

Material analysis using X-RAY fluorescence spectrometry

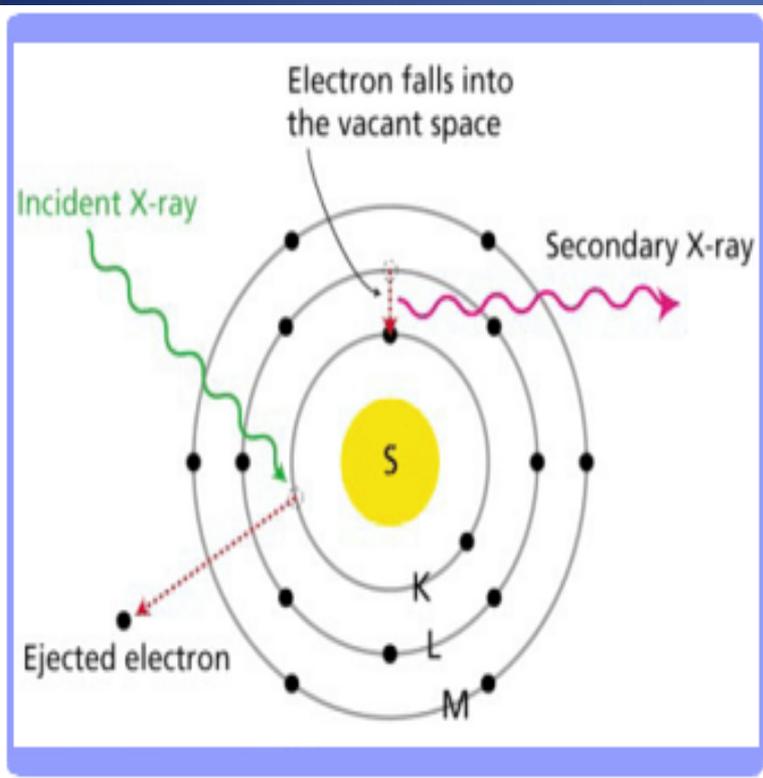
Qurat ul ann Bajwa
6th July 2012

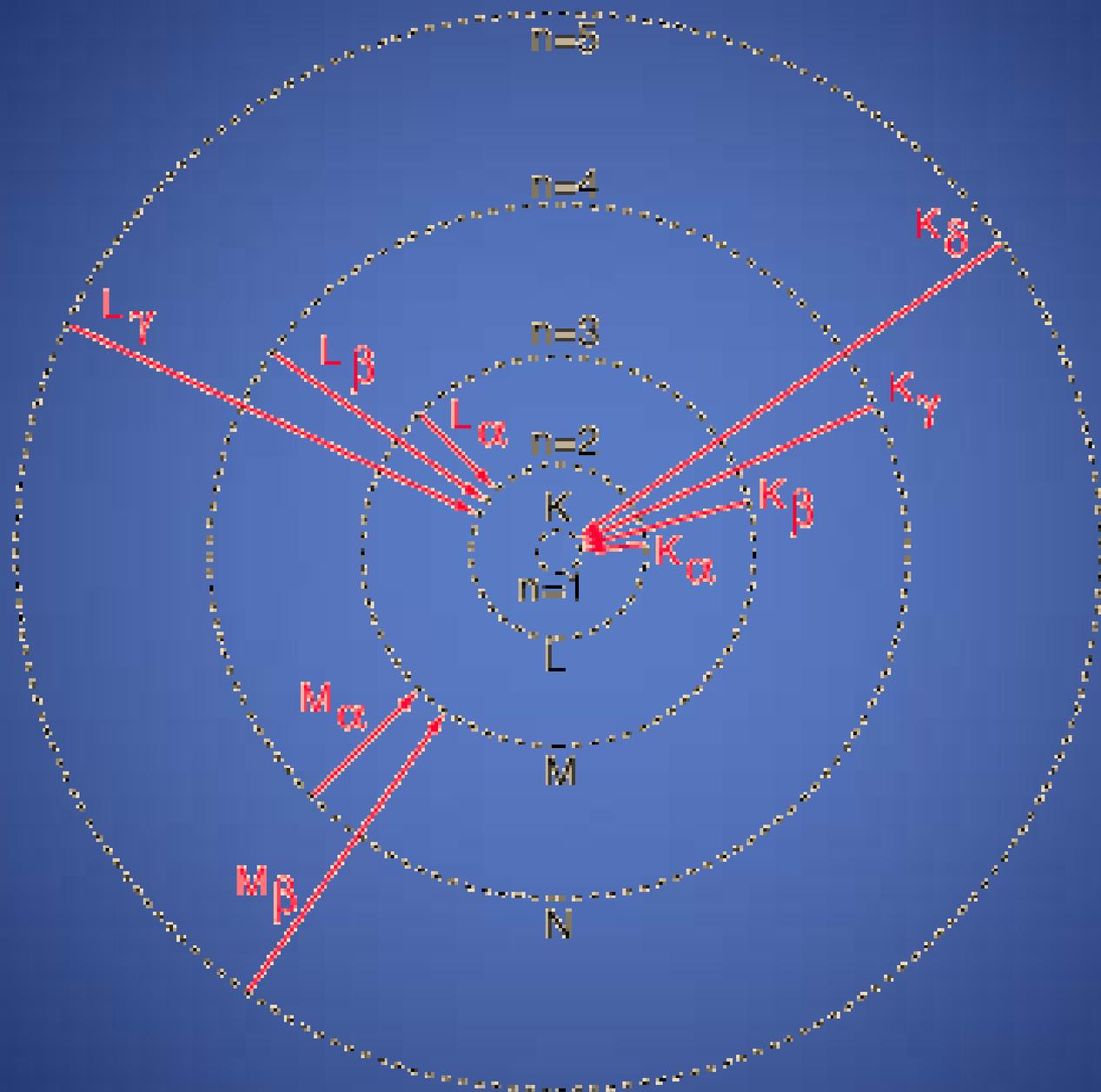
X-Ray Fluorescence

- X-Ray Fluorescence is defined as the emission of characteristic or 'secondary' X-rays from a material that has been excited by bombarding with high energy X-rays.
- This technique is widely used for material analysis.

What are characteristic X-Rays??

- When high energy photons are absorbed by atoms, inner shell electrons are ejected from the atom, becoming “photoelectrons”.
- This leaves the atom in an excited state, with a vacancy in the inner shell.
- Outer shell electrons then fall into the vacancy, emitting photons with energy equal to the energy difference between the two states in which transition takes place.
- Since each element has a unique set of energy levels, each element emits a pattern of X-rays characteristic of the element, termed “characteristic X-rays”.





XRF Spectrometer

- X-ray fluorescent(XRF) spectrometry uses the technique in which X-rays are used to excite electrons in a sample, thus generating secondary X-rays.
- XRF spectrometry helps to find out the compositions of major as well as trace elements in solids. Additionally, this technique can be used to determine thin film thickness.

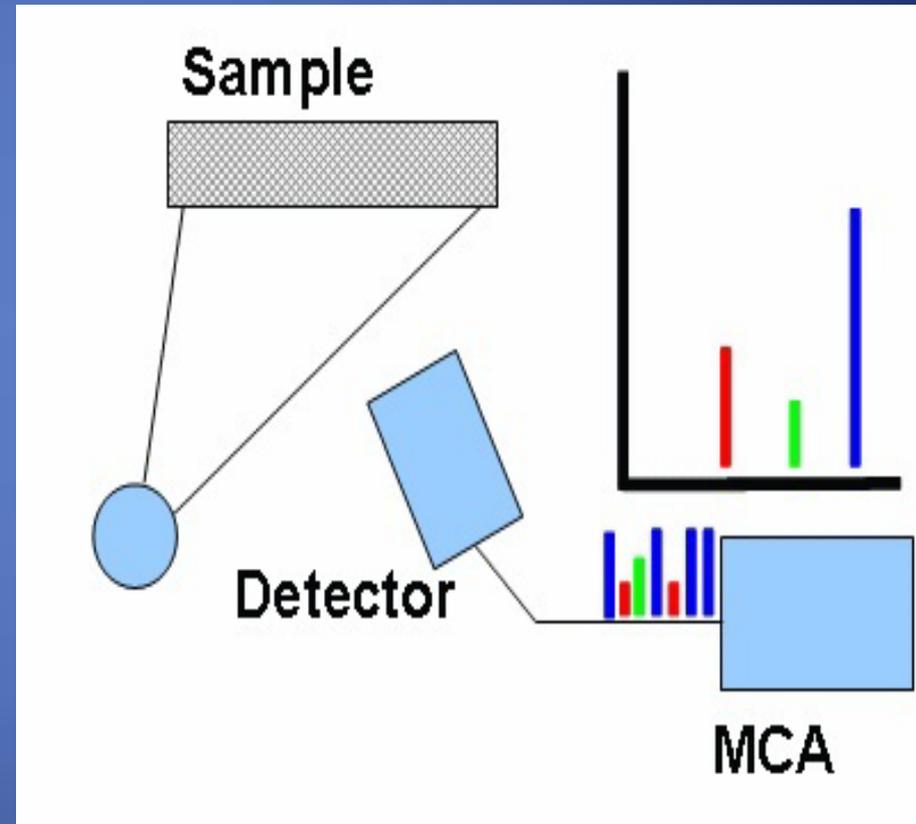
Types of spectrometry

- There are two types of spectrometry:
 1. Energy dispersive (EDXRF), using a solid-state detector (usually silicon) distinguishes each elemental peak according to its respective energy.
 2. Wavelength dispersive (WDXRF), which use a scanning crystal as the dispersive element separates each elemental peak according to its wavelength.
- EDXRF detects elements from sodium(Na) to uranium(U) while WDXRF extends down to beryllium(Be).

Working Principle of EDXRF

The working principle of the EDXRF is a three step process:

- STEP1: A secondary fluorescence photon is emitted by the sample, under the bombardment of primary photons emitted by the X-ray tube.
- STEP2: The secondary photon enters the detector.
It is converted to an electrical impulse.
The height (amplitude) of this pulse is directly proportional to the energy of the incoming photon.
- STEP3: the voltage impulse is processed by the Multi-channel analyzer.
This unit determines (measures) the pulse height (via a very fast analog-to-digital converter).
The pulse's height is converted into a specific channel address. The channel memory of concern is then incremented.



Amptek's Hardware Components

The XRF kit includes:

1. X-Ray generator (Mini X)
2. XR100 CR detector with Si-PIN diode
3. PX4 digital pulse processor
4. XRF mounting plate
5. Stainless steel SS-316 standard

X-Ray generator (Mini-X)

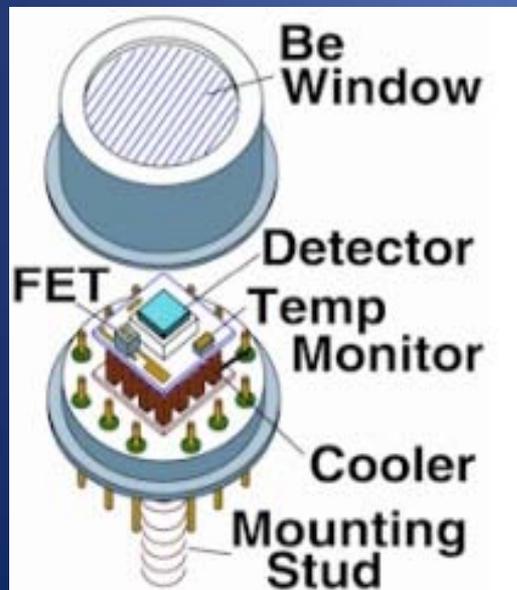
- The Mini-X (shown at top right) is a self-contained, packaged, miniature X-ray tube system, which includes:
 - an X-ray tube,
 - a 40kV/100 μ A power supply
 - silver(Ag) transmission anode
 - Beryllium window (transparent to X-Rays)
 - USB communication to the computer
- The X-ray source tube contains an electrically heated filament that generates electrons which are accelerated from the filament to the target Ag anode, by application of a high voltage.
- When these high velocity electrons are absorbed by the nuclei of the target atoms characteristic X-ray photons of high energy are produced.



XR-100 Detector



- The XR-100 is an X-Ray detector which contains:
 - a charge sensitive preamplifier
 - a thermoelectric cooler system
- Working principle:
 - The solid state detector consists of a semiconductor region sandwiched between a p-type and n-type material.
 - The X-ray photon absorbed in the detector creates an electron-hole pair.
 - The ejected electron will possess an amount of kinetic energy equal to the difference between energies of the incident photon and the band gap of the detecting material.
 - This electron will collide with other atoms causing ejection of charge carriers in the detector.
 - An electric field drifts the electrons and holes to the electrodes.
 - Charge transfer results in an electric pulse measurable in an outer circuit.
- This voltage across Si 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 pre-amplified 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 histogram memory, generating an energy spectrum.
 - The spectrum is then transmitted over the DP4's serial interface to the computer.



Experimental Setup



Quantitative and Qualitative analysis of the spectra

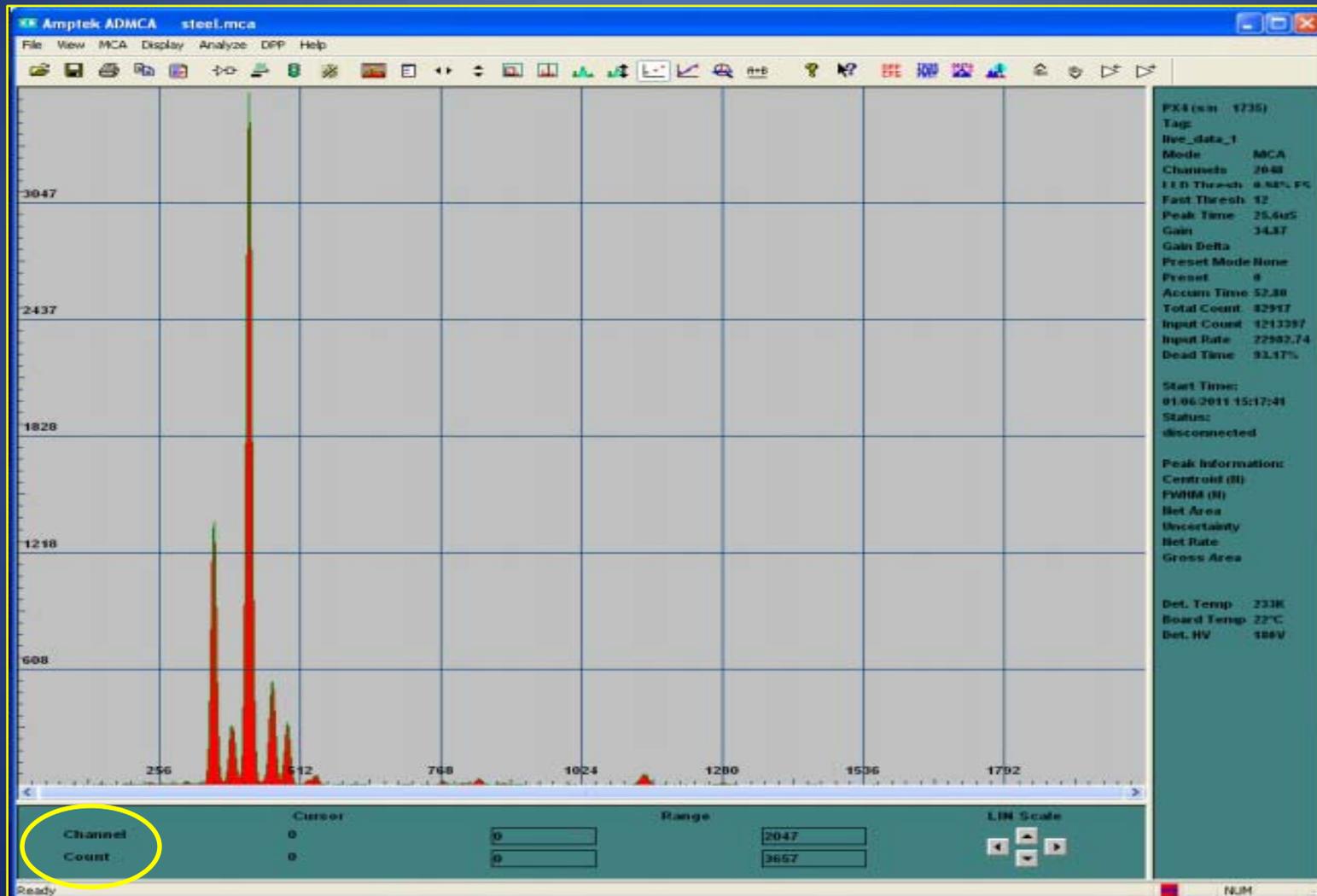
The following are used for the quantitative and qualitative analysis of the spectra obtained:

- ADMCA 2.0
- XRF-FP

ADMCA 2.0- Data and Acquisition Software

- It is a Windows software package that provides data acquisition, display, and control for Amptek's signal processor PX4.
- It provides full control of all hardware features available in the connected hardware (PX4 and detector),
- live display of the spectrum. Capable of displaying and calibrating up to 8142 channels of the MCA.
- Its spectral analysis features include
 - energy calibration,
 - setting up regions of interest (ROI), and
 - computing ROI information (centroid, net peak area,FWHM).
- It also possesses an active link to the XRF-FP Quantitative Analysis Software Package.

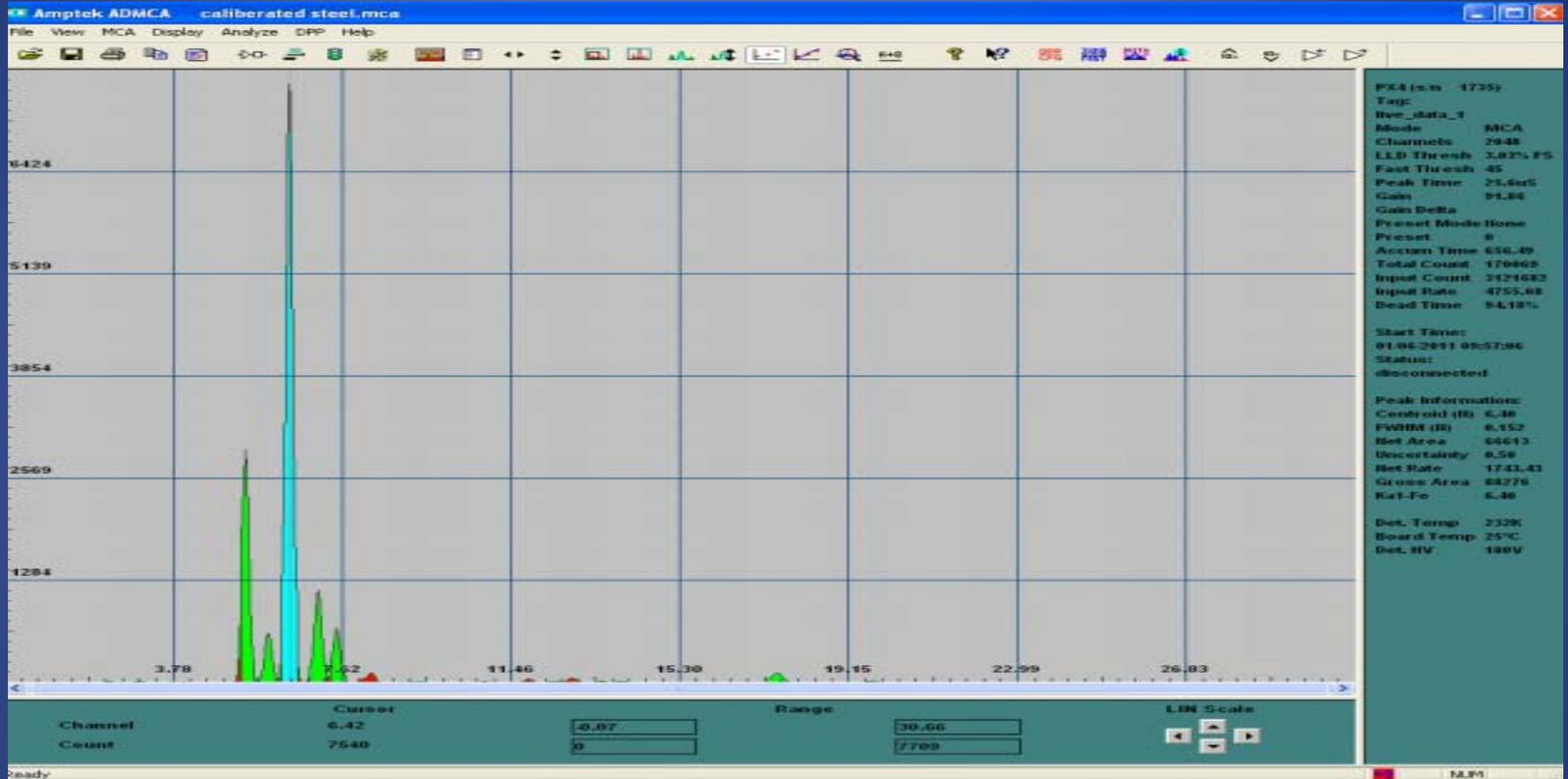
Steel spectrum on ADMCA



Calibration of the spectrum

- Calibration of the spectrum is crucial in determining the elemental concentrations in the sample.
- Calibration is a process in which specific energy values are assigned to the correct channel in the MCA. This is done by sending X-rays of known energy values to the MCA. Once the channels where the X-rays were sorted are identified, known energy values can be assigned to those channels.
- For accurate calibration of spectrum the test sample must contain at least two known peaks in the spectrum.
- For example for calibrating the steel spectrum, an iron (Fe) peak at 6.40 keV and molybdenum (Mo) peak at 17.48 keV.
- The two peaks must preferably be far off so that a better linear curve can be plotted and extrapolated for calibration.
- After locating the centroids of these two peaks, the values of x-ray energies are fed and the calibration is activated.

Calibrated steel spectrum



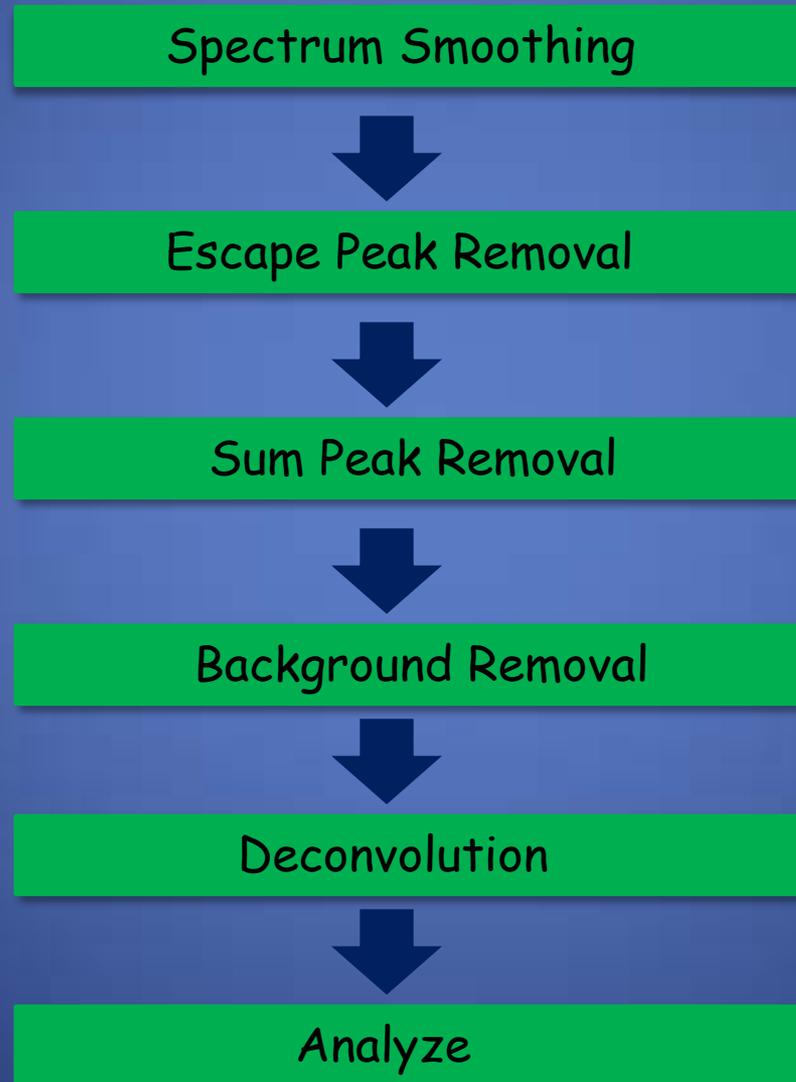
Regions of Interest Details

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	Kal-Cr
5.76	6.15	0.176	7200	8075	5.93	1.31	GOOD	Kal-Mn
6.25	6.54	0.152	66613	88276	6.40	0.50	GOOD	Kal-Fe
6.88	7.20	0.165	11010	14280	7.05	1.20	GOOD	Kal-Co
7.38	7.62	0.141	4412	7464	7.49	2.32	GOOD	Kal-Ni
17.24	17.71	0.247	1729	2149	17.48	2.93	GOOD	Kal-Mo

XRF-FP

- The XRF-FP is a quantitative analysis software package for X-ray fluorescence.
- It processes the raw X-ray spectral data from Amptek's detector, signal processing electronics and ADMCA spectrum to obtain
 - the elemental peak intensities
 - the elemental concentrations

Steps for Spectrum Processing



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 Peak Removal

- Escape peaks arise when internal fluorescence occurs, inside the detector material (Si) and a fraction of a parent characteristic X-ray gets lost as Si-K escape photons, with an energy of 1.75 keV.
- Hence every feature in the spectrum will have an associated escape feature at an energy lower by 1.75 keV.
- The software removes the escape peaks from the spectrum, and adds the equivalent original X-ray event at the parent peaks energy.

Sum Peak Removal

- Sum peaks arise because two incoming X-rays may arrive at the pulse processor within a time frame that is less than the minimum time interval required by the detector to discriminate two events.
- This results in peaks that have energies with the sum of the two incoming X-ray events.
- This correction is not as accurate as the escape peak removal, and may leave some residual sum peaks in the spectrum.

Background Removal

- The software uses the automatic background method to remove the background, which distinguishes fast-changing regions of the spectrum (peaks) from slowly changing regions (background).
- The background curvature arises primarily from bremsstrahlung X-ray continuum from an X-ray tube whose shape depends on the anode atomic number and incident electron-beam energy.

Deconvolution for Intensity extraction

- Deconvolution is the process of assigning areas to the peaks of interest and fitting the spectrum to a sum of separate peaks to calculate the net peak intensities for the elements of the sample material.
- We need net peak intensities which help convert each element's peaks to elemental concentrations.
- Peaks are synthesized for all the expected lines ($K\alpha$, $K\beta$, $L\alpha$, $L\beta$) in the region of the sample's peaks.
- The expected lines should already be provided by the user (using the ROI details from ADMCA) that will be used for the FP analysis.

Analysis command

- 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.

FP analysis of impure copper

XRS-FP File Acquire Load Setup Calibrate Process Help

Acquire Set kV/uA kV: (10->40) uA: (5->200) Preset: Time: %DT:

Specimen Component Table:

#	Component	Type	Conc.	Error	Units	Mole%	Error
1	Cu	Calc	92.054	0.860	wt.%	91.193	0.852
2	Zn	Calc	1.139	0.091	wt.%	1.096	0.088
3	Fe	Calc	6.371	0.182	wt.%	7.182	0.205
4	Co	Calc	0.000	0.000	wt.%	0.000	0.000
5	Cr	Calc	0.436	0.060	wt.%	0.528	0.073

Thickness Information:

Layer							Normalize	
Thick.	Type	Error	Units	Density	Fixed	OK	Total	
0.000	Bulk	0.000	mg/cm2	0.000	<input type="checkbox"/>	<input checked="" type="checkbox"/>	100.00	

Global Threshold Settings
 Conc Method

Element Table: Normal Coefficients

#	Element		Cond	Measurement							Threshold		Intensity	Ratio	ROI (keV)		Chi2	Quant	Calibration
	Elmt	Line		Code	Intensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value			Conc	Method			
2	Fe	Ka	1	43.896	1.25	0.00	6.3712	0.182	0.0000	7.182	0.0000	<input checked="" type="checkbox"/>	Gaussian	None	6.289	6.506	13.19	FP	0.00
3	Co	Ka	1	0.000	0.00	0.00	0.0000	0.000	0.0000	0.000	0.0000	<input checked="" type="checkbox"/>	Gaussian	None	6.811	7.034	2.56	FP	0.00
4	Cu	Ka	1	409.163	3.82	0.00	92.0536	0.860	0.0000	91.193	0.0000	<input checked="" type="checkbox"/>	Gaussian	None	7.919	8.157	232.81	FP	0.00
5	Zn	Ka	1	5.594	0.45	0.00	1.1387	0.091	0.0000	1.096	0.0000	<input checked="" type="checkbox"/>	Gaussian	None	8.504	8.750	3.57	FP	0.00

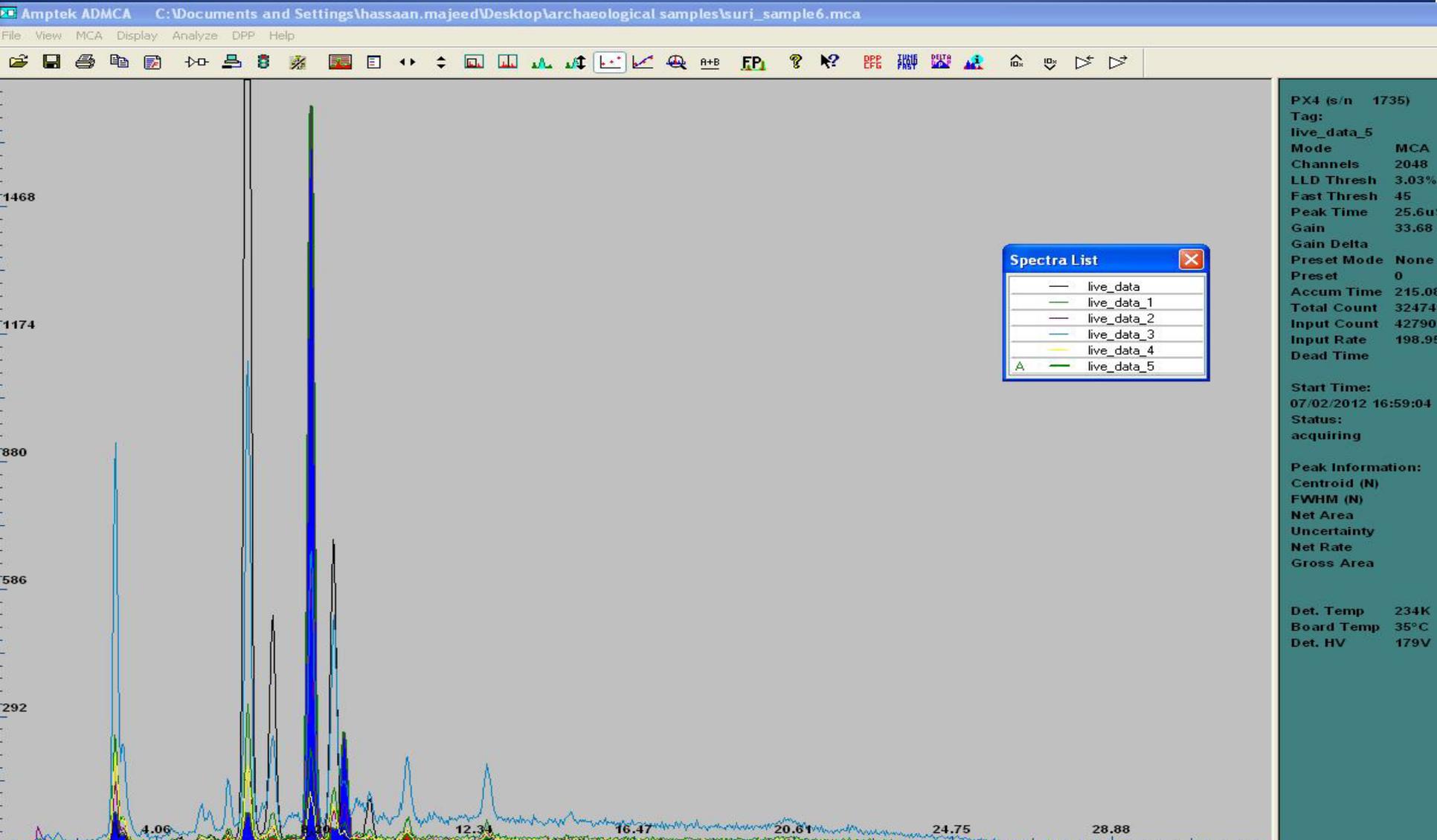
Measurement & Processing Conditions: Measurement Processing **Active Condition Code:**

Code	X-Ray Source					Detector			Chamber	Time (secs)	
	Target	Filter	Thick(um)	kV	uA	Type	Filter	Thick(um)		Atmos	Preset
1	Ag	None	0.00	30.0	15.0	Si pin	None	0.00	Air	0.0	112.0

Status: Completed MLSQ-FP Quantitative Analysis...

Comment:

Archaeological samples



References

- <http://www.amptek.com/products.html>
- http://users.skynet.be/xray_corner/xtb/chap011.html
- XRF Physlab manual, Jan 28 2011.