X-RAY FLUORESCENCE (XRF)

An introduction to the ED-XRF technique

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January 14th, 2011

X-Ray Fluorescence

- *X-Ray Fluorescence is defined as “The emission of characteristic "secondary" (or fluorescent) X-rays* from a material that has been excited by bombarding with high-energy X-rays.
- The phenomenon is widely used for elemental analysis.

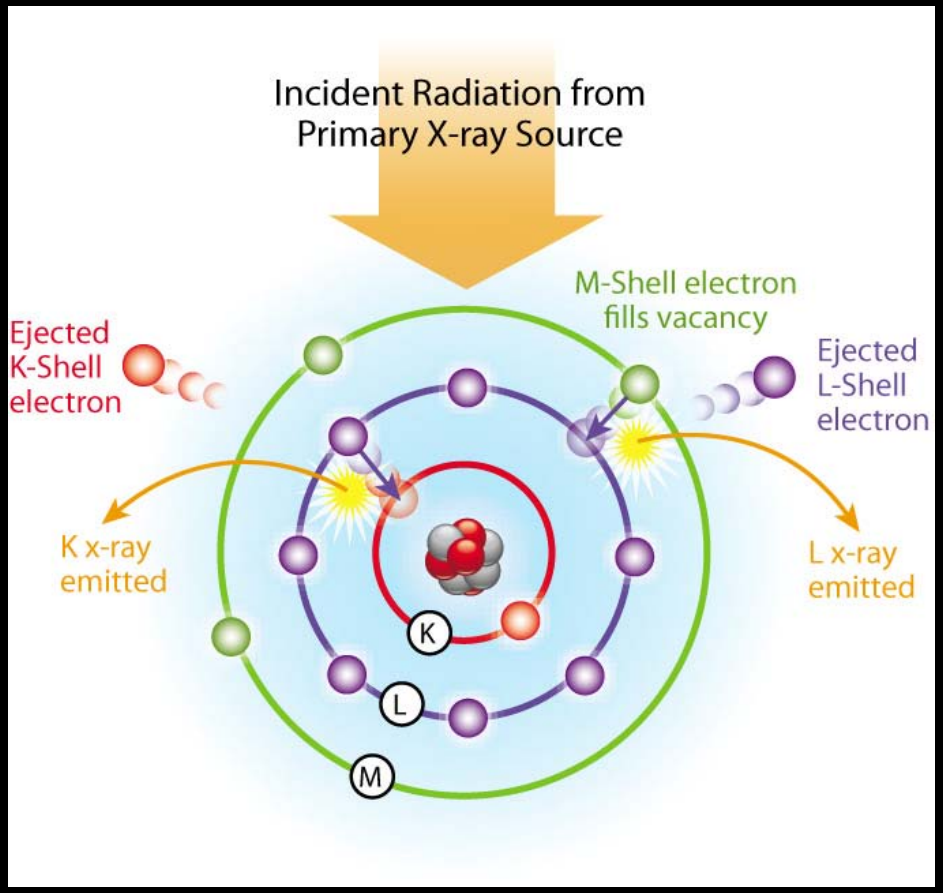
Characteristic X-Rays

- When high energy photons are absorbed by atoms, inner shell electrons are ejected from the atom.
- This leaves the atom in an excited state, with a vacancy in the inner shell.
- Outer shell electrons then fall into the vacancy
- High energy X-ray photons are emitted with energy equal to difference in the binding energies of the two shells involved in the transition $E_2-E_1=h\nu_{char}$.
- Each element has a unique set of energy levels, thus each element emits a pattern of X-rays characteristic of the element, termed “characteristic X-rays”.

The X-Ray Fluorescence Process

1) An electron in the K shell is ejected from the atom by an external primary excitation x-ray, creating a vacancy.

2) An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn.



XRF spectrometer and its types

- X-Ray Fluorescent (XRF) Spectrometers use a technique, in which x-rays are used to excite a sample and generate secondary x-rays.
- The technique provides determination of major and trace elements in solids.

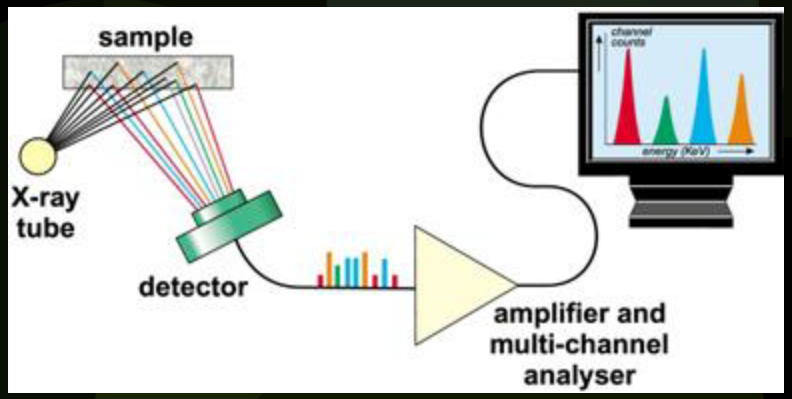
- The two main types of XRF spectrometers are

1. Energy dispersive (EDXRF), using a solid-state detector (usually silicon): distinguishes each elemental peak according to its Energy.
2. Wavelength dispersive (WDXRF), which use a scanning crystal as the dispersive element: separates each elemental peak according to its Wavelength.

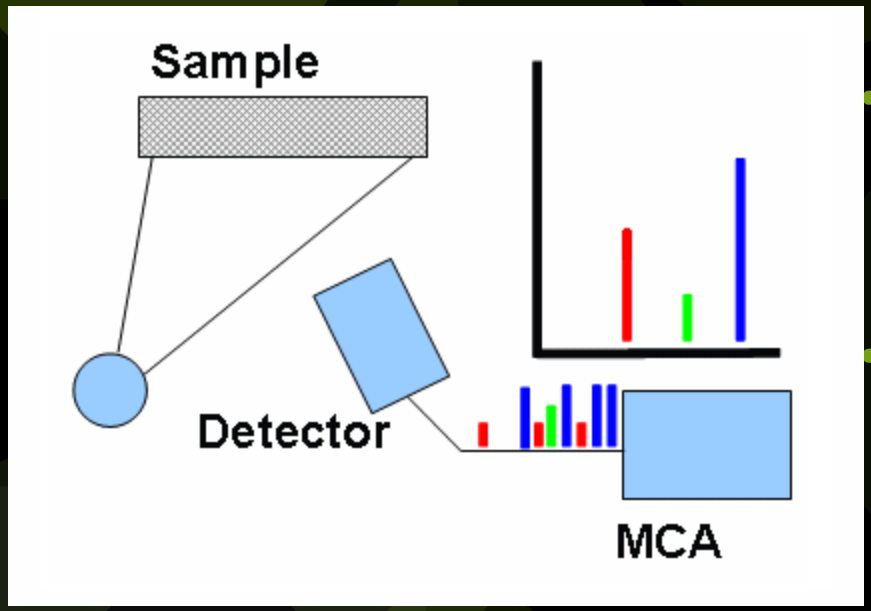
- EDXRF typically detects elements from at least sodium (Na) to uranium (U), while WDXRF can extend down to beryllium (Be).

Energy Dispersive XRF (EDXRF)

- The atoms in the sample are excited by X-Rays.
- All element specific X-Ray signals emitted are measured simultaneously in a fixed mounted semi-conductor detector.
- The radiation intensity of each signal, which is proportional to the concentration of the element in the sample, is calculated internally using a MCA.



Working principle of EDXRF spectrometer



- Step 1: A secondary fluorescence photon is emitted by the sample.
- Step 2: The secondary photon enters the detector.
  - It is converted to an electrical impulse.
  - The height of this pulse is directly proportional to the energy of the incoming photon.
- Step 3: The electrical impulse is processed by the Multi-channel analyzer.
  - MCA digitally determines the pulse height
  - The pulse's height is saved to a specific channel address. Each channel counts the numbers of impulses of a specific height.
  - The channel memory of concern (for e.g "red energy photons“) is then incremented.
  - At a given moment, the contents of all channels constitute an image of the measured spectrum.
- An EDXRF spectrometer is a simultaneous machine. It acquires the information of all elements simultaneously.

- X-ray generator (Mini-X)
- Si X-ray detector (XR100CR)
- Digital pulse processor (DP4)
- Base plate
- Calibration sample (stainless steel)

HARDWARE COMPONENTS IN AMPTEK XRF SYSTEM


XR-100CR
X-RAY DETECTOR


XR-100CR
X-RAY DETECTOR

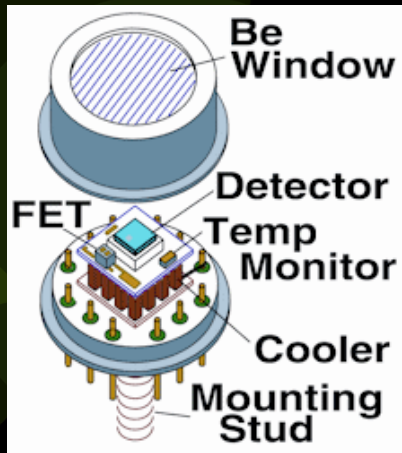

AMP TEK
PX4
DIGITAL PULSE PROCESSOR
AMP IN
XR-100
POWER
ON
OFF

Mini-X, X-ray generator

- Mini-X is a self-contained miniature X-ray tube system, which includes:
  - X-ray tube
  - High voltage supply
  - USB controller
- An electrically heated filament (cathode) within the X-ray tube generates electrons that are accelerated from the filament to the anode target by the application of a high voltage.
- X-rays are produced when these high velocity electrons are decelerated (slowed or stopped) or by the nuclei of high atomic number material and the difference in energy appears in the form of photons of high energy called X-rays or braking radiation.
- The Mini-X features
  - a 40 kV/100 µA power supply
  - silver (Ag) transmission target (Anode)
  - beryllium end window

XR100 Si Detector

- The XR-100CR is a high performance x-ray detector containing
  - a charge sensitive preamplifier
  - a thermoelectric cooler system
- Working:
  - Semiconductor (Si) exposed to radiation
  - Energy quanta absorbed by the lattice structure
  - If $E_{absobed} > E_{band\ gap}$, an electron-hole pair is generated for each quantum absorbed.
  - The number of electron-hole pairs is proportional to the energy transmitted by the radiation to the semiconductor.
  - An electric field, drifts the electrons and holes to the electrodes
  - Charge transfer results in a pulse that can be measured in an outer circuit.
- A 100-200 volt bias voltage across Si facilitates the transfer of charges
- This voltage is too high for operation at room temperature, so a thermoelectric cooler is provided to cool the system.



Digital Pulse Processor **DP4**

- The DP4 is a component in the complete signal processing chain, which consists of:
- MCA
- Power supply

- The input to the DP4 is the preamplified output from the Si detector.
- The DP4 performs the following tasks:
  - digitizes the preamplifier output (AD conversion)
  - detects the peak amplitude (digitally)
  - stores this value in its histogramm memory, generating an energy spectrum.
- The spectrum is then transmitted over the DP4's serial interface to the user's computer.

An introduction to the XRF analysis software

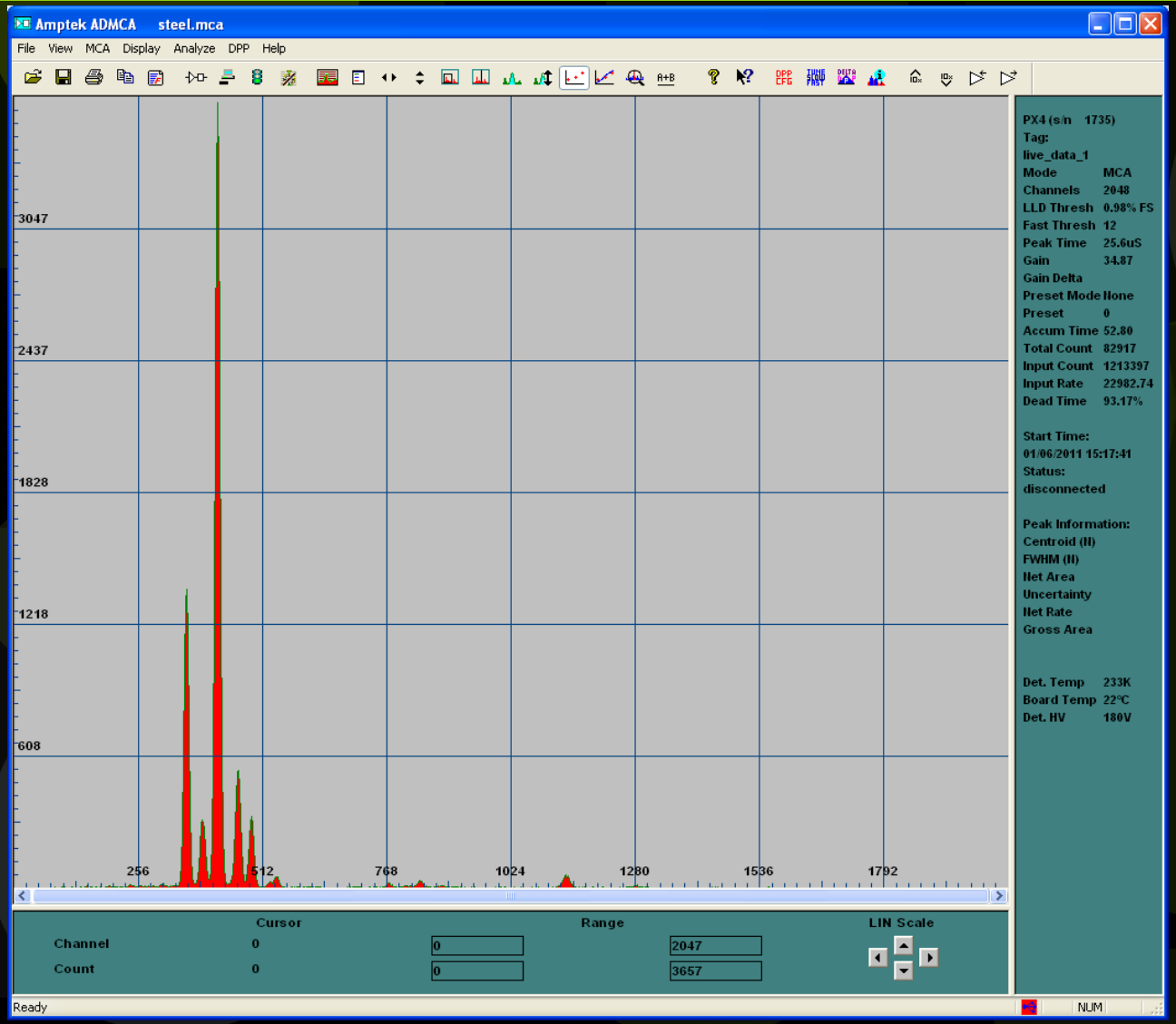
1. ADMCA 2.0
2. XRS-FP

QUANTITATIVE ANALYSIS OF SPECTRA

ADMCA 2.0 : Display and Acquisition Software

- ADMCA 2.0 is a Windows software package that
- Acquires the spectral data
- Displays the data
- Has got controls for signal processing.
- Spectral analysis features
  - Energy calibration
  - Setting regions of interest (ROI) to be examined
  - Computing ROI information (centroid, total area, FWHM)
  - Also performs spectrum fine tunning, subtraction and scaling of background.

Example spectrum

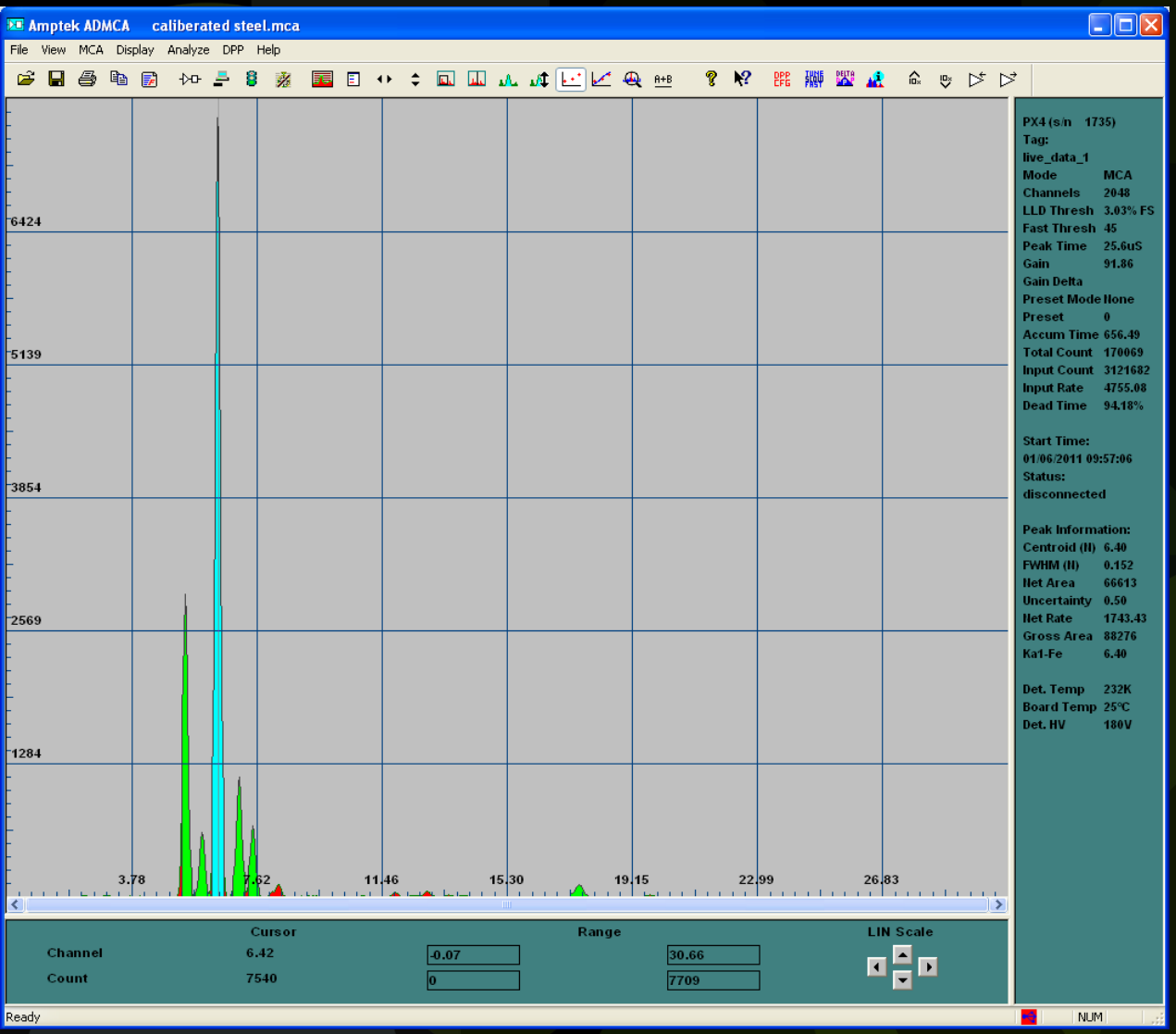


We have channels along the horizontal axis and counts along the vertical axis.

We need to calibrate the spectrum so that each peak lying along a particular channel corresponds to a specific characteristic x-ray energy.

Calibration: Changing the Channel scale to Energy in ADMCA

- The software calibration is an important step which changes the channel scale into an energy scale.
- For accurate calibration of spectrum the test sample must contain at least two known peaks in the spectrum.
- For example, an iron (Fe) peak at 6.40 keV and molybdenum (Mo) peak at 17.48 keV.
- After locating the centroids of these two peaks, the values of x-ray energies are fed and the caliberation is activated.
- The calibration is saved and is checked to be automatically loaded every time for future determination of unknown samples' compositions as well.

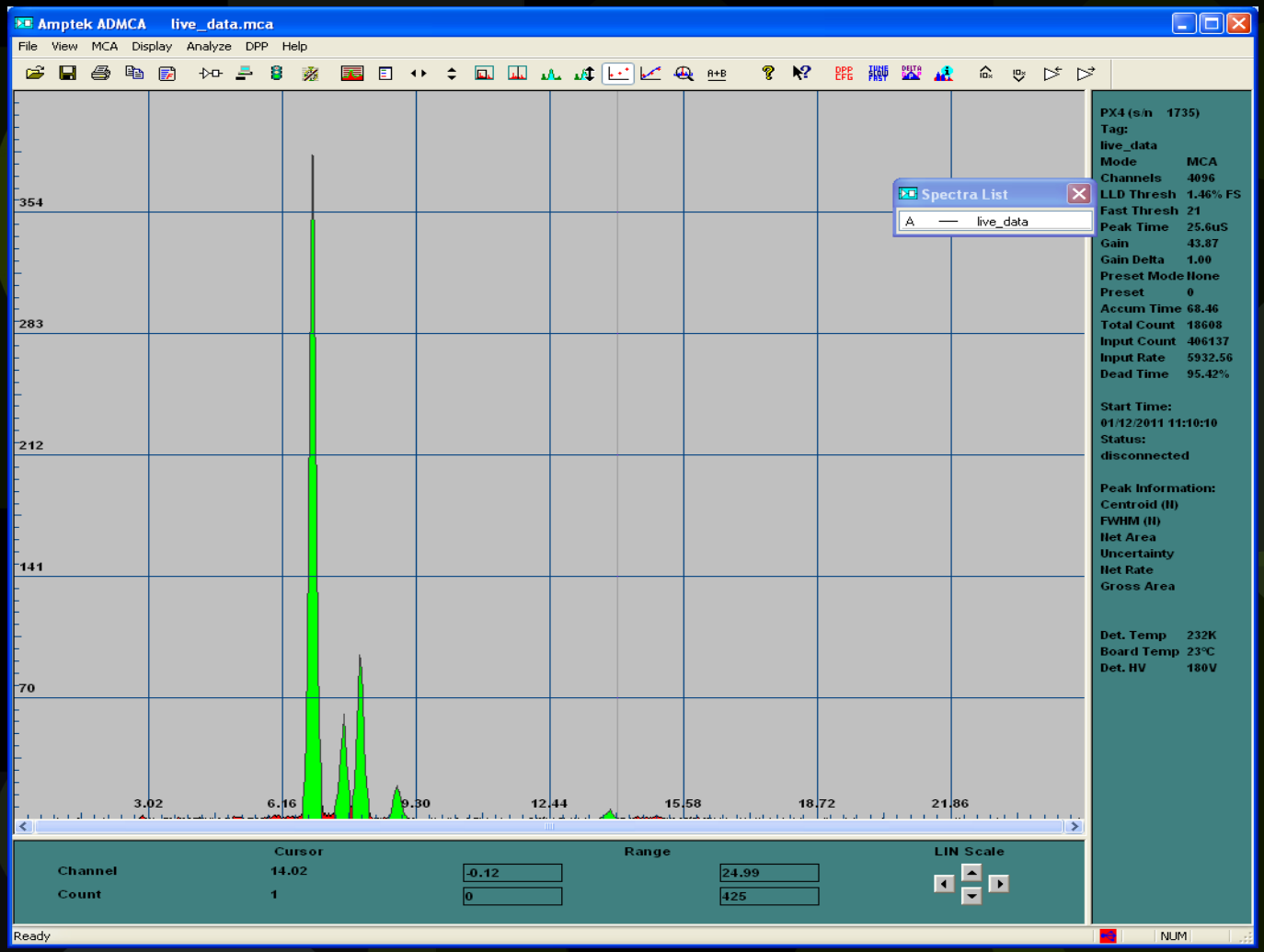


Stainless steel Energy calibrated Spectrum

After calibration, ROIs are defined and the ADMCA specifies a list of elements that corresponds to each ROI

Regions of Interest Details

Start	End	FWHM (N)	Net Area	Gross Area	Centroid (N)	Uncertainty	Status	Element
5.34	5.55	0.115	13095	27557	5.43	1.57	GOOD	Ka1-Cr
5.76	6.15	0.176	7200	8075	5.93	1.31	GOOD	Ka1-Mn
6.25	6.54	0.152	66613	88276	6.40	0.50	GOOD	Ka1-Fe
6.88	7.20	0.165	11010	14280	7.05	1.20	GOOD	Ka1-Co
7.38	7.62	0.141	4412	7464	7.49	2.32	GOOD	Ka1-Ni
17.24	17.71	0.247	1729	2149	17.48	2.93	GOOD	Ka1-Mo



Cobalt film deposited on Cu plate

The analysis of Co-film using calibration scale set for Steel

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Regions of Interest Details

Start	End	FWHM (N)	Net Area	Gross Area	Centroid (N)	Uncertainty	Status	Element
6.66	7.05	0.153	10491	11688	6.87	1.08	GOOD	Ka1-Co
7.41	7.71	0.110	1165	1655	7.58	3.98	GOOD	Ka1-Ni
7.82	8.16	0.153	2395	2908	7.99	2.44	GOOD	Ka1-Cu
8.66	9.05	0.061	584	647	8.86	4.56	GOOD	Ka1-Zn
13.66	14.02	0.010	108	166	13.82	13.86	GOOD	No match

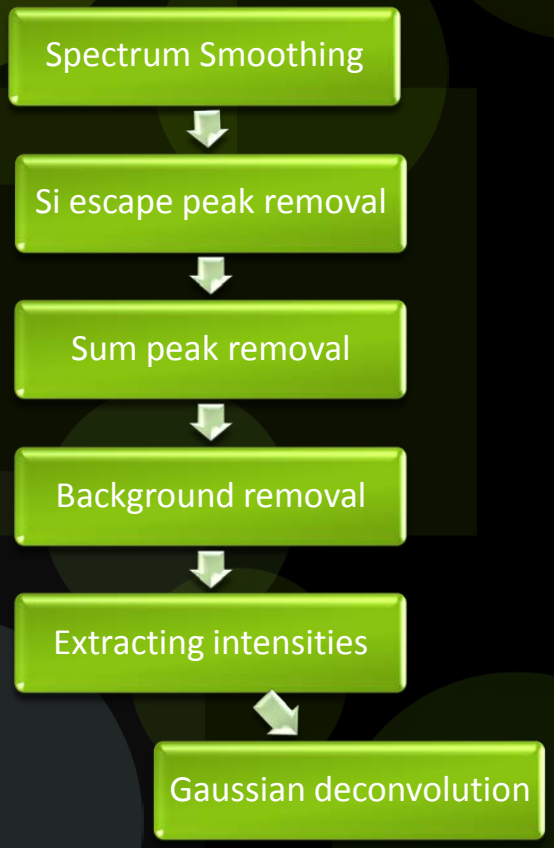
XRS-FP: Fundamental Parameters analysis software

- The ADMCA 2.0 has an active link to FP software.
- Purpose of FP software:
  - Interrelate the intensities of the characteristic X-ray lines to the concentration of the element in the sample.

Significance of the software

- The peaks in the spectrum correspond to the elements in the sample.
- The number of X-rays in each peak is proportional to the number of atoms.
- The software
  - Detects which peaks are present
  - Finds the relative intensity of each peak
  - Computes the concentration of each element in the sample.

Sequence of processing functions



- In general, an XRF spectrum consists of peaks, corresponding to
  - Various elements in the sample
  - Superimposed background
- It is the job of “spectrum processing” to effectively remove the signal (i.e., net peak intensity) from the noise.
- The spectrum processing in XRS-FP sequentially performs the functions illustrated in the figure.

Spectrum smoothing

- A **Gaussian** smoothing is the result of smoothing an image by a Gaussian function implemented to
  - reduce noise
  - reduce extra details

- This operation typically performs a Gaussian smooth of each channel in the spectrum, for the specified number of times.

Escape peaks removal

- Escape peaks arise when a fraction of parent characteristic X-rays gets absorbed as Si-Kα escape (1.75 keV) photons.
  - The deposited energy is reduced.
  - e.g. a 6.4 keV X-ray (Fe Kα) deposits only 4.65 keV.
- Every feature in the spectrum will have an associated escape feature at 1.75 keV lower energy.
- The software removes the effect by adding the equivalent x-ray event at the parent peak's energy.

Sum Peak Removal

- Sum, or pileup, peaks arise because two incoming x rays arrive at the pulse processor within a time frame that is less than peak discriminating time of two events.
- For example, two incoming Fe-Kα photons (each with an energy of 6.4 keV), which pileup, would produce a count at 12.8 keV.
- This correction is not as accurate as the escape peak removal, and may leave some residual sum peaks in the spectrum.

Background Removal

- The only method used, in the current software, is the **Automatic background method**.
- The method distinguishes fast-changing regions of the spectrum (i.e., peaks) from slowly changing regions (i.e., background).
- The background curvature arises primarily from scattered x-ray continuum from an x-ray tube whose shape depends on the anode atomic number and incident electron-beam energy (high voltage, in kV).

Intensity Extraction by Gaussian Deconvolution

- Deconvolution: Process of fitting the spectrum to a sum of separate photopeaks.
- Purpose: We need net peak intensities which help convert each element's peaks to elemental concentrations.
- Method: peaks are synthesized for all the expected lines (K_{α}, K_{β}, L_{α}, L_{β}) in the region of the sample's peaks.
- Note: The expected lines should already be provided by the user (using the ROI details from ADMCA) that will be used for the (FP) analysis.

Analyze

- This is the main command for the quantitative analysis of samples using the FP software.
- Using all the previous steps' information this command will convert the elemental intensities to composition, using required libraries and other information (geometric parameters, calibration).

- After this command is completed, the elemental compositions will be updated in a list as shown below in example for stainless steel.

XRS-FP analysis of steel

Amptek Inc XRF Report

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Layer Table

#	Thick	Type	Error	Units	Density	Norm.	Total
1	0.00	Bulk	0.00	mg/cm2	0.00	On	100.00

Sample Table

Layer	Component	Type	Concn.	Error	Units	Mole%
1	Ti	Calc	0.044	0.003	wt.%	0.055
1	Cr	Calc	25.399	0.127	wt.%	29.060
1	Fe	Calc	13.787	0.101	wt.%	14.688
1	Ni	Calc	43.569	0.192	wt.%	44.162
1	Nb	Calc	0.883	0.039	wt.%	0.566
1	Mo	Calc	6.352	0.118	wt.%	3.939
1	Cu	Calc	1.865	0.030	wt.%	1.746
1	Co	Calc	3.580	0.051	wt.%	3.614
1	Mn	Calc	0.933	0.019	wt.%	1.010
1	W	Calc	3.588	0.106	wt.%	1.161

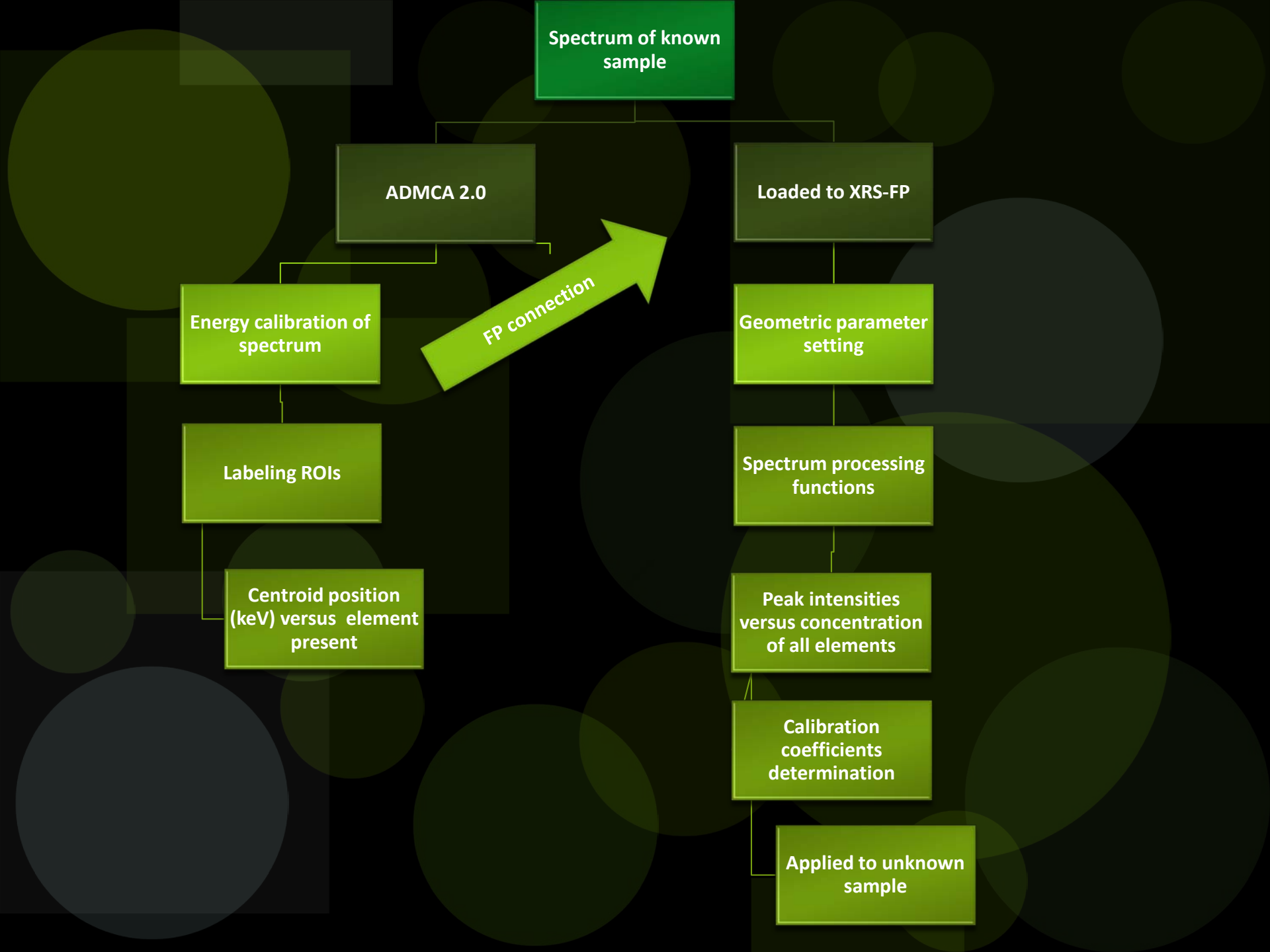
Element Table

Elmt	Line Code	Cond. Code	Intensity (c/s)	Error (c/s)	Conc.	Calib. Coeff.
Ti	Ka	1	0.06	0.079	0.044	2548.8
Cr	Ka	1	755.25	8.892	25.399	4734.2
Mn	Ka	1	28.16	1.717	0.933	8944.5
Fe	Ka	1	1960.49	14.326	13.787	23343.4
Co	Ka	1	0.00	0.000	0.000	0.0
Ni	Ka	1	184.21	4.391	43.569	774.2
Cu	Ka	1	7.28	0.873	1.865	718.8
Nb	Ka	1	0.40	0.205	0.883	164.3
Mo	Ka	1	53.17	2.359	6.352	4681.7
W	La	1	3.97	0.644	3.588	1274.2

Condition Table

#	Target	Filter	Thick. (um)	kV	uA	---Detector--- Type	Filter	Thick. (um)	Atmos	Preset Time(s)	Actual Time(s)
1	Ag	None	0.0	30.0	30.00	Si pin	None	0.0	Air	0.0	38.2

This is a detailed analysis using the FP software, in which we first set all the geometric parameters of the system,
then load the calibrated spectrum and finally perform different functions on the spectrum to get a chart of elemental concentrations in the given sample.


Spectrum of known sample
ADMCA 2.0
Loaded to XRS-FP
Energy calibration of spectrum
FP connection
Geometric parameter setting
Labeling ROIs
Spectrum processing functions
Centroid position (keV) versus element present
Peak intensities versus concentration of all elements
Calibration coefficients determination
Applied to unknown sample

References

- http://www.amptek.com/products.html
- http://users.skynet.be/xray_corner/xtb/chap011.html
- http://www.microsemi.com/brochures/pindiodes/appendix%20f.pdf
- http://www.panalytical.com/index.cfm?pid=137
- http://www.spectro.com/pages/e/p0105wp01.htm