

# Quantitative XRF analysis

**Introduction**

**Matrix effects**

**Corrections/influence coefficients**

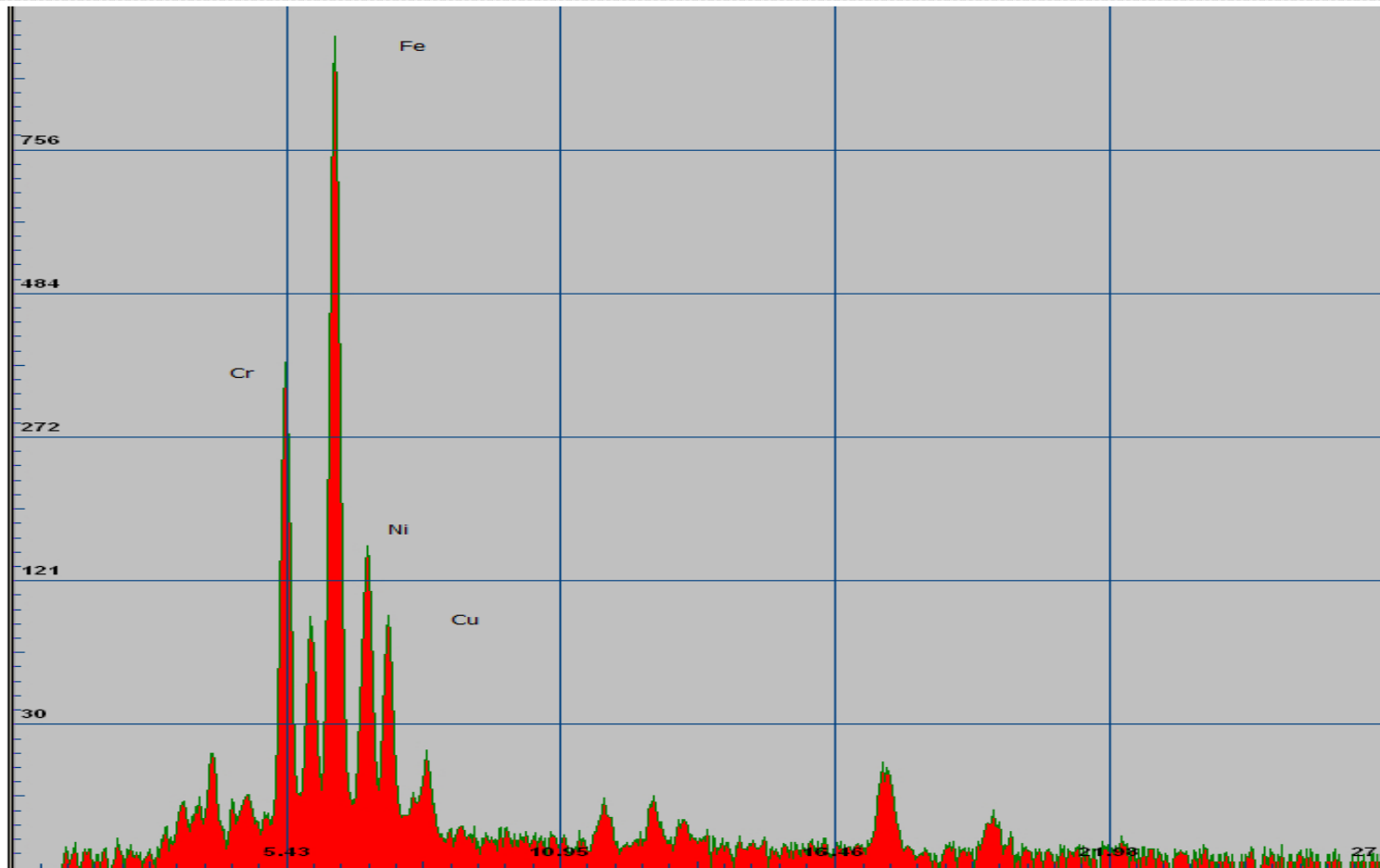
**Standard comparison method**

**FP algorithm**

**Thin film algorithm**

An introduction to the ED-XRF technique

<http://physlab.lums.edu.pk/images/d/de/XRF-v6.pdf>

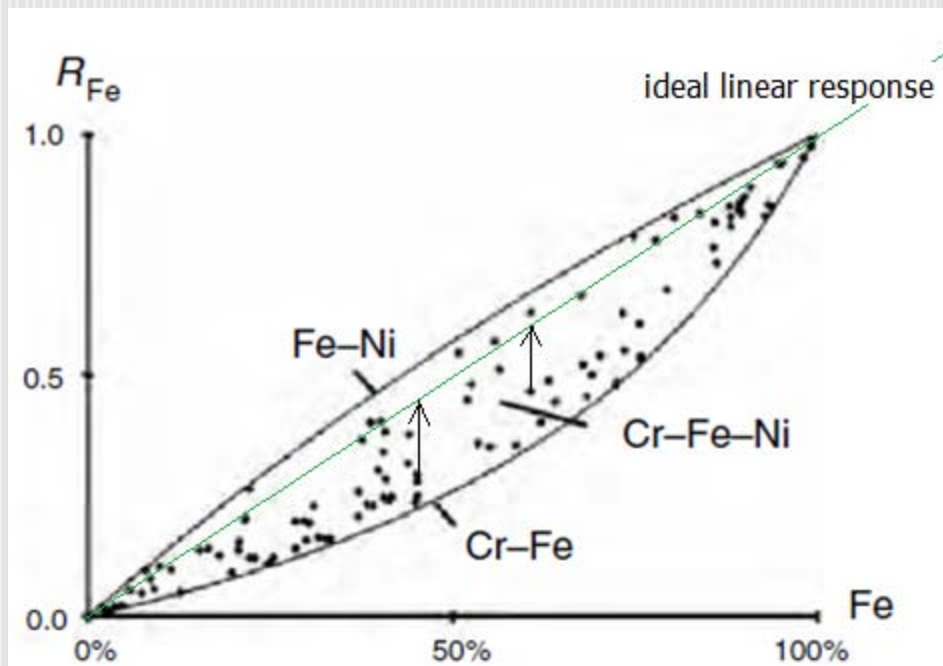


- XRF spectrum reveals the relation between the intensity of an element to its concentration in the sample.
- The most intense peak 'Fe' corresponds to the element with greatest concentration and so on.

# Analyte and sample

- Analyte: element of interest, whose concentration we want to measure,
- Matrix: the sample or composition in which the particular analyte is present.
- Characteristic/ Fluoresced X-rays of an analyte  $i$ ,
- Incident/Primary X-ray beam ( $E, \lambda$ )

- Ideally Intensity of an element in a sample (pure sample or compound) should be a linear function of its concentration but the experimental data shows deviation.



$E_{X\text{-ray,Fe}} < E_{X\text{-ray,Ni}}$   
 (6.4keV)      (7.48keV)  
 Enhancement in Fe

$E_{X\text{-ray,Cr}} < E_{X\text{-ray,Fe}}$   
 (5.41keV)      (6.4keV)  
 Absorption in Fe.

# Purpose of QA

- The general principle is that the “ideal” calibration curve is assumed to be in principle linear, however the matrix effects make it nonlinear.
- The aim of quantitative XRF analysis is to apply corresponding counteracting “corrections,” so that the experimental curve is again linearized.
- The coefficients, which account for these (mathematical) corrections for each matrix element, are called *influence coefficients* (denoted by  $\alpha_{ij}$ ).
- *If  $i=\text{Fe}$ ,  $j=\text{all other elements in the sample}$ ,  $\alpha_{ij}$  would represent the combined effect of all elements on  $i$ .*

# Matrix response/correction and its determination \*

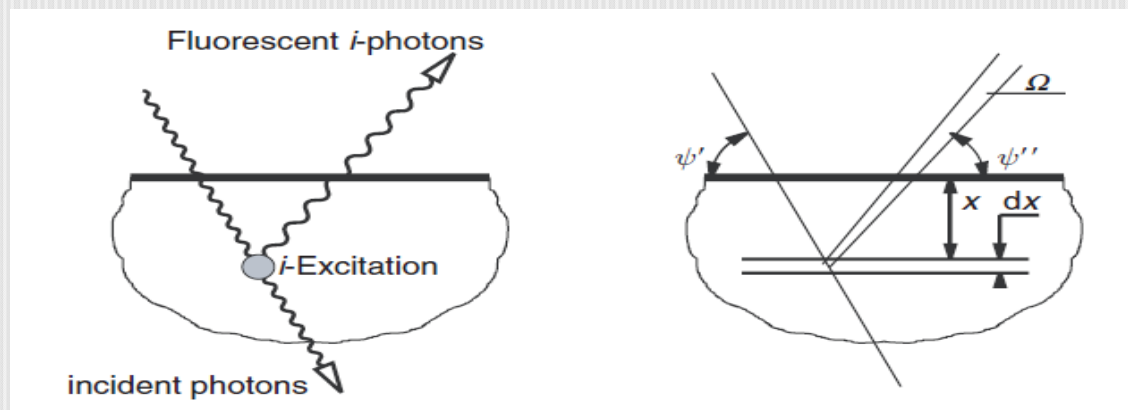
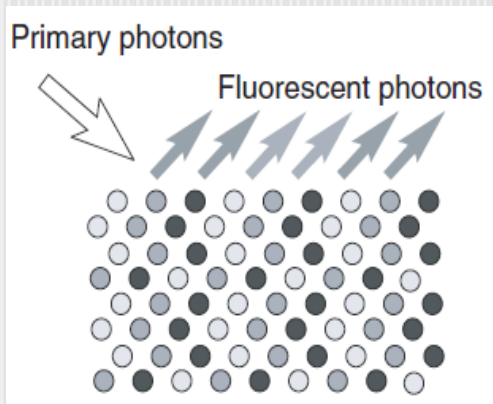
\*Handbook of Practical X-Ray Fluorescence Analysis, B. Beckhoff B. Kanngießner N. Langhoff R. Wedell H. Wolff, Chapter 5: Quantitative Analysis

# Matrix effects

1. Primary radiation penetrates into a specimen & absorbed,
  2. Characteristic X-rays are emitted,
  3. Characteristic X-rays can also be absorbed in the sample in going toward the detection system.
  4. Characteristic X-rays of higher energy may act to enhance the intensity of lower-energy ch X-rays.
- The absorption of primary radiation and characteristic X-rays into the sample is termed **Matrix effects**.

# Direct /primary excitation

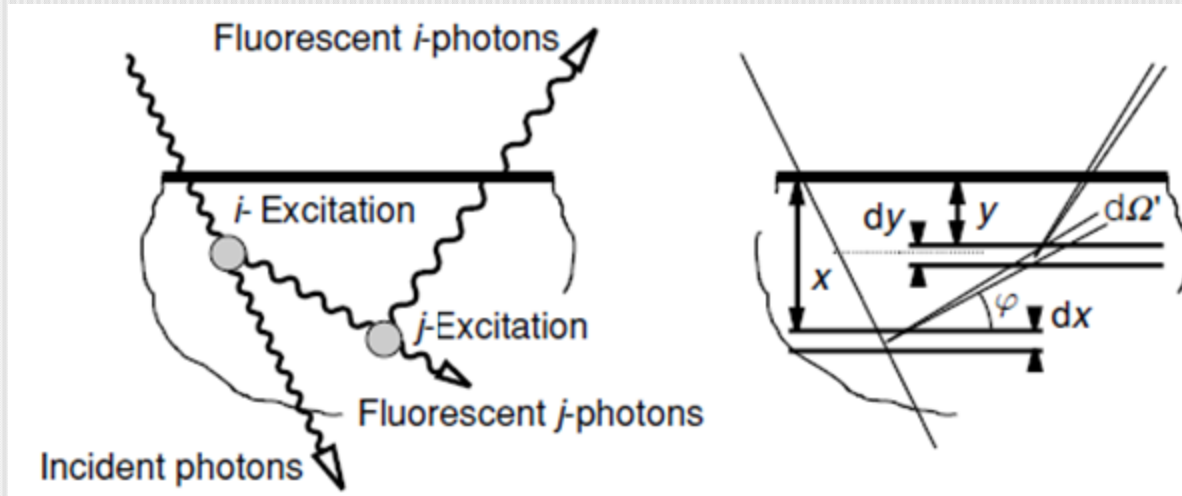
- A process by which incident X-rays from the source excite *primary Characteristic radiation* from atoms of the specimen.





# Indirect excitation

- When primary characteristic photons have sufficient energy to excite fluorescence radiation of other atoms in the specimen.



- In the range of transition elements, secondary excitation is particularly strong for elements differing by 2 in atomic numbers. For e.g., in stainless steel (Cr–Fe–Ni) is the usual example for demonstrating this ( $\text{Fe} \rightarrow \text{Cr}$ ,  $\text{Ni} \rightarrow \text{Cr}$ , and  $\text{Ni} \rightarrow \text{Fe}$ ).

# Determination of $M$

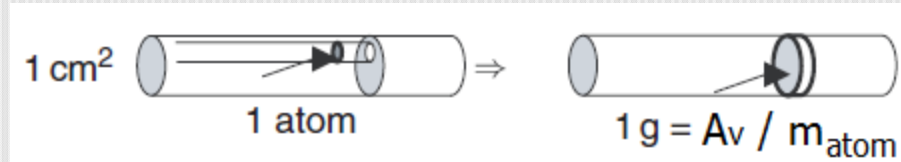
For monochromatic incident X-ray beam  
Considering absorptions only

- The mathematical starting point is the formal relationship

$$C_i = R_i M(C_1, C_2, \dots, C_n)$$

- a dominating linearity  $C_{Fe} = R_{Fe}$
- *modified by a function  $M(C_{Cr}, C_{Mn}, \dots, C_{Mo})$  (in case of SS)*
- **M** takes the corrective role of moving the scattered data-points to a straight line.

# Attenuation law



- The photon counts  $N$  after attenuation in specimen (absorber) is a function of penetrated *mass or thickness*.

$$N(m) = N_0 e^{-\mu m}$$

- Where  $m$  is mass per unit area (Areal density) &  $\mu$  is the mass attenuation coefficient.

$$\mu = \mu_{\text{Atom}} A_v / m_{\text{atomic}}$$

- $\mu_{\text{atom}}$  is the *total atomic cross-section (interaction of atom with radiation)* and an *attenuation coefficient*

# Attenuation by materials composed of several kinds of atoms

- We will use the fractional masses of elements as  $C_j$ , and their mass attenuation coefficients  $\mu_j$ ,
- $(\sum C_j = 1)$ ,
- Total mass attenuation coefficient of the specimen is the weighted sum of the individual atomic attenuation coefficients

$$\mu = \sum_j C_j \mu_j$$

# Influence coefficients determination

- For a monochromatic incident X-rays, the relation between the count rate and concentration is,

$$R_i = C_i \frac{\mu^*}{\mu_i^*} \quad M = M(C_1, C_2, \dots, C_n) = \frac{\mu^*}{\mu_i^*}$$

- *M is interpreted as the influence of the matrix on the analyte i count rate.*
  - $\mu^*$ : total mass absorption coefficient for **incident** X-rays,
  - $\mu_i^*$ : mass absorption coefficient of **i emerging** fluorescent photons by the matrix elements.

$$\mu^* = \frac{\mu_{S,E}}{\sin \psi'} + \frac{\mu_{S,i}}{\sin \psi''} = \mu'_S + \mu''_S$$

$$\begin{aligned}
\mu^* &= \sum_{j=1}^n C_j (\mu'_j + \mu''_j) = \sum_{j=1}^n C_j \left( \frac{\mu_{j,\lambda}}{\sin \psi'} + \frac{\mu_{j,i}}{\sin \psi''} \right) \\
&= C_i \mu_i^* + \sum_{j=1, j \neq i}^n C_j \mu_j^* = \left( 1 - \sum_{j=1, j \neq i}^n C_j \right) \mu_i^* + \sum_{j=1, j \neq i}^n C_j \mu_j^* \\
&= \mu_i^* \left( 1 + \sum_{j=1, j \neq i}^n C_j \frac{\mu_j^* - \mu_i^*}{\mu_i^*} \right) \\
\mu^* &= \mu_i^* \left( 1 + \sum_{j=1, j \neq i}^n C_j \alpha_{ij} \right)
\end{aligned}$$

$$\alpha_{ij} = \frac{\mu_j^* - \mu_i^*}{\mu_i^*} = \frac{\left( \frac{\mu_{j,\lambda}}{\sin \psi'} + \frac{\mu_{j,i}}{\sin \psi''} \right) - \left( \frac{\mu_{i,\lambda}}{\sin \psi'} + \frac{\mu_{i,i}}{\sin \psi''} \right)}{\left( \frac{\mu_{i,\lambda}}{\sin \psi'} + \frac{\mu_{i,i}}{\sin \psi''} \right)}$$

- $\alpha_{ij}$  are called the FPs and are a function of the sample composition.
- The expression for  $M$  modifies from,

$$M = M(C_1, C_2, \dots, C_n) = \frac{\mu^*}{\mu_i^*}$$

to

$$M_{\text{mono}} = 1 + \sum_{j=1, j \neq i}^n C_j \alpha_{ij}$$

- The  $\alpha_{ij}$  terms represent the influence of absorption by all other elements  $j$  on analyte  $i$ .

$$C_i = R_i \left( 1 + \sum_{j \neq i} \alpha_{ij} C_j \right) = C_{i, \text{apparent}} (1 + \text{correction terms})$$

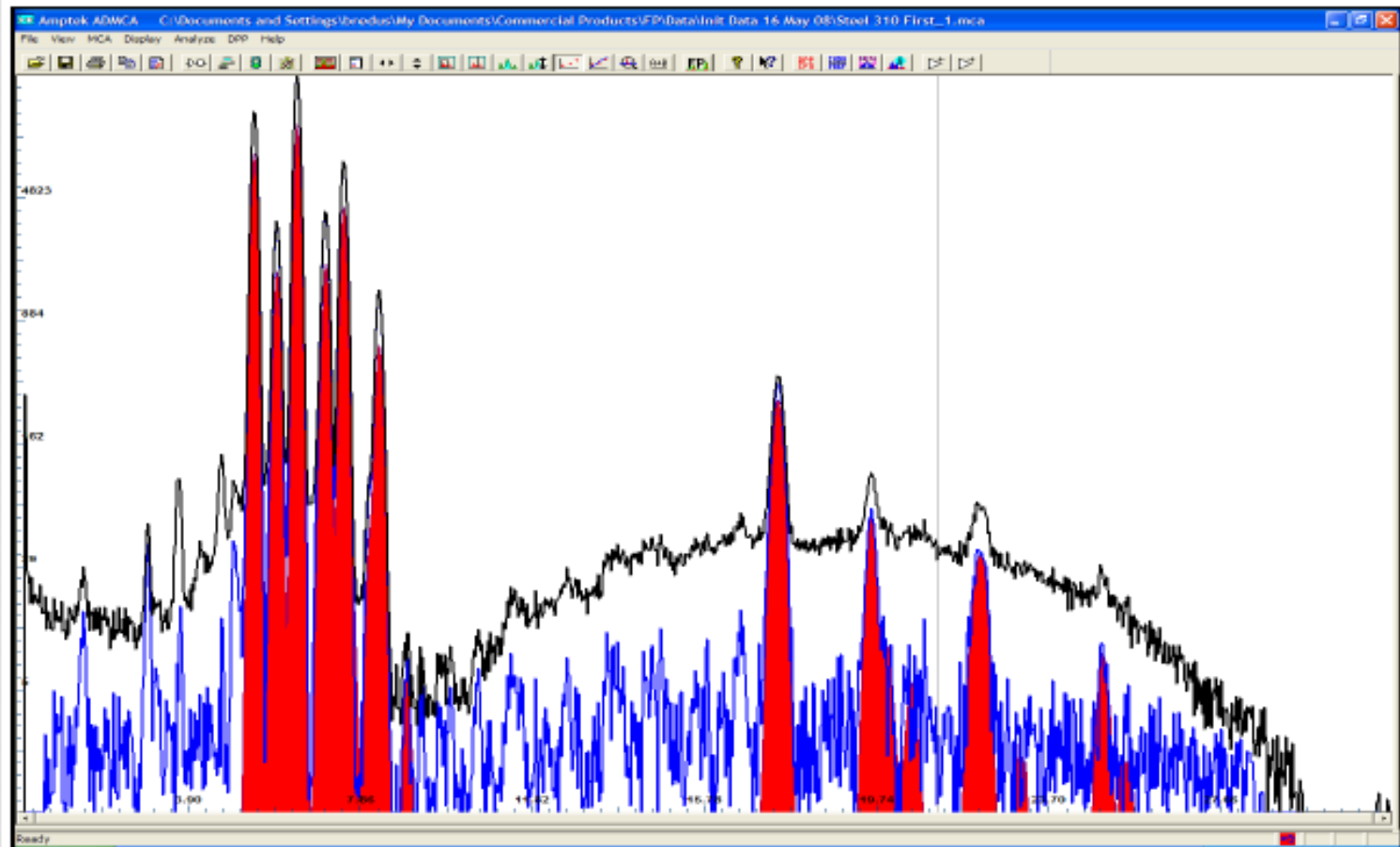


- Fundamental parameters  $\alpha_{ij}$  and the combined matrix effect  $M$  depend on,
  - The analyte element and the analyte line;
  - The matrix elements,
  - On the geometry ( $\psi'$  and  $\psi''$ ).

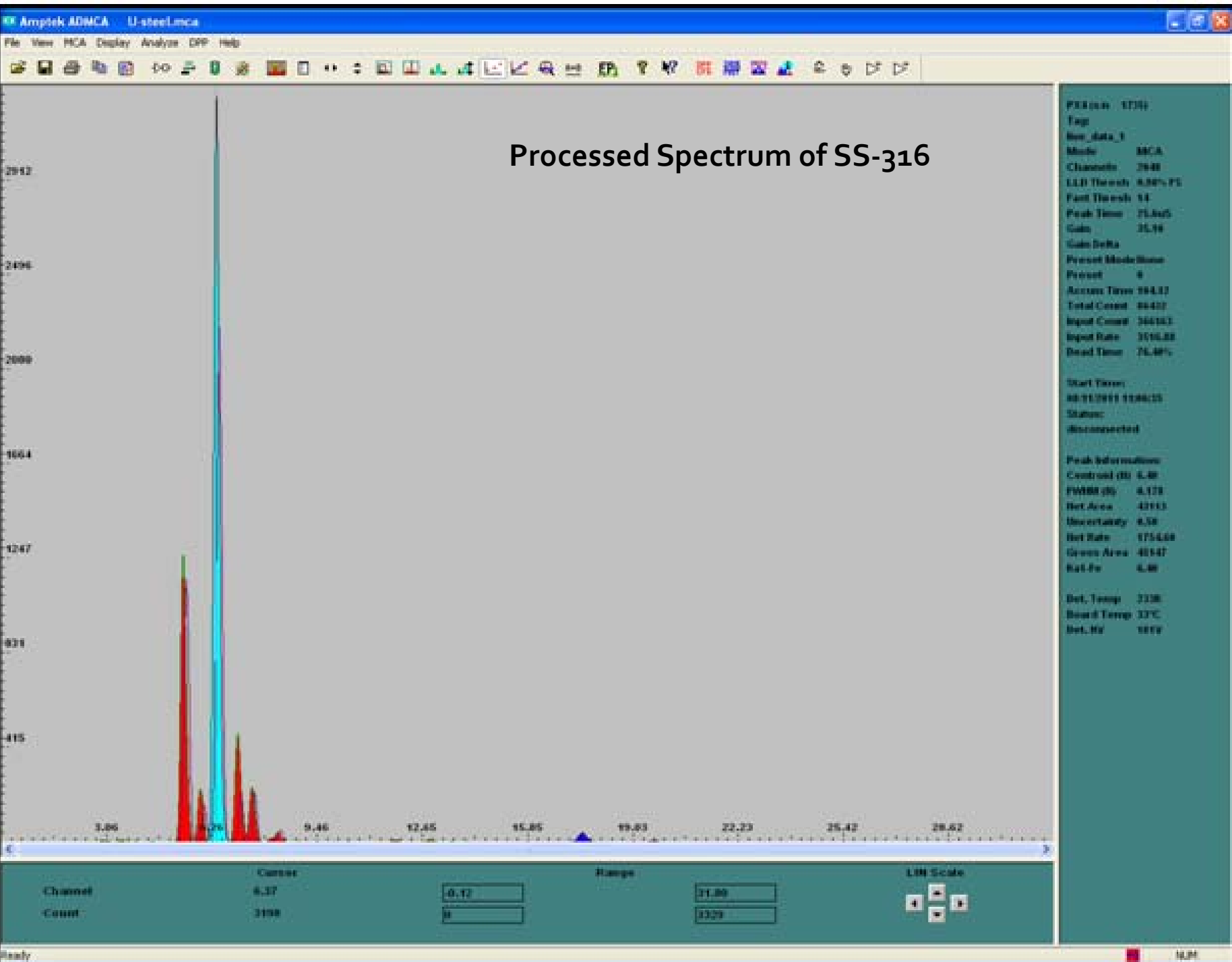
# XRS-FP: Scheme of using standard materials for the concentration analysis

1. PROCESSing by the XRS software: peak fitting and intensity calculation,
2. FP calibration: removing the matrix effects,
3. ANALYZing the concentrations by the software: comparing the intensities.

# 1. Extraction of relative intensities



*Processing: 1)back ground removal, 2)Gaussian peak fitting, 3)extracting intensities*



## ADMCA information

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### Regions of Interest Details

Start	End	FWHM (N)	Net Area	Gross Area	Centroid (N)	Uncertainty	Status	Element
5.14	5.64	0.180	15243	15785	5.40	0.84	GOOD	Ka1-Cr
5.76	6.07	0.180	2381	2723	5.92	2.33	GOOD	Ka1-Mn
6.15	6.73	0.178	43113	45147	6.40	0.50	GOOD	Ka1-Fe
6.81	7.77	0.192	9189	9189	7.20	1.04	GOOD	Ka1-Co
17.24	17.74	0.170	606	838	17.48	5.40	GOOD	Ka1-Mo

## XRS-FP intensity information

$$I_i = \frac{\text{area of } i^{\text{th}} \text{ element}}{\text{Total area covered by spectrum}} \times (\text{Peak counts})_i$$

# 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	0.017	0.007	wt.%	0.020
1	Cr	Calc	20.667	0.435	wt.%	22.508
1	Fe	Calc	60.393	0.857	wt.%	61.239
1	Ni	Calc	13.874	0.602	wt.%	13.385
1	Nb	Calc	0.107	0.050	wt.%	0.065
1	Mo	Calc	4.088	0.328	wt.%	2.413
1	Cu	Calc	0.185	0.043	wt.%	0.165
1	Co	Calc	0.000	0.000	wt.%	0.000
1	Mn	Calc	0.000	0.000	wt.%	0.000
1	W	Calc	0.669	0.137	wt.%	0.206

## Element Table =====

Elmt	Line	Cond.	Intensity	Error	Conc.	Calib.
	Code	Code	(c/s)	(c/s)		Coeff.
Ti	Ka	1	0.96	0.395	0.017	58000.1
Cr	Ka	1	367.96	7.740	20.667	9508.9
Mn	Ka	1	0.00	0.000	0.000	15102.0
Fe	Ka	1	808.63	11.473	60.393	9154.1
Co	Ka	1	0.00	0.000	0.000	9194.0
Ni	Ka	1	86.41	3.751	13.874	5890.0
Cu	Ka	1	3.06	0.706	0.185	13343.2
Nb	Ka	1	0.73	0.346	0.107	11716.7
Mo	Ka	1	25.35	2.032	4.088	11634.8
W	La	1	0.87	0.794	0.669	17001.8

## Condition Table =====

#	Target	Filter	Thick.	kV	uA	---Detector---	Thick.	Atmos	Preset	Actual
			(um)			Type Filter	(um)		Time (s)	Time (s)
1	Ag	None	0.0	30.0	15.00	Si pin None	0.0	Air	0.0	24.6

Net intensities are tabulated by the software.

The intensities in the column do not represent the absolute counts along the y-axis, but the percentage of the total peak heights.

$$R_i = \frac{I_i}{\sum I_n}$$

## 2. FP calibration

- The  $R_i \propto C_i$  and provide rough estimates of the concentration.
- The  $R_i$  have contributions from the Matrix effects.
- So now we need the FP mathematical model to account for the effect of matrix on the analyte.

# Matrix corrections for standard sample

$$C_i^{\text{original}} = M(C_1, C_2, \dots, C_n) \times R_i$$

$$\frac{C_i}{\sum C_n} \times 100\% = \frac{I_i}{\sum I_n} \times M_i$$

- Since we have the  $C_i$ 's fractional wt %age for all the elements of the standard and the uncorrected relative intensity from the spectrum, we can find the matrix correction coefficients  $M$  using the ***Calibrate FP*** command.



# Saving the FP calibrated file

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Amptek Inc XRF Report
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9:2

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 Conc. Error Units Mole%
1 Ti Calc 0.017 0.007 wt.% 0.020
1 Cr Calc 20.667 0.435 wt.% 22.508
1 Fe Calc 60.393 0.857 wt.% 61.239
1 Ni Calc 13.874 0.602 wt.% 13.385
1 Nb Calc 0.107 0.050 wt.% 0.065
1 Mo Calc 4.088 0.328 wt.% 2.413
1 Cu Calc 0.185 0.043 wt.% 0.165
1 Co Calc 0.000 0.000 wt.% 0.000
1 Mn Calc 0.000 0.000 wt.% 0.000
1 W Calc 0.669 0.137 wt.% 0.206

Element Table =====
Elmt Line Cond. Intensity Error Conc. Calib.
Code Code (c/s) (c/s) Coeff.
Ti Ka 1 0.96 0.395 0.017 58000.1
Cr Ka 1 367.96 7.740 20.667 9508.9
Mn Ka 1 0.00 0.000 0.000 15102.0
Fe Ka 1 808.63 11.473 60.393 9154.1
Co Ka 1 0.00 0.000 0.000 9194.0
Ni Ka 1 86.41 3.751 13.874 5890.0
Cu Ka 1 3.06 0.706 0.185 13343.2
Nb Ka 1 0.73 0.346 0.107 11716.7
Mo Ka 1 25.35 2.032 4.088 11634.8
W La 1 3.87 0.794 0.669 17001.8

Condition Table =====
```

The correction coefficients are  
saved into the software for all the  
elements of the standard sample  
and are used for the future  
analysis of same elements in a  
unknown composition.

### 3. ANALYZing: Standard comparison method to find unknown concentrations

- The unknown sample is compared with a standard sample by this method.
- This comparison algorithm is applied in two steps.

1. The effective coefficients  $\alpha_{ij}^*$  (or  $M$ ), corresponding to the standard sample, are introduced into the concentration equation for the standard,

$$C_i^* = R_i^* \left( 1 + \sum_{j \neq i} \alpha_{ij}^* C_j^* \right)$$

2. The same FPs  $\alpha_{ij}^*$  are used for the unknown sample in the following equation,

3. For an initial guess of concentrations  $C_i^*$  is used from the saved file,

$$C_i = R_i \left( 1 + \sum_{j \neq i} \alpha_{ij}^* C_j \right)$$

# Iteration scheme

$$C_i^{\text{new}} = \frac{R_i^m}{R_i} C_i^{\text{old}}$$

- The iteration equation is used at present in the fundamental parameters calculations.
- XRS makes initial estimate of mass fractions and then compare the corresponding calculated relative intensities with those actually measured.
- Successively better estimates of composition are found by an iteration procedure.
- The most common method for finding the next estimate of concentration,  $C'_t$ , from the present estimate,  $C_t$ , for each element  $i$ , is to ***use the equation***

# Fundamental parameter Algorithm (FA) for bulk samples

A short note on the mathematical formulation and physical interpretation of the FP algorithm.

# History

- Sherman 1955: equation to calculate net X-ray intensities emitted by each element from a specimen of known composition.
  - It is a combination of theoretical physics and experimental results.
- Rousseau 1982: Deduced FA from Sherman equation, Rousseau proposed FA to accurately correct for matrix effects that modify the measured net intensity emitted by an analyte in a specimen.
  - Considers the spectrum of incident radiation,
  - Geometry of the spectrometer,
  - Addresses all matrix effects  $M$  (enhancement and absorption).
  - Calculates influence coefficients  $\alpha$ 's.

$$N_{i, \text{observed}} = N_{i, \text{prim}} + N_{i, \text{sec}}$$

$$= g_i C_i \frac{\tau_i(\lambda) I_0(\lambda)}{\mu'_S(\lambda) + \mu''_S(\lambda_i)} \left( 1 + \sum_{\text{Elements } j} C_j \delta_{ij}(\lambda) \right)$$

- $\lambda$  is the wavelength of the incident monochromatic beam,
- $I_0(\lambda)$  is the original intensity of the incident beam,
- $g_i$  is the product of
  - the fluorescent yield of the analyte photon,
  - probability of  $i^{\text{th}}$ -photon production and
  - absorption edge energy for a (K or L) shell electron.
- $\tau_i(\lambda)$  is photo-absorption coefficient of incident X-ray photons by the analyte.
- $\delta_{ij}(\lambda)$  is a function of various parameters including
  - the probability of  $j$  characteristic photon production,
  - mass attenuation of fluorescent X-rays,
  - fluorescent yields of  $j$  photons (from  $i$  photons) and
  - incident and emission angles.

# Fundamental algorithm

$$R_i = C_i \frac{1 + \sum_j \varepsilon_{ij} C_j}{1 + \sum_j \alpha_{ij} C_j},$$

- The intensity is proportional to the concentration  $C_i$  and also to a ratio on the right-hand side.
  - The numerator contains all the enhancement coefficients  $\varepsilon_{ij}$  of each element  $j$  of the matrix
  - the denominator contains all the absorption coefficients  $\alpha_{ij}$  of each element  $j$ .
- Thus,  $R_i$  will increase with the enhancement effects and decrease with the absorption effects.
- Above expression is called the *fundamental algorithm* and is used by the *XRS-FP* software for concentration analysis.



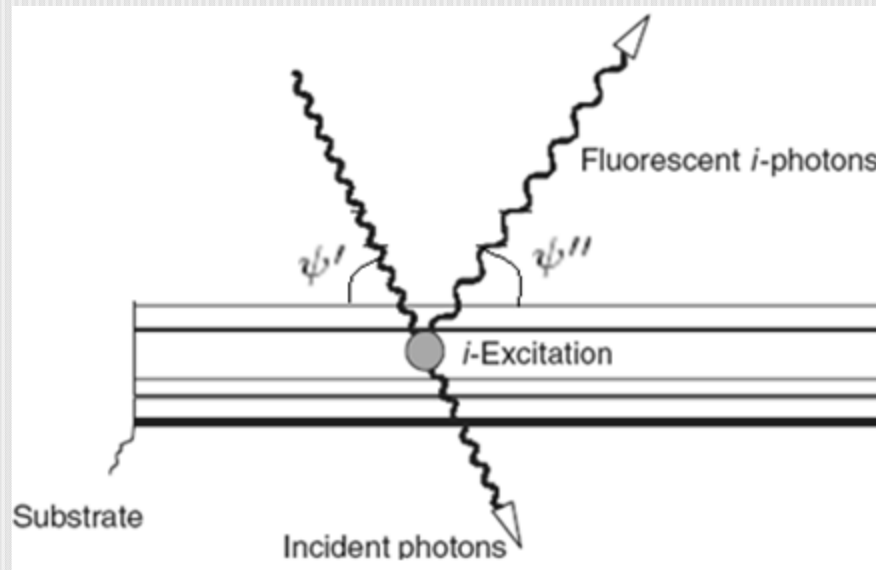
# FP equations for thin film analysis

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- XRF is an attractive technique for the analysis of thin and layered samples.
- The photon rates originating from thin and layered specimens depend on
  - the composition of layers,
  - thickness of the layers.
- => simultaneous determination of the composition & thickness.

# Reference (standard) sample

- Quantification can be accomplished using calibration thin film standards with composition close to that of the unknown film.
- Special FP-based analysis is demanded for thin and layered samples.



- The count rate for a film of element  $i$ , *for incident radiation of wavelength  $\lambda$  is given by,*

$$N_{i,\text{observed}}^{\text{Layer}} = G_i C_i \frac{\tau_{i,\lambda} [1 - \exp(-\mu^* \rho T)] N_0(\lambda)}{\mu^*}$$

- In cases of very thin layers, the approximation
  - $1 - \exp(-\mu^* \rho T) \approx \mu^* \rho T$ ,
- So for  $T \rightarrow 0$ , the count rate in terms of  $C_i$  and  $T$  is,

$$N_{i,\text{observed}}^{\text{Layer}} \approx G_i C_i \tau_{i,\lambda} \rho T N_0(\lambda)$$

- This means that the count rate of a very thin layer is linear proportional to the thickness of the layer.

# Back-Calculation Schemes

- For thin film samples, an iterative method is used to calculate the composition and the thickness of the layers.
- This method minimizes the difference between the measured and the calculated count rates of the analytes.
- The iteration process starts with an initial guess of the composition and thicknesses of the layers (from a standard).

- The composition and thicknesses are varied until the weighted difference between the calculated and the observed intensities is minimal.
- *The objective is*

$$\text{Minimize } \sum_i \left( \frac{N_i^m - N_i^c(C, T)}{\sigma_i} \right)^2$$

- where  $C$  and  $T$  are all unknown concentrations and thicknesses.
- For the weighting, the counting statistical error of the measured rate,  $\sigma$ , can be used.

# Amptek Inc XRF Report

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## Layer Table =====

#	Thick	Type	Error	Units	Density	Norm.	Total
1	32.33	Calc	0.00	nm	19.30	On	100.00

## Sample Table =====

Layer	Component	Type	Concn.	Error	Units	Mole%
1	Au	Calc	100.000	3.911	wt.%	100.000

## Element Table =====

Elmt	Line	Cond.	Intensity	Error	Conc.	Calib.
	Code	Code	(c/s)	(c/s)		Coeff.
Au	La	1	80.34	3.142	100.000	24110.0

## Condition Table =====

#	Target	Filter	Thick.	kV	uA	---Detector---	Thick.	Atmos	Preset	Actual
			(um)			Type Filter	(um)		Time (s)	Time (s)
1	Ag	None	0.0	30.0	30.00	Si pin None	0.0	Air	0.0	32.6