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Light Element Analysis

Hans Dijkstra

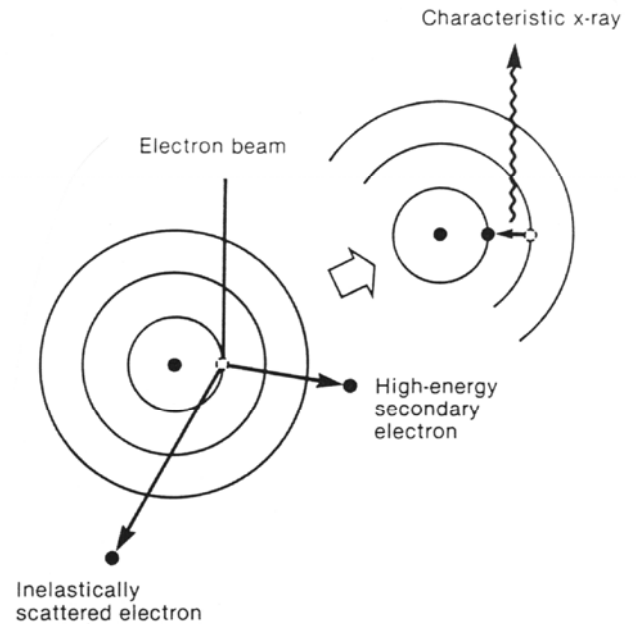
**Thermo Fisher Scientific
Breda, the Netherlands**

Overview

- Analysis of B, C, N, O and F with EDS and WDS
- Specimen preparation
- Wavelength Dispersive Spectroscopy (WDS)
- Energy Dispersive Spectroscopy (EDS)
- Quantification
- Conclusions

The light elements

- The analysis of light elements is similar to other heavier elements
- The light elements only generate $K\alpha$ type X-rays
- The M-shell is empty, so no $K\beta$ or $L\alpha$ lines
- No analysis of H and He (no characteristic X-rays)
- No analysis of Li (no permitted electron transition)
- Low-energy X-rays are strongly absorbed by other elements
- X-ray yield (fluorescence yield) is very low; Auger yield is high
- Ionization energies are very low
- Incoming electron can generate many X-rays



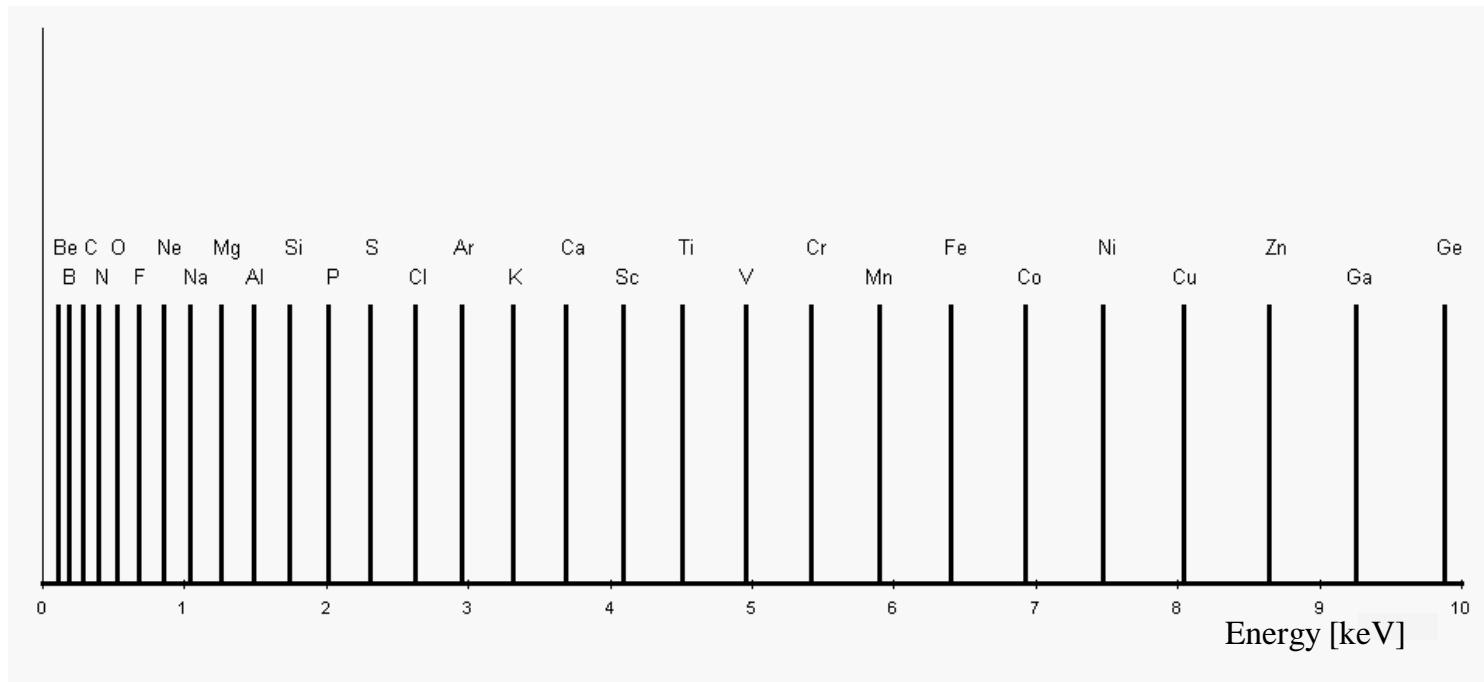
The light elements

- Energies and wavelengths

Element	Z	Wavelength [nm]	Energy [eV]	Critical excitation energy [eV]
Be	4	11.40	109	112
B	5	6.76	183	192
C	6	4.47	277	284
N	7	3.16	392	400
O	8	2.36	525	532
F	9	1.83	677	687

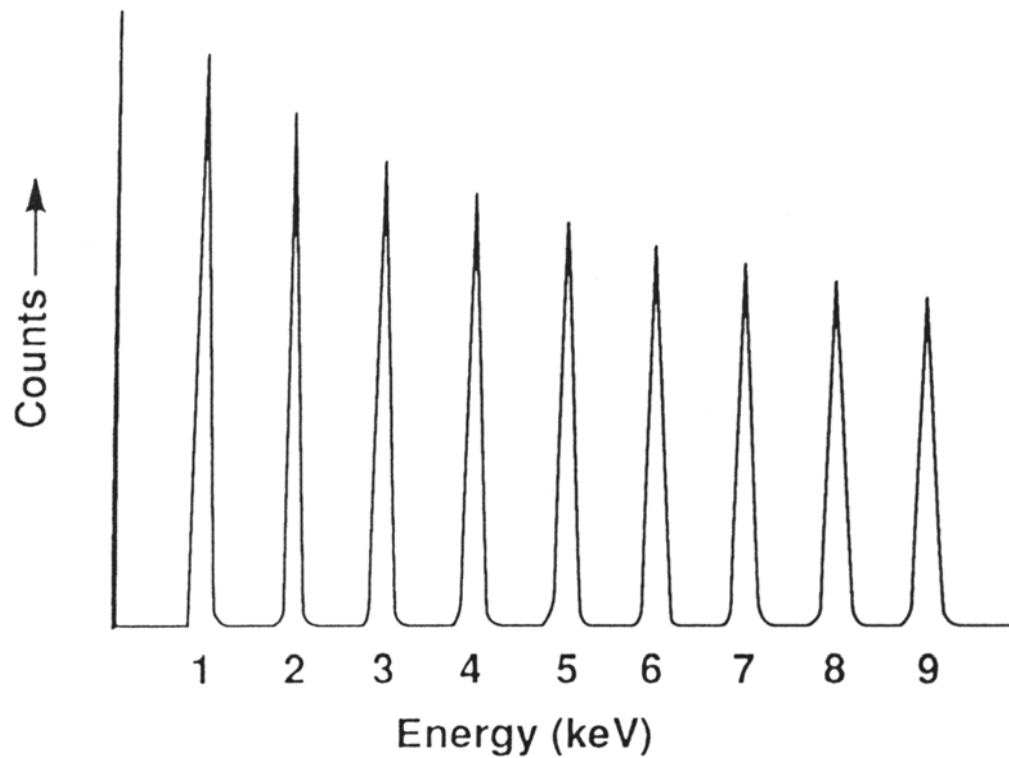
The light elements

- X-ray lines in the low-energy region tend to be close together
- Separation is still good enough for EDS analysis



The light elements

- Fortunately: Energy resolution of EDS decreases with lower energies

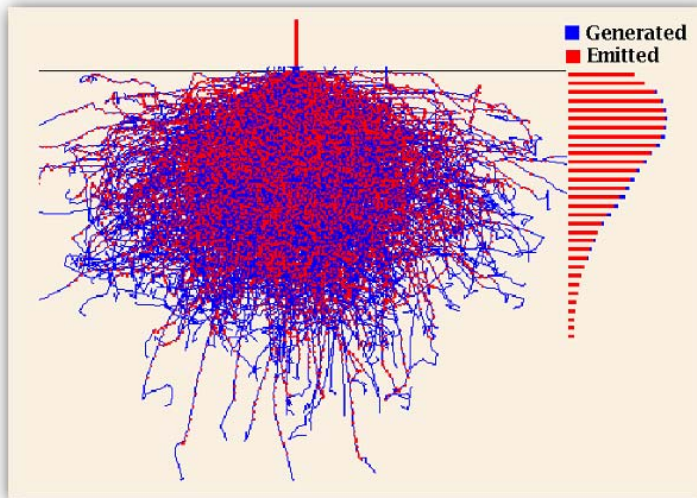


- Cu-Ka 150 eV
- Mn-Ka 130 eV
- Al-Ka 90 eV
- F-Ka 70 eV
- C-Ka 55 eV

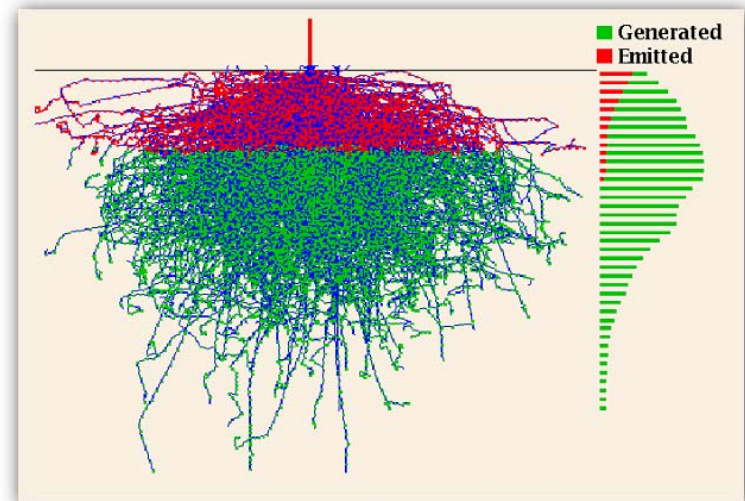
Specimen preparation

- The light element signal comes generally from close to the surface

Fe-K in Fe_3C



C-K in Fe_3C



- So the C signal in a spectrum comes more from the surface than the Fe signal !
- Surface quality becomes very important
- For quantitative analysis a well-polished surface is required

Specimen preparation

- Contamination of the sample can seriously affect results
- Contamination is caused by hydrocarbons getting 'cracked' under the electron beam, generating locally a carbon coating
- N-K α is strongly absorbed by carbon
- B-K α is strongly absorbed by carbon

- Solutions:
 - Two main sources of contamination: microscope + sample
 - Get clean microscope vacuum
 - Samples need to be clean: use gloves!
 - Be careful when embedding samples: no cracks or slits
 - Beware with porous samples
 - Place samples in dessicator (or SEM chamber ?) for 24 hours before you plan to analyze them

Wavelength Dispersive Spectroscopy (WDS)

- Low energy X-ray lines require large 2d-spacing crystals

$$\text{Bragg equation: } 2d \cdot \sin(\theta) = n \cdot \lambda$$

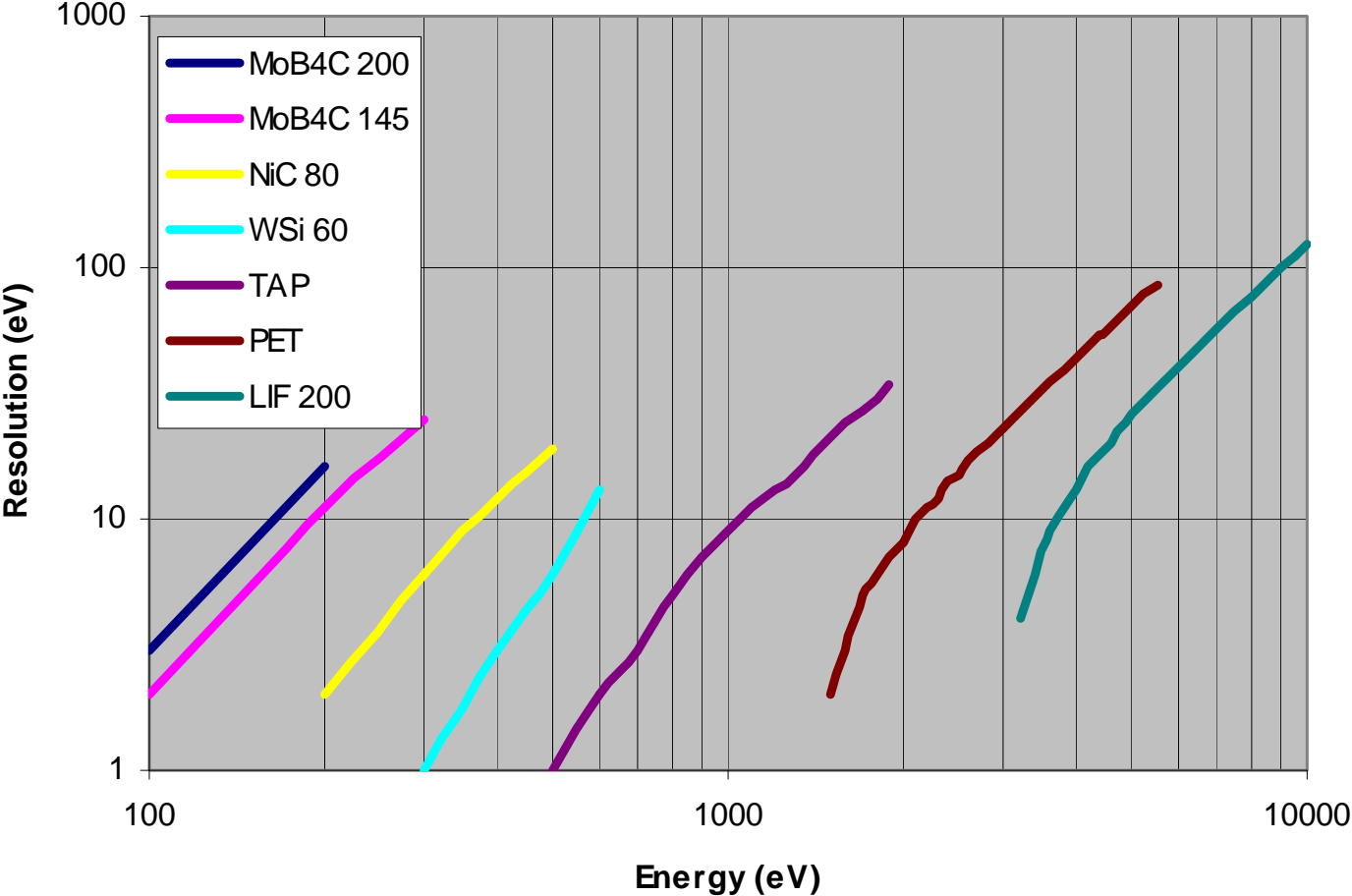
- Only some natural crystals are suitable:
 - KAP (Potassium phtalate)
 - RAP (Rubidium phtalate)
 - TAP (Thallium phtalate)
- These crystals have a 2d-spacing of about 26 Angstrom, allowing detection of F-K and on some spectrometers O-K.
- In the 1970's new synthetic crystals were developed, such as:
 - Lead-stearate (STE)
 - WSi
 - NiC
 - MoB4C
 - CrSc
- These crystals have large or very large 2d spacings, allowing detection of down to Beryllium.

Wavelength Dispersive Spectroscopy (WDS)

- In general a high Bragg angle (low energy for a given diffractor) will give the best resolution
- In general a low Bragg angle (high energy for a given diffractor) will produce the best count rate
- So it is nice to have 2 crystals for each light element:
 - Use high-resolution for peak overlap situations
 - Use high-countrate for trace element analysis
- Absorption by the materials in a diffractor negatively effect the count rate at energies just above the absorption edge of the elements in the diffractor. For example a NiC diffractor will have reduced count rates just above the Nickel and Carbon absorption edges. This is advantages for measuring some elements such as Nitrogen where a CrSc diffractor enhances the N-K α intensity but suppresses the Ti-L α .

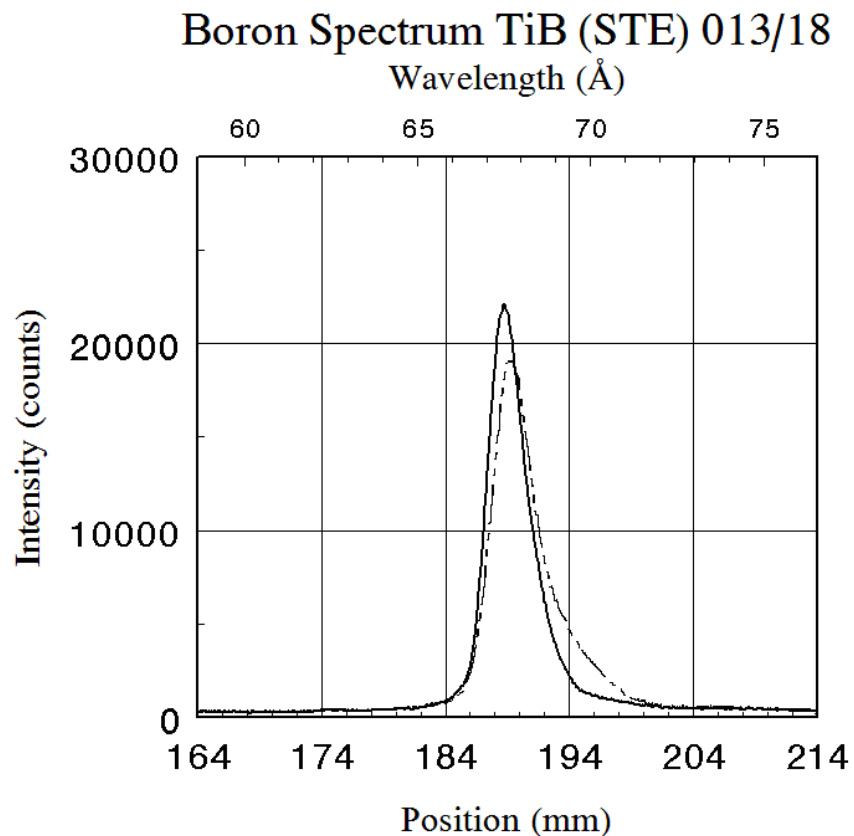
Wavelength Dispersive Spectroscopy (WDS)

MAXrayER Resolution Estimates



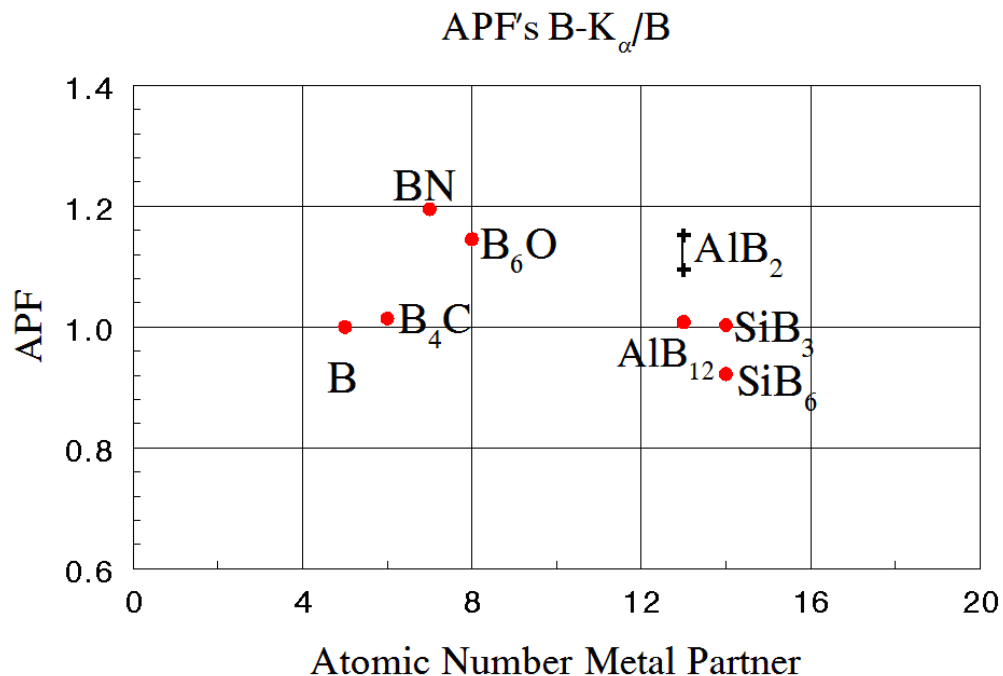
Wavelength Dispersive Spectroscopy (WDS)

- Peak shapes can depend on the matrix elements, and for the same material can even depend on the orientation of the sample compared to the WDS spectrometer.

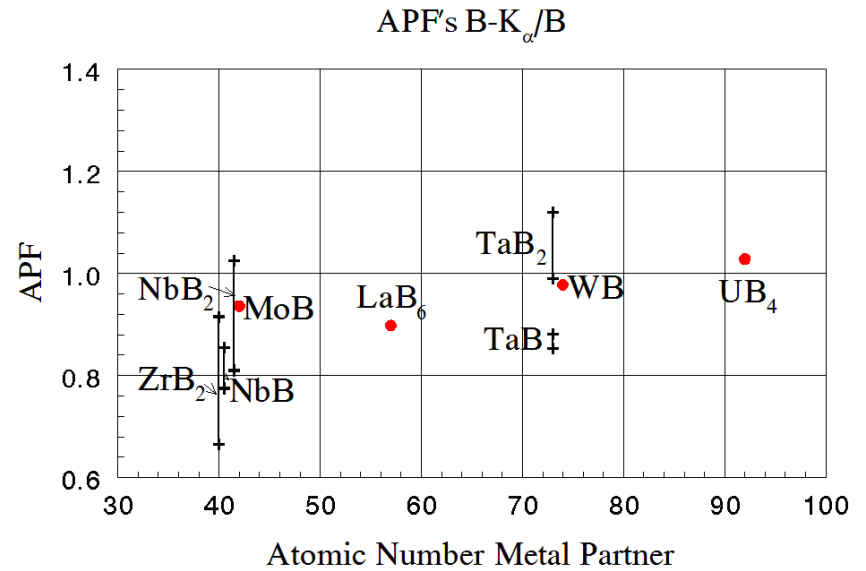
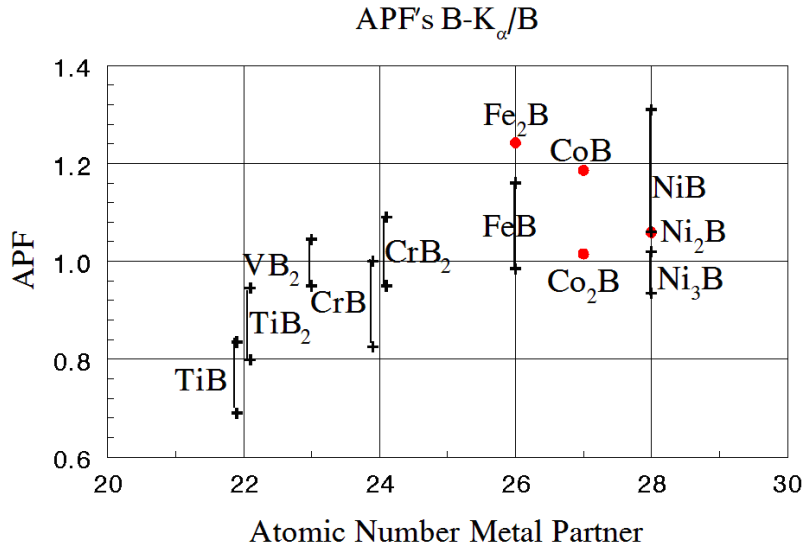


Wavelength Dispersive Spectroscopy (WDS)

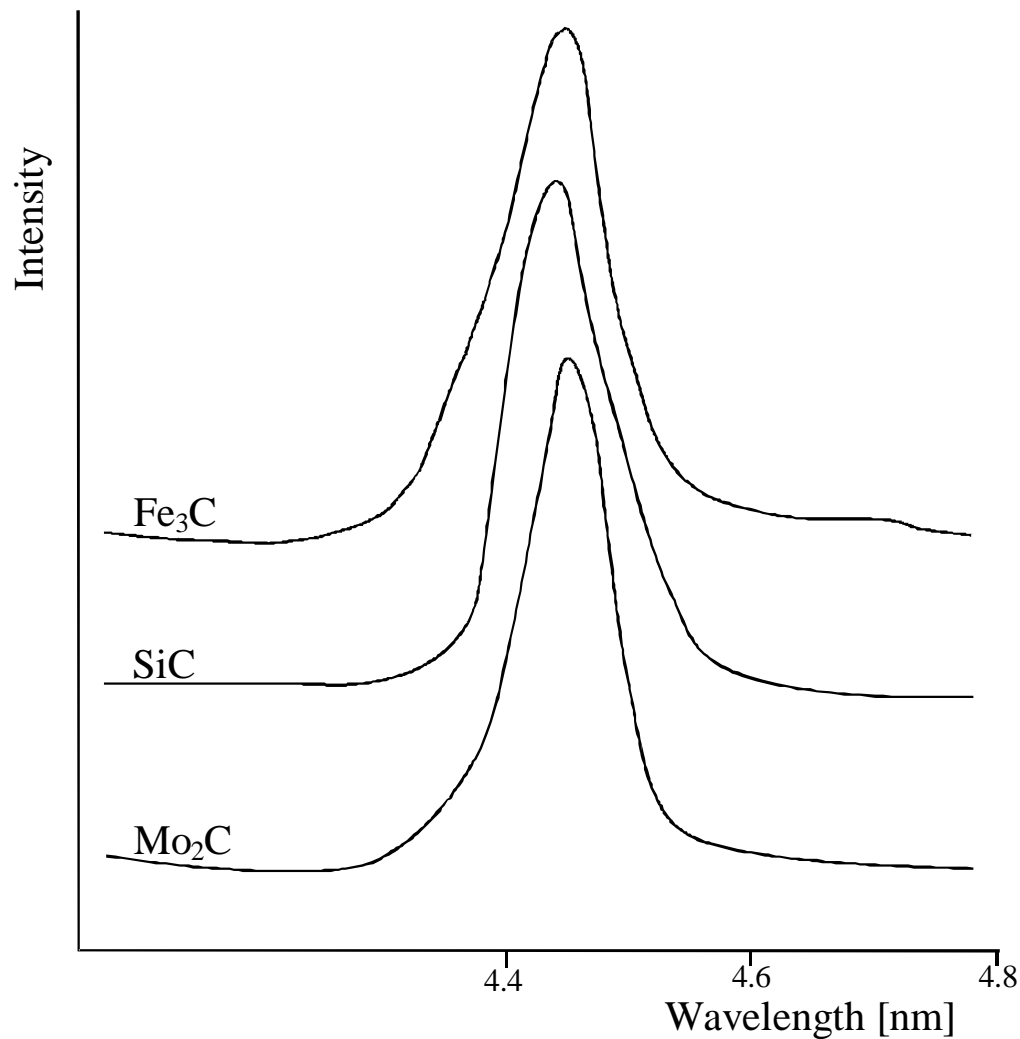
- As a result of these peak shape changes, you need to measure the complete integral peak intensities.
- If you use the same type of material frequently, then you can use Area-Peak factors.
- Area-peak variations are most common with Be, B and C, but less significant with N and nearly non-existent with O.



Wavelength Dispersive Spectroscopy (WDS)

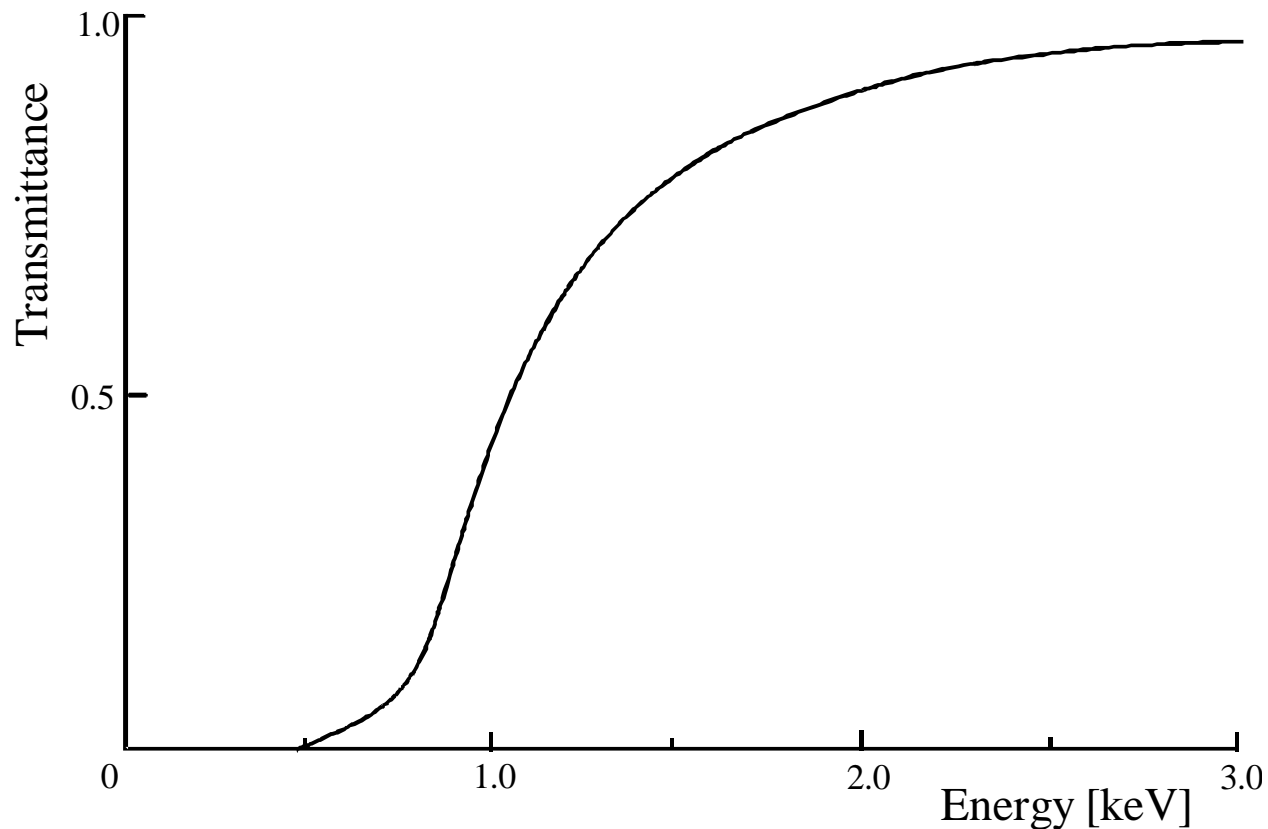


Wavelength Dispersive Spectroscopy (WDS)



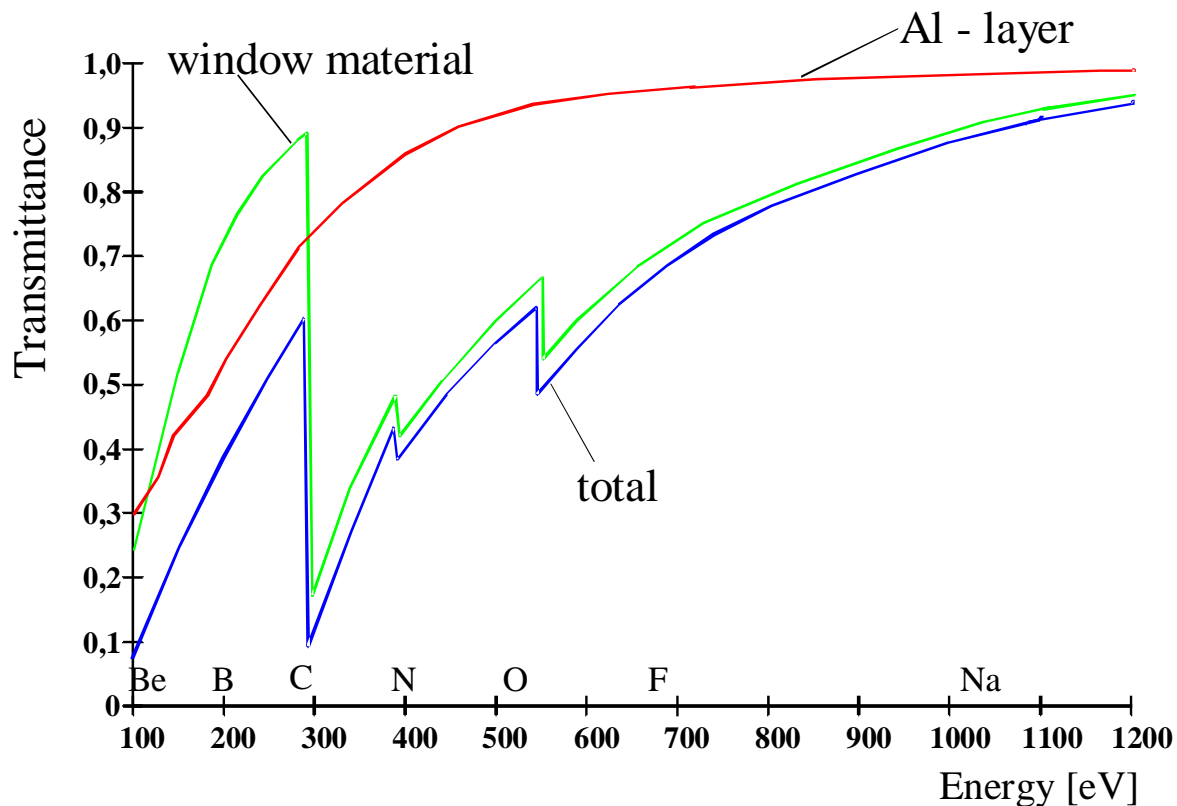
Energy Dispersive Spectroscopy (EDS)

- The traditional beryllium window absorbs all X-ray with energy < 1 keV
- Modern EDS detectors are equipped with a thin (0.3 micron) polymer windows
- These windows transmit light-element X-rays



Energy Dispersive Spectroscopy (EDS)

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Quantification

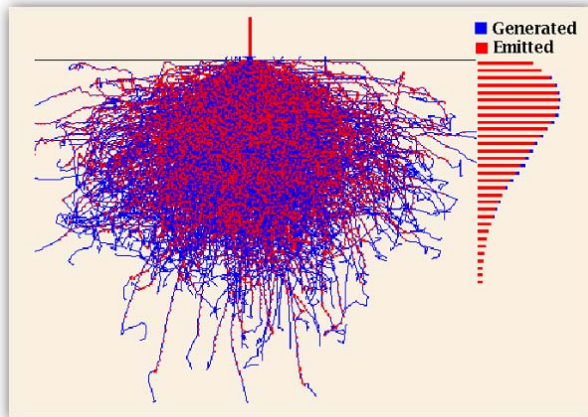
The traditional ZAF approach is not accurate enough if strong absorption is involved. In general, if the MAC is larger than 1000 cm²/gr we call it strong absorption. If the MAC is larger than 5000 cm²/gr then we call it very strong absorption

Mass Absorption Coefficients (cm²/g) for **Boron-K α** X-rays according to various sources.

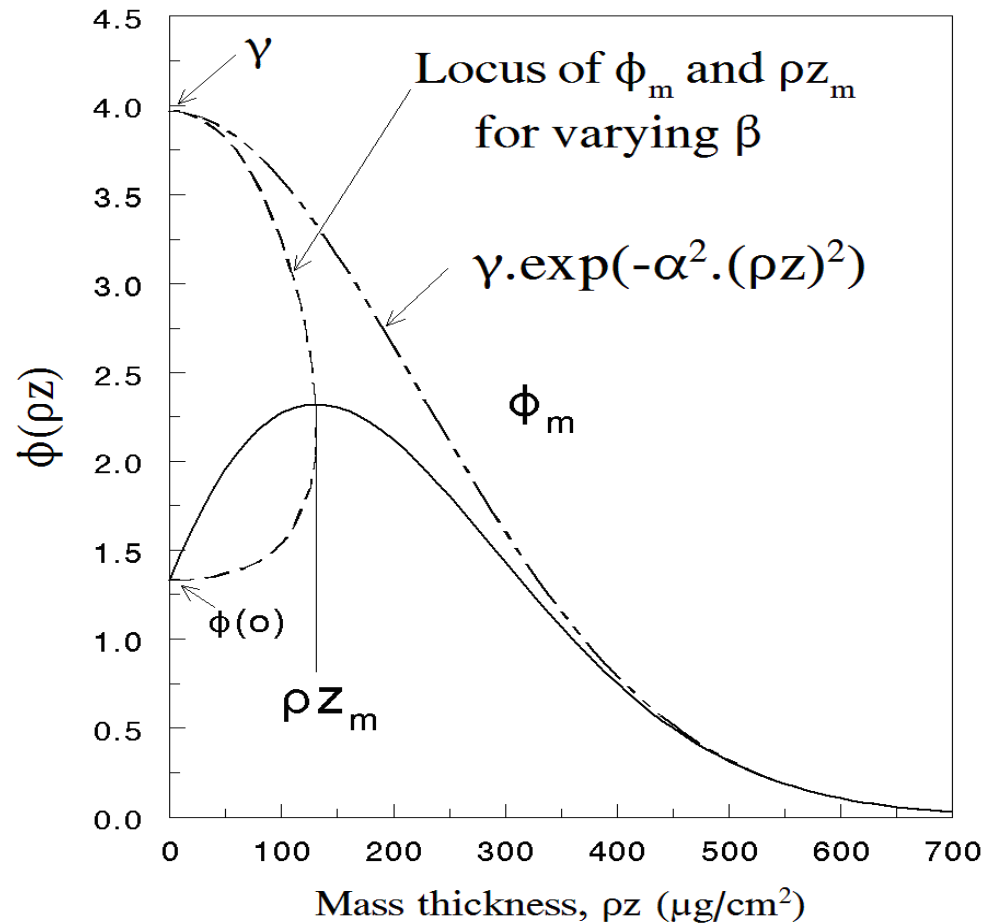
Absorber	Henke	Henke	Henke	Bastin
B	3353	3350	3350	3350
C	6456	6350	6400	6450
N	10570	11200	10900	10400
O	16530	16500	18500	16500
Al	65170	64000	77300	64000
Si	74180	84000	86100	81400
Ti	15280	15300	16800	15100
V	16710	16700	19900	18250
Cr	20670	20700	22400	20200
Fe	25780	27600	31000	27000
Co	28340	30900	30900	33000
Ni	33090	35700	39600	41500
Zr	38410*	8270	7240	4330
Nb	4417	6560	5470	4600
Mo	4717	5610	5710	4400
La	3826	3730	3400	2900
Ta	20820	20800	20800	21800
W	19660	19700	19400	20400
U	2247	9020	9600	8000

Quantification

Phi-Rho-Z methods have been developed in the 1980 and 1990 to improve quantification of light elements

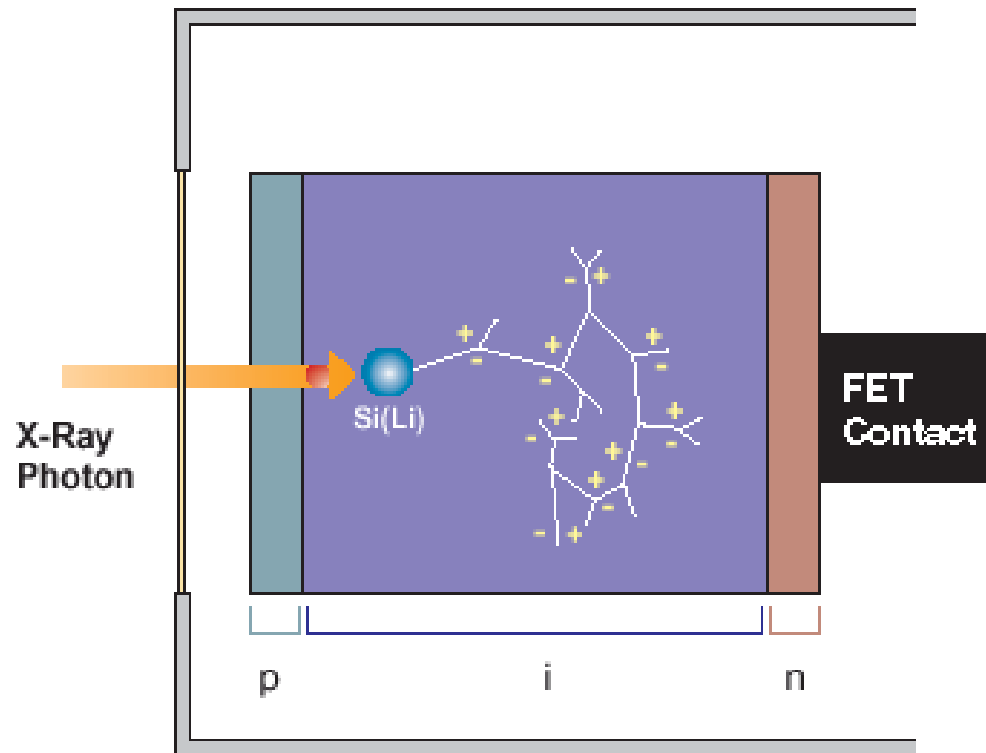


$\phi(\rho z)$ curve Al-K $_{\alpha}$ /Al 15 kV
Surface-centered Gaussian



Quantification

To get accurate EDS analysis, you need to calibrate the detector efficiency. The calibration method depends on the EDS manufacturer.



Conclusions

- Both WDS and EDS are capable of analyzing light elements
- Specimen preparation is very important
- Quantification can reach a good accuracy, but only with very careful operation. The quality of light-element analysis depends strongly on the operator, not on the hardware or software !

Thank you very much for your attention !!