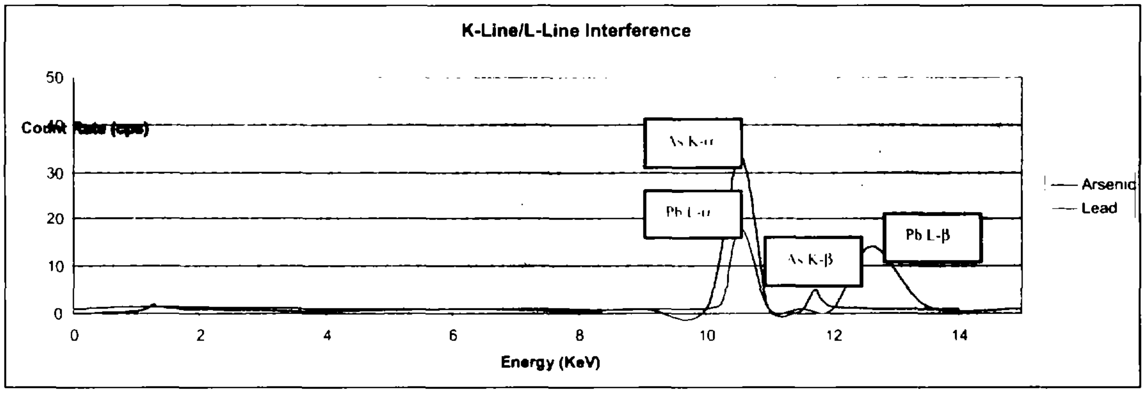
Lead-Arsenic Interferences with XRF

XRF elemental analysis of soils is based on the detection of x-rays released by heavy metals within the soil. Each element has a set of unique x-ray energy levels which allow for their identification. When an element is bombarded with a gamma ray from the XRF unit, an electron is removed from one of the inner electron shells.(1) An electron from an outer shell then moves in to fill the gap.(1) As the electron moves from an outer shell to an inner shell, it releases energy in the form of an x-ray.(1) The rays are labeled as K,L, M or N with a corresponding α, β or γ to denote which electron shell the x-ray originated from and which shell the electron moved inwards from, respectively.(1) The further an electron moves, the greater the amount of energy is released.(1) Therefore, if an electron is moved into the K shell from the N shell, the largest amount of energy will be released. Slightly lower energy levels are observed for movement into the L shell, and nearly immeasurable levels are detected at the M shell.(1) Measurements are typically read from the K and L-line α and β waves. For arsenic and lead those values are:(1)

	K-α	K- β	L-α	L-β
Arsenic	**10.54**	11.73	1.28	1.32
Lead	74.96	84.92	**10.55**	12.61

From this table you can see that the strongest peak for As (K-α) is overlapped by the Pb L-α peak. This could cause a potential interference issue, making it difficult to determine the correct amount of lead and arsenic in the soil. This is better illustrated in the following diagram.(2)



You can see that the K-α peak for arsenic overlaps the L-α peak for lead. This leads to error in elemental analysis. While there will be a degree of uncertainty in the measurements, the XRF is capable of identifying whether the element represented by the peak at 10.5 KeV is lead or arsenic as well as reducing the amount of error in the reported concentrations. There are three techniques that allow the XRF to reduce the error in measurements.

The first is the original calibration of the instrument, which is based on pure samples.(3) When the instrument measures a pure lead sample, it memorizes what the lead spectrum is supposed to look like when there are no other elements interfering or overlapping it.(3) The same is true for all other elements, including arsenic. Then, when a multi-element sample is being analyzed, the XRF program looks within a particular region of interest (ROI) for the Pb peaks. (3) When it sees something in that ROI it recognizes anything that isn't pure Pb and removes it from its calculation of Pb concentration. (3) The same is true of arsenic. Therefore, the arsenic peak will be removed from the lead calculation and the lead peak will be removed from the arsenic calculation.

Second, interference between lead and arsenic are minimized because their ROI's are programmed to be as far apart as possible.(3) The XRF analyzer uses the K-α peak of As (10.54 KeV) and the L-β peak of Pb (12.61 KeV) as defined ROI's. (3) This means that the lead concentration calculation is not based on the L-α peak that is overlapped by arsenic, thus allowing for accurate measurements of lead.

Third, a spectral deconvolution is performed prior to any quantification of the elements based on the constant ratio maintained between the peaks of the same element.(3) In other words, when the instrument examines the Pb L-β region, it is able to estimate the size of the Pb L-α peak based on the ratio that exists between the two. (3) When quantifying for As, it can subtract the estimated Pb L-α peak from the spectrum and determine that the leftover peak is As. (3)

Uncertainty in measurements increases as lead levels increase. Any large amounts of Pb will increase background in the general area of the As region of interest. This will be reflected in the calculated precision of the As analysis, leading to higher uncertainty. (3) Because Limit of Detection (LOD) is a direct calculation from uncertainty, high Pb presence can increase the absolute limit of detection of As. (3) Finally, the overlapping peaks may actually enhance each other, inflating the reported concentration of arsenic. (3) The magnitude of inflation is reflected in the error of the reading.

Typically arsenic readings will be accurate until lead is 5,000 ppm or greater, although the exact value depends on the specific sample being tested. (3) A typical limit of detection in soil for lead is 30 ppm after 60 seconds and 20 ppm after 120 seconds. (2) For arsenic it is 25 ppm after 60 seconds and 15 ppm after 120 seconds. (2) However, values that low may not actually be measurable with any accuracy. The Limit of Quantitation (LOQ) is the lowest concentration that can be reliably measured and is typically reported as 3.33 times the LOD.(4) For arsenic this would be about 45 ppm. XRF arsenic concentration accuracy for different lead levels can be established by testing the unit with the provided NIST samples.

The following measurements of Arsenic can be expected for the correlating Lead values. All information is obtained from the NIST Standard Reference Material Montana Soil samples accompanying the XLP 712[5,6,7].

Sample 2709	Sample 2709	Sample 2710	Sample 2710	Sample 2711	Sample 2711
Lead	Arsenic	Lead	Arsenic	Lead	Arsenic
18.9 +/- 0.5	17.7 +/- 0.8	5532 +/- 80	626 +/- 38	1162 +/- 31	105 +/- 8

These values are for ideal soil samples that are not often encountered in the field. Additional factors that could affect XRF readings are soil moisture, particle size, and matrix homogeneity. Due to the sensitivity for inflated arsenic values with high errors, care should be taken in preparing field samples for analysis. While in situ measurement is fastest, for the most accurate concentrations below 50 ppm, ex situ sample preparation is preferred. In situ analysis may still be useful if certain steps are followed. 1. Remove any debris 2. Loosen soil to 2.5 cm over an area of at least 10 cm diameter 3. Stir the sample to achieve homogenization 4. Allow to dry in the sun for 2-3 hours.(8) These steps can be taken while the site is being flagged for sample locations. Just before taking the measurement the soil should be mixed again, combed with a 2mm mesh, leveled and gently packed down.(8) A sample time of 120 seconds should be enough time to get accurate readings, but experimenting with longer sample times could be valuable. Ex situ sampling should follow EPA Method 6200 guidelines.

References:

1.*X-Ray Fluorescence Spectroscopy (XRF)*(November, 2005). See website ttp://www.amptek.com/xrf.html

2. Debbie Schatzlein, Volker Thomsen andDavid Mercuro, *Theory and Use of Field Portable X-Ray Fluorescence for Soil Analysis workshop* (2003).

3. Communication with Laura Stupi, Applications Chemist, Niton Corporation (July, 2005)

4. Voler Thomsen, Debbie Schatzlein, and David Mercuro, *Limits of Detection in Spectroscopy*, Spectroscopy, v. 18, n. 12 pp. 112-114. (December, 2003).

5. National Institue of Standards and Technology Certificate of Analysis Standard Reference Material 2710. July 18, 2003

6. National Institue of Standards and Technology Certificate of Analysis Standard Reference Material 2709. July 18, 2003

7. National Institue of Standards and Technology Certificate of Analysis Standard Reference Material 2711. July 18, 2003.

8. Stephen Shefsky, *Comparing Field Portable X-Ray Fluorescence (XRF) to Laboratory Analysis of Heavy Metals in Soil* (1997).