



**Tech Talk**

# Quantification of Energy Dispersive Spectrum (EDS)

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Reference book: Transmission Electron Microscopy—A Textbook for Materials Science  
written by David B. Williams and C. Barry Carter

# Outline

- **Acquisition of high-quality EDS dataset**
- **Procedures of EDS quantification**
- **Why EDS quantification is inaccurate?**

# Acquisition of high-quality EDS dataset

## Tips and tricks for EDS acquisition

- Maximize probe current if the sample can endure high dose (maximize the generated X-rays)
- Tilt your sample to around  $10\text{-}15^\circ$  to face the detector (maximize the collection efficiency)
- Do not forget to remove the objective aperture (reduce artifact)
- Tilt your sample to avoid the two-beam condition (reduce the channeling effect)
- Use a shorter time constant ( $\tau \sim 5\text{-}100 \mu\text{s}$ ) to maximize the counting rate
- Regions cannot be too thick ( $> 600 \text{ nm}$ ) or too thin ( $< 50 \text{ nm}$ )
- Dead time cannot be too large ( $> 50\text{-}60\%$ ) or too small ( $< 3\%$ )
- Your sample should not have carbon contamination

# Procedures of EDS quantification

## Concept of EDS quantification and Cliff-Lorimer ratio method

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \text{ and } C_A + C_B = 1$$

$C_A / C_B$  : atomic percentage or weight percentage of elements A/B;

$I_A / I_B$  : EDS peak intensity of elements A/B;

$k_{AB}$  : not a constant but related to the following three parameters:

a> Z, the atomic number

b> A, the absorption of X-rays within the sample

c> F, the fluorescence of X-rays within the specimen

Thin-foil criterion: For TEM samples, we usually assume that the specimen is thin enough to ignore the absorption and fluorescence.

# Procedures of EDS quantification

## Steps of EDS quantification

- Identification of each peak
- Remove background
- Peak integration
- How to obtain the  $k_{AB}$ ? (Standard sample or calculation method)

# Procedures of EDS quantification—Peak identification

- Si escape peak (signal detection artifact)

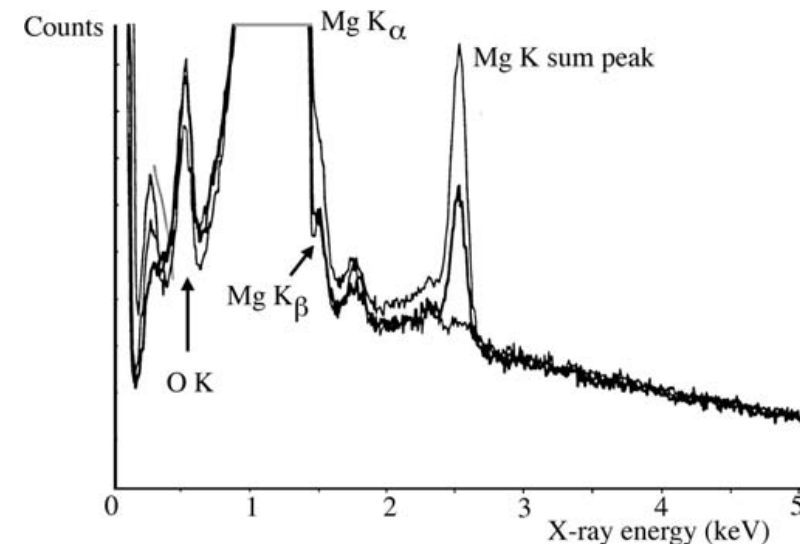
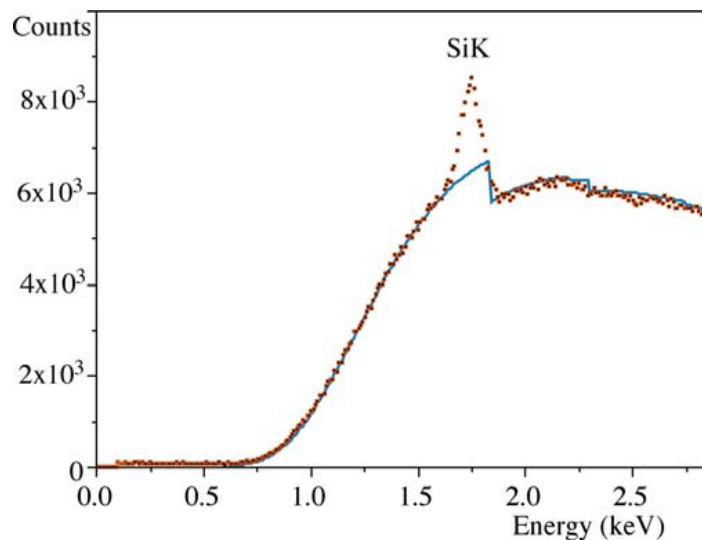
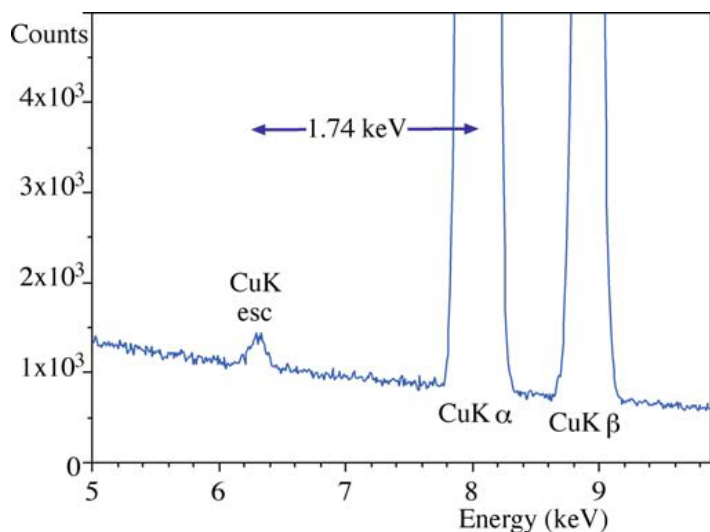
Detector is not a perfect sink. Incoming photon with energy  $E$  is not transformed into electron-hole pairs but fluoresces a Si  $K\alpha$  X-ray with a 1.74 keV energy.

- Internal fluorescence peak (signal detection artifact)

Incoming photons fluoresce atoms in the dead layer of the detector and result in Si  $K\alpha$  peak

- Sum peak (signal processing artifact)

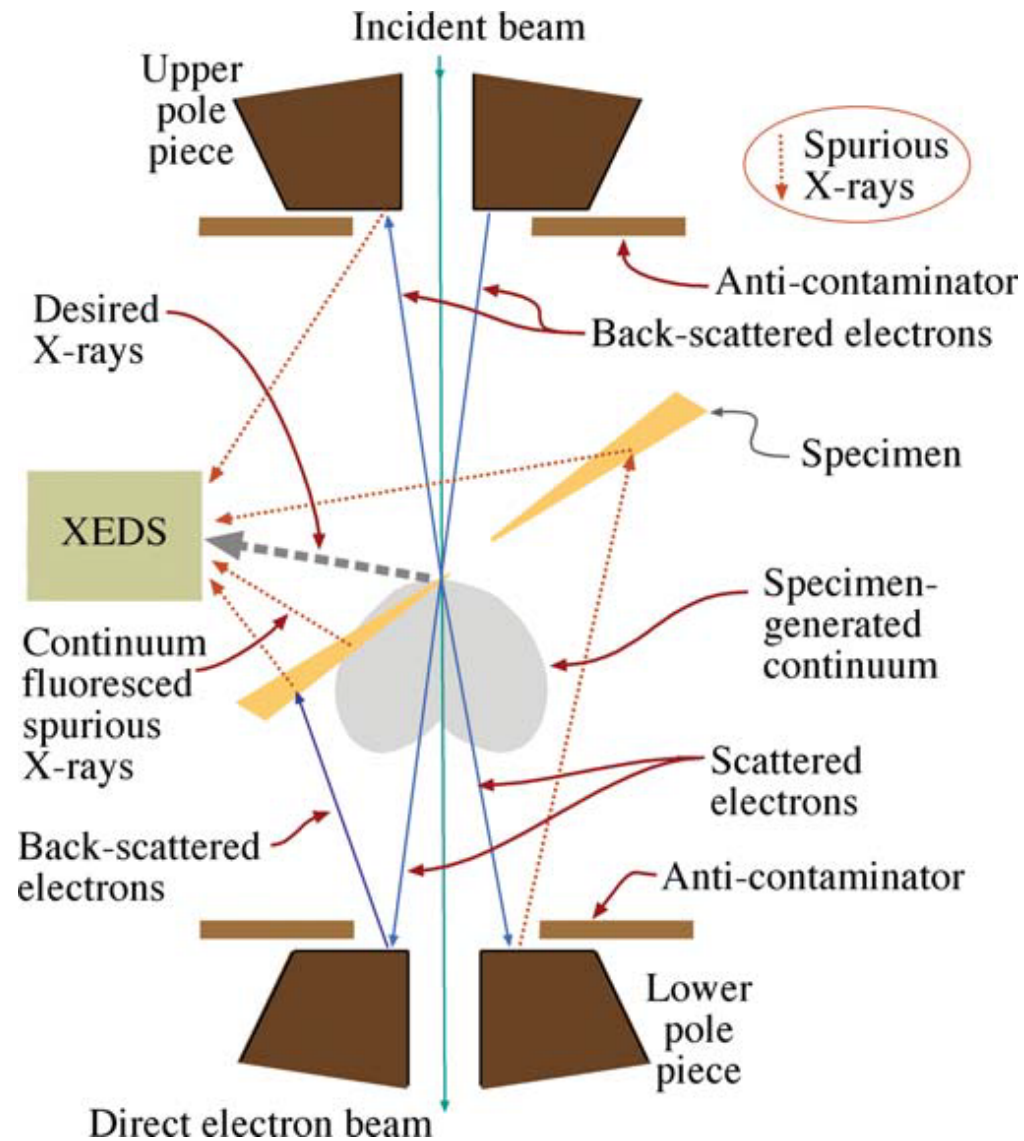
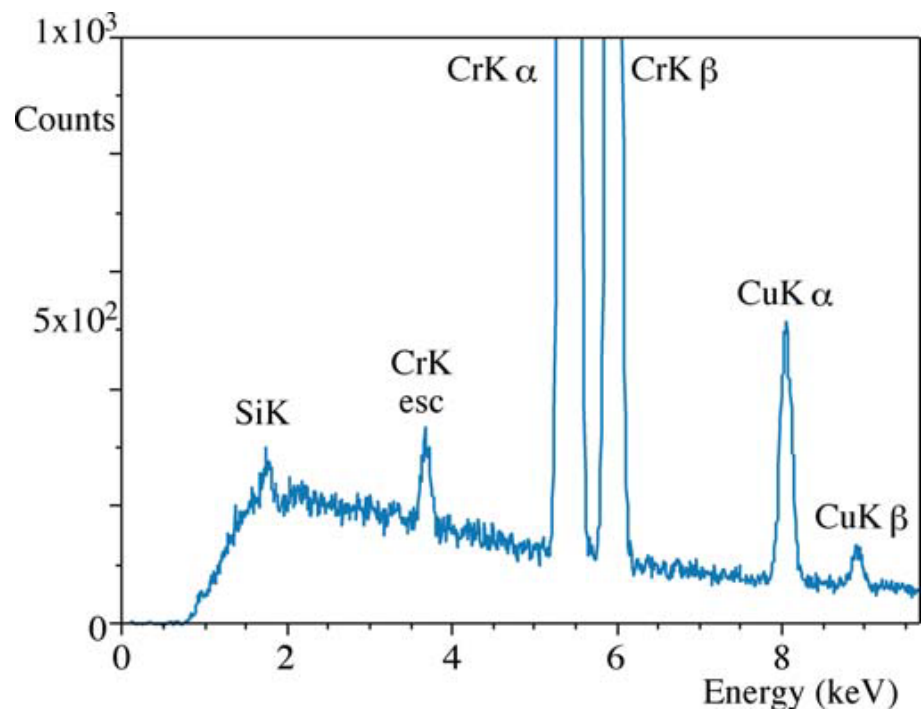
Sum peak occurs when the count rate exceeds the electronics' ability to discriminate all the individual pulses and so-called 'pulse pile-up'. **Reduce the dead time!!**



# Procedures of EDS quantification—Peak identification

## System X-rays

- Cu is everywhere
- Remember to remove the objective aperture before taking EDS signal
- Operate as close to zero tilt as possible



# Procedures of EDS quantification—Peak identification

## Coherent Bremsstrahlung (CB)

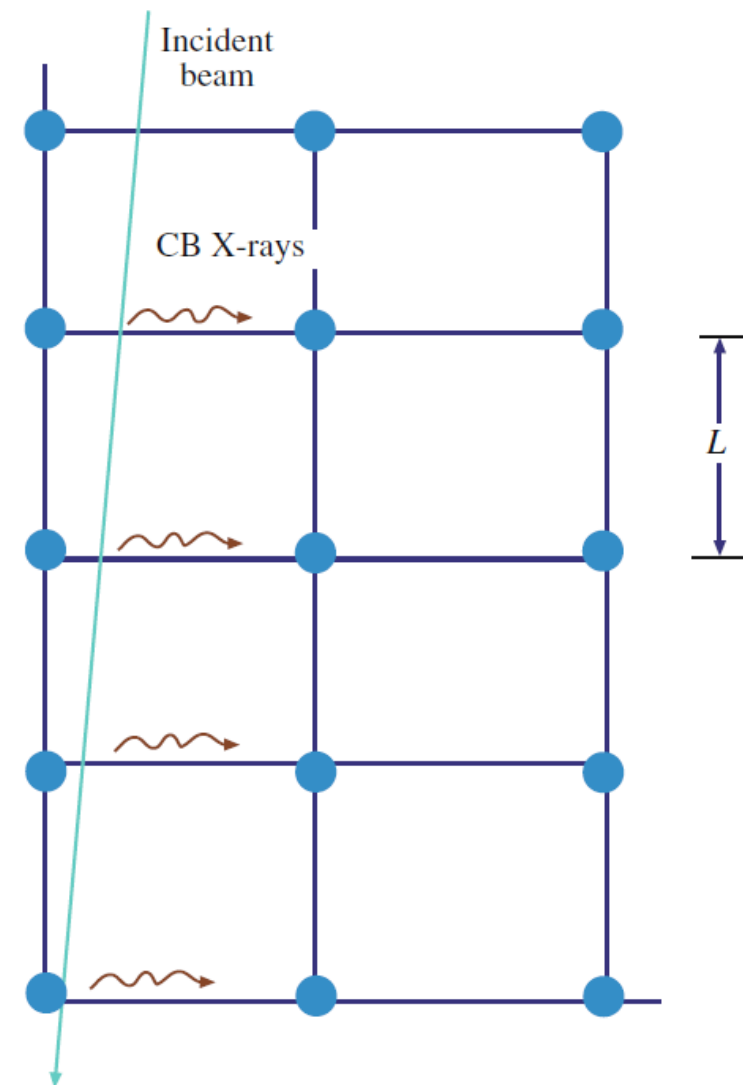
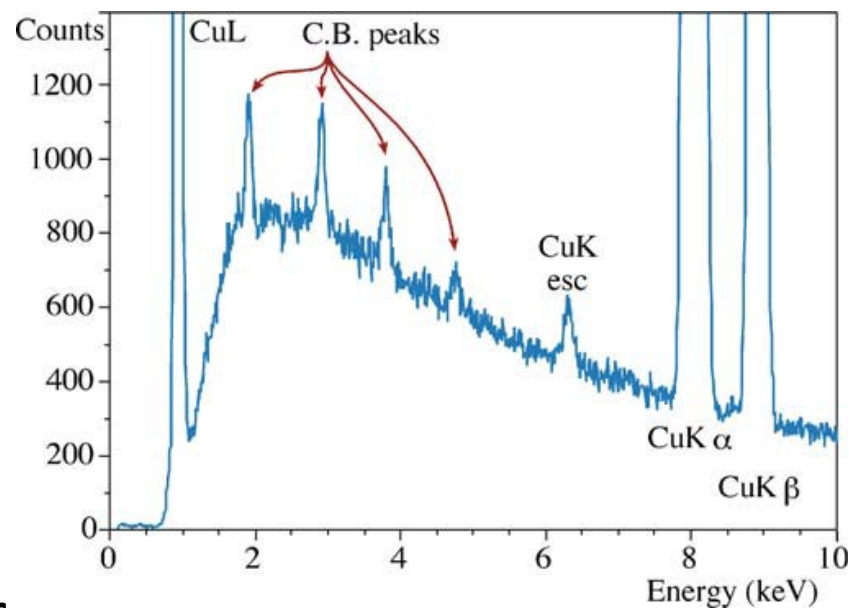
- Continuous bremsstrahlung spectrum usually happens bulk polycrystalline materials by electrons with lower energy (< 30 ekeV)
- Within TEM, for single crystalline specimens, CB likely will occur.

$$E_{CB} = \frac{12.4\beta}{L(1-\beta\cos(90+\alpha))}$$

$\beta$ : electron velocity divided by the velocity of light

$L$ : Lattice spacing in the beam direction

$\alpha$ : take-off angle of the detector

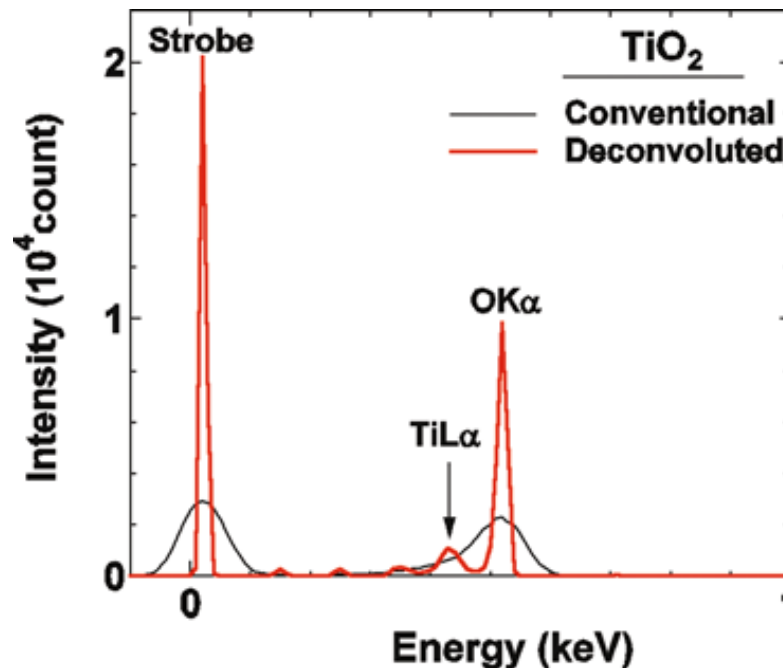
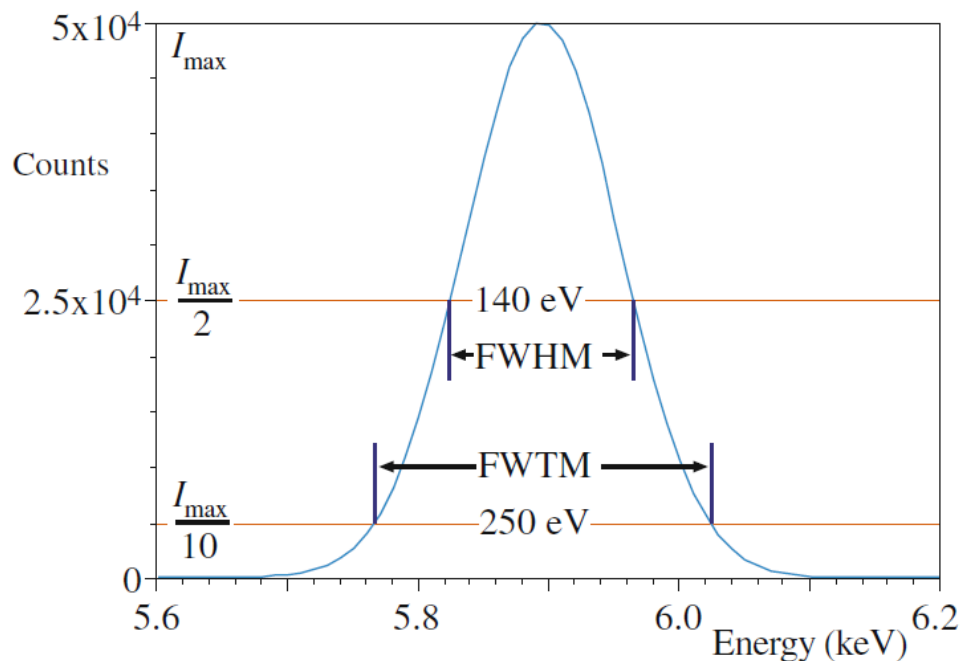




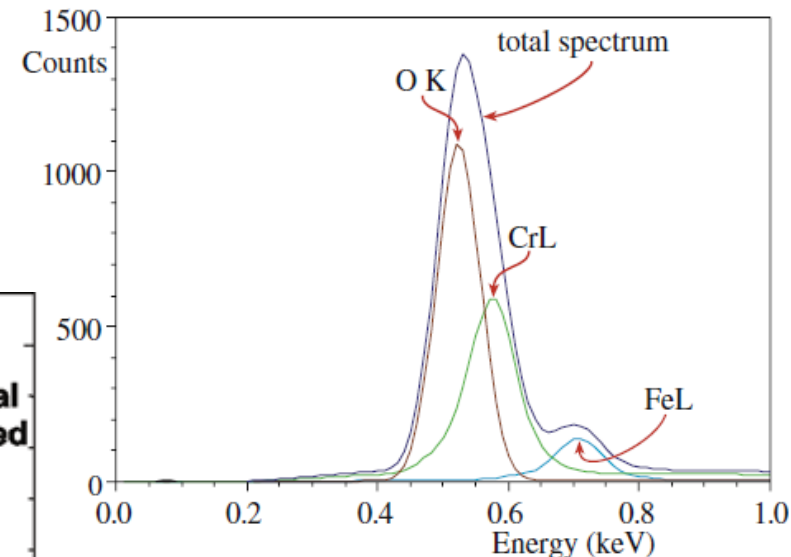
# Procedures of EDS quantification—Peak identification

Deconvolution for resolving overlapped peaks and improvement of energy resolution

## Very low energy resolution



## Deconvolution overlap



Deconvolute the point-spread function to remove the electronic-noise component of the characteristic peak width

# Procedures of EDS quantification—Remove background

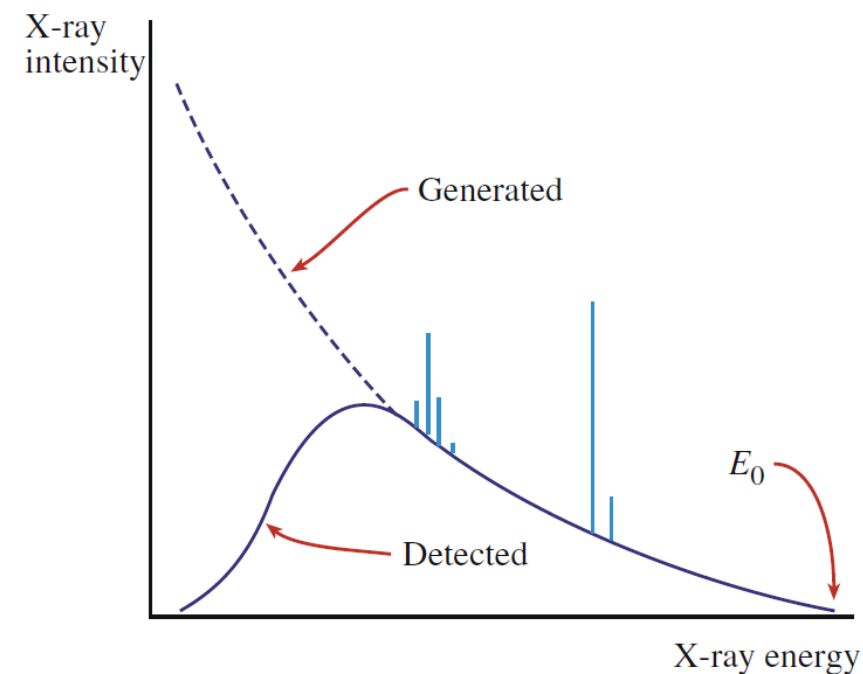
- **Bremsstrahlung X-rays (braking radiation)**
- When electrons interact with the Coulomb field of nucleus, there will be substantial momentum changes and it may emit an X-ray during this process.
- The approximate expression used is:

$$N(E) = \frac{KZ(E_0 - E)}{E}$$

N(E): number of bremsstrahlung photons with energy E;

Z: atomic number;  $E_0$ : electron energy

K: Kramers' constant including Kramer's original constant, collection efficiency and processing efficiency of detector, absorption of X-rays within specimen



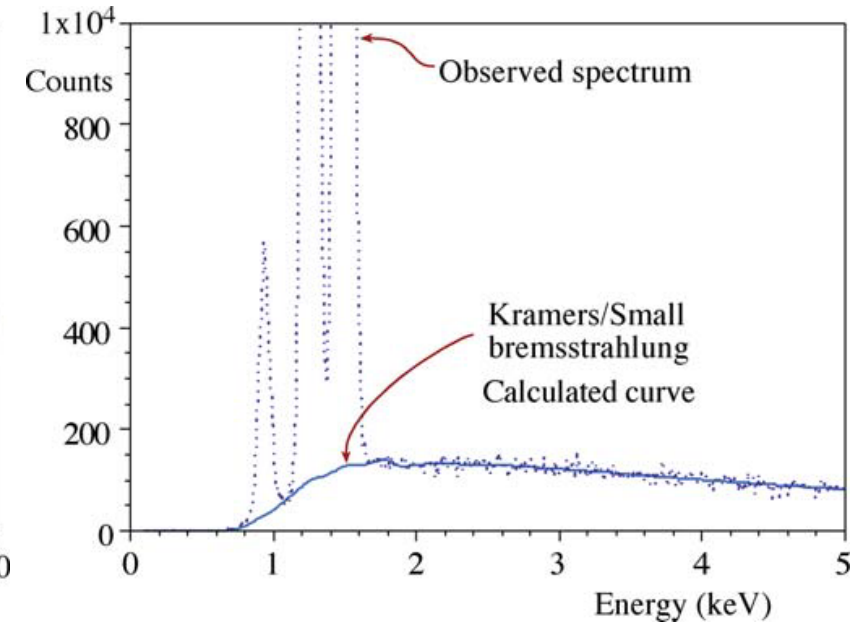
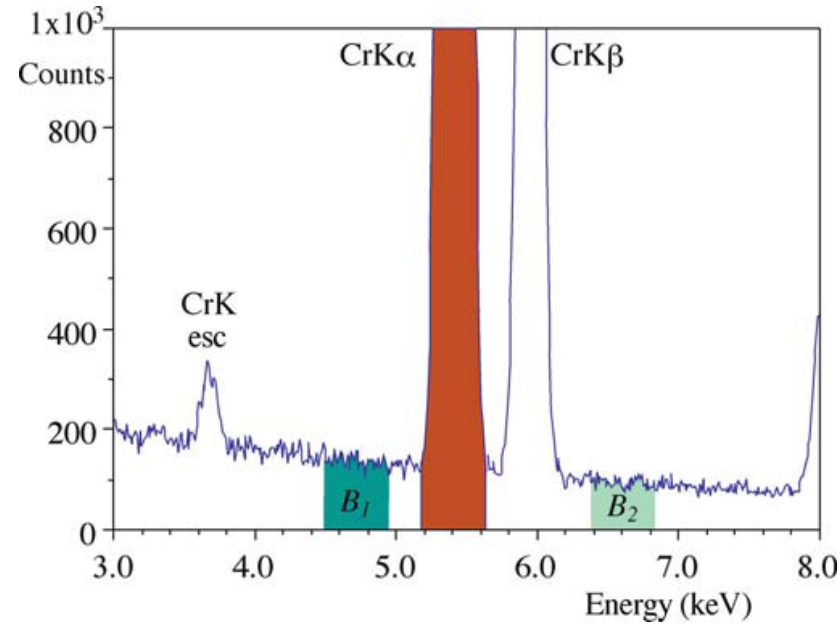
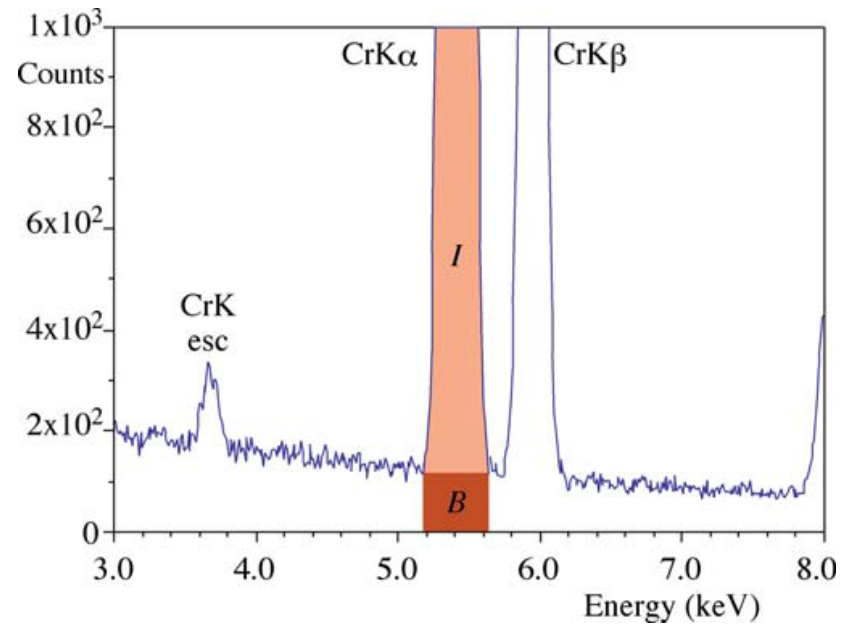
# Procedures of EDS quantification—Remove background

## a> Window methods

Simple but no physical meaning; optimum window width is 1.2 FWHM;

## b> modeling the background

At low-energy region, peak overlap and absorption are strong; Modeling background is a better solution



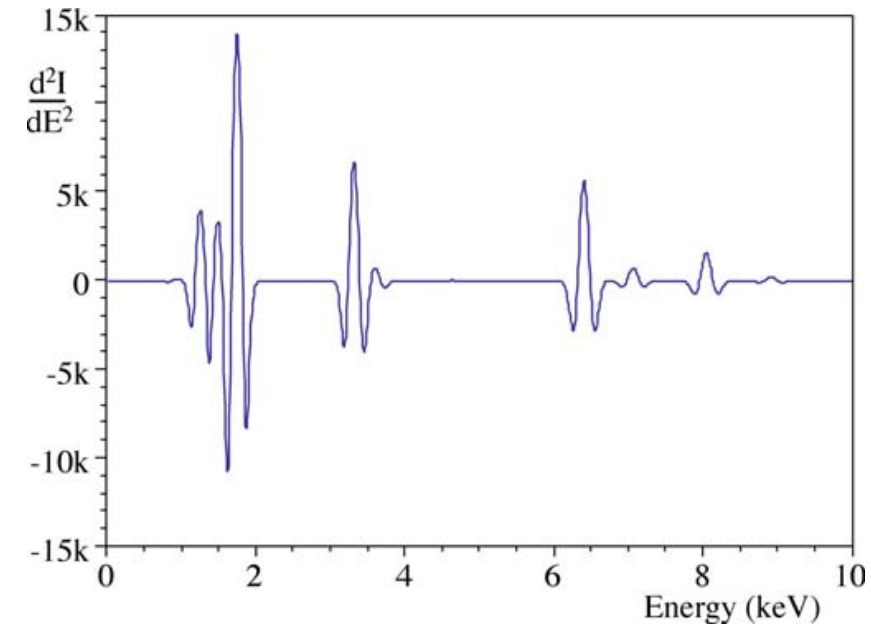
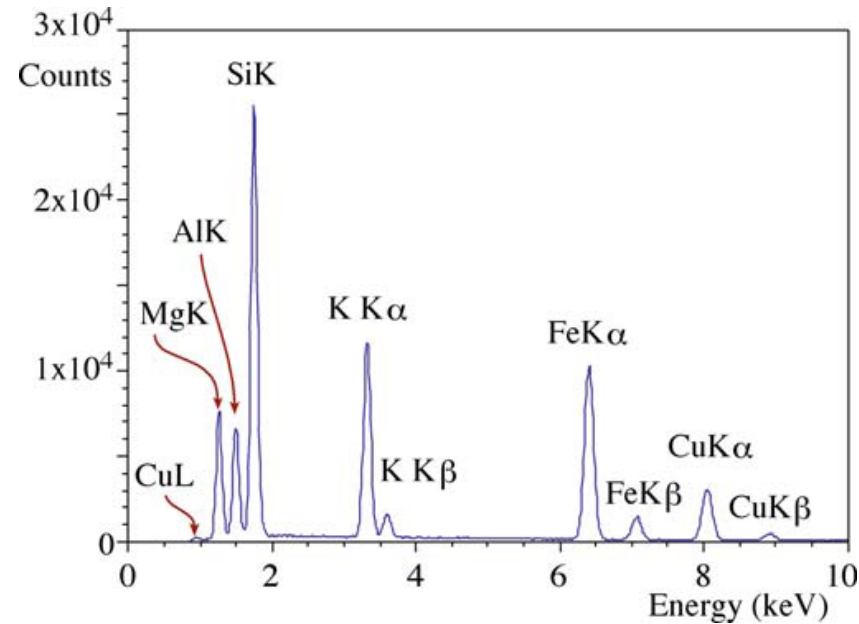
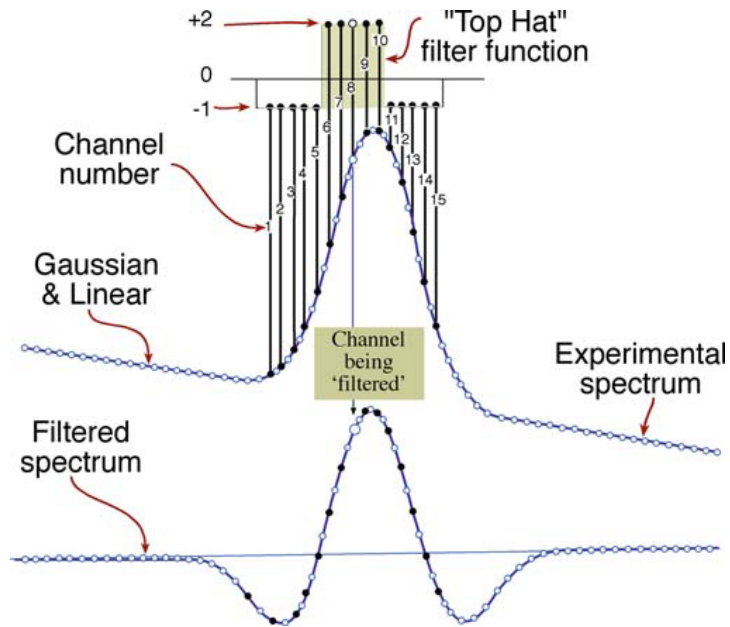
# Procedures of EDS quantification—Remove background

## c> Filtering out the background (Top-hat filter)

no physical meaning;

The characteristic peaks show a rapid variation of counts as a function of energy ( $\frac{dI}{dE}$  is large);

Background has a relatively small  $\frac{dI}{dE}$  ( $\frac{d^2I}{d^2E} \sim 0$ )



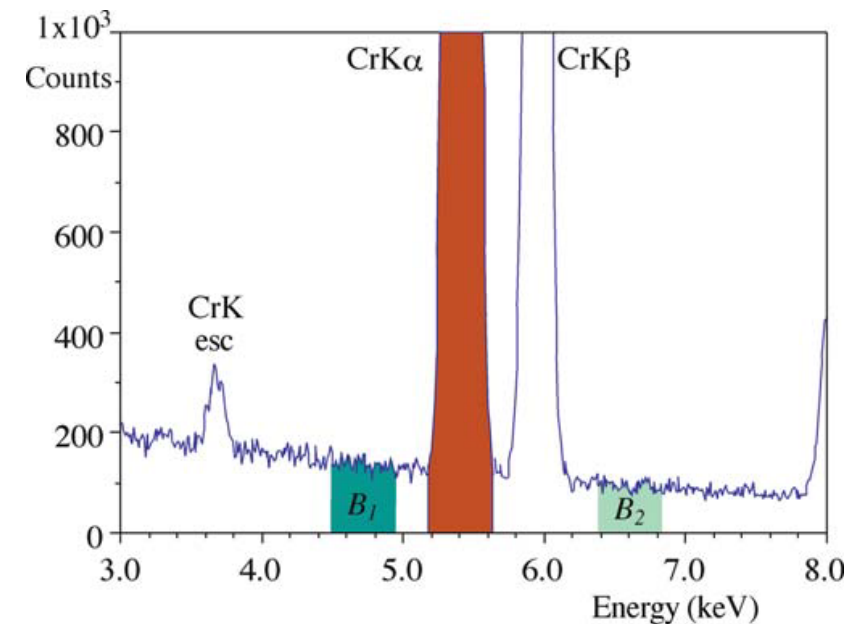
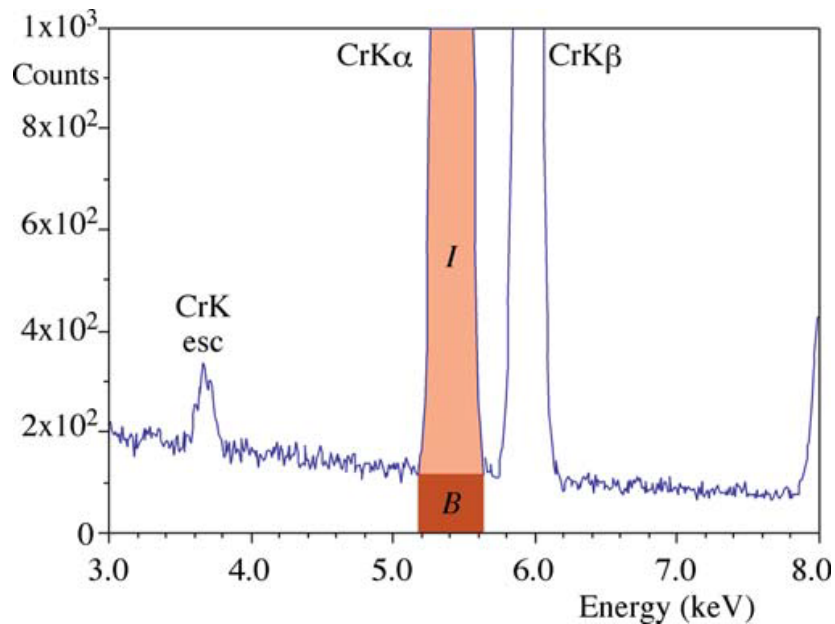
# Procedures of EDS quantification--Peak integration

a> Window methods

Remember to use the same window width as background subtraction

b> modeling the background and filtering background

Fit the peaks using a slightly modified Gaussian function and integrate the counts under the Gaussian



# Procedures of EDS quantification—Determination of $k_{AB}$

- **How to obtain the  $k_{AB}$ ?**

a> Experimental determination

\*Use standard sample with the required elements and known chemical compositions (not easy to find);

\*Make sure using the sample experimental parameters and processing parameters as the ones for your samples

b> Theoretical calculation

$$k_{AB} = \frac{(Qwa)_A A_B \epsilon_A}{(Qwa)_B A_A \epsilon_B}$$

$A_A, A_B$ : atomic weight

$Q_A, Q_B$ : ionization cross sections

$w_A, w_B$ : fluorescence yield

$a_A, a_B$ : relative transition probability

$\epsilon_A, \epsilon_B$ : detector efficiency

# Procedures of EDS quantification-- $\zeta$ -factor method

## Concept of EDS quantification and $\zeta$ -factor method

$$(\rho t)_A = \zeta_A \frac{I_A}{C_A} \quad \zeta_A = \frac{A}{C_A N_0 Q w a i} \quad C_A + C_B = 1$$

$$\frac{C_A}{C_B} = \frac{I_A \zeta_A}{I_B \zeta_B} \text{ and } C_A / C_B : \text{ atomic percentage or weight percentage of elements A/B;}$$

$I_A / I_B$ : EDS peak intensity of elements A/B

i: beam current;  $N_0$ : Avogadro's constant; Q: ionization cross section; w: fluorescence yield

a: relative transition probability

Advantage: preparation of standard sample is easy; pure-element with known composition

# Why EDS quantification is inaccurate?

## ➤ Statistics error

$$\left(\frac{\sigma_C}{C_A/C_B}\right)^2 = \left(\frac{\sigma_{k_{AB}}}{k_{AB}}\right)^2 + \left(\frac{\sigma_{I_A}}{I_A}\right)^2 + \left(\frac{\sigma_{I_B}}{I_B}\right)^2$$

$$\text{Relative Error} = \frac{3\sigma}{N} * 100\% = \frac{3N^{0.5}}{N} * 100\%$$

**Increasing the total counts and multiple measurement points are ways to reduce the statistics error.**

This error exists for both calculated  $k_{AB}$  or experimentally determined  $k_{AB}$



# Why EDS quantification is inaccurate?

## ➤ Absorption and fluorescence

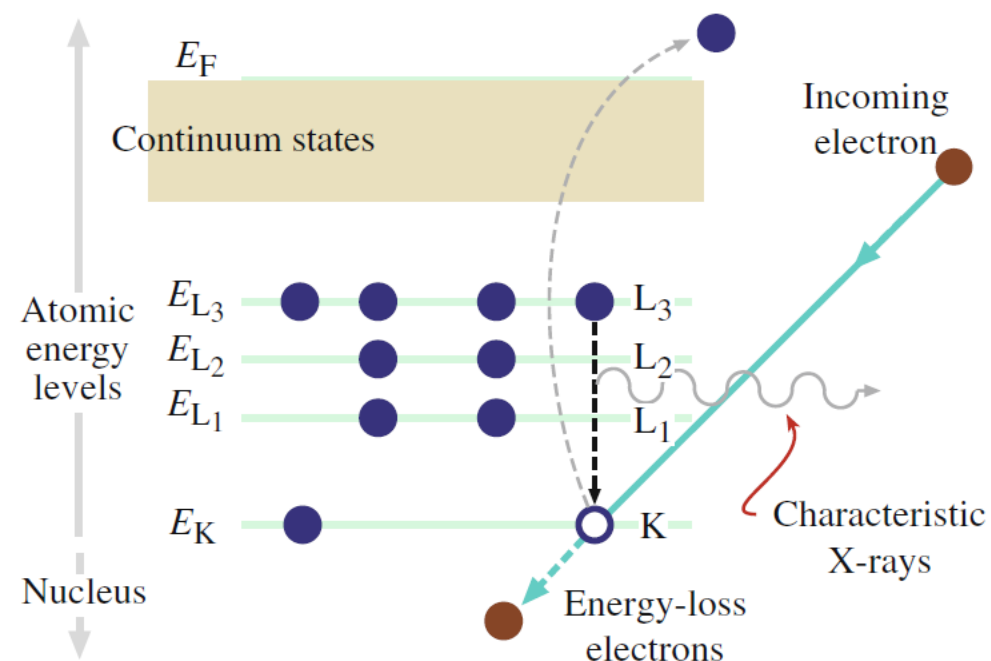
- An ionized atom does not have to lose energy by giving off a characteristic X-ray but can emit an Auger electron instead.
- Fluorescence yield ( $\omega$ ) describes the probability of X-ray versus Auger emission.

$$\omega = \frac{Z^4}{a+Z^4} \quad (\text{for K shell, } a \sim 10^6)$$

For C-K edge,  $\omega \sim 10^{-3}$ ;

For Ge-K edge,  $\omega \sim 0.5$ ;

**That's also why EDS is not the best way to analyze the light elements such as Li, Be and B.**



# Why EDS quantification is inaccurate?

- Significant peak overlap
- For calculated  $k_{AB}$ , the calculation of ionization cross sections  $Q$  is inaccurate particularly for L, M lines (calculation error no better than  $\pm 10 - 20\%$ )
- For calculated  $k_{AB}$ , detector efficiency  $\varepsilon$  is difficult to accurately determined
- For experimental determination, it is difficult to prepare the standard sample
- Possible sample degeneration and contamination under electron beam
- Inaccurate background subtraction and peak integration
- .....

**Thank you for your attention!**

**Q.&A.**