CHEMICAL ANALYSIS IN THE
ELECTRON MICROSCOPES:
QUANTITATIVE X-RAY MICROANALYSIS

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Chemical Analysis (Microanalysis)

- Analysis performed on a very small part of a large specimen
- In principle, one can determine two things from the x-ray spectrum emitted by any specimen:
  - (i) measurement of wavelength or energy of each characteristic x-ray enables us to find out which elements are present, i.e., qualitative analysis
  - (ii) measurement of how many x-rays of any type are emitted per second should tell us how much of the element is present, i.e., quantitative analysis
- However, due to instrumental and specimen requirements quantitative analysis is not easy
Qualitative Analysis

- EDS is a parallel collection technique
- All X-ray energies are collected simultaneously and X-ray spectrum of energy vs number of counts produced.
- From the energy of peaks the elements present can be deduced
- From the size of the peaks the relative amounts of elements in the sample can be estimated

QUANTITATIVE ANALYSIS

- Two questions to answer:
  - (i) What is the smallest amount of element X which could be detected
  - (ii) What is the amount of an element in a specimen
THE LIMIT OF DETECTABILITY

- Should know minimum detectable concentration (MDC)
- If the count rate in the background is $b$ counts per second, if the counting time is $t$, then the background level is $bt$ and the smallest detectable peak is $2\sqrt{bt}$ above the background.
- What concentration of an element in the specimen would give this peak. To answer this we must compare our peak height with the peak height $(P-B)$ given by a standard specimen consisting of the pure element. MDC is given by:

$$MDC = \frac{(P-B)_{\text{specimen}}}{(P-B)_{\text{standard}}} \times 100 = \frac{2\sqrt{bt} \times 100}{pt-bt} \text{ weight%}$$

- To lower the MDC, reduce $b$, increase $p$ and $t$. The easiest is to increase the time of analysis.
- EDX system have poorer peak-to-background ratios than WDX.
- Both systems have worse p/b ratios for the lighter elements.

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For the lighter elements, MDC is around 0.1% in EDX and an order of magnitude lower for WDX. The precise figure will depend on the atomic weight of the trace element compared to that of the specimen since the soft x-rays from a light element will be strongly absorbed by a matrix of high atomic weight.
If one wants to quantify the relative amounts of different elements present in a complex sample one has to account for a number of factors and carry out a correction of the data.

One must account for other elements present in the sample and whether their individual peaks overlap with each other creating a “shoulder” that can mask the presence of one element or distort the midpoint of another.
Several methods to correct the spectra. ZAF takes into account the Atomic Weight (Z), effects of Absorbance (A) and effects of Fluorescence (F) in adjusting the data to give the correct values.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>K-RATIO</th>
<th>Z</th>
<th>A</th>
<th>F</th>
<th>ZAF</th>
<th>WT %</th>
<th>Chem</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-K</td>
<td>0.01320</td>
<td>0.9297</td>
<td>2.8395</td>
<td>0.9996</td>
<td>2.6387</td>
<td>3.48</td>
<td>4.00</td>
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<td>Ti-K</td>
<td>0.02310</td>
<td>1.0077</td>
<td>1.0663</td>
<td>0.9378</td>
<td>1.0077</td>
<td>2.33</td>
<td>2.26</td>
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<tr>
<td>Cr-K</td>
<td>0.16190</td>
<td>1.0083</td>
<td>1.0357</td>
<td>0.9185</td>
<td>0.9592</td>
<td>15.53</td>
<td>14.76</td>
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<tr>
<td>Fe-K</td>
<td>0.01070</td>
<td>1.0051</td>
<td>1.0430</td>
<td>0.8541</td>
<td>0.8954</td>
<td>0.96</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni-K</td>
<td>0.68650</td>
<td>0.9868</td>
<td>1.0233</td>
<td>0.9963</td>
<td>1.0060</td>
<td>69.06</td>
<td>68.12</td>
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<td>Mo-L</td>
<td>0.01450</td>
<td>1.1151</td>
<td>1.2994</td>
<td>0.9924</td>
<td>1.4379</td>
<td>2.08</td>
<td>1.91</td>
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<td>Ta-M</td>
<td>0.01360</td>
<td>1.1893</td>
<td>1.5030</td>
<td>0.9975</td>
<td>1.7830</td>
<td>2.42</td>
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<td>W-M</td>
<td>0.01900</td>
<td>1.1912</td>
<td>1.4660</td>
<td>0.9971</td>
<td>1.7412</td>
<td>3.31</td>
<td>3.91</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99.18</td>
<td>97.87</td>
<td></td>
</tr>
</tbody>
</table>

DIFFICULTIES OF X-RAY ANALYSIS IN SEM

- not always possible to excite the K series in an SEM
- when the atomic number increases the energy required to knock-out a K-shell e⁻ also increases
- For example: for elements heavier than tin (Z=50) 75 keV energy is required to produce K x-rays
- There is another way of x-ray production: x-rays passing through a specimen can emit characteristic x-rays with a slightly lower energy
- For example: in a brass specimen zinc Kα x-rays with an energy of 8.64 keV can excite extra copper Kα x-rays with an energy of 8.05 keV
- This effect is known as FLUORESCENCE
DIFFICULTIES OF X-RAY ANALYSIS IN SEM

- It makes quantitative analysis very difficult
- The interaction volume is smallest for low energy e⁻ and heavy elements
- Energy of the x-rays are also important: soft x-rays (low energy, long wavelength) such as carbon Kα are readily absorbed by solids and therefore relatively less escape from the surface
- ZAF correction
QUANTIFICATION

To estimate the amount of an element present, we first determine the number of characteristic x-ray counts from the specimen in a fixed time interval, \( N_{\text{spec}} \), and compare this with the number arriving from a standard of known composition in a similar time, \( N_{\text{std}} \).

The concentration of this element in the specimen, \( C_{\text{spec}} \), should then be given by:

\[
C_{\text{spec}} = \frac{N_{\text{spec}}}{N_{\text{std}}} \times C_{\text{std}} = k \times C_{\text{std}}
\]

Where \( C_{\text{std}} \) is the accurately known concentration of this element in the standard, and each value of \( N \) is a peak count minus a background count.

QUANTITATIVE ANALYSIS

Difficulties

As the two counts \( N_{\text{spec}} \) and \( N_{\text{std}} \) have to be collected at different times, we must be certain that the analysis conditions have not changed.

The specimen is not the same as the standard:

In most of the cases specimen contains several elements.

Its density and average atomic weight of the specimen likely to differ. Therefore: the equation must be corrected for three factors known as atomic number effect (Z), absorption (A) and fluorescence (F).

- **ZAF technique**-

\[
C_{\text{spec}} = k \times Z \times A \times F
\]
QUANTITATIVE ANALYSIS

Z is concerned with the efficiency with which an element generates x-rays. It depends on two factors:

- (i) how far the electrons penetrate before they lose too much energy to excite further x-rays
- (ii) how many electrons are backscattered without exciting any x-rays

When the mean atomic number of the specimen differs considerably from that of the standard, the count rate for an element will not be linearly proportional to the amount present and Z will therefore not be equal to 1.

QUANTITATIVE ANALYSIS-Z Correction

There are two parts to the Z correction: a BS component and a stopping power component.

Remember that as the mean Z of the sample increases the number of electrons that are backscattered (BS coefficient) also increases, and this is what gives rise to contrast in backscattered electron images.

The electrons that are backscattered are ejected from the sample and cannot generate X-rays from it, so if the sample has a different mean atomic number than the standard a correction to the measured X-ray intensity must be made.
QUANTITATIVE ANALYSIS

- The stopping power is the rate of energy loss by the incident electrons per unit of mass penetrated in the sample, and it decreases with increasing mean atomic number, Z.
- The mass penetrated increases with increasing Z, and more X-rays are generated from samples with higher Z.
- The stopping power correction has the opposite sense to the backscatter correction, and the sum of the two corrections makes up the mean atomic number correction, Z.

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QUANTITATIVE ANALYSIS-Absorption Correction

- The X-rays generated within the sample travel in all directions through it, and may be absorbed within it.
- X-rays are either absorbed within the sample or they pass through it – they do not gradually lose energy as electrons do.
- In the SEM, X-ray absorption is most commonly due to the photo-electric effect.
- This means that if the energy of the Characteristic X-ray is equal to the ionization energy of an electron shell of an atom in the sample, there is a strong probability that the X-ray photon will be absorbed and a photo-electron will be generated.

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An X-ray photon interacts with the electron cloud around an atom in the sample. The X-ray photon is absorbed if its energy is close to the binding energy of an electron orbital in an atom of the target. The X-ray photon is absorbed and an electron, a photo-electron, is ejected from the atom.

Clearly, the probability of the X-ray being absorbed is dependent on the other elements in the sample and their ionization energies.

- The probability of the X-ray being absorbed also depends on the distance that it travels through the sample before it escapes and enters the X-ray detector.
- The path length of the X-ray through the sample is given by $z \csc \psi$ where $z$ is the depth in the sample from which the X-ray is generated and $\psi$ is the takeoff angle of the detector.
- The absorption correction factor is given by $\mu \csc \psi$ where $\mu$ is the Mass Absorption Coefficient (MAC).
In general, MACs increase as the energy of the absorbed X-ray decreases so corrections for low Z elements are large while those for high Z elements are smaller.

Also, high Z elements tend to be strong absorbers so large corrections are required for low Z elements in a matrix containing high Z elements.

Specimen and standard would have a different coefficient and the amount of absorption will differ.

The magnitude of this correction can be quite large.

Especially where soft x-rays are emitted from specimens containing heavier elements.

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The X-rays produced in the sample by the electrons of the primary beam have the potential to produce a second generation of X-rays. This process is known as secondary fluorescence, or just fluorescence.

Fluorescence occurs when Characteristic X-rays produced by the primary-beam electrons from one element in the sample have an energy greater than the critical ionization energy of an electron shell in another element present in the sample.
QUANTITATIVE ANALYSIS - Fluorescence Correction

For example, Fe Kα X-rays (E = 6.40 keV) are able to fluoresce Cr Kα X-rays (E_c = 5.99 keV), but Cr Kα X-rays (E = 5.41 keV) cannot fluoresce Fe Kα X-rays (E_c = 7.11 keV). In this case, in an Fe-Cr alloy, the measured intensity of the Cr Kα X-ray will be too high although there will be little effect on the measured intensity of the Fe Kα X-ray.

F cannot occur within a pure elemental standard. Fortunately, it is a very inefficient process and only a very small proportion of high energy x-rays excite lower energy fluorescent radiation.

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QUANTITATIVE ANALYSIS

However, when elements of nearby atomic number are present, as tends to happen for example in steels (Cr=24, Mn=25, Fe=26 and Ni=28) fluorescence effect can be important. One of the worst cases is that of chromium in steels where a correction of %15 (F=0.85) may be needed.

With ZAF correction using computers, concentrations to be calculated to about + -2% with WDX and 6% with an EDX

For quantitative analysis the specimens must be flat. This is especially a must in WDX due to the Rowland circle

Also, it is difficult to find pure standards: gases, low density vs
SUMMARY

- EDS analyses X-rays emitted from a region of the sample—typically about 1 micron in size
- X-rays have an energy characteristic of the element from which they are emitted
- EDS detectors use a Si or Ge crystal to detect the X-rays and their energies
- From the EDS spectrum, the peaks can be identified to determine what elements are in a sample
- The number of X-rays is proportional to the amount of an element in a sample

Transverse section of Pinus sylvestris (Scots pine) showing the latewood portion of the growth ring. This surface shows latewood tracheids (transportation and structural cells) and also part of a ray (cells for storage of food substances). EDX spot analysis of this wood sample using Oxford Instrument’s INCA Energy shows a small chlorine peak, which results from treatment of the wood with a preservative.

The sample charges excessively unless carbon coated. Other types of coating cannot be used due to the very low levels of chlorine used in the preservative, with which the wood is treated.

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XRD

e⁺ gun
sample
target

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SEM microanalysis with WDX

e⁺ gun
sample

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