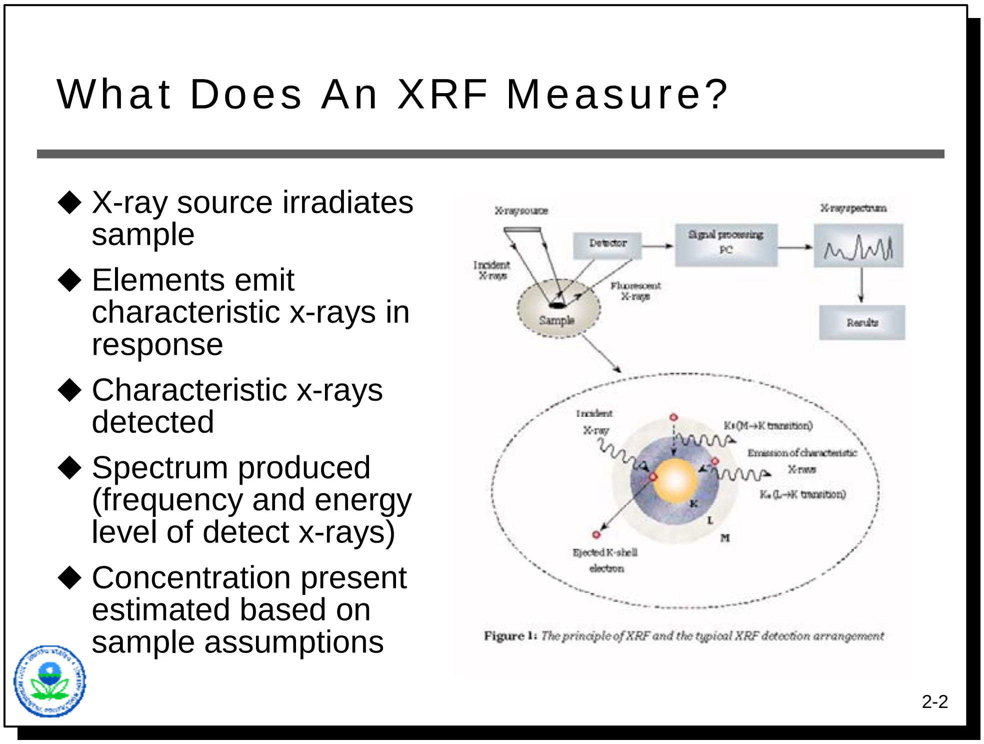
Module 2:

Basic XRF Concepts



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*

Notes

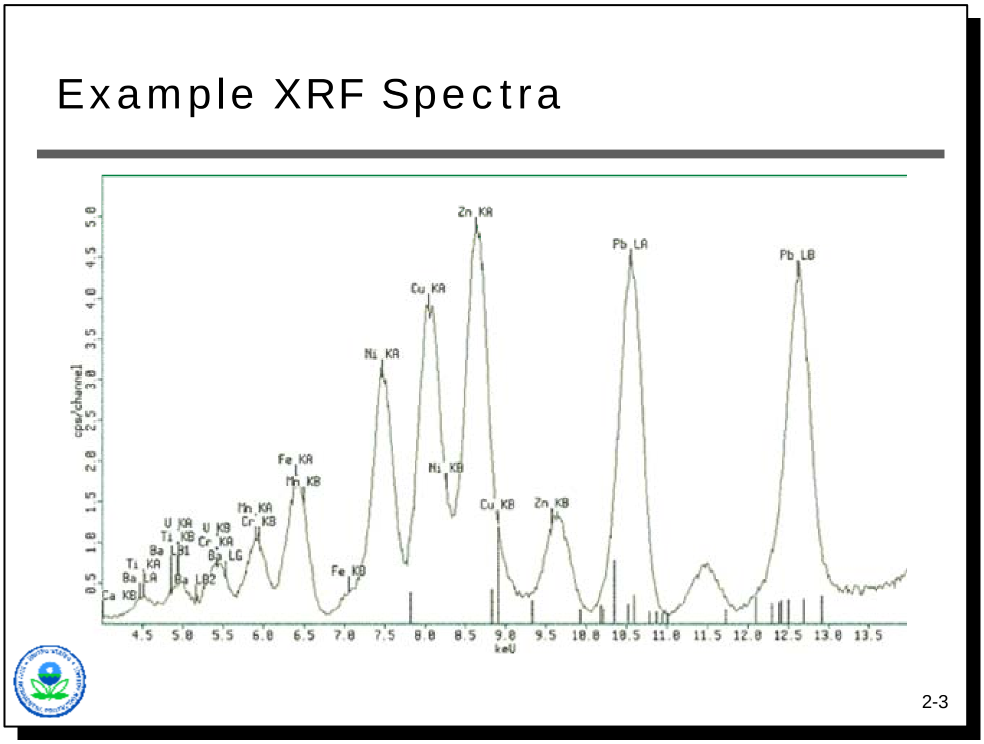
- **X-ray source irradiates sample:** Modern XRF systems include basically three components: an x-ray source, a detector, and a signal processing unit. The x-ray source produces x-rays that irradiate the sample of interest. Traditionally x-ray sources were sealed radionuclide sources such as Fe-55, Cd-109, Am-241, or Cm-244. Each sealed source type emitted x-rays of a particular energy level. The selection of a sealed source depended on the elements of interest, since different elements respond best to different irradiating x-ray energy levels. Sealed sources, however, presented practical challenges: some had relatively short half-lives meaning that they had to be changed on a regular basis to maintain XRF performance; they often required special licenses to be used; and each only addressed a relative small set of inorganic contaminants of concern. Consequently manufacturers of XRF units have been moving to electronic x-ray tubes for producing the required x-rays.

- **Elements emit characteristic x-rays in response:** When a sample is irradiated with x-rays, the x-rays interact with individual atoms, and these atoms respond by “fluorescing”, or producing their own x-rays whose energy levels and abundance (number) are different for each element.

- **Characteristic x-rays detected:** The XRF detector captures these fluorescent x-rays, counting each and identifying their energy levels.

- **Spectrum produced (frequency and energy level of detect x-rays):** The signal processing unit takes the detector information and produces spectrum. Additional software processing converts the spectrum into element-specific estimates of the concentrations present.

- **Concentration present estimated based on assumptions:** Additional software processing converts the spectrum into element-specific estimates of the concentrations present based on sample assumptions.

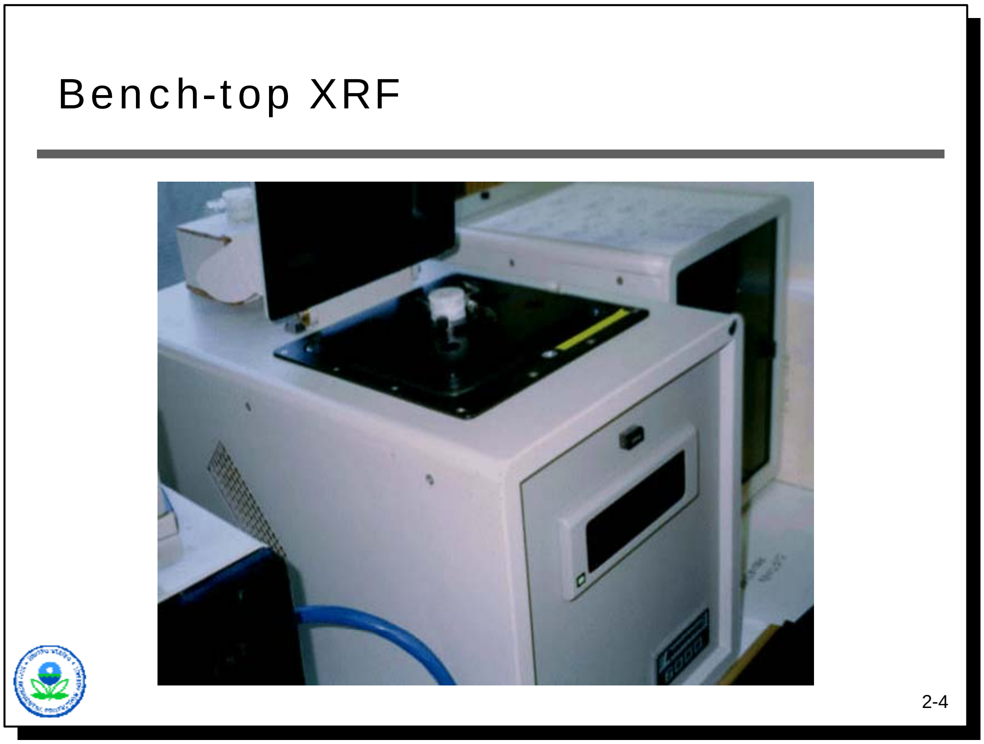


Example XRF Spectra

Notes

◆ This slide shows an example of an x-ray spectra produced by an XRF measurement. The x-axis is x-ray energy, and the y-axis shows the number of x-rays observed at each energy level. The peaks are indicative of the presence of unique elements. The heights of the peaks are proportional to the number of x-rays counted, which in turn is proportional to the mass of the element present in the sample. The width of the peaks, in general, is an indication of the detector's ability to "resolve" x-ray energies it observes, or in other words, to correctly identify the energy level of the x-ray it detected. The better the resolution, the tighter these peaks will be, the better the XRF will be in terms of performance (i.e., correctly identifying and quantifying the presence of a particular element).

This spectrum has a couple of features of interest. As this spectrum demonstrates, any particular element can have more than one peak associated with it, for example lead, or zinc, or iron in this spectrum. As this spectrum also demonstrates, peaks for individual elements may be so close that for all practical purposes they are indistinguishable. The Fe/Mn peak around 6.5 KeV is a good example. This is what causes what is known as interference, which is something that will be discussed later.



Bench-top XRF

Notes

- This slide shows a bench-top XRF unit. Samples from the field are brought to the unit which can be located in a trailer. XRF is a well-established analytical technique with a long history of use in a laboratory environment. In the last decade advances in electronics have allowed the development and refinement of field-deployable units. XRF analysis is different from most other inorganic techniques in that it is a non-destructive analysis. In other words, the original sample is not destroyed by the analytical process. There are no extraction or digestion steps. Consequently the same material can be analyzed repeatedly by an XRF unit, or analyzed by an XRF unit and then submitted for some other analysis.

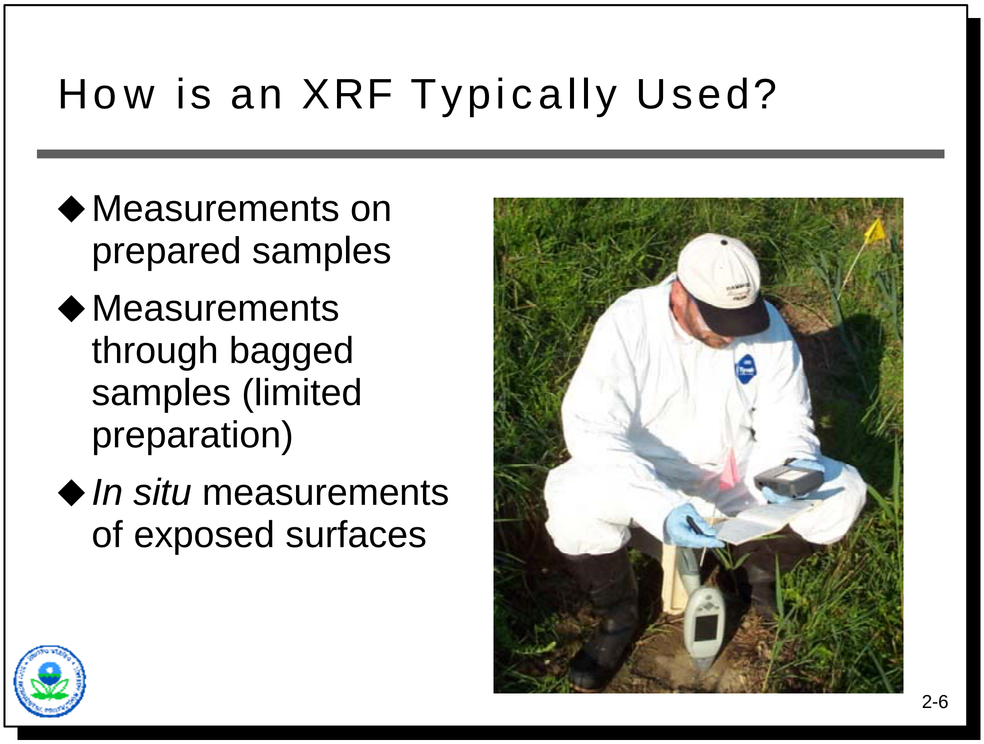
How is an XRF Typically Used?

- Measurements on prepared samples
- Measurements through bagged samples (limited preparation)
- *In situ* measurements of exposed surfaces

(continued)

Notes

- **Measurements on prepared samples:** The XRF can be used to take measurements on samples that are prepared by drying and grinding. The sample measured consists typically of a few grams of soil contained in a special cup designed for XRF use.
- **Measurements through bagged samples (limited preparation):** The XRF can also be used to take measurements on bagged samples that have undergone very little preparation.
- **In situ measurements of exposed surfaces:** The XRF can also be used to take measurements of exposed surfaces in the field. Only surface measurements can be made using this method.



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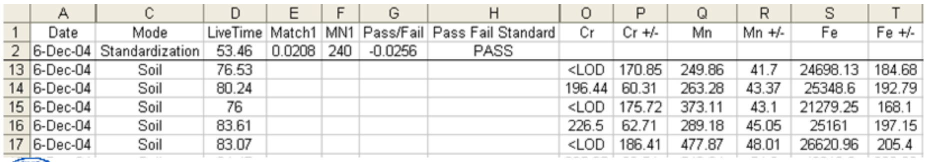
What Does an XRF Typically Report?

- ◆ 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

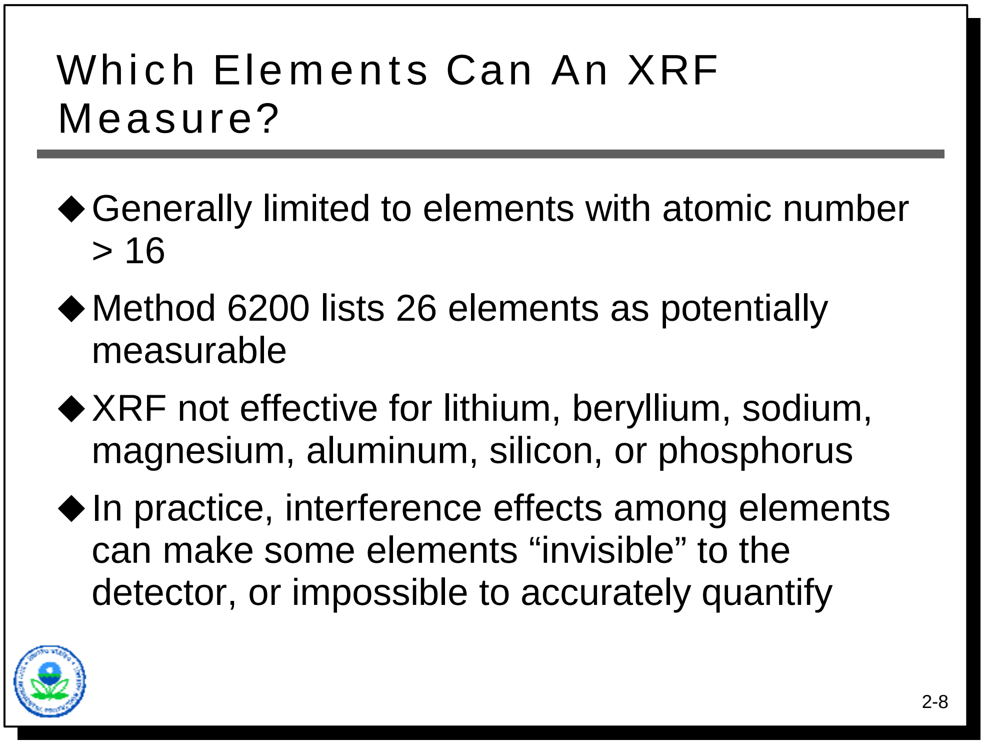
Notes

◆ **What does an XRF typically report:** The following items are typically reported by the XRF:

- » Measurement date
- » Measurement mode – which includes the type of sample measured
- » “Live time” for measurement acquisition – which indicates the number of seconds the detector was actually collecting information. This is a subtle but important point. In the case of Innov-X instruments, a measurement time is selected and the measured acquired for that duration. The live time for an Innov-X unit is something less (typically 80%) than the measurement time. In contrast, for a Niton instrument the measurement time selected by the user corresponds to the live time, and consequently a Niton measurement will actually take longer than specified measurement time (typically around 20% longer).
- » Concentration estimates. Consistent with SW846 Method 6200, a “<LOD” is typically reported when the measured result is less than 3 times the standard deviation for that measurement as estimated by the instrument. For both Niton and Innov-X, the software can be set to force the instrument to report measured values no matter their error. The pros and cons of doing this will be discussed later.

- Analytical errors associated with estimates. Two important notes here. In the case of an Innov-X unit, the reported error is an estimate of the one standard deviation error associated with the reported value. In the case of a Niton unit, the reported error is actually twice the estimated standard deviation error associated with the measurement. For both instruments, if a <LOD is reported as a result, the error column will contain the estimated detection limit for that measurement rather than the error. The estimated detection limit is three times the error. One can see this in the case of Cr. The first measurement reports Cr as an <LOD with a detection limit of 170 ppm. The second measurement reports Cr as 196 ppm with an error that is approximately a third of the detection limit reported by the previous measurement.

- User defined fields – which may include comparison to a certain concentration



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

- ◆ **Generally limited to elements with atomic number > 16:** The XRF is generally limited to elements which have an atomic number greater than 16. However, the XRF cannot necessarily measure all elements with an atomic number greater than 16 at concentrations that would be considered acceptable for environmental applications.

- ◆ **Method 6200 lists 26 elements as potentially measurable:** EPA Method 6200 for Field Portable X-Ray Fluorescence Spectrometry lists the following elements as being potentially measurable:

  - » Antimony (Sb)
  - » Arsenic (As)
  - » Barium (Ba)
  - » Cadmium (Cd)
  - » Calcium (Ca)
  - » Chromium (Cr)
  - » Cobalt (Co)
  - » Copper (Cu)
  - » Iron (Fe)
  - » Lead (Pb)
  - » Manganese (Mn)
  - » Mercury (Hg)
  - » Molybdenum (Mo)
  - » Nickel (Ni)
  - » Potassium (K)
  - » Rubidium (Rb)
  - » Selenium (Se)

  - Silver (Ag)
  - Strontium (Sr)
  - Thallium (Tl)
  - Thorium (Th)
  - Tin (Sn)
  - Titanium (Ti)
  - Vanadium (V)
  - Zinc (Zn)
  - Zirconium (Zr)

- **XRF not effective for lithium, beryllium, sodium, magnesium, aluminum, silicon, or phosphorus:** The XRF cannot detect common elements that are considered to be “light” elements, such as lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus.

- **In practice, interference effects among elements can make some elements “invisible” to the detector, or impossible to accurately quantify:** In practice, the performance of the XRF (as measured by detection limits and ability to accurately quantify an element) is highly variable from element to element. One of the factors contributing to variations in performance is the interference among elements whereby the elevated presence of one element may mask the elevated presence of another. A common example is arsenic being masked by the presence of lead. Interference effects are real, element-specific, and at times significant.

How Is An XRF Calibrated?

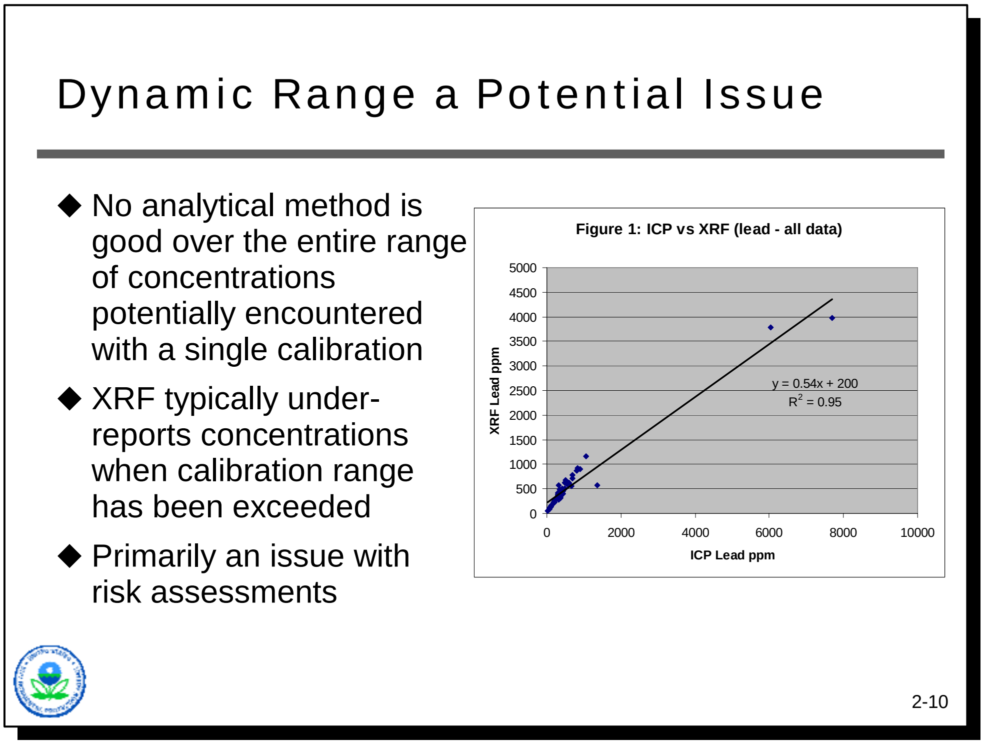
- **Fundamental Parameters Calibration** – calibration based on known detector response properties, “standardless” calibration, what is commonly done
- **Empirical Calibration** – calibration calculated using regression analysis and known standards, either site-specific media with known concentrations or prepared, spike standards

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

Notes

- Most, in not all, XRF vendors today are more than happy to help users develop site-specific calibrations for their XRF applications. These can be particularly important where site-specific matrix effects are of particular concern, and/or when the element of interest is not one of the standard set used for factory standardless calibrations.

- It is important to remember that the XRF is no different than any other analytical method. Properly calibrated, it will have a range of concentrations over which the linear calibration is assumed to hold for any particular element. That range typically runs from the instrument’s detection limits up to the percent range of concentrations. One should not expect the XRF to accurately report concentrations above its calibration range. In a standard laboratory the solution to this problem is to dilute the sample. Unfortunately dilution is not an option with a field-deployed XRF. The issue of calibration range is typically not a problem if one is simply screening soils for concentrations above or below some decision-making threshold. It can become an issue, however, if one is interested in estimating the average concentration over an area using multiple XRF measurements, and when some of those measurements include high levels of contamination. It can also be an issue when one is trying to establish comparability between an XRF result and a corresponding laboratory analysis, and that comparison involves highly contaminated samples.

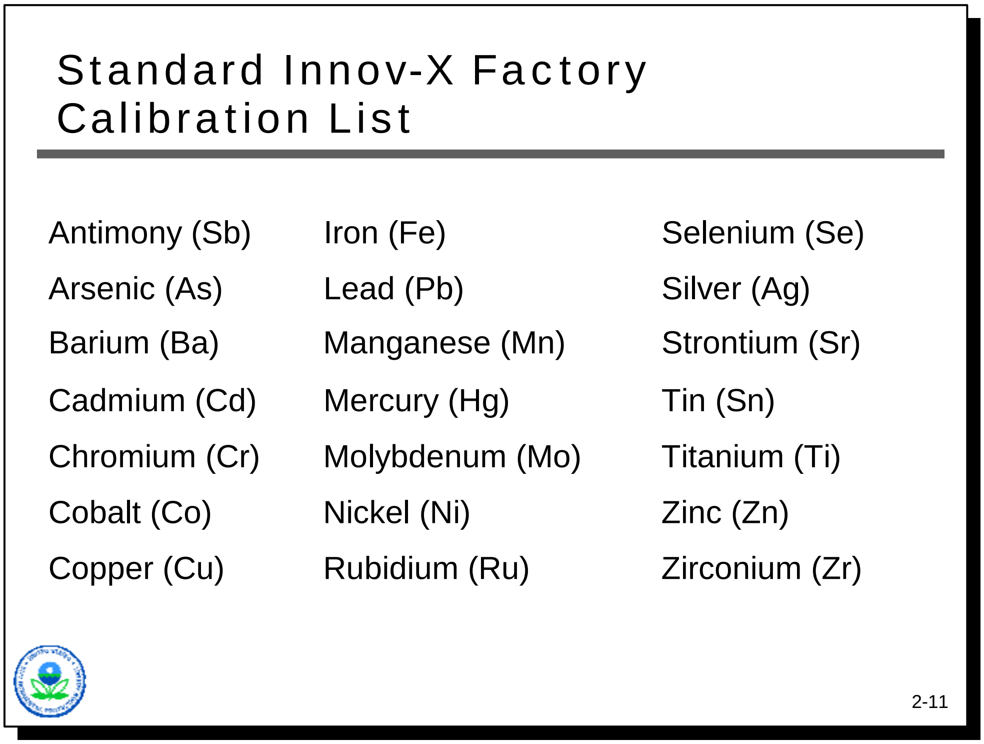


Dynamic Range a Potential Issue

- 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

Notes

- **No analytical method is good over the entire range of concentrations potentially encountered with a single calibration:** As the graph shows, there is good agreement between the XRF and ICP analysis at the lower end of the concentration range but not at the higher end of the concentration range.
- **XRF typically underreports concentrations when calibration range has been exceeded:** As the graph shows, the XRF reports lower concentrations of lead than the ICP analysis at concentrations above 6,000 parts per million (ppm).
- **Primarily an issue with risk assessments:** This phenomenon is an issue when the data are to be used in a risk assessment because underreporting concentrations may underestimate the actual risk associated with the contamination.

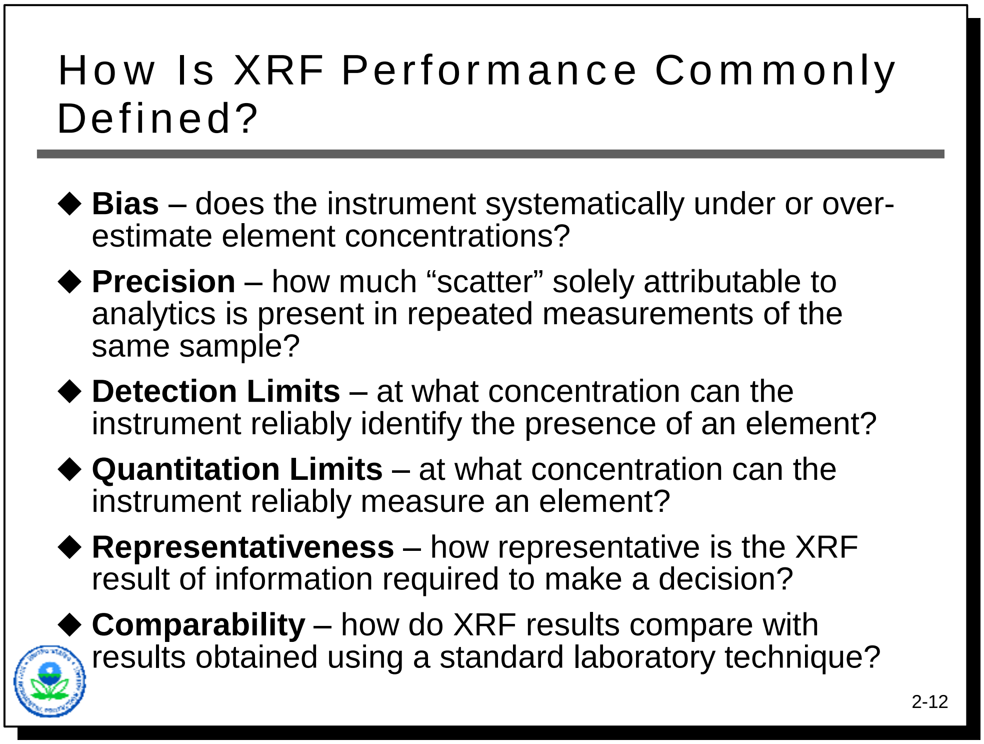


Standard Innov-X Factory Calibration List

- 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)

Notes

◆ This slide shows the list of compounds available for the standard Innov-X factory calibrations.



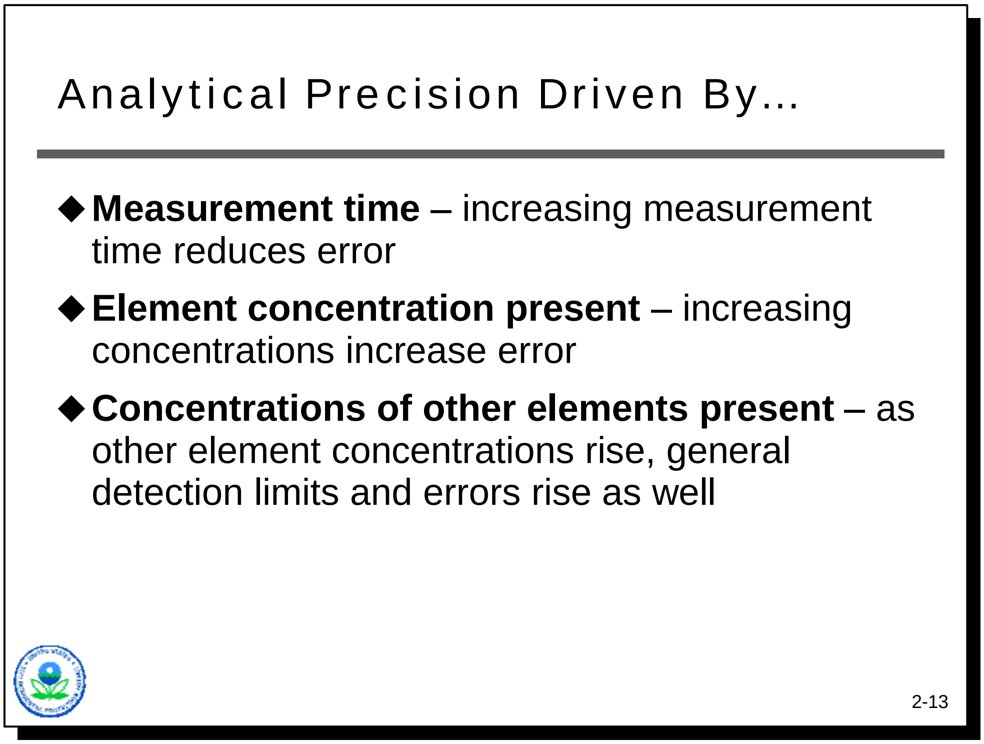
How Is XRF Performance Commonly Defined?

- **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?

2-12

- **How is XRF performance commonly defined:** The following factors are used to define how an XRF performs:
  - **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 concentrations can the instrument reliably identify the presence of an element?
  - **Quantitation Limits** – at what concentrations 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?

The following slides will discuss precision, detection limits, and comparability in more detail.



Analytical Precision Driven By…

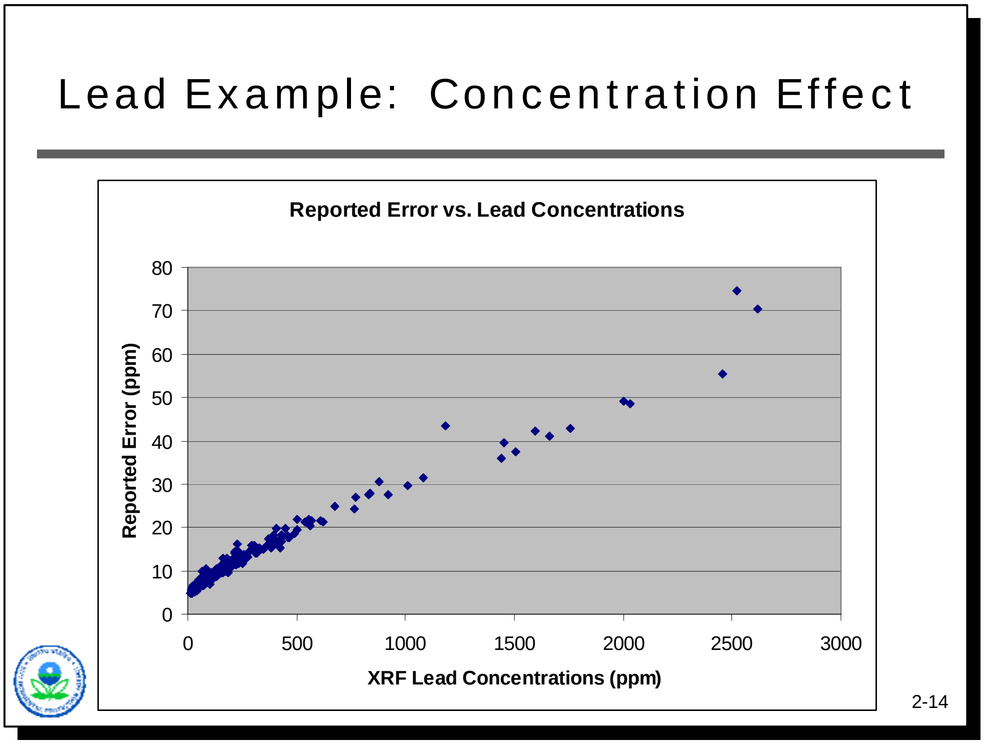
- **Measurement time** – increasing measurement time reduces error
- **Element concentration present** – increasing concentrations increase error
- **Concentrations of other elements present** – as other element concentrations rise, general detection limits and errors rise as well

Notes

- **Measurement time:** Measurement time affects precision. Increasing the measurement time reduces error and increases precision.

- **Element concentration present:** The amount of the element of concern affects precision. Generally, increasing concentrations result in increased error and decreased precision.

- **Concentrations of other elements present:** The presence of other elements affects precision. As the concentration of other elements rise, general detection limits and errors rise, decreasing analytical precision.

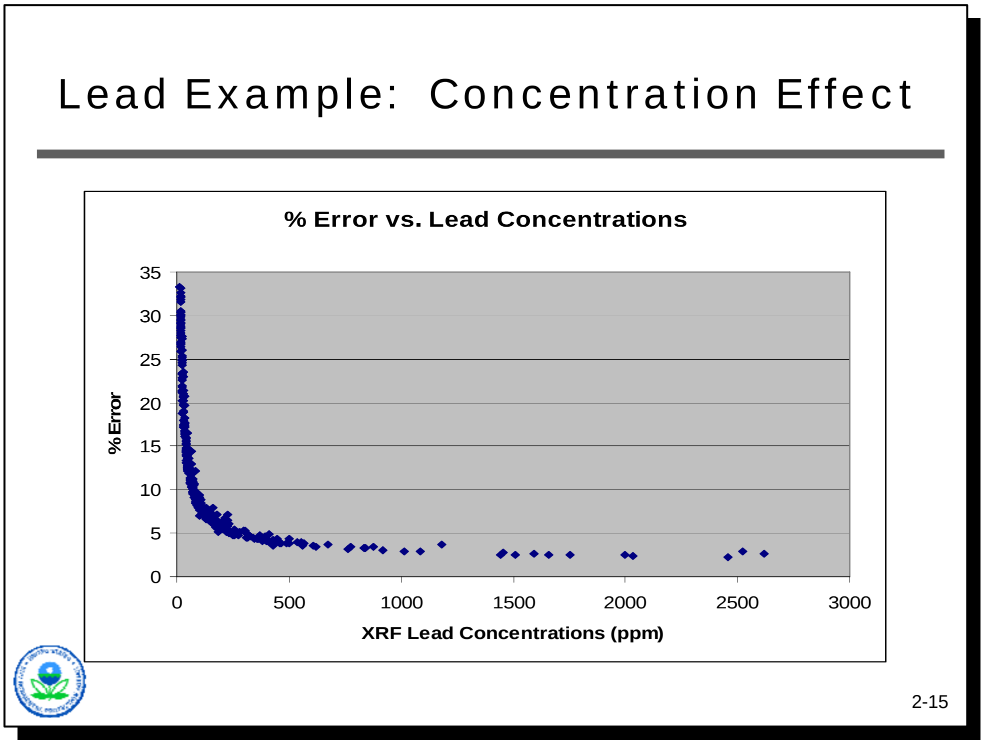


Lead Example: Concentration Effect

Notes

- The next two slides show two graphs that illustrate the effects of concentrations on reported measurement errors in the case of 434 lead measurements with an XRF. In the first graph, the x-axis shows lead concentrations while the y-axis shows their associated reported errors. One gets the general relationship that one would expect: error grows as the square root of concentration. In other words, to double the error one needs to quadruple the concentration.

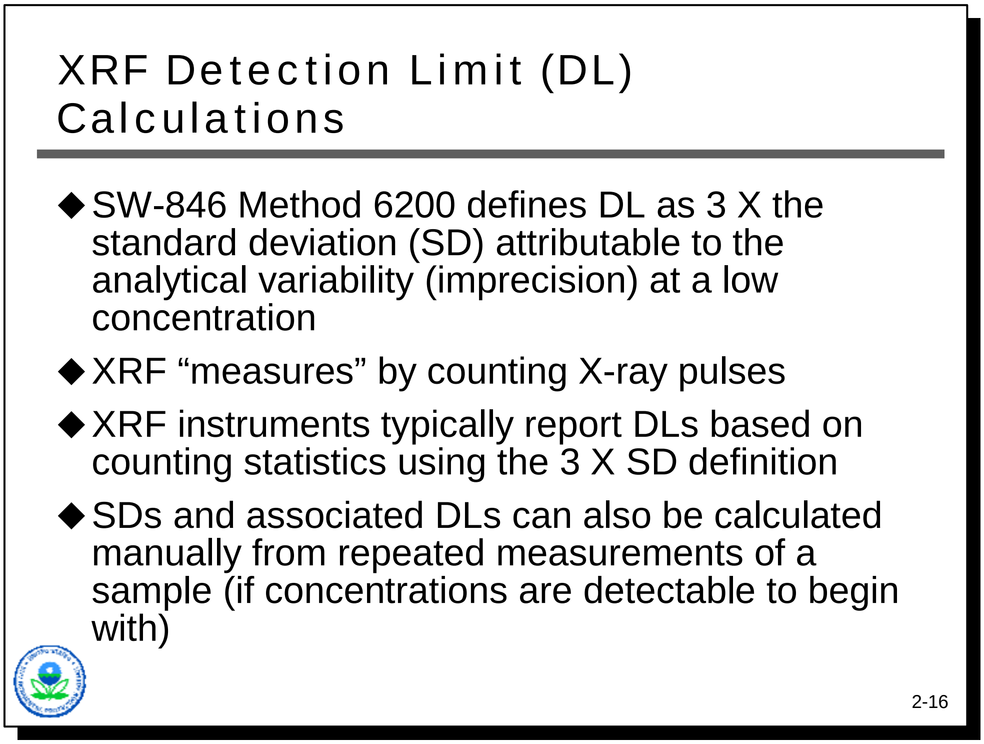
  Notice too that these relationships start to fall apart as XRF lead values become high, reflecting the contribution of other sources of error to measurement error (e.g., the presence of other elements that are very elevated).



Lead Example: Concentration Effect

Notes

- This graph also illustrates the effects of concentrations on reported measurement errors in the case of 434 lead measurements with an XRF. Percent error is plotted as a function of concentration. Notice that % error is a maximum at the detection limits of the instrument, and is never more than approximately 30%. For lead values in the range of what is typically of interest (e.g., 400 ppm), percent error is less than 5%. This is an important fact to keep in mind. The expectation for standard laboratory analytical precision is less than 10%. In the case of this XRF example, the XRF meets that expectation for lead values greater than approximately 100 ppm. A general rule of thumb for any particular element is that for concentrations that are10 times the XRF's detection limit, the analytical error of XRF measurements will be less than 10%.



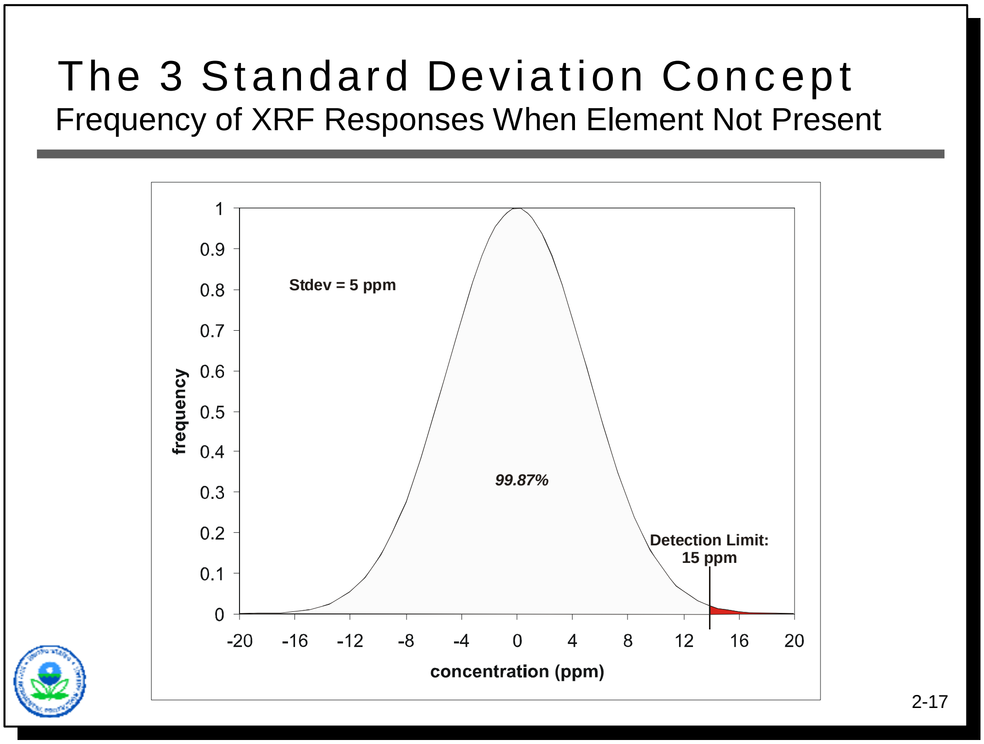
XRF Detection Limit (DL) Calculations

- ◆ SW-846 Method 6200 defines DL as 3 X the standard deviation (SD) attributable to the analytical variability (imprecision) at a low concentration
- ◆ XRF "measures" by counting X-ray pulses
- ◆ XRF instruments typically report DLs based on counting statistics using the 3 X SD definition
- ◆ SDs and associated DLs can also be calculated manually from repeated measurements of a sample (if concentrations are detectable to begin with)

Notes

- ◆ **XRF detection limit (DL) calculations:** Remember that relative error or percent error (error divided by the concentration) falls as concentration increases. What this means is that using this definition of detection limits, the percent error associated with an XRF measurement will never be more than approximately 30%, and usually will be significantly less.

- ◆ A common question people ask is what the detection limit is for a measurement where the element of interest was detected and reported by the XRF. A common mistake is for the detection limit to be estimated, in this case, by taking the error of the measurement and multiplying the error by three. This can significantly over-estimate the detection limits of the instrument. The reason is that analytical error increases as concentrations increase. Consequently the error for a quantifiable concentration will be greater than the error if the element had not been present.



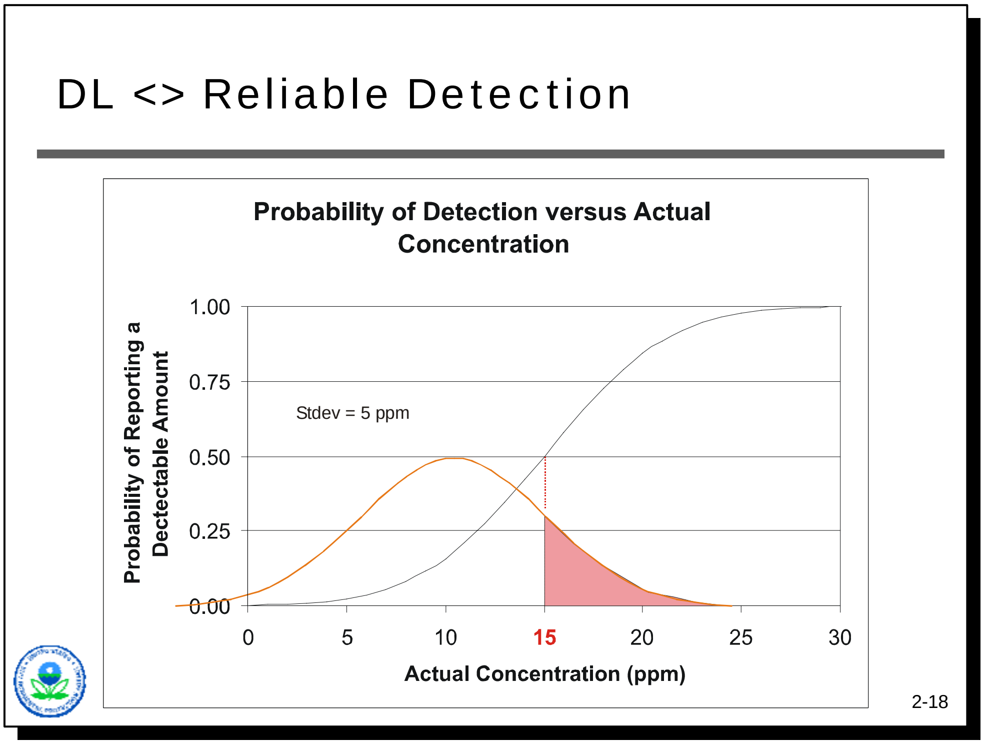
The 3 Standard Deviation Concept

Frequency of XRF Responses When Element Not Present

2-17

Notes

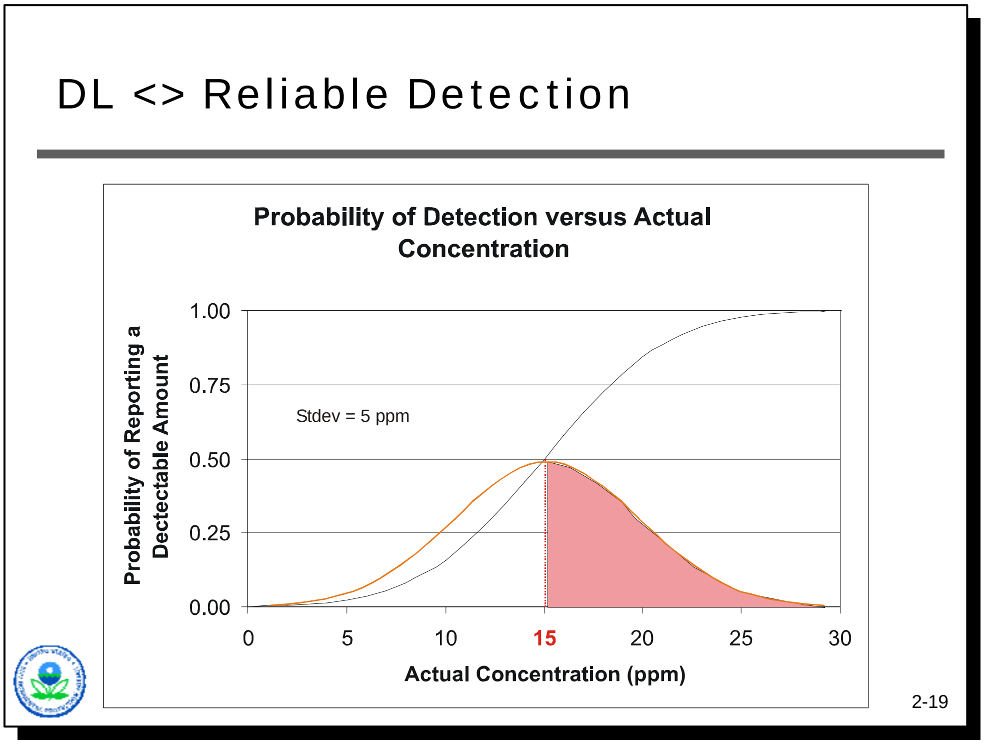
◆ The graphic above illustrates the frequency of XRF responses when the element is not present. Assume that a sample does not have an element present (or that it is present at trace levels). If one were to take a measurement of the sample with the XRF, the XRF would record a concentration present for that element just because of the random nature of x-ray counting statistics. If one did a large number of repeat measurements, one could generate a distribution or frequency plot of those “random” concentrations such as is shown here, with a measurable standard deviation. Notice that the frequency distribution is centered around zero, indicating that this instrument is providing an unbiased estimate of the concentration for the element of interest. Notice too that half the time the instrument would report positive values, and half the time it would report negative values…an important fact that will be discussed later. If one moves three standard deviations up from zero and calls that the detection limit (consistent with SW846 Method 6200), then almost 100% of the concentration values generated when the element is not present would be less than the detection limit. In other words, if the instrument records a result greater than this detection limit, then it is very likely that in fact the element is present.



DL <> Reliable Detection

Notes

- As defined and implemented, the detection limit for an XRF is not the same as the concentration that can be reliably detected. The graphics on this and the next two slides illustrate that fact. We start with the same scenario as the previous slide, an element with a XRF detection limit of 15 ppm. In these slides, the x-axis is actual concentration, while the y-axis is the probability the XRF will detect the element. The three red bell-shaped frequency curves show what the XRF response might be for three different actual concentrations (10 ppm, 15 ppm, and 20 ppm). The portion under the curves shaded red represents the fraction of repeated measurements at that concentration that would have yielded a result above the detection limit (15 ppm). As show in Slide 2-18 above, if the actual concentration were 10 ppm, about a third of the measurements would have yielded a "detection" (an XRF result > 15 ppm). The probability of reporting a detection, as a function of actual concentration, is shown by the black S-shaped curve.

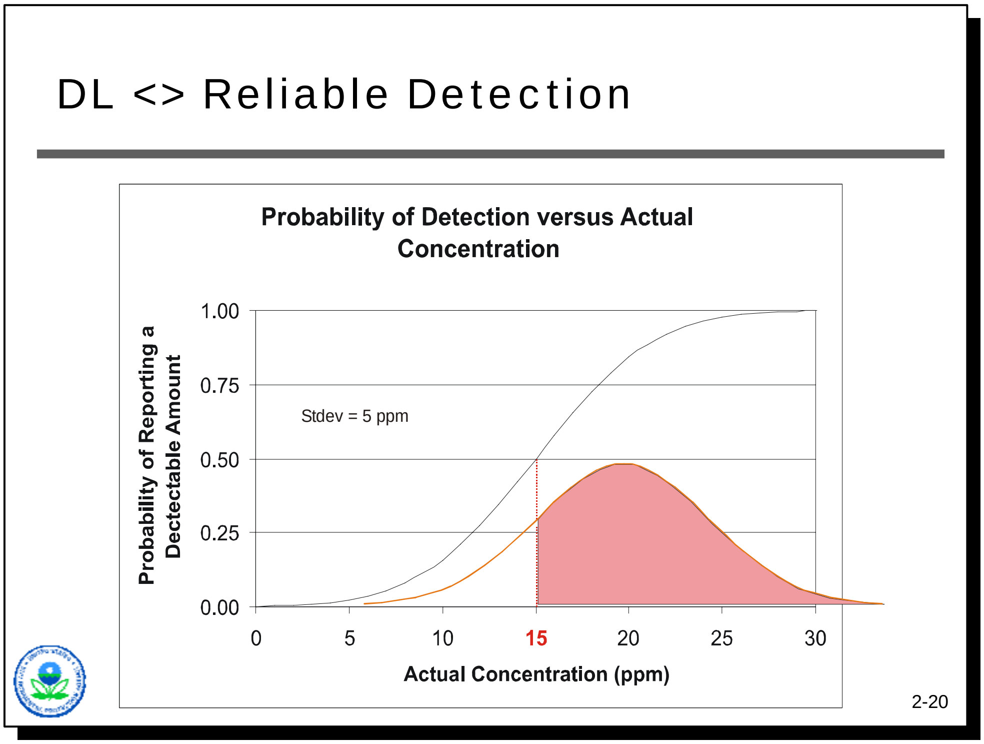


DL <> Reliable Detection

Probability of Detection versus Actual Concentration

Notes

- As shown in Slide 2-19 above, if the actual concentration were 15 ppm (at the detection limit), the XRF would have detected the element only 50% of the time. The probability of reporting a detection, as a function of actual concentration, is shown by the black S-shaped curve.



DL <> Reliable Detection

Notes

- As shown in Slide 2-20 above, if the actual concentration was 20 ppm, the XRF would have reported a detected value about two thirds of the time. In this particular case, it is not until the actual concentration reaches 30 ppm (or twice the DL) that the XRF will report a detectable value almost all of the time. The probability of reporting a detection, as a function of actual concentration, is shown by the black S-shaped curve.

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

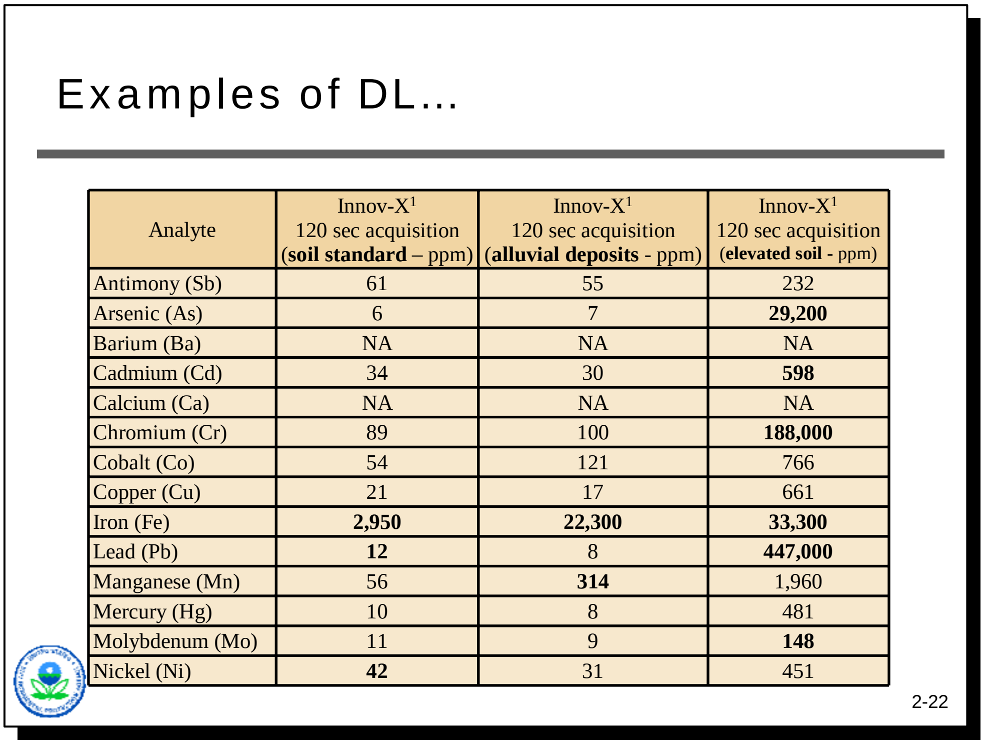
Consequently, the DL for any particular element will change, sometimes dramatically, from one sample to the next, depending on sample characteristics and operator choices

Notes

- ◆ **Measurement time:** The precision or reproducibility of a measurement will improve with increasing measurement time. Increasing the count time by a factor of 4 will provide 2 times better precision. Consequently increasing the count time by a factor of 4 will cut detection limits by a factor of two. Of course, increasing count time decreases sample throughput, so selecting the appropriate measurement time is a trade-off between the desired detection limits and per-sample measurement costs.

- ◆ **Matrix effects:** Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. One way to reduce error associated with variation in particle size is to grind and sieve all soil samples to a uniform particle size. Differences in matrix effects can result in differences in detection limits from one sample to the next.

- ◆ **Presence of interfering or highly elevated contamination levels:** Chemical matrix effects result from the differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, iron tends to absorb copper x-rays, reducing the intensity of the copper measured by the detector, while chromium will be enhanced at the expense of iron because the absorption edge of chromium is slightly lower in energy than the fluorescent peak of iron. When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The presence of interference effects will raise detection limits.



Examples of DL…

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

Notes

- The table illustrates the fact that detection limits can change dramatically from sample to sample. Here we see three different sets of results from the same Innov-X unit, in each case collected with a 120-second acquisition time. The bold numbers in this table are actually quantified values (i.e., detects), while the plain text numbers are detection limits for elements that were not detectable. Results for three different samples are presented. The first is for a spiked matrix (the spiked element is not present in this table). The second is for a background soil sample taken from alluvial deposits. The third is for a highly contaminated sample taken beneath a leaking waste sewer line at a chemical facility.

  The effect of highly elevated lead and chromium on the detection limits for other elements is severe. The detection limit for mercury jumps from around 10 ppm to almost 500 ppm, a 50 times factor change.

  One other note about these data. The concentration levels reported for chromium and lead for the contaminated sample fall outside the calibrated range. These values would and should be taken with a large dose of skepticism…the levels of lead and chromium in this sample are undoubtedly extremely high, but the ability of the XRF to accurately quantify them at these levels would be very suspect.

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

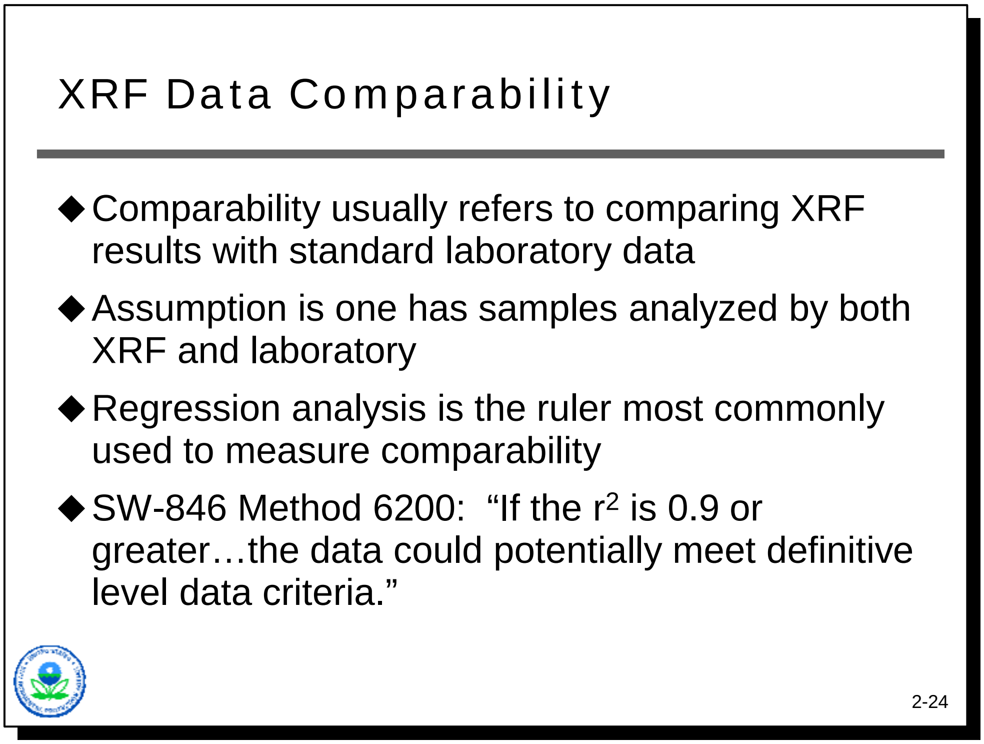
- ◆ Not all instruments/software allow the reporting of XRF results below detection limits
- ◆ For those that do, manufacturer often recommends against doing it
- ◆ Can be valuable information if careful about its use…particularly true if one is trying to calculate average values over a set of measurements

Notes

◆ **Not all instruments/software allow the reporting of XRF results below detections limits:** Some instruments and associated software do not allow the reporting of measurement results that are below detection limits.

◆ **For those that do, manufacturer ofter recommends against doing it:** For those instruments that do allow reporting of results below detection limits, the manufacturer usually advises against it. Within the chemistry analytical world, the approach has been to not report values less than detection limits. Within the radionuclide analytical world, the approach has been to report values less than detection limits. The XRF is an analytical technique that has its roots in the radionuclide world (e.g., gamma and alpha spectroscopy), but has applications to the chemical world (e.g., elemental metals).

◆ **Can be valuable information if careful about its use . . . particularly true if one is trying to calculate average values over a set of measurements:** Values below detection limits can be useful when calculating average values over a set of measurements. If the instrument's calibration is unbiased for low levels of the element of interest, using measured values below the instrument's detection limits can yield more accurate assessments of average concentrations that flagging readings as non-detects and substituting some arbitrary value such as the detection limit, or half the detection limit, in average value calculations. Great care and full disclosure are necessary when using values below detection limits.



XRF Data Comparability

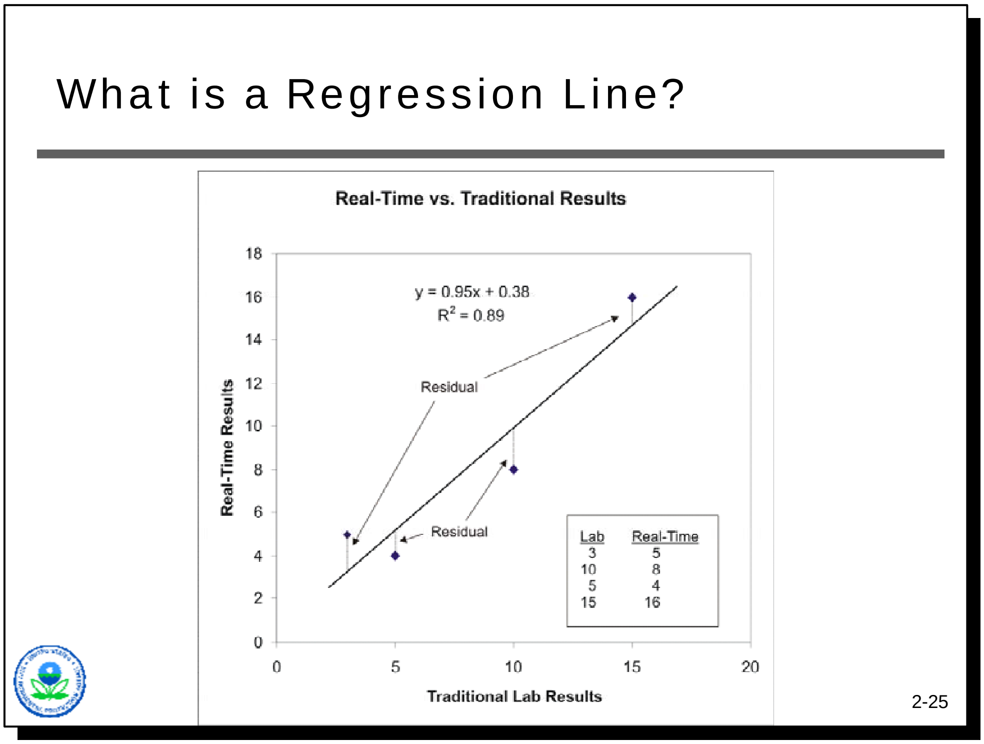
- ◆ Comparability usually refers to comparing XRF results with standard laboratory data
- ◆ Assumption is one has samples analyzed by both XRF and laboratory
- ◆ Regression analysis is the ruler most commonly used to measure comparability
- ◆ SW-846 Method 6200: "If the r^2 is 0.9 or greater…the data could potentially meet definitive level data criteria."

- ◆ **Comparability usually refers to comparing XRF results with standard laboratory data:** The comparability of the XRF analysis is determined by submitting XRF-analyzed samples for analysis at a laboratory. The XRF results are then compared with the laboratory results.

- ◆ **Assumption is one has samples analyzed by both XRF and laboratory:** The confirmatory samples must be splits of well homogenized sample material. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the XRF. They should also include samples with element concentrations at or near the site action levels.

- ◆ **Regression analysis is the ruler most commonly used to measure comparability:** The results of the confirmatory analysis and XRF analyses are usually evaluated with a least squares linear regression analysis.

- ◆ **SW-846 Method 6200: "If the r^2 is 0.9 or greater . . . the data could potentially meet definitive level data criteria.":** Method 6200 states that the method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The method also suggests that the r^2 for the results should be 0.7 or greater for the XRF data to be considered screening level data. Finally, the method states that if the r^2 is 0.9 or greater and inferential statistics indicate the XRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.



What is a Regression Line?

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

Notes

- The scatter-plot in this slide illustrates how a regression analysis works. The data in the lower-right table represents our collaborative data set: four samples, with each having both a traditional laboratory result and a real-time result (e.g. XRF). Plotting these data give us the scatter-plot shown. Assuming there's a linear relationship between results generated by the laboratory and results generated by the real-time technique, the question is finding that linear relationship.

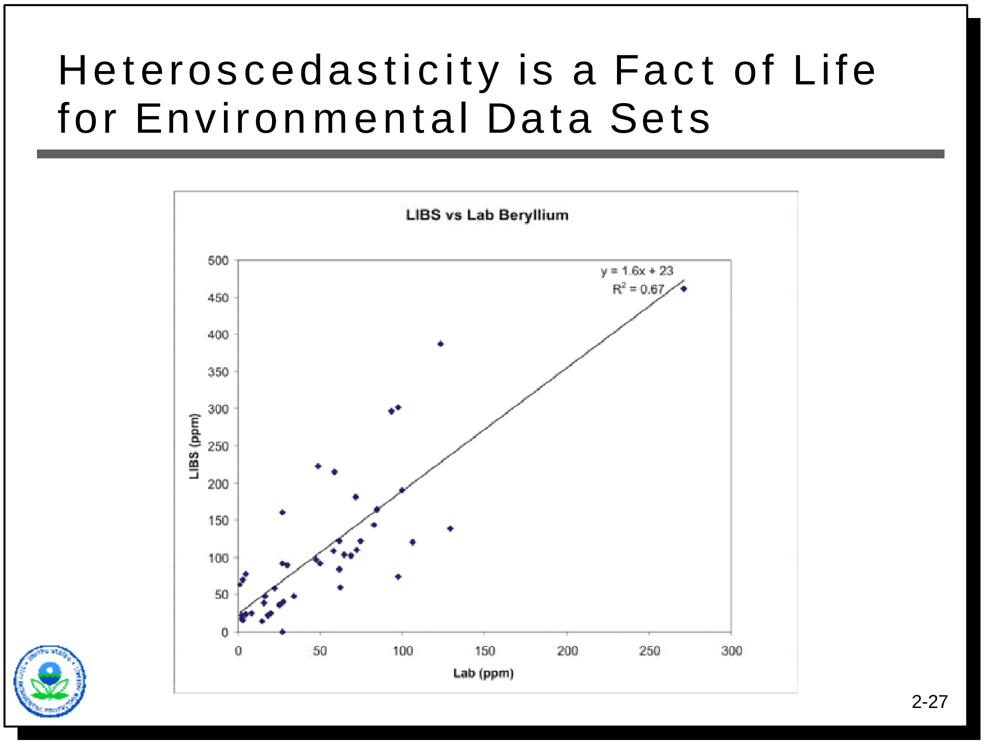
  The line shown represents the results from a regression using these data. The regression line represents the "best fit" line. "Best fit" here is defined as the line that minimizes the sum of the squared residuals. A residual is the vertical distance separating a regression line and a data point.

Regression Terminology

- Scatter Plot: graph showing paired sample results
- Independent Variable: x-axis values
- Dependent Variable: y-axis values
- Residuals: difference between dependent variable result predicted by regression line and observed dependent variable
- Adjusted R^2: a measure of goodness-of-fit of regression line
- Homoscedasticity/Heteroscedasticity: Refers to the size of observed residuals, and whether this size is constant over the range of the independent variable (homoscedastic) or changes (heteroscedastic)

Notes

- **Regression terminology:** The following are regression terms:
  - Scatter Plot – graph showing paired sample results
  - Independent Variable – x-axis values, usually the lab result
  - Dependent Variable – y-axis values, usually the XRF result
  - Residuals – difference between dependent variable result predicted by regression line and observed dependent variable
  - Adjusted R^2 – a measure of goodness-of-fit of regression line
  - Homoscedasticity/Heteroscedasticity – refers to the size of observed residuals, and whether this size is constant over the range of the independent variable (homoscedastic) or changes (heteroscedastic)



Heteroscedasticity is a Fact of Life for Environmental Data Sets

LIBS vs Lab Beryllium

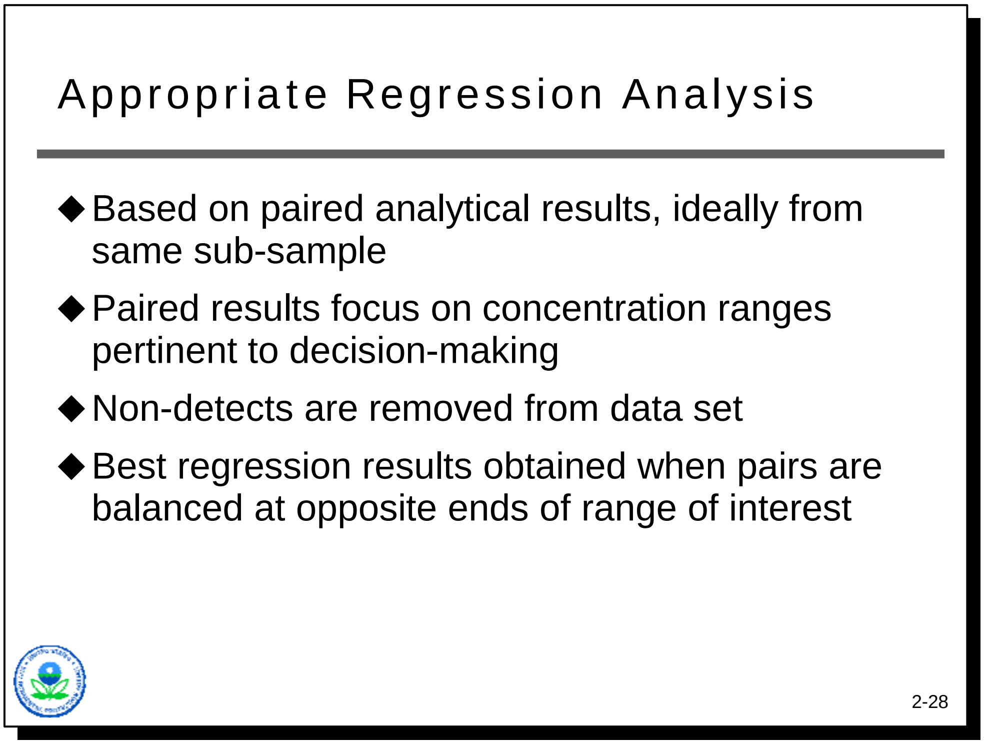
2-27

Notes

- Heteroscedasticity is unfortunately a fact-of-life for environmental collaborative data sets. The LIBS/laboratory scatter-plot illustrates the concept of heteroscedasticity. We can fit a regression line to these data, with the resulting line and its equation shown. The orange lines bracketing the regression line above and below given a sense for how the size of residuals change as concentrations increase. For low concentrations, the scatter-plot points are tightly clustered around the regression line, giving rise to relatively small residuals. As concentrations increase, the “scatter” of points around the line steadily increases. The result is that residuals for higher-concentration points are much larger than what they are for lower concentration values. This increasing residual size as concentrations increase is called heteroscedasticity.

  The concept is important because regression analyses often include UCL lines or UTL lines that bracket the regression line. The problem with this is that UCL and UTL calculations derived from a regression analysis are only valid if the underlying data are homoscedastic…which environmental collaborative data never are. The warning: beware of trying to extract too much from a regression analysis’s results.

  There is a simple physical explanation for heteroscedasticity in environmental collaborative data…analytical error tends to increase as concentrations increase.



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

Notes

◆ **Based on paired analytical results, ideally from same sub-sample:** Such an analysis should be based on paired results, ideally with the analytical work done on the same sub-sample where possible to minimize the effects of sample preparation. Poor comparability results are often the result of poorly prepared samples and not analytical issues.

◆ **Paired results focus on concentration ranges pertinent to decision-making:** The paired results should focus on the concentration range pertinent to decision-making. Often times field analytical methods have a more limited dynamic range within which they provide accurate results. This means that it is unreasonable to expect a good, strong linear relationship for two methods over the complete range of concentrations (which may span several orders of magnitude) present at a site. What is important is to determine whether such a relationship exists over the range in which making decisions is important.

◆ **Non-detects are removed from data set:** Non-detects should be removed from a regression analysis because they will skew regression results.

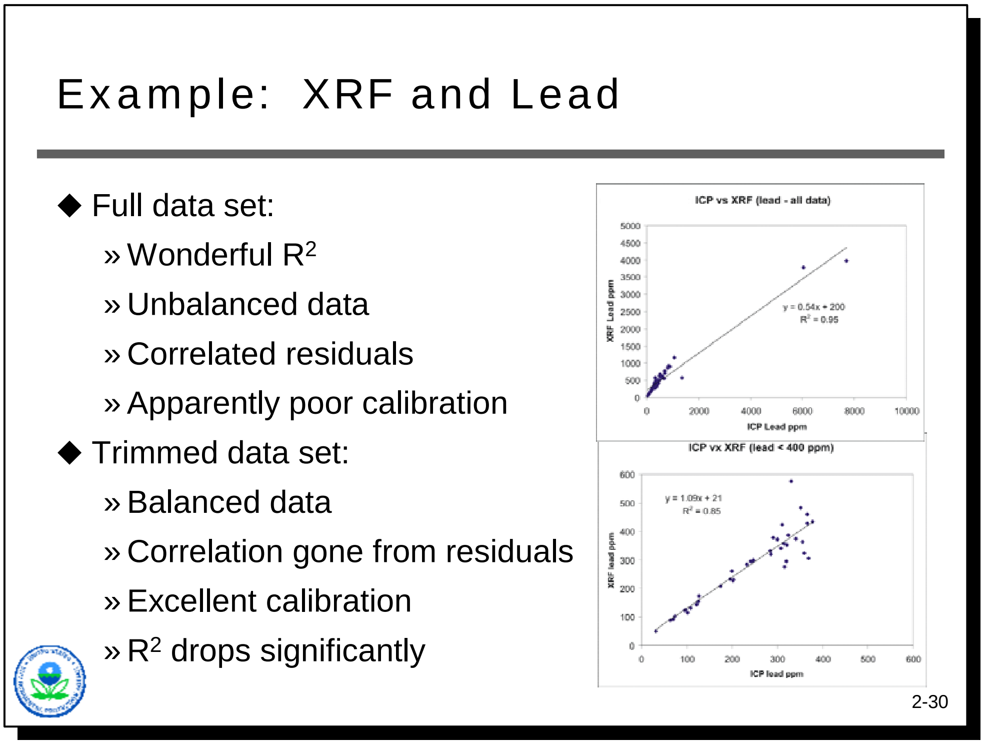
◆ **Best regression results obtained when pairs are balanced at opposite ends of the range of interest:** The best regression results are obtained when the data used are balanced, i.e., half are at the lower end of interest, and half are at the higher end of interest. WARNING: unbalanced data sets (i.e., data sets where most of the points are clustered at the low end with one or two high value) will yield unstable and likely misleading regressions.

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)

Notes

- **No evidence of inexplicable outliers:** There should be no evidence of outliers. Outliers are points that clearly fall well away from the regression line and appear to be different than the rest.
- **Balanced data sets:** Data sets should be balanced.
- **No signs of correlated residuals:** There should be no signs of correlated residuals. Correlated residuals refer to the situation where a group of points consistently fall above or below the regression line.
- **High R^2 values (close to 1):** A good regression should have a high R^2 value, preferably close to 1 (will range between 0 and 1).
- **Constant residual variance (homoscedastic):** A good regression should also have constant residual variance across the concentration range, or in other words the data should be homoscedastic. Unfortunately for environmental collaborative data sets, this is never the case.



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

2-30

Notes

- Here's an example based on XRF analyses of lead in soil samples. The top graphic shows a scatter plot based on the complete data set collected. The regression line has a wonderful R^2 value, but has several obvious visual deficiencies. These include unbalanced data (most of it clustered at the low end with only two points at the high end), correlated residuals, and what appears to be a poor calibration for the XRF based on the slope of the line.

  The second data set has had its data trimmed to include only those concentrations that fall within the range truly of interest from a decision-making perspective. These data are balanced across the concentration range of interest. The correlations are gone from the residuals. The slope corresponds to what one would expect from a calibrated XRF. Note that the R^2 value is actually less, though, then the first example, even though the second regression is clearly superior, underscoring the problems with simply using R^2 values as a measure of regression performance and hence field analytic data quality and usability.

  Also, in the second scatter plot the spread of the data around the line increases as concentrations increase. This is called heteroscedasticity, and indicates that the variance of the data is not constant over the range of observed concentrations. The presence of heteroscedasticity is a given in environmental data, and complicates the interpretation of regression results. Therefore, interpreting UCLs and UTLs for regression lines when heteroscedasticity is present should be done very carefully.

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

Notes

- **Purpose:** Some times XRF data are “converted” using a regression line to make them “comparable” to laboratory data. One might do this if one wants to pool the XRF data with lab data for risk assessment purposes.

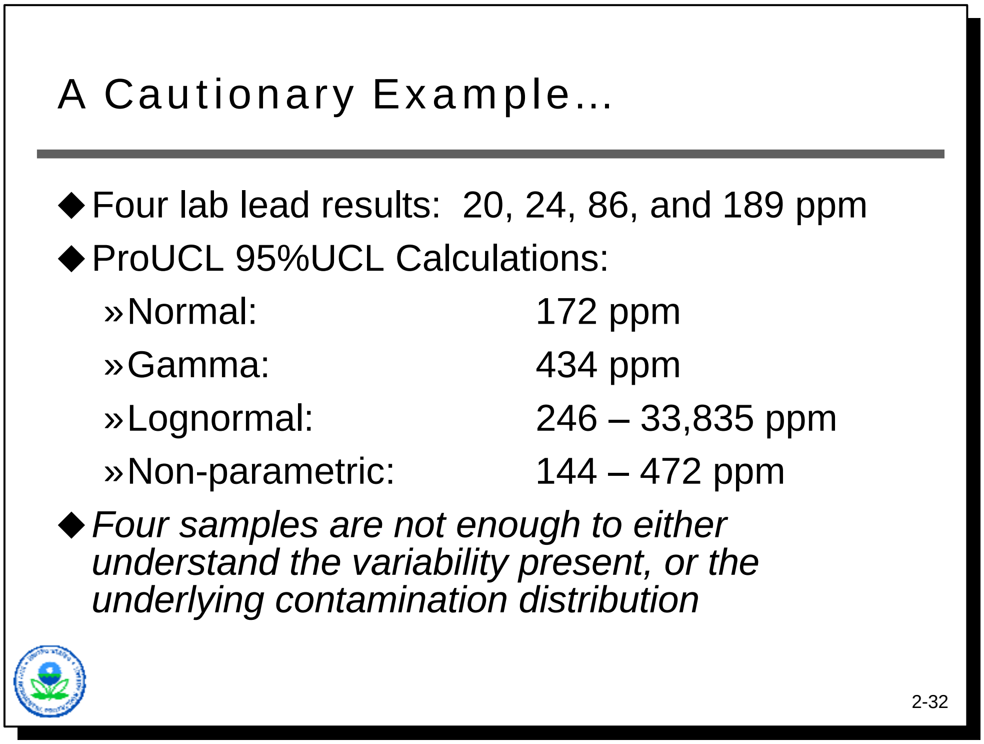
- **To consider:** Before “transforming” XRF data in this fashion, the following should be considered:

  - » Need for “conversion” may be an indication of a bad regression

  - » XRF calibration are not linear over the range of concentrations potentially encountered

  - » Extra variability in XRF data should not be an issue (captured in upper concentration limit (UCL) calculations when estimating the exposure point concentration (EPC))

  - » Contaminant concentration distributions are typically skewed . . . a large volume of XRF data may provide a better UCL/EPC estimate than a few laboratory results even if the regression is not great.

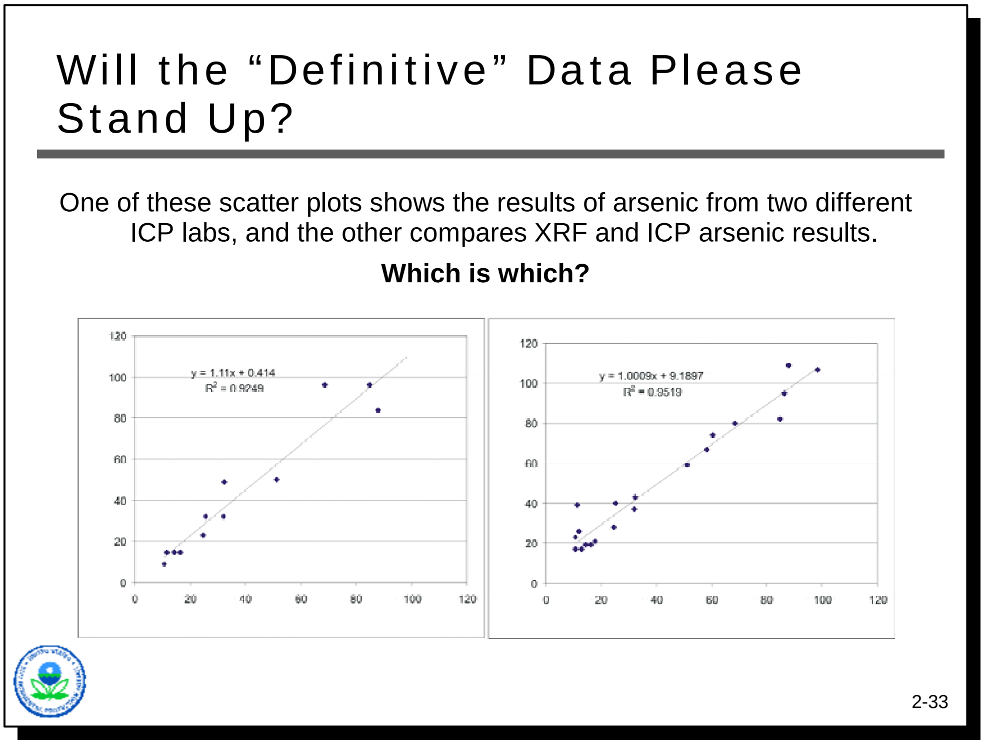


A Cautionary Example…

- Four lab lead results: 20, 24, 86, and 189 ppm
- ProUCL 95%UCL Calculations:
  - »Normal: 172 ppm
  - »Gamma: 434 ppm
  - »Lognormal: 246 – 33,835 ppm
  - »Non-parametric: 144 – 472 ppm
- *Four samples are not enough to either understand the variability present, or the underlying contamination distribution*

Notes

- This example shows that four samples are not enough to either understand the variability present, or the underlying contamination distribution, no matter how “high quality” the laboratory data are. If the action level for this site were 400 ppm, the decision about whether the area posed a risk or not would be ambiguous. A larger volume of measurements, even if they were from an XRF with analytical quality not quite as good as the lab’s, would provide a better understanding of variability and contaminant distribution, and consequently a better UCL estimate, assuming the XRF was properly calibrated for the element of interest.



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.

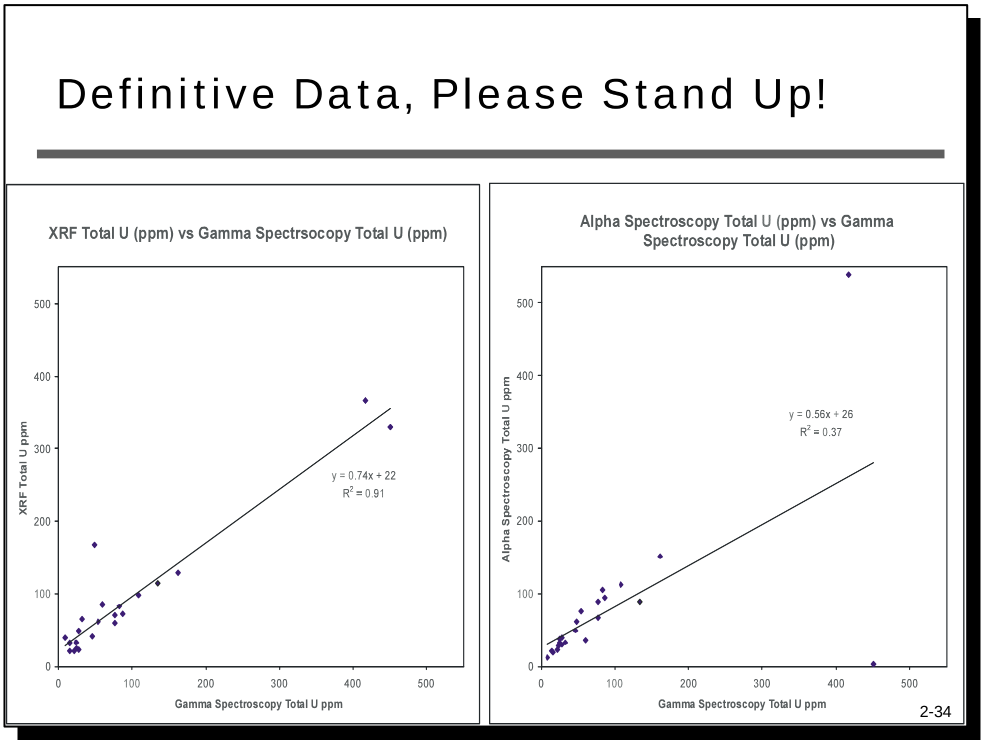
Which is which?

Notes

- These two scatter plots show paired data results for arsenic. In one case, samples first analyzed by XRF were then sent off for ICP analyses. In the other case, the same sample was split and sent for ICP analyses to two different labs. Which of these two corresponds to the ICP/ICP comparison, and which to the XRF/ICP comparison?

  The answer is that the scatter plot on the right compares XRF to ICP, while the scatter plot on the left shows ICP versus ICP results for two different labs for the same set of samples.

  The take home point is quite simple. Traditional analyses are often treated as though they are "definitive" and free from error. When the results of an alternative analysis such as an XRF are compared to those from a traditional lab, any differences observed are attributed to poor performance on the alternative analysis's part. The reality is not so simple. Traditional analyses also include "errors" that need to be recognized.



Definitive Data, Please Stand Up!

Notes

- This slide shows results from a set of samples analyzed with three different methods for uranium, via XRF (very limited sample preparation), gamma spectroscopy (sample preparation, but no extraction), and alpha spectroscopy (sample preparation with extraction required). The plot on the left compares XRF and gamma spectroscopy data with a resulting R^2 of 0.91. The plot on the right compares alpha spectroscopy and gamma spectroscopy data with a resulting R^2 of 0.37. Both gamma spectroscopy and alpha spectroscopy are well-established methods for measuring uranium in soils. In this particular case, if the XRF had just been compared to alpha spectroscopy results, the likely conclusion would have been that there were performance problems with the XRF. The availability of gamma spectroscopy data as well helped to identify alpha spectroscopy as the problem for at least two of the samples.

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

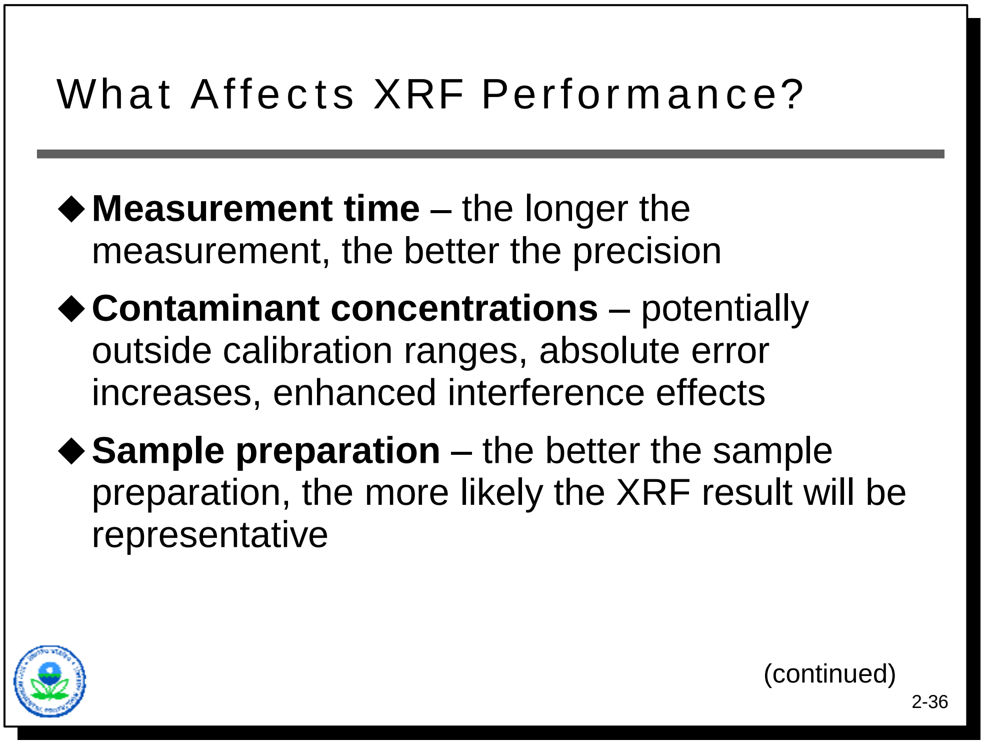
Notes

◆ **Standard laboratory data can be “noisy” and are not necessarily an error-free representation of reality:** It is a mistake to believe that standard laboratory data are free of errors. This can be seen when laboratory analyses from two different laboratories are compared to one another in the same way that XRF and laboratory data are compared.

◆ **Regression R^2 values are a poor measure of comparability:** Regression performance should be judged using a number of factors, not just the R^2 value.

◆ **Focus should be on decision comparability, not laboratory result comparability:** Decision comparability judges whether or not data is suitable for the decision at hand. XRF data may be suitable for decisions about whether an action level has been exceeded or for calculating UCL/EPC even when the regression is not perfect.

◆ **Examine the lab duplicate paired results from traditional QC analysis:** Frequently the regression from duplicate paired results is poor. It is unreasonable to expect the split field (XRF) versus laboratory regression to be better than the laboratory’s duplicate versus duplicate regression.



What Affects XRF Performance?

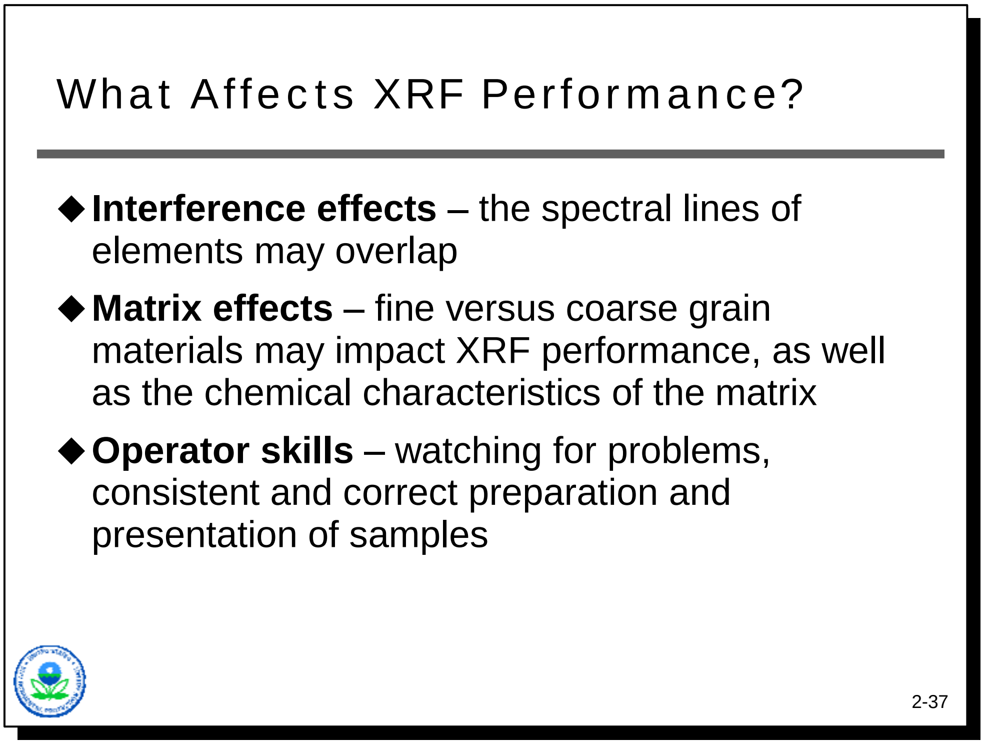
- ◆ **Measurement time** – the longer the measurement, the better the precision
- ◆ **Contaminant concentrations** – potentially outside calibration ranges, absolute error increases, enhanced interference effects
- ◆ **Sample preparation** – the better the sample preparation, the more likely the XRF result will be representative

(continued)

2-36

Notes

- ◆ **Measurement time:** The longer the measurement time or count time, the better the precision will be.
- ◆ **Contaminant concentrations:** Contaminant concentrations may be outside of the calibration ranges. Other contaminants may cause interference effects.
- ◆ **Sample preparation:** The better the sample preparation, the more representative the XRF results will be of actual conditions.

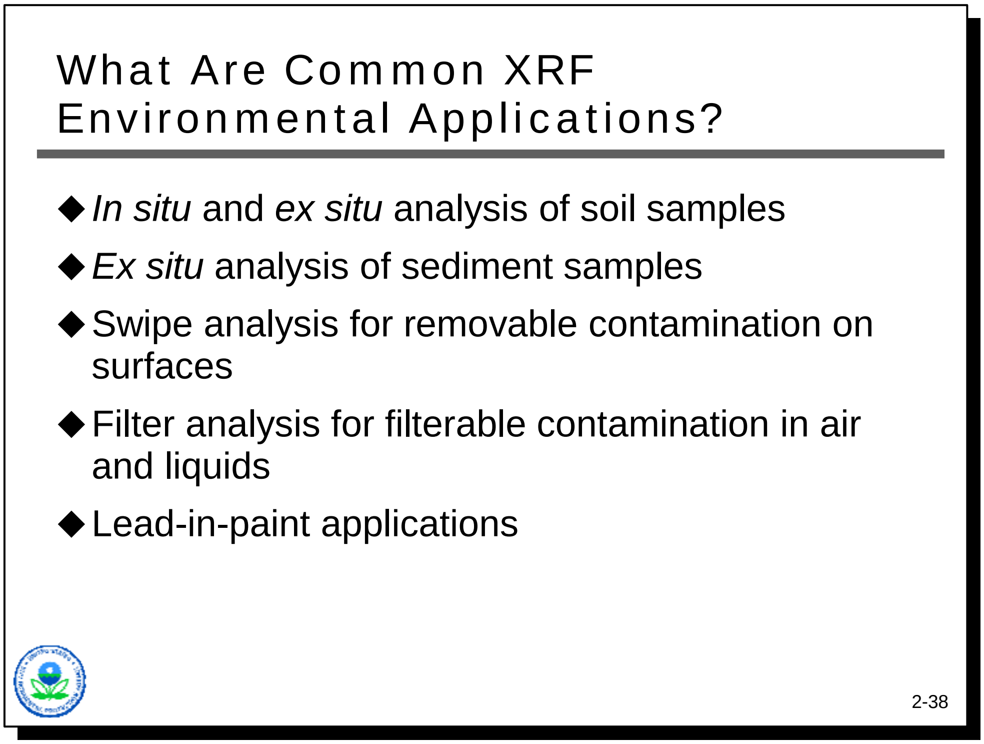


What Affects XRF Performance?

- **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

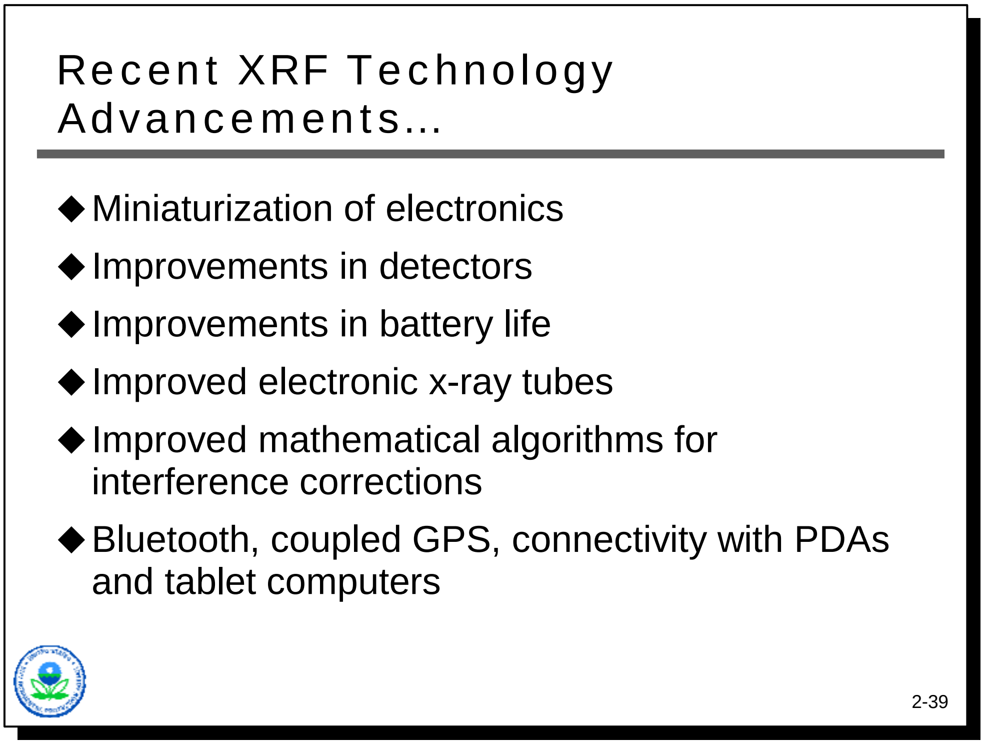
Notes

- **Interference effects:** The spectral lines of elements may overlap distorting results for one or more elements.
- **Matrix effects:** Physical matrix effects, such as fine versus course grain materials, may impact XRF performance. In addition, chemical characteristics of the matrix may also impact XRF performance.
- **Operator skills:** The level of operator skill can affect XRF performance. The operator should watch for problems and should practice consistent and correct preparation and presentation of samples.



What Are Common XRF Environmental Applications?

- *In situ* and *ex situ* analysis of soil samples
- *Ex situ* analysis of sediment samples
- Swipe analysis for removable contamination on surfaces
- Filter analysis for filterable contamination in air and liquids
- Lead-in-paint applications



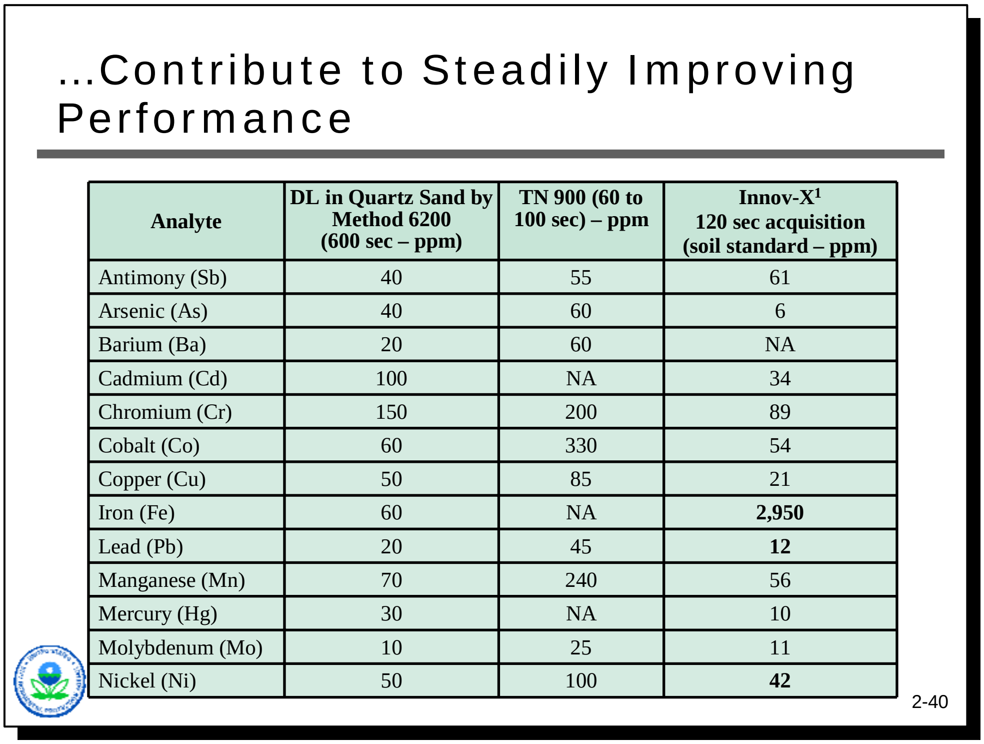
Recent XRF Technology Advancements…

- Miniaturization of electronics
- Improvements in detectors
- Improvements in battery life
- Improved electronic x-ray tubes
- Improved mathematical algorithms for interference corrections
- Bluetooth, coupled GPS, connectivity with PDAs and tablet computers

Notes

◆ **Recent XRF technology advancements:** The following advancements in XRF technology have improved the performance of the technology:

- » Miniaturization of electronics – this has made the instruments more portable
- » Improvements in detectors – with a corresponding lowering of detection limits
- » Improvements in battery life – which increases sample throughput by reducing instrument downtime and improves general field application
- » Improved electronic x-ray tubes – which improves performance of the units
- » Improved mathematical algorithms for interference corrections – which expands the applicability of the technology
- » Bluetooth, coupled GPS, connectivity with PDAs and tablet computers – which enhances data collection, management, and storage

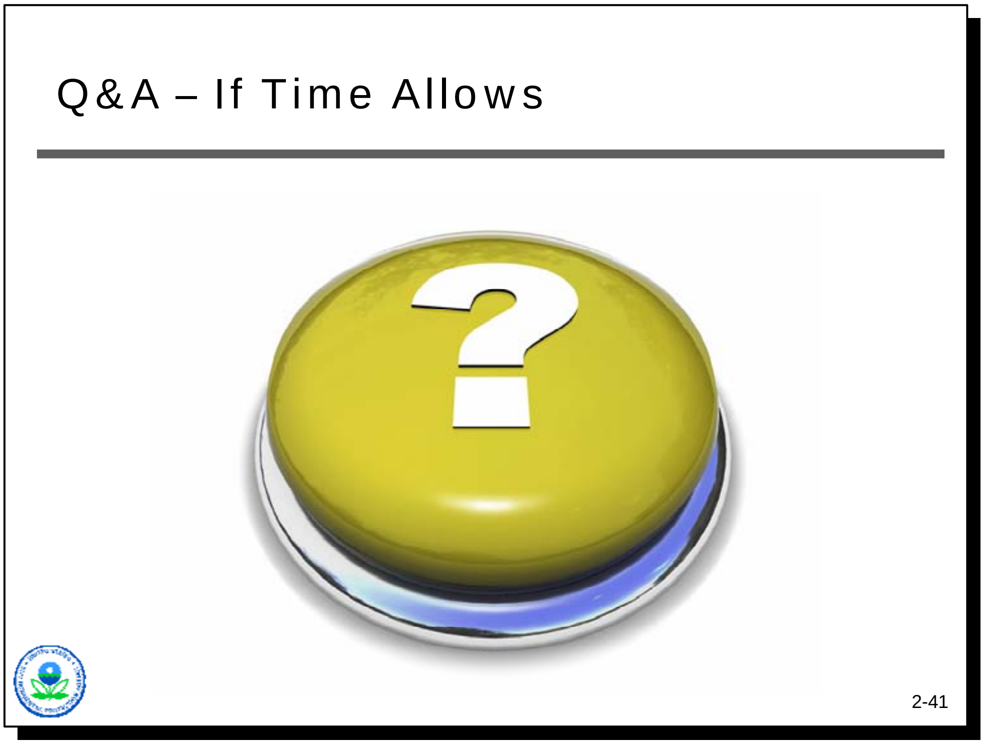


...Contribute to Steadily Improving Performance

Analyte	DL in Quartz Sand by Method 6200 (600 sec – ppm)	TN 900 (60 to 100 sec) – ppm	Innov-X[1] 120 sec acquisition (soil standard – ppm)
Antimony (Sb)	40	55	61
Arsenic (As)	40	60	6
Barium (Ba)	20	60	NA
Cadmium (Cd)	100	NA	34
Chromium (Cr)	150	200	89
Cobalt (Co)	60	330	54
Copper (Cu)	50	85	21
Iron (Fe)	60	NA	**2,950**
Lead (Pb)	20	45	**12**
Manganese (Mn)	70	240	56
Mercury (Hg)	30	NA	10
Molybdenum (Mo)	10	25	11
Nickel (Ni)	50	100	**42**

Notes

◆ This last table shows the results of XRF technology improvements over the years. The first data column shows XRF detection limits as reported in Method 6200 in the best of conditions - quartz sand with a 600 second acquisition. The second column shows the performance of a TN 900 XRF in the mid to late 1990s (the table containing these results is dated 1998) with a 60 to 100 second acquisition. One would expect these values to be less than half of what is reported if a 600 second acquisition time had been used. The last column shows data collected with an Innov-X unit in 1996 for a spiked soil standard (the spiking element is not present in this table). Results in bold indicate actual measured data. Plain text results are reported detection limits. The detection limit differences are marked for a number of samples. For example, in the case of arsenic the Innov-X detection limit is one tenth that of the TN 900 back in the 1990s. This improvement is not vendor-specific…in fact all vendors of portable XRF technologies have made significant strides in improving instrument performance in the last decade. One would expect those improvements to continue and be reflected in falling detection limits and better handling of interference effects.



Q&A – If Time Allows