration** – calibration based on known detector response properties, "standardless" calibration, what is commonly done
- **Empirical Calibration** – calibration calculated using regression analysis and known standards, either site-specific media with known concentrations or prepared, spike standards
- **Compton Normalization** – calibration calculated using a combination of fundamental parameters and empirical calibration, most common for general environmental applications when concentrations are below % range

In any case, the instrument will have a dynamic range over which a linear calibration is assumed to hold.

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Dynamic Range a Potential Issue

- 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)

$y = 0.54x + 200$
$R^2 = 0.95$

(XRF Lead ppm vs ICP Lead ppm scatter plot)

Standard Innov-X Factory Calibration List

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

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?
- **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?

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Where Does Bias Come From?

- Soil moisture effects on XRF
- Problems with XRF calibration
- Problems with XRF performance
- Concentrations outside calibration range of XRF
- Interference effects (e.g., lead impacting arsenic values)
- Matrix effects
- Extraction issues with laboratory procedure (e.g., antimony, barium)

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Effect of Water Content For Various Elements

Effect of Water Content on Signal for Various Elements
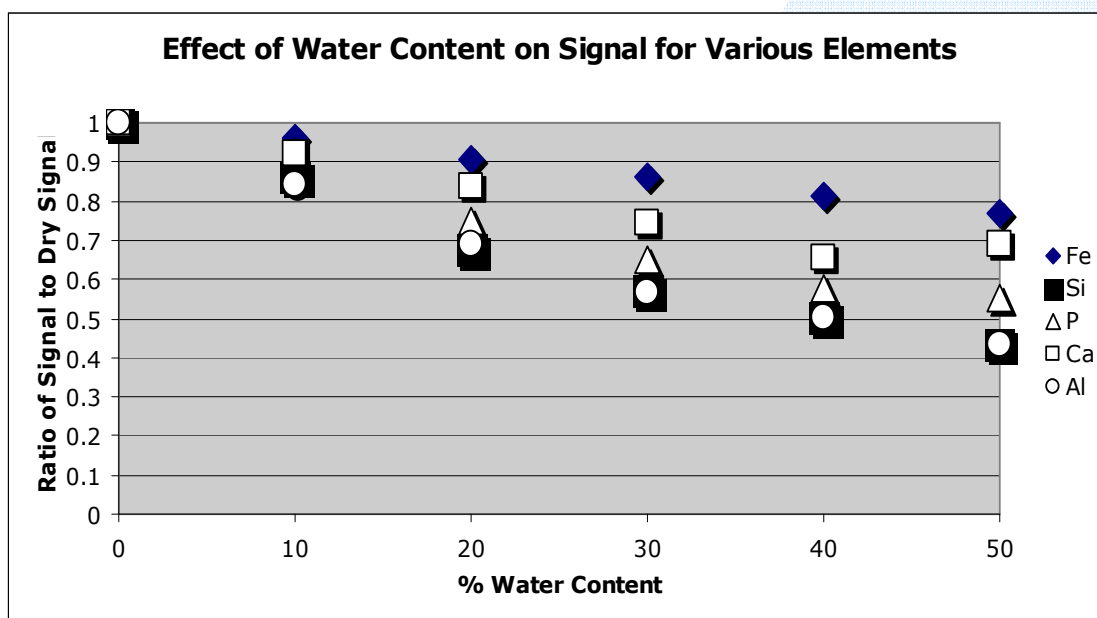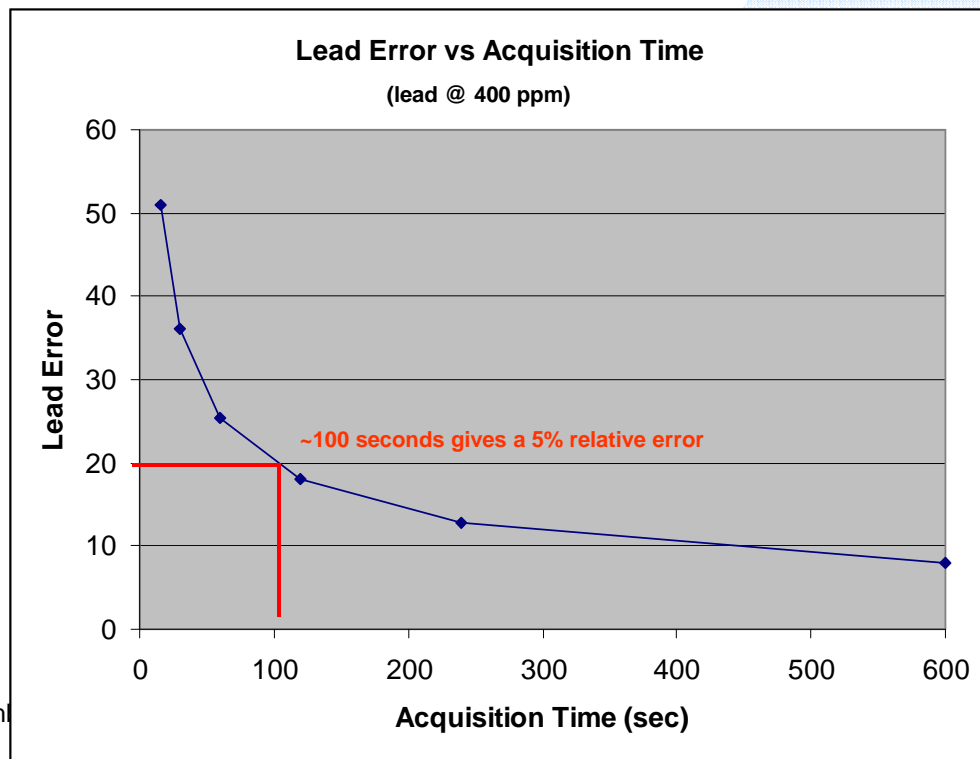
Analytical Precision Driven By...

- **Measurement time** – increasing measurement time reduces error

- **Element concentration present** – increasing concentrations increase error

- **Concentrations of other elements present** – as other element concentrations rise, general detection limits and errors rise as well
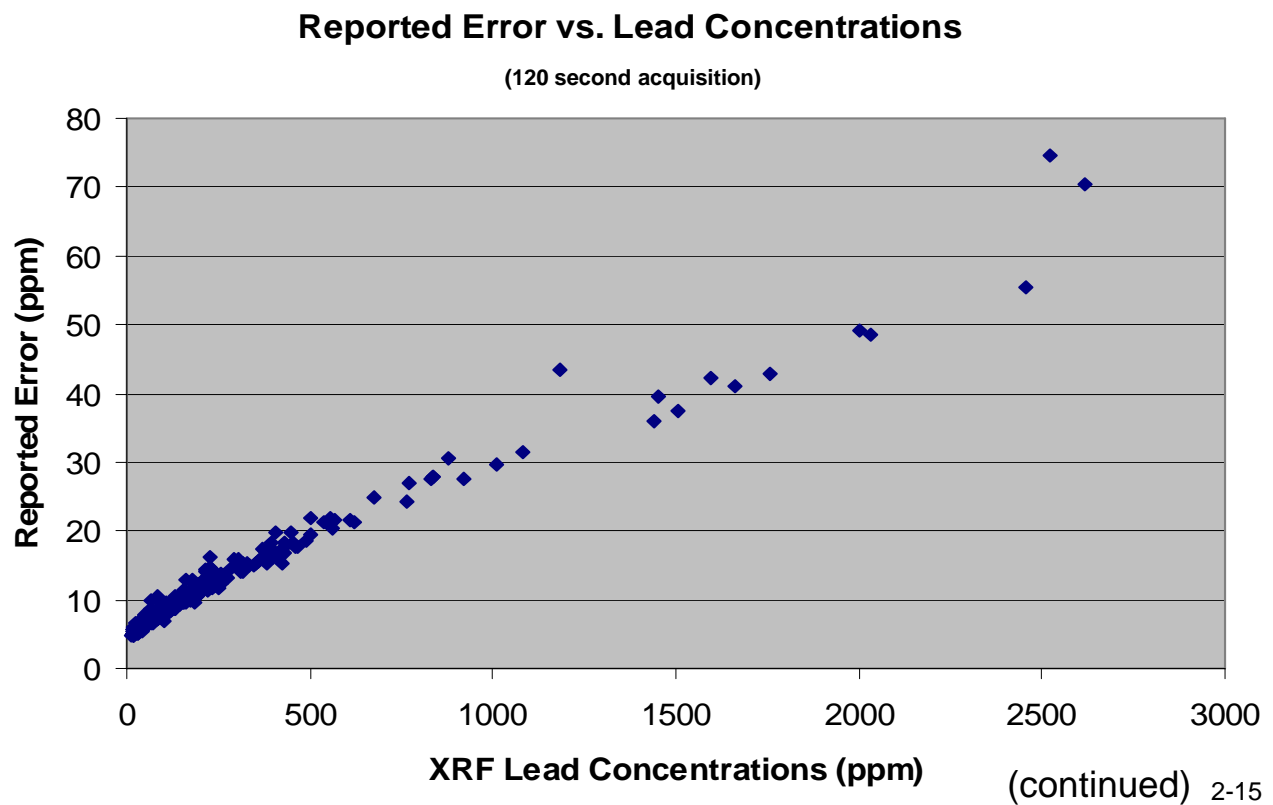
Precision Increases as Measurement Time Increases

Lead Error vs Acquisition Time

(lead @ 400 ppm)

~100 seconds gives a 5% relative error

Lead Error

Acquisition Time (sec)

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Lead Example: Concentration Effect

Reported Error vs. Lead Concentrations

(120 second acquisition)

(continued) 2-15

Lead Example: Concentration Effect

% Error vs. Lead Concentrations

(120 second acquisition)
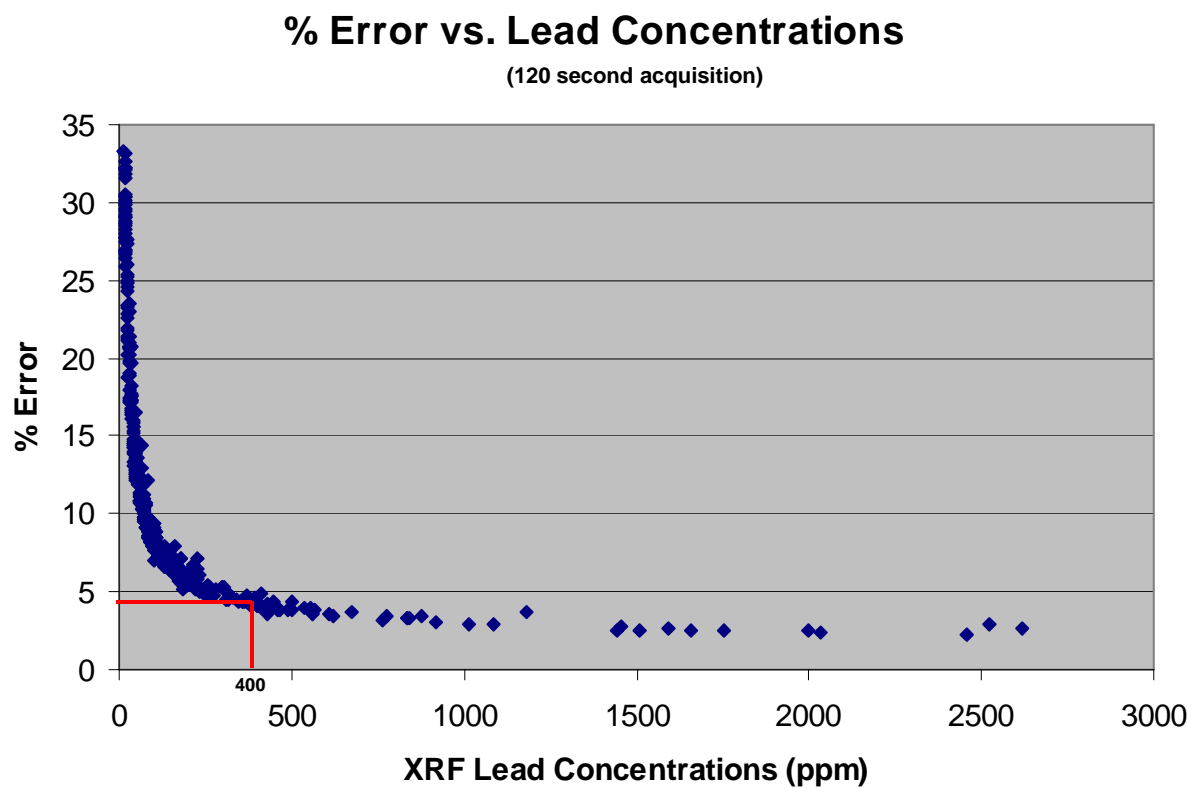
For Any Particular Instrument, Detection Limits Are Influenced By…

- Measurement time (quadrupling time cuts detection limits in half)

- Matrix effects

- Presence of interfering or highly elevated contamination levels
  Consequently, the DL for any particular element will change, sometimes dramatically, from one sample to the next, depending on sample characteristics and operator choices

Examples of DL…

(detection limits in black, "hits" in italicized **red**)

Analyte	Innov-X[1] 120 sec acquisition (**soil standard** – ppm)	Innov-X[1] 120 sec acquisition (**alluvial deposits** - ppm)	Innov-X[1] 120 sec acquisition (**elevated soil** - ppm)
Antimony (Sb)	61	55	232
Arsenic (As)	6	7	*29,200*
Barium (Ba)	NA	NA	NA
Cadmium (Cd)	34	30	**598**
Calcium (Ca)	NA	NA	NA
Chromium (Cr)	89	100	*188,000*
Cobalt (Co)	54	121	766
Copper (Cu)	21	17	661
Iron (Fe)	*2,950*	*22,300*	*33,300*
Lead (Pb)	*12*	8	*447,000*
Manganese (Mn)	56	*314*	1,960
Mercury (Hg)	10	8	481
Molybdenum (Mo)	11	9	*148*
Nickel (Ni)	*42*	31	451

To Report, or Not to Report: That is the Question!

- Not all instruments/software allow the reporting of XRF results below detection limits

- For those that do, manufacturer often recommends against doing it

- Can be valuable information if careful about its use…particularly true if one is trying to calculate average values over a set of measurements
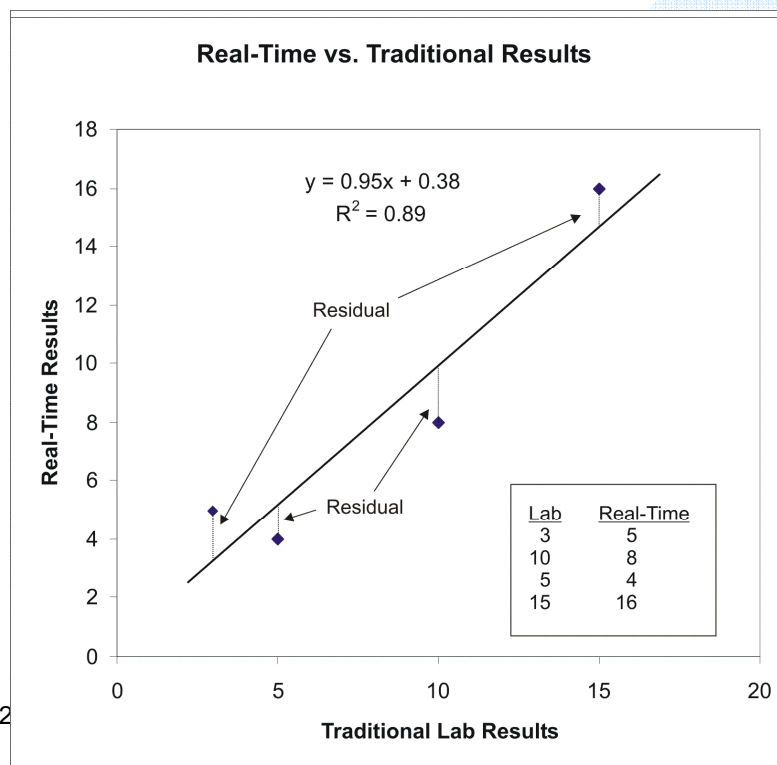
XRF Data Comparability

- Comparability usually refers to comparing XRF results with standard laboratory data

- Assumption is one has samples analyzed by both XRF and laboratory

- Regression analysis is the ruler most commonly used to measure comparability

- SW-846 Method 6200: "If the r^2 is 0.9 or greater…the data could potentially meet definitive level data criteria."

What is a Regression Line?

Real-Time vs. Traditional Results

$y = 0.95x + 0.38$
$R^2 = 0.89$

Residual

Residual

Real-Time Results (y-axis): 18, 16, 14, 12, 10, 8, 6, 4, 2, 0

Traditional Lab Results (x-axis): 0, 5, 10, 15, 20

Lab	Real-Time
3	5
10	8
5	4
15	16

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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

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Evaluating Regression Performance

- No evidence of inexplicable "outliers"

- Balanced data sets

- No signs of correlated residuals

- High R^2 values (close to 1)

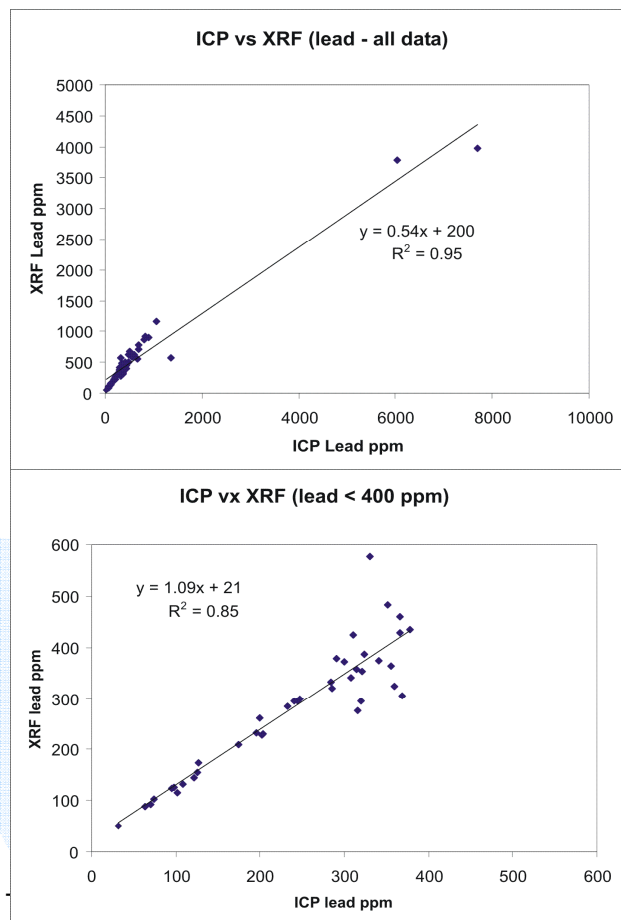- Constant residual variance (homoscedastic)

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

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ICP vs XRF (lead - all data)

$y = 0.54x + 200$
$R^2 = 0.95$

XRF Lead ppm (y-axis: 0 to 5000)
ICP Lead ppm (x-axis: 0 to 10000)

ICP vx XRF (lead < 400 ppm)

$y = 1.09x + 21$
$R^2 = 0.85$

XRF lead ppm (y-axis: 0 to 600)
ICP lead ppm (x-axis: 0 to 600)

Converting XRF Data for Risk Assessment Use

- Purpose: making XRF data "comparable" to lab data for risk assessment purposes
- To consider:
  - Need for "conversion" may be an indication of a bad regression
  - XRF calibrations not linear over the range of concentrations potentially encountered
  - Extra variability in XRF data not an issue (captured in UCL calculations when estimating EPC)
  - Contaminant concentration distributions are typically skewed… lots of XRF data may provide a better UCL/EPC estimate than a few lab results even if the regression is not great

Will the "Definitive" Data Please Stand Up?

One of these scatter plots shows the results of arsenic from two different ICP labs, and the other compares XRF and ICP arsenic results.
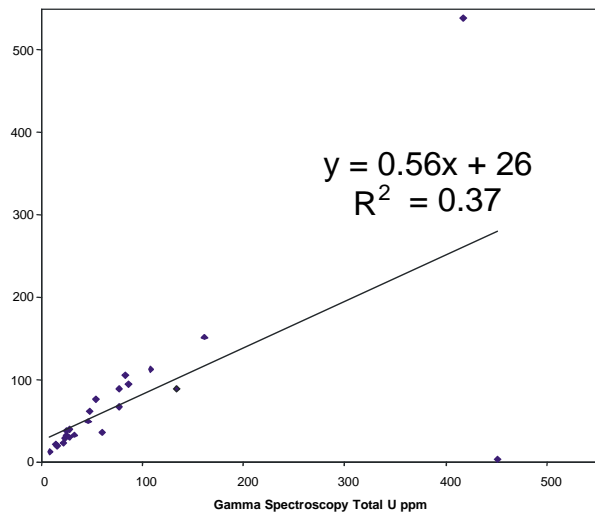**Which is which?**
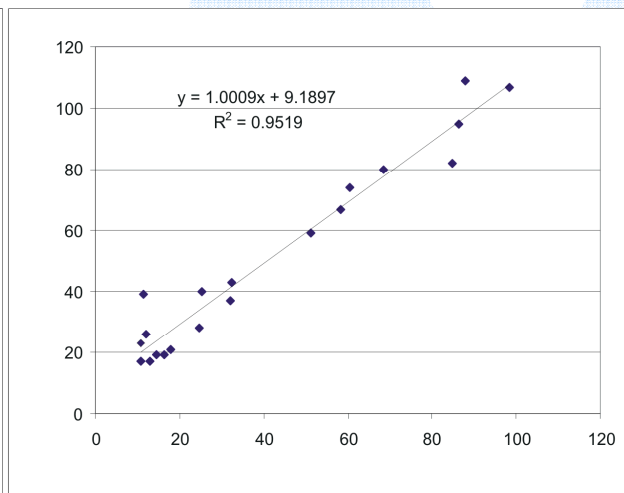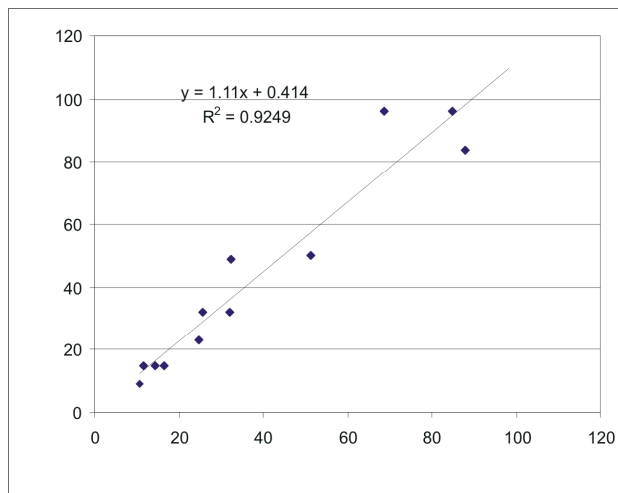
Definitive Data, Please Stand Up!

Alpha Spectroscopy Total U (ppm) vs Gamma Spectroscopy Total U (ppm)

$y = 0.56x + 26$
$R^2 = 0.37$

Gamma Spectroscopy Total U ppm

XRF Total U (ppm) vs Gamma Spectrsocopy Total U (ppm)

$y = 0.74x + 22$
$R^2 = 0.91$

Gamma Spectroscopy Total U ppm
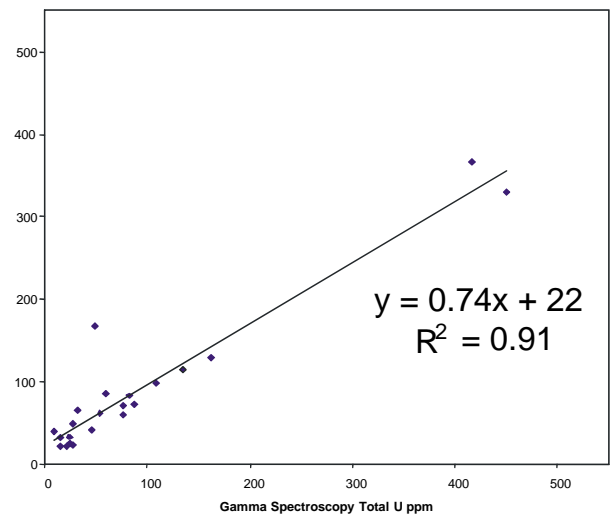
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How Good Can an XRF Be?

XRF Total U vs. Lab Total U

$y = 0.97x + 4.9$
$R^2 = 0.98$

(X-axis: Alpha Spectroscopy Total U (ppm), 0 to 700)
(Y-axis: XRF Total U (ppm), 0 to 700)
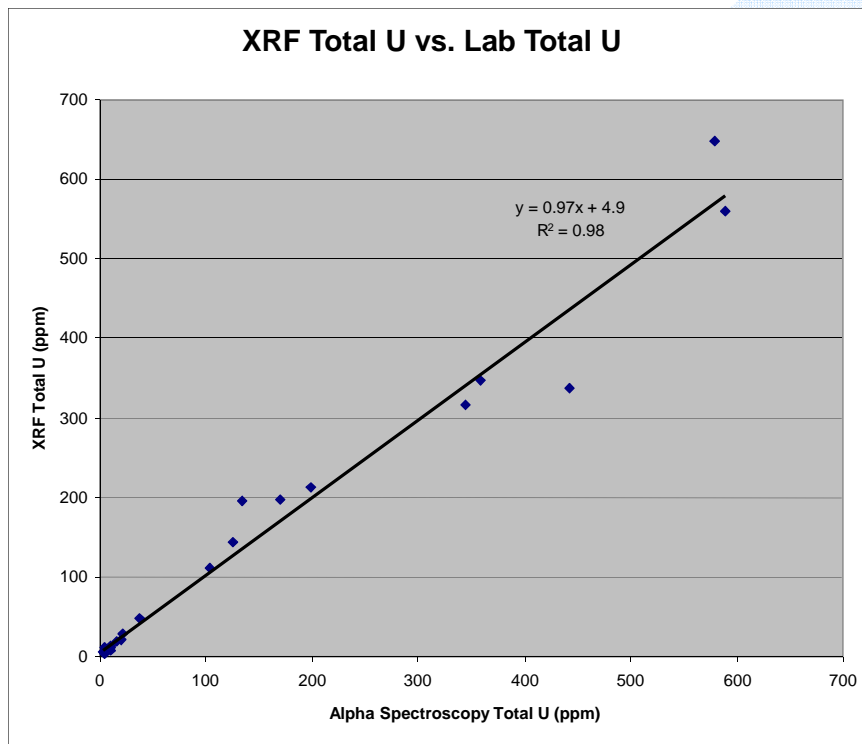
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Take-Away Comparability Points

- Standard laboratory data can be "noisy" and are not necessarily an error-free representation of reality
- Regression R^2 values are a poor measure of comparability
- Focus should be on decision comparability, not laboratory result comparability
- Examine the lab duplicate paired results from traditional QC analysis - the split field vs. lab regression cannot be expected to be better than the lab's duplicate vs. duplicate regression

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What Affects XRF Performance?

- **Measurement time** – the longer the measurement, the better the precision

- **Contaminant concentrations** – potentially outside calibration ranges, absolute error increases, enhanced interference effects

- **Sample preparation** – the better the sample preparation, the more likely the XRF result will be representative

What Affects XRF Performance?

- **Interference effects** – the spectral lines of elements may overlap

- **Matrix effects** – fine versus coarse grain materials may impact XRF performance, as well as the chemical characteristics of the matrix

- **Operator skills** – watching for problems, consistent and correct preparation and presentation of samples

XRF and Dynamic Work Strategies

- XRF is truly a "real-time" field-deployable instrument
- "Real-time" aspect means XRF is ideal for supporting dynamic work strategies
- Dynamic work strategies based on XRF:
  - Changing the number of XRF measurements taken
  - Changing the locations of data collection
  - Determining how many samples are sent for lab analysis
  - Determining which samples are sent for lab analysis
  - Selecting samples for QC work

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Improving Data Representativeness with XRF

- Sample support
  - matching sample support with decision needs
  - field of view for *in situ* analyses
- Controlling within-sample heterogeneity
  - Appropriate sample preparation important (see EPA EPA/600/R-03/027 for additional detail)
  - XRF applications to within-sample heterogeneity issues
- Controlling short-scale heterogeneity
  - aggregating *in situ* measurements

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Bagged-Sample Measurements Can Substitute for Sample Preparation

- Goal is to get an accurate estimate of the metal concentration within a sample as quickly and cheaply as possible
- Primary cost associated with an XRF is sample preparation
- Measuring through bag walls multiple times and averaging result substitutes for sample preparation
- How many shots through bag walls are required and what should the measurement times be?

Same Concept Applies to XRF
In Situ Measurements

- XRF *in situ* measurements:
  - Rapid means for quickly estimating concentration present in surface soils
  - Short scale heterogeneity can be severe for impacted soils
  - As with bagged samples, more shorter-acquisition-time measurements systematically across area of interest gives a more accurate assessment of the average concentration present

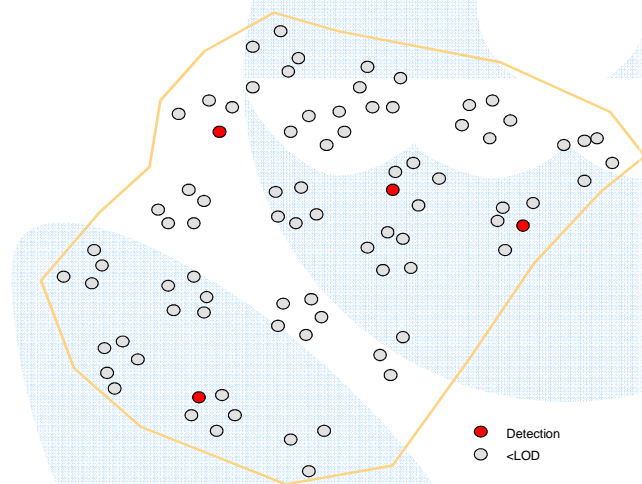September 11, 2012   Portsmouth Training   35

One Additional XRF Not-So-Basic Concept…

- Recall that XRF relative measurement error and DL decrease with increasing count time
- Suppose one has established a DL goal and determined a necessary count time to achieve it
- *It doesn't matter whether one long shot is taken, or repeated shorter measurements with an average concentration determined from the shorter measurements!*
- This is why reporting <DL XRF results can be very useful…we need those results to calculate meaningful averages for short acquisition times
- Particularly important for repeated *in situ* measurements or repeated measurements of bagged samples

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Working with <LOD Results: Exposure Units/Area Averages

- 5 acre exposure unit

- Uranium issue

- 84 XRF samples

- All but 4 non-detects
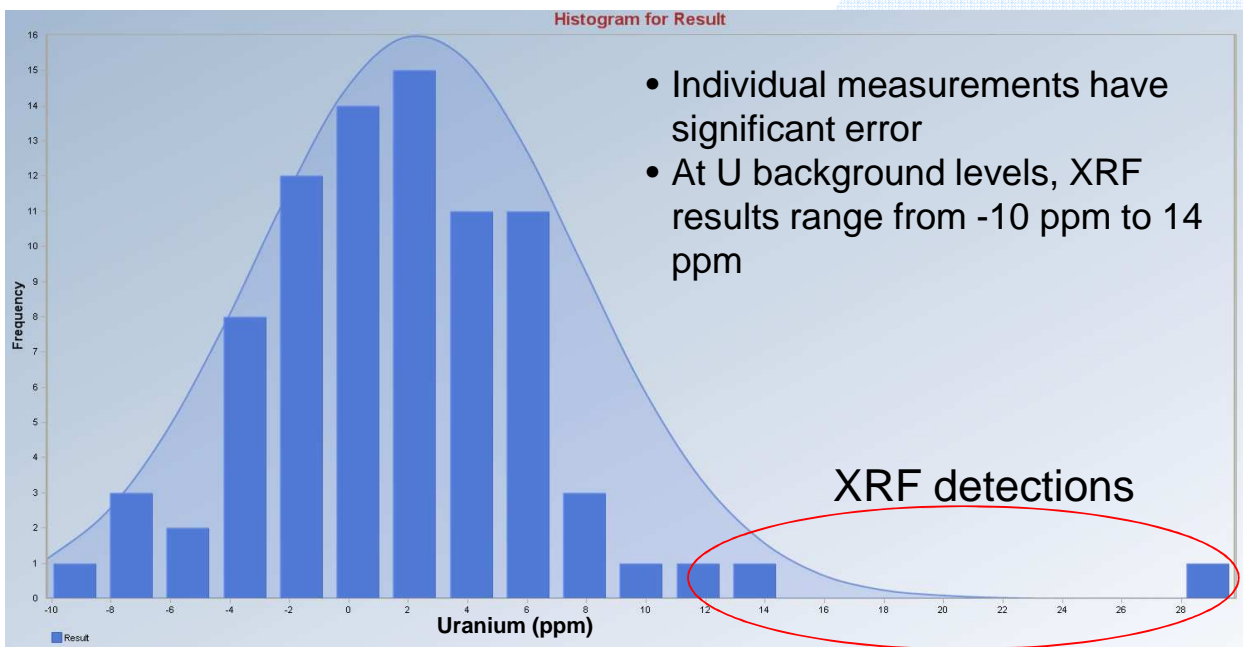
- DL: ~15 ppm w/ 120 sec reading

- Background: ~ 3 ppm

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XRF U Result Distribution Is Ugly…

Improving Representativeness

Histogram for Result

- Individual measurements have significant error
- At U background levels, XRF results range from -10 ppm to 14 ppm

XRF detections

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…But EU Average U Calculation Provides Usable Results

- With raw U XRF data:
  - average: 2.3 ppm
  - 95%LCL-UCL: 1.1 - 3.5 ppm
- Standard guidance would have discarded <LOD values when calculating mean
- End result would either mean rejecting XRF data, or using a much less accurate approach for estimating mean concentration (e.g., set <LOD results to LOD or ½ of LOD)

Working with <LOD Results: Bagged Sample Estimates

Bag ID	Sample	Result	Error	Flag
BS-18	TOP-1	10.9	3.7	<LOD
	TOP-2	5.4	3.7	<LOD
	TOP-3	0.0	3.6	<LOD
	TOP-4	2.0	3.8	<LOD
	TOP-5	7.1	3.6	<LOD
	BOTTOM-1	6.2	3.8	<LOD
	BOTTOM-2	1.3	3.7	<LOD
	BOTTOM-3	3.5	3.8	<LOD
	BOTTOM-4	8.8	3.8	<LOD
	BOTTOM-5	9.0	3.5	<LOD

- Uranium concerns
- 30-sec readings
- DL: ~11 ppm/reading
- Averaging 10 readings for bag
- Equivalent to 300-sec reading
- Average = 5.4 ppm +/- 1.2 ppm
- DL for average: ~3.6 ppm

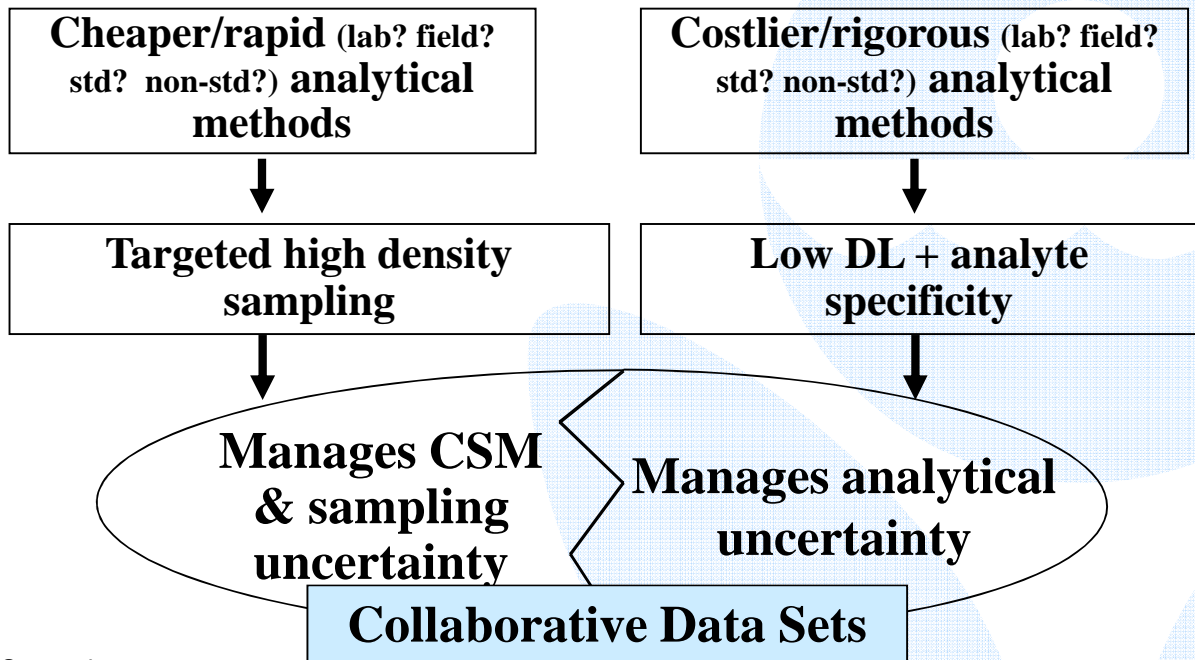September 11, 2012   Portsmouth Training   40

Aggregating XRF Measurements

- Can be done either automatically by the XRF unit (if set up to do so) or manually by recording multiple measurements, downloading, and calculating averages for sets of measurements in a spreadsheet

- If automatically, *be aware that the XRF-reported error and DL will be incorrect for the measurement aggregate*

"Driving" Sampling Programs Based on XRF Data

- XRF data can be used to "delineate" lateral footprints of contamination
- XRF data can be used to determine soil core depths on-the-fly
- XRF data can be used to select samples for off-site analysis
- XRF data can be used to determine the number of XRF measurements/samples required

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Collaborative Data Sets Address Analytical and Sampling Uncertainties

Cheaper/rapid (lab? field? std? non-std?) **analytical methods**

Costlier/rigorous (lab? field? std? non-std?) **analytical methods**

Targeted high density sampling

Low DL + analyte specificity

Manages CSM & sampling uncertainty

Manages analytical uncertainty

Collaborative Data Sets

Collaborative Data Sets: Supplementing Lab Data with XRF

- Goal: Identify areas of concern and estimate their mean concentration
- Assumptions:
  - Two methods, one cheap/less accurate (e.g., XRF), one expensive/"definitive" (e.g., alpha spec)
- XRF data identifies areas of concern
- XRF data used to estimate number of more expensive analyses required to estimate mean accurately
- More expensive, higher analytical quality data used to estimate average concentrations

A Simple Example…

- 4 residential backyards screened by XRF for arsenic w/ action level of 25 ppm averaged over yard
- Regulator insists final release decision be based on lab data
- Use XRF to determine:
  - whether each yard is likely above or below action level, and
  - if below, how many lab samples are required to statistically show it?

Here's what the yards look like:
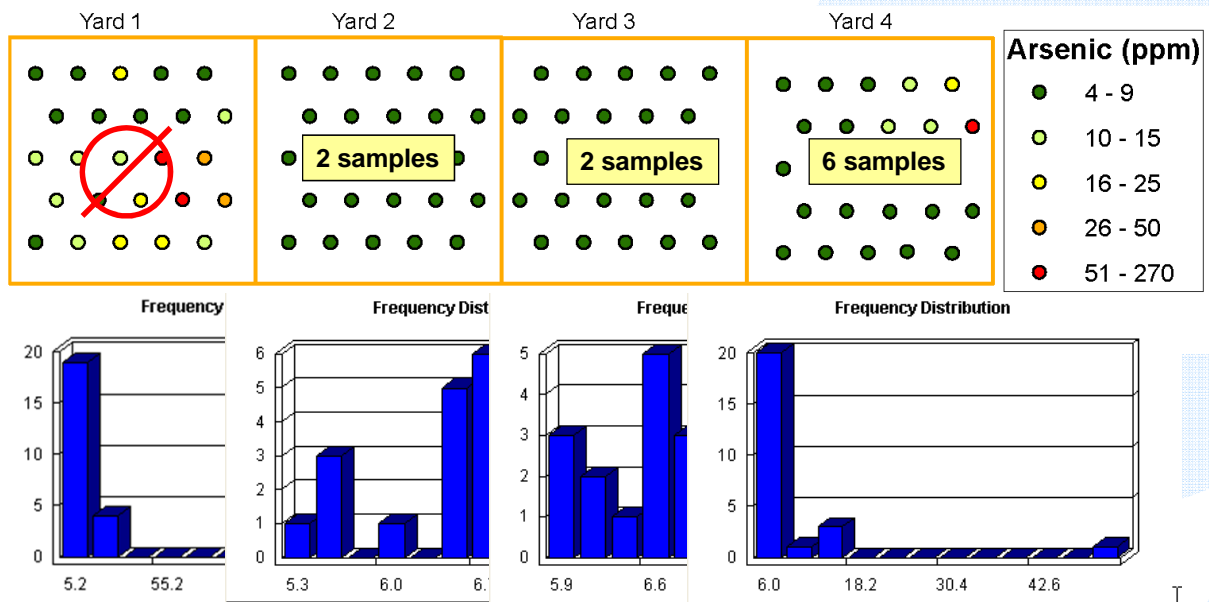
An Example of Determining Lab Sample Selection and Sample Depth

- Looking for contaminated sediment layer

- Uranium used as a proxy for primary COC (which is not measurable by real-time technique)

- Every 6-in interval of 3-ft cores screened by XRF

  – Highest impacted interval submitted to lab for analysis

  – If last interval has impacts above background, core down an additional 3 feet

Stratified Sampling Programs Using XRF

- XRF is the primary data source

- Goal is to determine whether average concentration is above or below standard for a decision unit

- Spatial patterning expected to be present within the decision unit

- Decision unit is stratified (cut into strata), each potentially receiving a different number of XRF measurements

- Numbers determined by initial rounds of XRF results

Any Questions?