Overview of XRF Instrumentation:
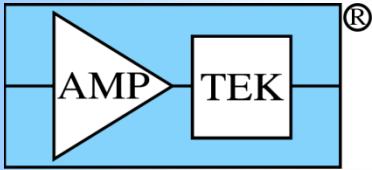
Software

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Instrument

- Excitation source
  - X-ray tube or radioisotope

- Spectrometer
  - X-ray detector
  - Signal processing electronics

- Software
  - Spectrum correction and processing software
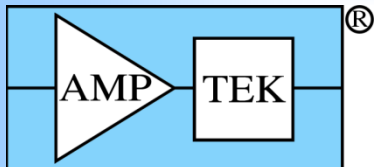
- Other
  - Radiation shielding
  - Sample fixture

What does the software do?

- **Acquisition software**
  - Configures the hardware
  - Starts and stops data acquisition
  - Reads the raw pulse height spectrum from spectrometer
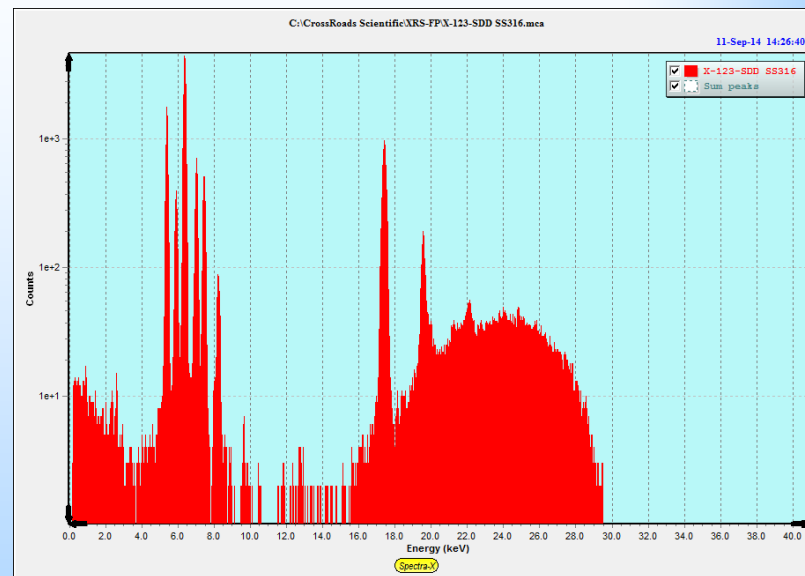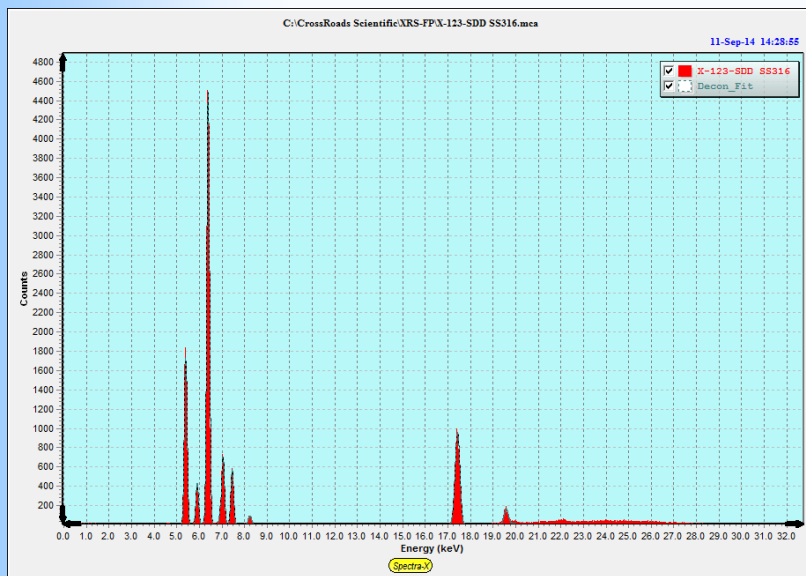- **Analysis software**
  - Applies energy calibration
  - Corrects raw spectrum for various physical effects and artifacts
  - Identifies photopeaks
  - Computes intensity (counts/sec) of each photopeak
    - Subtracts background
    - Subtracts counts due to overlapping peaks
  - Computes concentrations
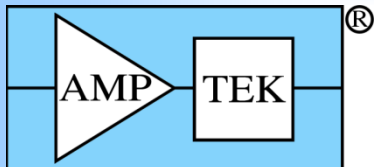   - Corrects for matrix effects
    - Applies calibration factors

What the software does, part 1: Acquires the raw spectrum

Raw spectra of stainless steel: linear (left) shows the main peaks while log plot (right) shows background and artifacts
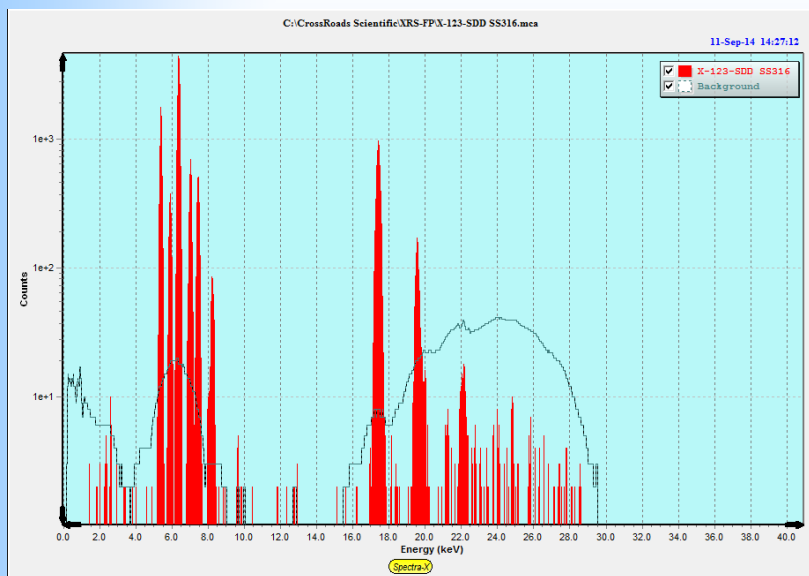
Measured using Amptek Experimenter's Kit, Ag anode tube, W/Al filter, X-123-SDD spectrometer, and XRS-FP analysis software
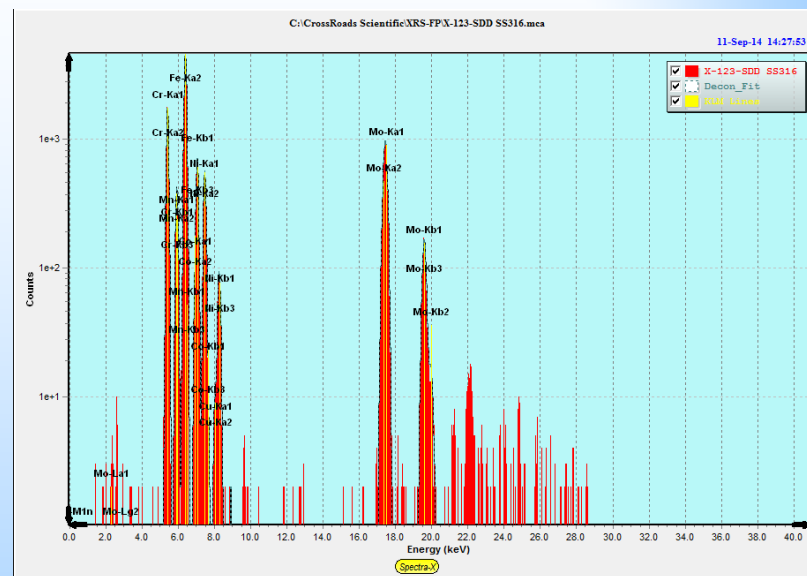
Software

What the software does, part 2: Processes the spectrum
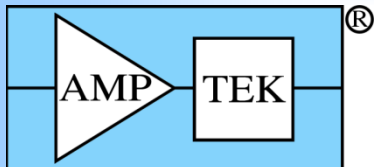

After background removal

After peak deconvolution

Corrects for physical effects (pileup, escape peaks, scatter)

Removes background continuum

Fits to sum of peaks

Software

What the software does, part 3: Quantifies results

Element	Intensity (cts/sec)
V	0.8 + 0.8
Cr	359.8 + 7.3
Mn	16.2 + 2.1
Fe	975.2 + 12.0
Co	0.0 + 1.2
Ni	128.6 + 4.4
Cu	2.6 + 0.9
Mo	461.1 + 8.3

Element	Concentration
V	0.06% + 0.07%
Cr	19.20% + 0.39%
Mn	0.81% + 0.10%
Fe	64.66% + 0.80%
Co	0.00% + 0.00%
Ni	12.05% + 0.42%
Cu	0.17% + 0.06%
Mo	3.05% + 0.05%

Peak intensities   Elemental concentrations

Deconvolution → intensity (X-rays/sec) in each peak

Applies calibrations and matrix corrections

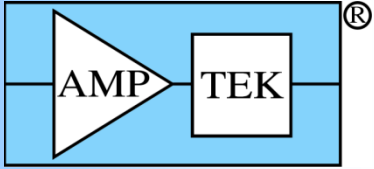Computes elemental concentrations (final answer)
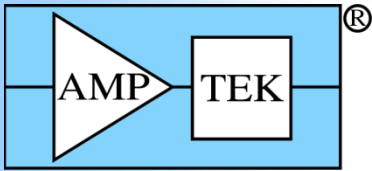
Types of XRF analyses

- Qualitative analysis
  - Identifies which elements are present (above a detection limit)

- Semi-quantitative analysis
  - Measures elements concentration using a Fundamental Parameters (FP) method to correct for matrix effects
  - *Standardless FP*: Algorithm estimates calibration and matrix factors
  - *Hybrid FP*: Use mix of calibration and algorithm
  - Relative accuracy of 5-10% (hybrid) to 10-20% (standardless)

- Quantitative analysis
  - Strict reference method: X-ray intensity is compared to a calibration curve from standard reference materials
  - Calibration must use same matrix

- All methods apply equally to bulk concentration, layer density (mg/cm^2), layer thickness, etc.

Energy Calibration

Energy Calibration

What is energy calibration?

- The spectrometer outputs a "pulse height spectrum", a histogram of the number of X-rays in each pulse height bin or "channel"

- Spectrometer does not "know" the energy associated with each pulse height bin; this can depends on many instrument parameters

- Energy calibration finds relationship between pulse height and energy: the "gain" (eV/channel) and "offset" (generally not zero)
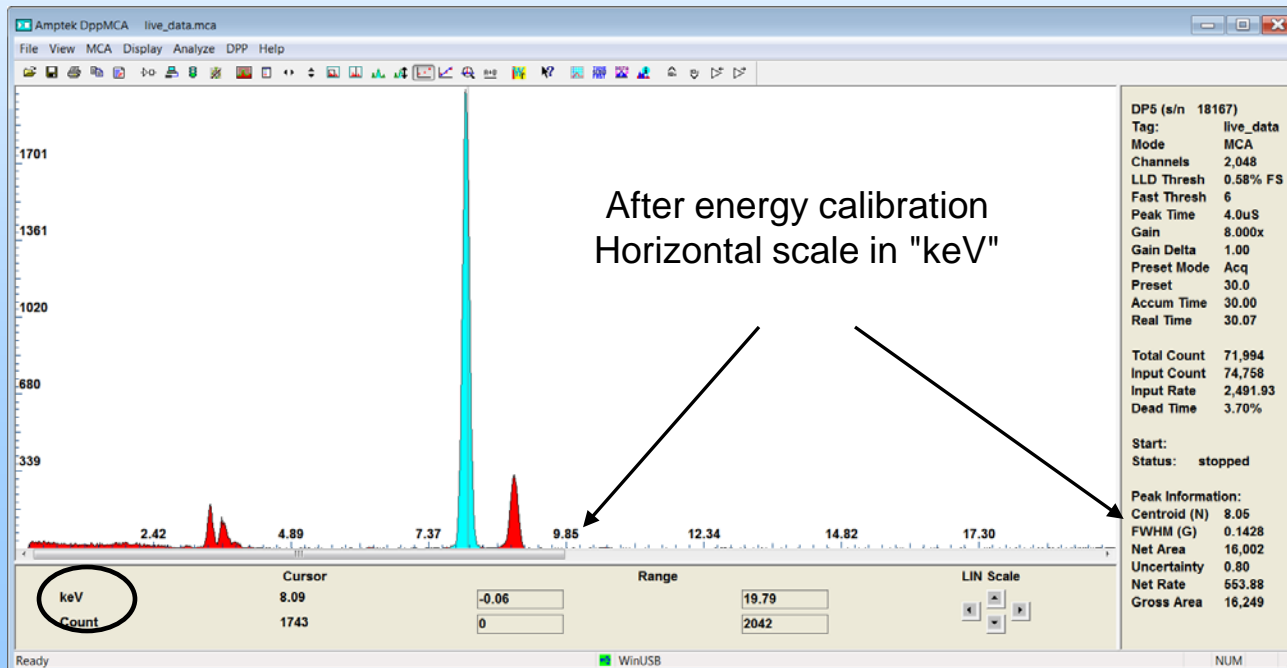

Before energy calibration
Horizontal scale in "channel number"
Not in physical units

Energy Calibration

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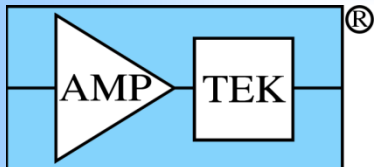

After energy calibration
Horizontal scale in "keV"

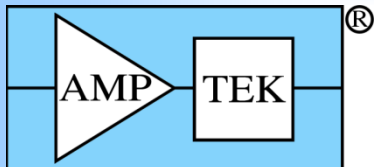# Energy Calibration

How is an energy calibration done?

– In a turn-key analyzer, usually done by manufacturer but user may need to check

– Start with a known spectrum, and do linear fit between known energy and channel number

– Should be at least two peaks which are (a) well above background, (b) separated from overlapping peaks, and (c) far apart in energy
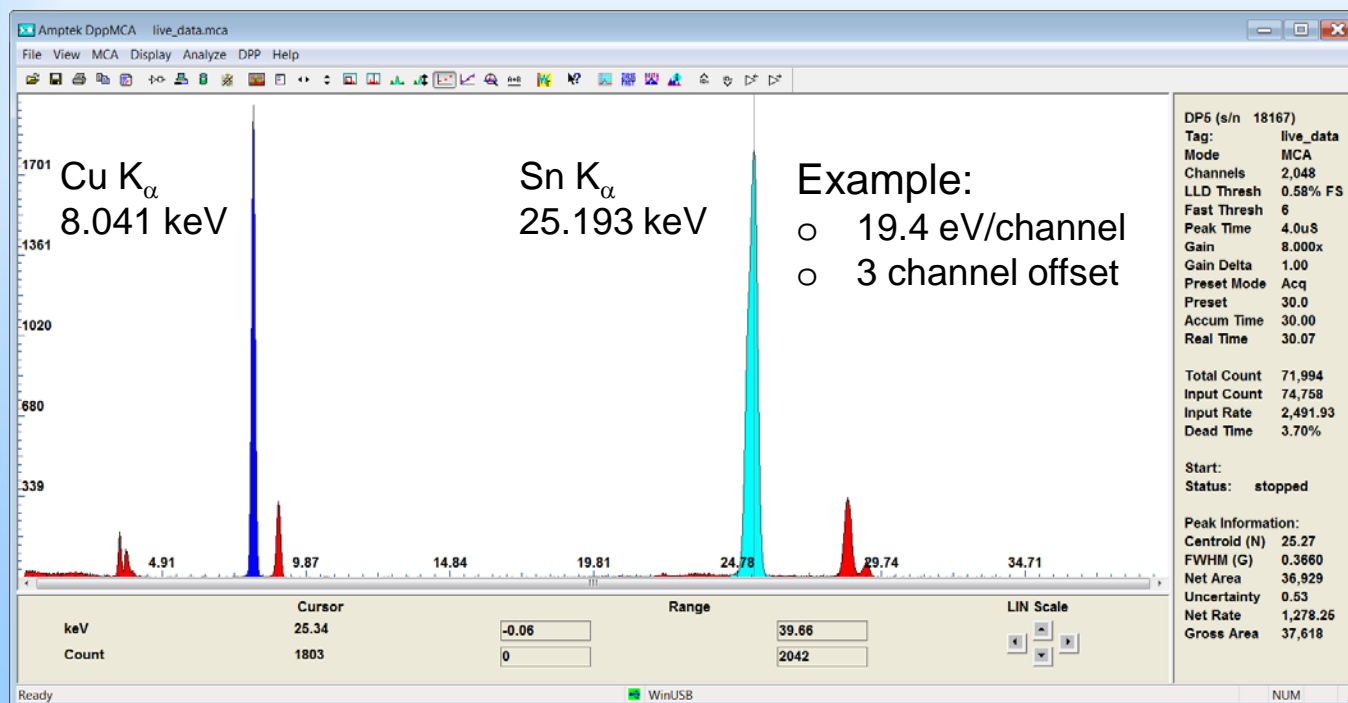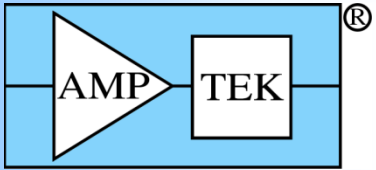
Cu K$_\alpha$
8.041 keV

Sn K$_\alpha$
25.193 keV

Example:
o 19.4 eV/channel
o 3 channel offset

Photopeak spectra

What are the energies of the photopeaks?

- Moseley's law gives approximate values; exact values are given in various tables
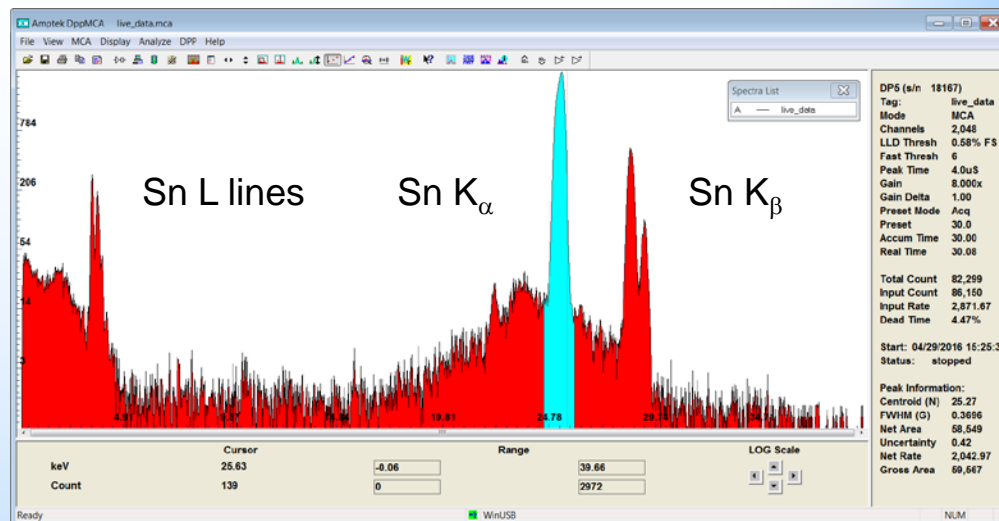- Energy of each X-ray peak equals difference between atomic energy levels
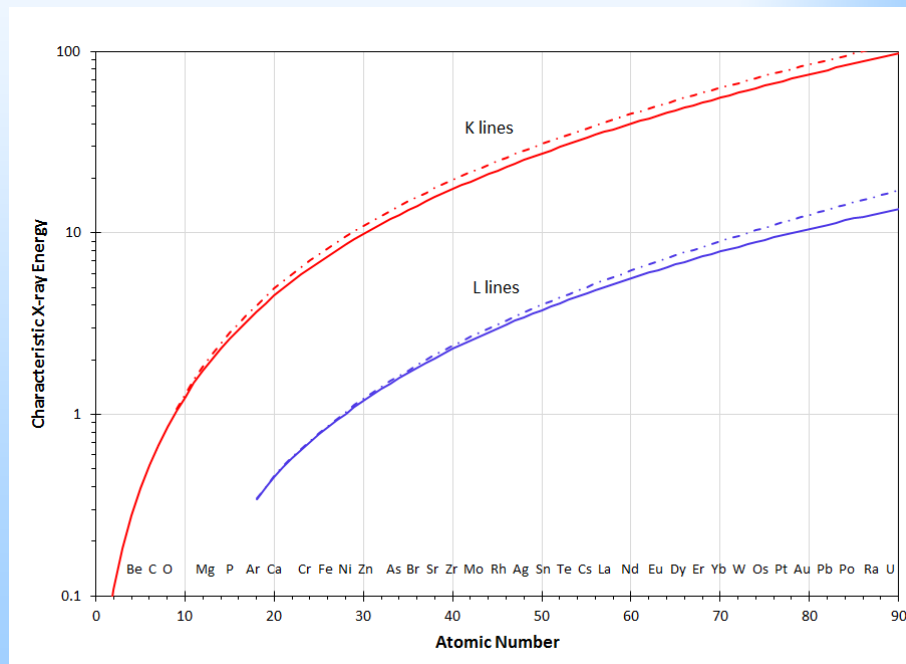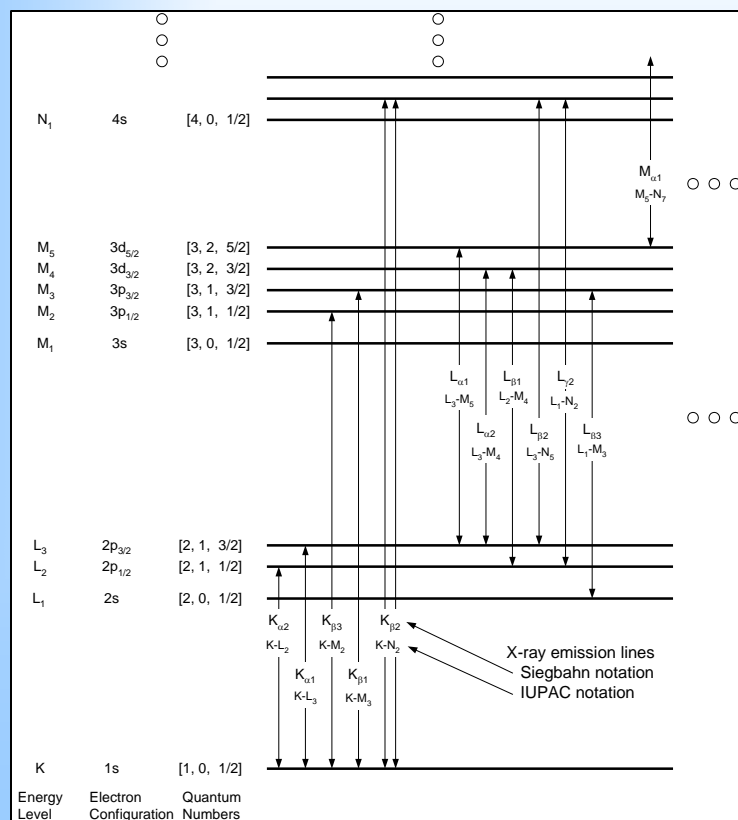
Example spectra
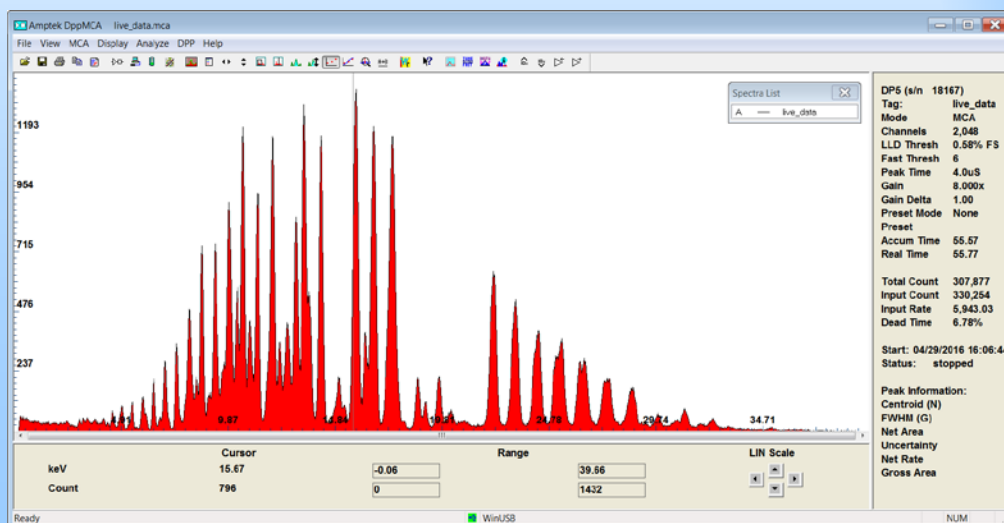
Tin spectrum

Multielement spectrum
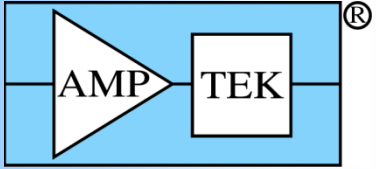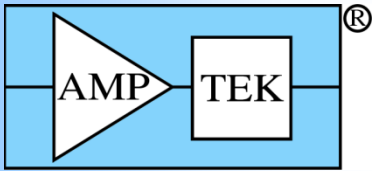
Spectrum Processing

What does the processing do?

- There are features in the spectrum, in addition to photopeaks from sample, which must be addressed for accurate analysis
  - Escape peaks
  - Escape continuum
  - Compton and Rayleigh scatter peaks
  - Brehmstrahlung continuum
  - Sum peaks
  - Overlapping peaks (a.k.a. interferences)
- Some of these cause photopeak counts to occur in other energy channels. The software adds these "lost" counts back into the photopeak
- Some of these can obscure real peaks. The software "cleans" the spectrum so real peaks are clearer
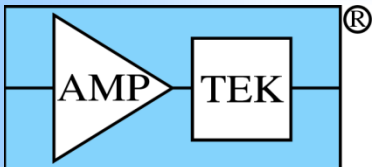
Spectrum Processing

Escape peaks

- When an X-ray stops in a detector, by photoabsorbtion, a silicon atom in the detectors is in an excited state, so emits Si characteristic X-rays
- Some Si K_α X-rays escape the detector → false peak 1.75 keV below primary peak
- Must be corrected in software: reassigns lost counts to photopeak and away from background region
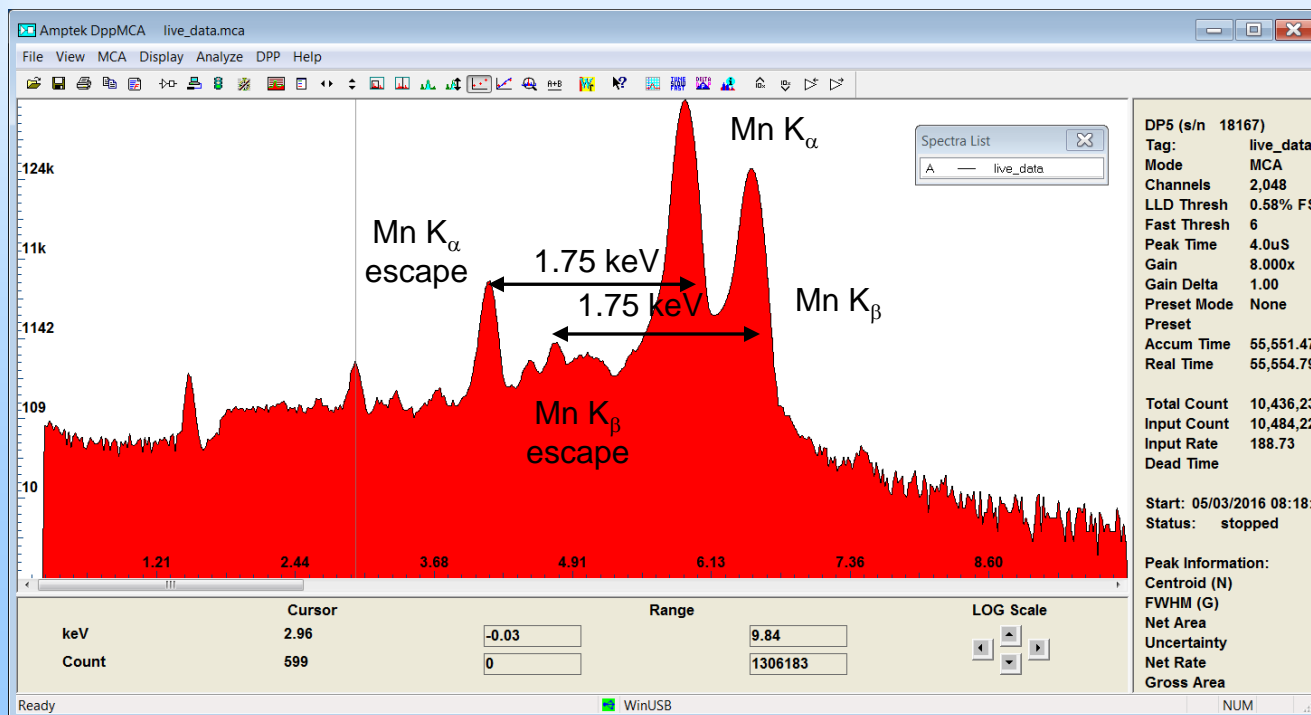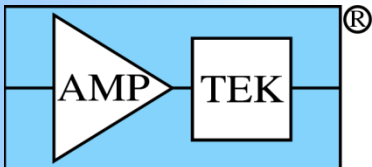
Background

- – Several processes produce a background contiuum:
    - Brehmstrahlung X-rays from tube scatter from sample or target
    - Photoelectrons escaping detector form a continuum
    - Continuum is mostly smooth but has steps, curves, etc – complex shapes
- – Background obscures real peaks and degrades measurement precision/accuracy
- – Software must distinguish background counts from real counts in same region
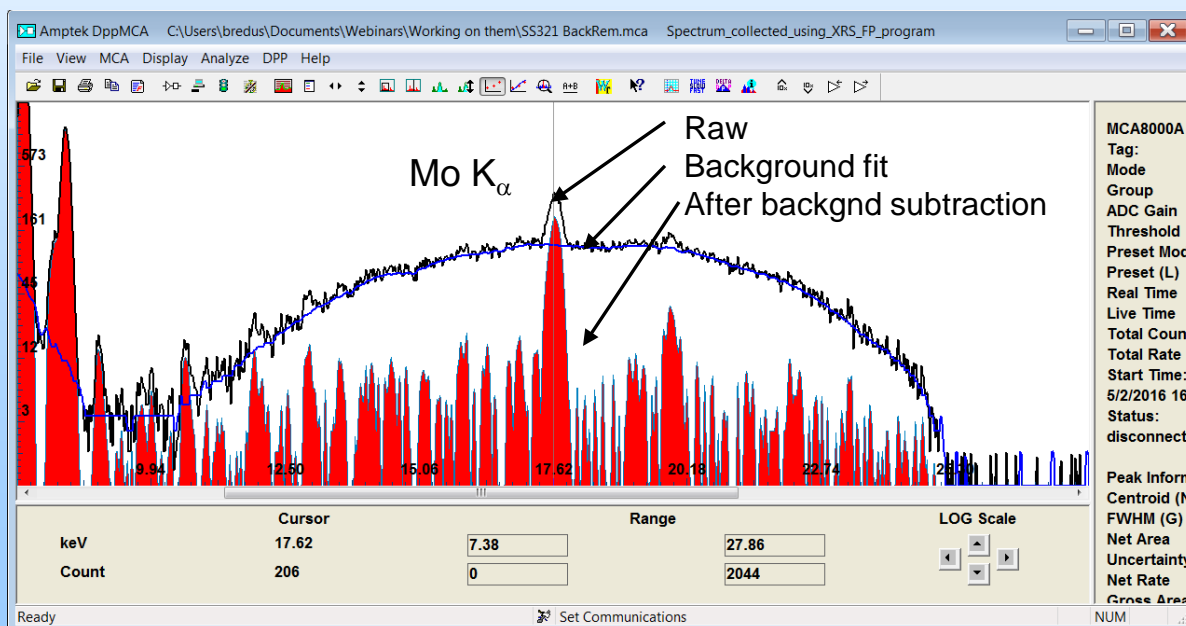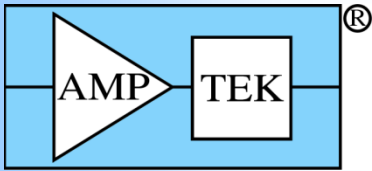
Spectrum Processing

Sum peaks

- If two X-rays interact in detector at same time, detector sees one pulse with sum of energies
- Most important for the major peaks and at the highest count rates
- The sum peaks can obscure real peaks and counts there are lost from main peak
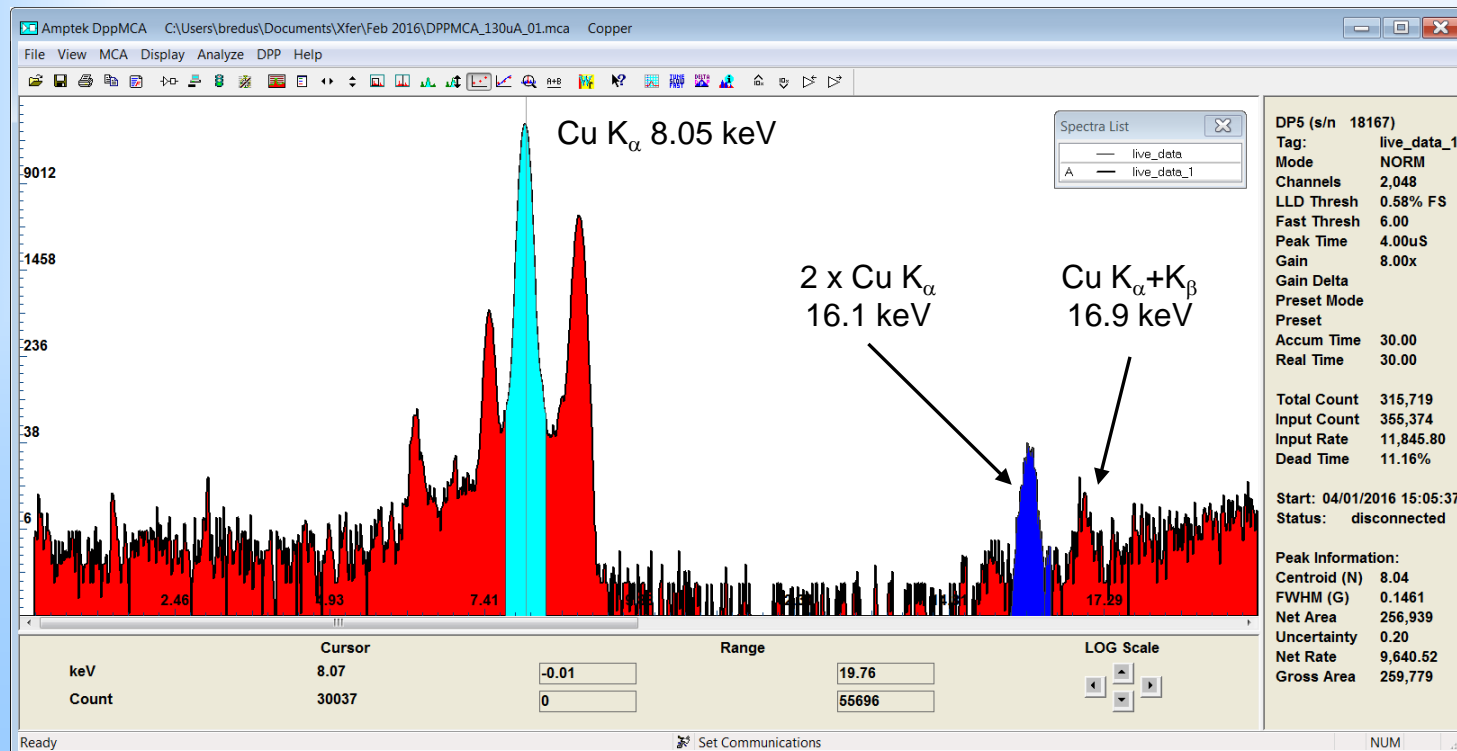
Spectrum Processing

Overlapping peaks

- If another peak overlaps the spectral peak (region of interest) of the element to be analyzed, this is termed an "interference"

- Overlapping peaks can arise from sample itself (e.g. Fe K_α peak overlaps Mn K_β peak) or from the environment (air contains Ar so measurement in air show Ar K_α)

- Software must account for the overlap to obtain the correct intensity
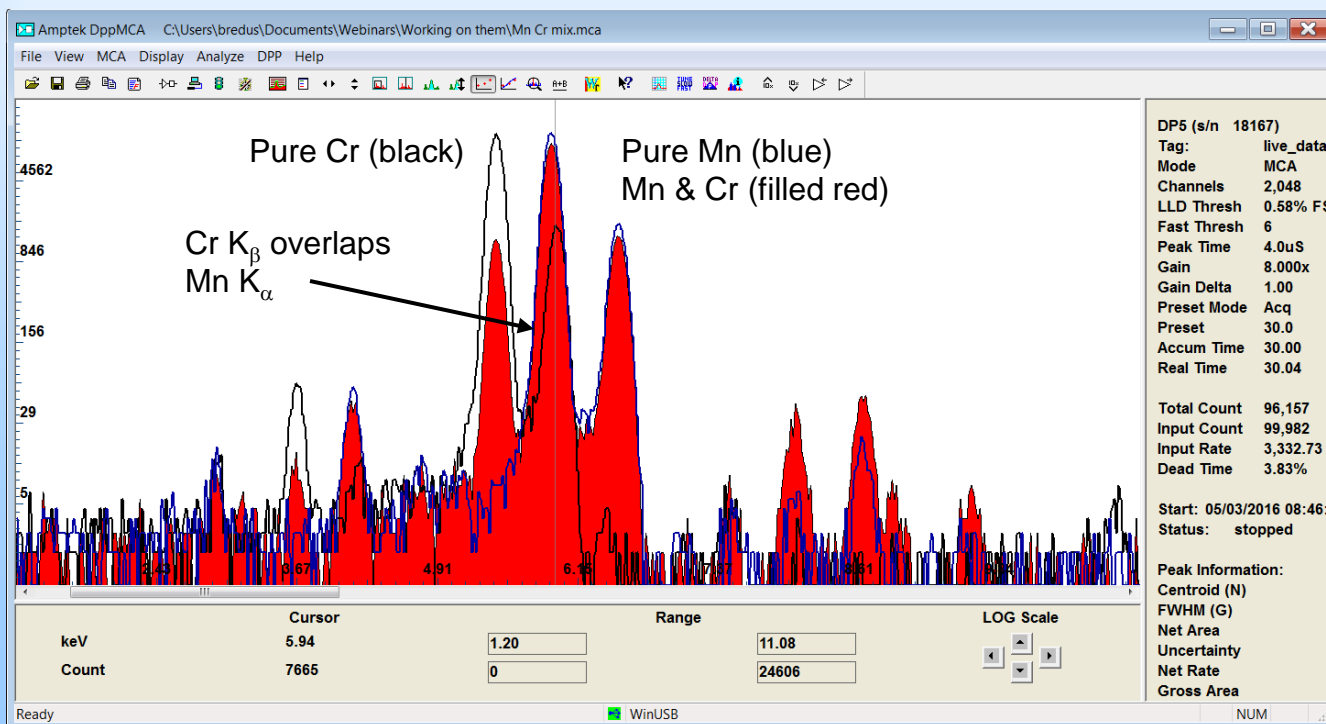
How does one determine the area of the photopeak?

Several different methods can be used

- Direct sum of counts within a region of interest (ROI)
- Fit photopeak shape to a Gaussian, using a predetermined centroid and width
- Fit photopeak shape to a Gaussian, adjusting centroid and width during fit
- Fit photopeak shape to a more complicated theoretical curve (e.g. to include a tail or other features)
- Fit photopeak shape to a measured curve (reference spectrum)

Which is best?

- Simpler ones are quick and work well for large, separated peaks
- More complicated ones help with overlapping peaks, complex spectra, and intensities near the detection limits

Quantification

Quantification

Calibration factors

- Intensity of each element's X-ray peak is proportional to the number of the atoms excited, i.e. concentration

- Only true if **everything** is held constant.

- Calibration factors depend on geometry, excitation energy, absorption in sample, many other factors

- An error in calibration → poor accuracy
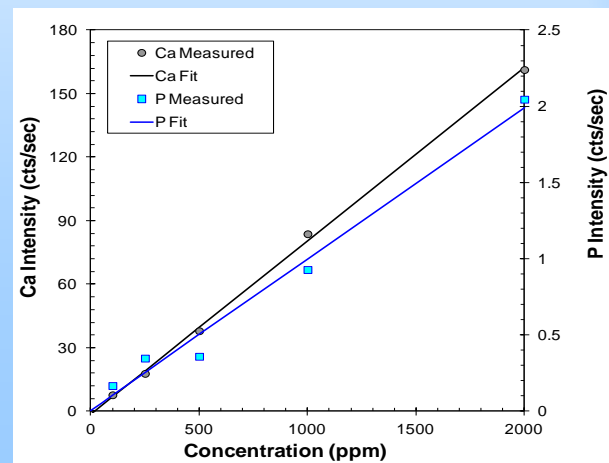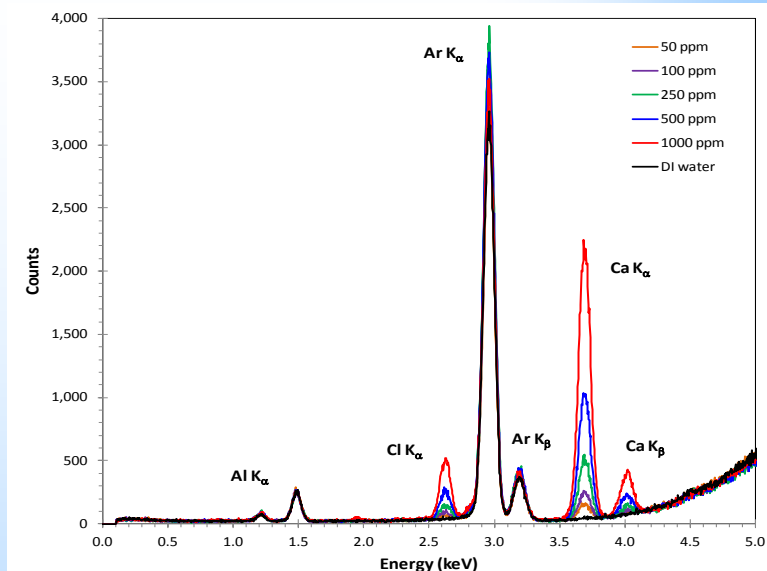
Matrix effects

- – Every atom in the sample affects the intensity of X-rays from the analyte
- – Attenuation
    - • X-rays produced in the sample are attenuated by the sample
    - • Attenuation depends on composition of sample
- – Enhancement
    - • If you add a high-Z element to a sample, it will excite the lower Z elements, thus increasing the intensity
- – You must know the composition of the matrix to correct matrix effects
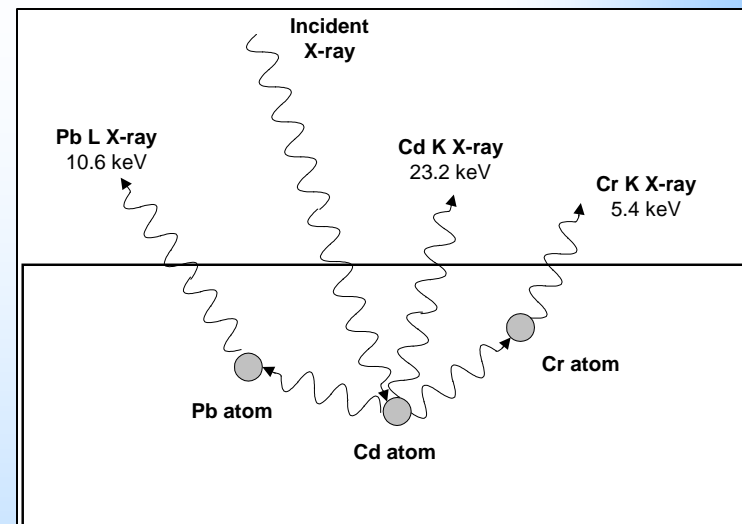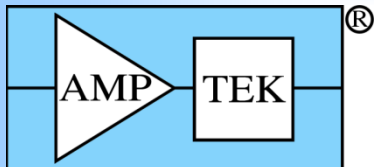
Incident X-ray

Pb L X-ray
10.6 keV

Cd K X-ray
23.2 keV

Cr K X-ray
5.4 keV

Cr atom

Pb atom

Cd atom

How to approach calibration & matrix effects

- **Strict "quantitative" analysis**
  - A reference based method, requiring standards with compositions that are well known and similar to those of material to be analyzed
  - Standards are analyzed, intensities obtained, and a calibration plot is generated for elements of interest

- **Comparative analysis**
  - In many practical applications, one does not need concentrations per se but can compare to a reference
  - In manufacturing, one often is often comparing items to predetermined reference samples which set limits
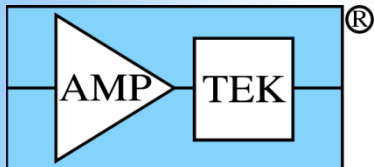
How to approach calibration & matrix effects

– **Standardless fundamental parameters (FP) analysis**

- Theory is used to compute calibration factors and matrix corrections. Based on the "Sherman Equation"

- No calibration needed, so very easy. One does not need to obtain reference samples similar to what will be measured

- Equations are approximate, does not include real world tolerances, so relative accuracy is limited to ~10% best case

– **Hybrid FP or FP with standards**

- Calibration is used to determine some factors while others, e.g. matrix corrections, are derived from theory

Measurement equations

$$C_i = I_i \cdot K_i \cdot M \cdot S \qquad [1]$$

$$I_i = \left(G_i - B_i - P_i + \gamma_i \right)/T \qquad [2]$$
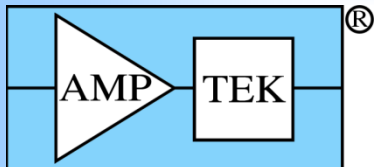
Simplified but illustrative

– Equation [1]

- C_i is the concentration of element i
- I_i is the X-ray intensity of element i (in counts/sec)
- K_i is the calibration coefficient
- M is a matrix correction factor
  - The "matrix" is all the other elements in the sample besides the analyte
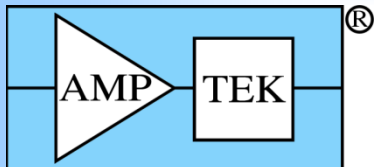 - X-rays emitted by every element in the sample interact with the atoms from all the other elements

– Equation [2]

- G_i is the gross or total counts in a region of interest (ROI) for the peak of element I
- B_i is the background counts
- P_i is counts from overlapping or interfering peaks
- γ_i is correction for artifacts
- T is the measurement time

Software

Measurement uncertainty

- Every term in equations [1] and [2] contributes to measurement uncertainty

- There will be random errors (affecting precision)
  - Dominant source is usually from random counting statistics
  - If there are 100 counts in photopeak, relative precision will be 10%
  - To get 0.1% precision you need 1 million counts in peak

- There will be systematic errors if anything changes from calibration/model
  - If sample geometry changes, then calibration factor changes
  - If you change T_{peak}, HV on tube, filter on tube, etc then errors results

- There will be systematic errors due to approximations in models
  - Photopeaks are never truly Gaussian. A Gaussian deconvolution is only approximate
  - Escape peak models, sum peak models, background models only approximate
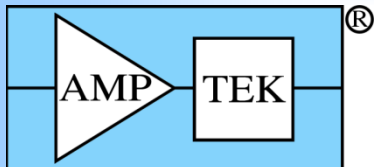 - These errors are largest when a small peak of interest is on a large peak to be modeled

Measurement uncertainty

- Expanded uncertainty

$$\frac{\sigma_C^2}{C^2} = \frac{\sigma_K^2}{K^2} + \frac{\sigma_M^2}{M^2} + \frac{\sigma_S^2}{S^2} + \frac{\left(\sigma_G^2 + \sigma_B^2 + \sigma_P^2 + \sigma_\gamma^2\right)}{I^2}$$

- Each term includes random errors (due to counting statistics), systematic errors due to changing conditions (i.e. geometry), and systematic errors due to approximations in the models
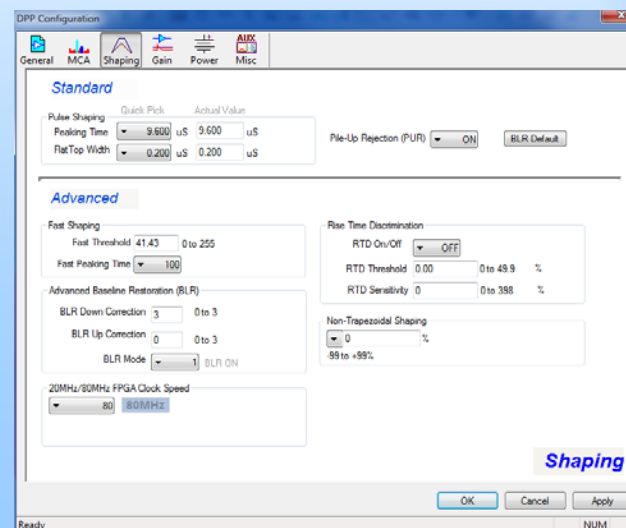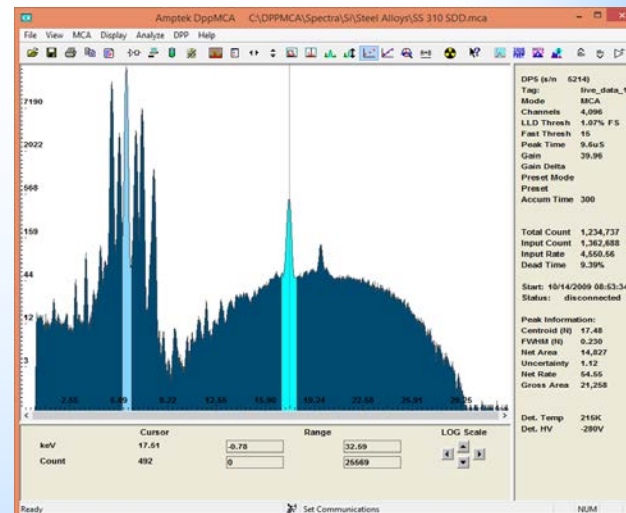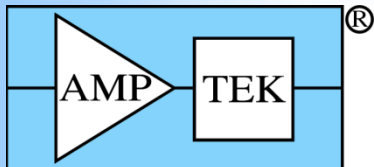
Amptek Software

DPPMCA

- Data acquisition & control
- Limited analysis
  - Energy calibration
  - Define ROIs, compute net counts
- Free with processor

Software developer kit

- User can integrate Amptek DPP with their analysis & display
- Cross-platform available for non-Windows

Amptek Software

XRS-FP

- Full analysis software
  - Processes spectra, fits photopeaks to get intensity, applies matrix corrections & calibration factors

- Many options
  - Standardless FP, FP with standards, purely standards based
  - Multiple excitation conditions, scattered intensity corrections, multiple thin film analyses
  - Gaussian peaks, ROI, reference spectra

- Can be customized for specific applications or user interfaces