INCAEnergy

Spectrum Synthesis – Accurate estimation of the
Limit of Detection for any sample

What affects limits of detection:

- A common question heard by many microanalysts is “what is your limit of detection?”
- In the electron microscope, there are a large number of parameters which can effect the limit of detection:
- Analysis conditions
  - Count time
  - Beam current
  - Beam accelerating voltage
- Detector geometry
  - Take off angle
  - Solid angle
- X-ray absorption
  - Composition of the matrix
  - X-ray line measured
- This makes practical experimental determination of limits difficult and time consuming. Therefore, most published detection limits are based on spectra collected from simple pure or binary materials, and calculated by mathematical extrapolation. This can make the published data misleading when analyzing real samples
- For applications where reliable detection of elements at very low concentration is important, we need to accurately know:

1. The limit of detection for the element in the matrix being analyzed
2. The optimum analysis conditions to use to ensure efficient detection of that element

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How can we determine the limit of detection?

- A useful theoretical estimate of detection limit can be calculated from a spectrum using the following equation:

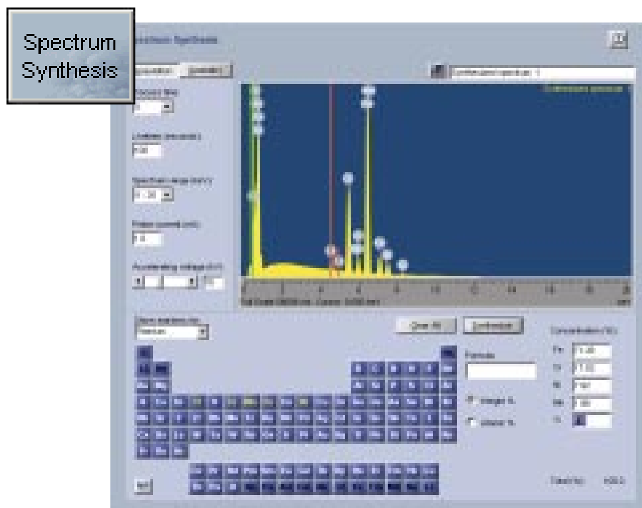
$$\text{3sigmaLOD}=3*\sqrt{B}*C/P$$

Where:
B is the number of background counts and $3\sqrt{B}$ is the 3 sigma error on the background measurement
C is the concentration of the element in the sample measured
P is the number of counts in the X-ray line measured after subtracting background

Therefore the LOD is the level of C the concentration, when the number of counts in the X-ray line P is the same as the 3 sigma error of the background measurement. This theoretical estimate assumes that in an unknown sample, background subtraction will be perfectly accurate and that P and B are measured by integrating over an energy window of the same width. It also ignores the effect of the matrix.

- A more practical solution is provided by the **INCA**Energy Spectrum Synthesis software, which
  - Predicts full spectrum and absolute cps/nA/sterad
  - Works for 5-30keV for elements Z=6-92
  - Proven Peak/Total area intensity accurate to within 7% standard deviation
- Using this software a spectrum can be accurately calculated for any composition under any range of collection parameters and geometry conditions

Spectrum synthesis



Acquisition | Geometry
Working distance (mm): 12
Tilt (degrees): 0
Azimuth (degrees): 0
Detector retraction (mm): 3
Detector area (mm2): 10
Solid angle (mstr): 14.5
Take-off angle (deg): 35.0
Restore defaults

To generate a spectrum for limit of detection estimation using Spectrum Synthesis:

- Enter the composition of the sample matrix
- Add 1wt% of the element to be analyzed (this is sufficient to calculate a precise value without significantly changing the matrix composition)
- Select the acquisition parameters to be used
- Check the geometry parameters are consistent with the microscope that will be used for analysis
- Synthesize the spectrum

Quant

Quant

Summary results :

Element	Weight%	Atomic%
Ti	1.07 +/- 0.03	1.23
Cr	18.51 +/- 0.07	19.65
Mn	1.93 +/- 0.06	1.94
Fe	70.80 +/- 0.11	69.96
Ni	7.69 +/- 0.09	7.22
Totals	100.00	100.00

- A realistic estimate of the detection limit for the element is calculated in the summary quant results window
- The +/- value shows the 1 sigma error, therefore in this example the 3 sigma detection limit for titanium in a steel matrix for the collection and geometry parameters chosen would be 0.09wt%
- This value also takes into account the errors resulting from the processing of the spectra:
  - Background subtraction
  - Filtered least squares fitting (FLS)
- Peak overlap, a common issue in EDS, is also accounted for using this technique

Using Spectrum Synthesis to show how detection limits can vary when measured in different materials or under different conditions

- Using the method above, limits of detection have been calculated for the element zinc when:
  - Analyzed in Stainless steel and organic matrices
  - Analyzed using 25, 12, and 5kV
  - Analyzed using Zn K and Zn L series
  - The results of this analysis clearly show that one detection limit calculation for zinc would not be applicable for every material, or all collection parameters
- For example
  - Lower detection limits are achievable for zinc in organic materials
  - Use Zn L lines for measurement unless using a high accelerating voltage
  - At 12kV the overvoltage is insufficient to detect small amounts of zinc using the K lines

Matrix	kV	ZnL	ZnK
Steel	25	0.39	0.15
Steel	12	0.33	1.5
Steel	5	0.45	
Organic	25	0.15	0.09
Organic	12	0.15	1.02
Organic	5	0.12	

*3 sigma limits of detection in weight% estimated using **INCA**Energy quantitative analysis software from spectra synthesized with 1% of the element and 99% of the matrix present. Matrix composition in weight%; Steel: Fe 71.28, Cr 17.82, Ni 7.92, Mn 1.98; Organic: C 84.88, O 14.13. Collection parameters: 0.5nA beam current, 200s live time, 35deg take off angle, 7.5 milli steradians solid angle, resolution 133eV at 5.9keV

Using Spectrum Synthesis to show the effects of X-ray absorption

In reality it is not easy to predict the effect of X-ray absorption from the mean atomic number of the matrix. The proximity of the measured element line to an absorption edge can have a large influence. This effect is strongest at energies very slightly higher than the absorption edge. For example, if we study small amounts of aluminum, phosphorus and sulfur in a silicon matrix at 20kV, the effect of absorption by the silicon matrix is clear:

- Al K lines are below the Si K absorption edge, and show minimal absorption
- S K lines are notably higher than the Si K absorption edge and show some absorption
- P K lines are very slightly higher than the Si K absorption edge and show the highest absorption
- The effects on detection limits, calculated using Spectrum Synthesis, are shown below:

Matrix	kV	Al K*	P K*	S K*
Si	20	0.18	0.42	0.3

Using Spectrum Synthesis to optimize collection parameters for efficient detection of trace elements

- Spectrum Synthesis can also be used to determine what microscope conditions would give the lowest detection limit
  - For example from the data calculated for zinc in an organic matrix, the best limit of detection would be attained by measuring the Zn K series using an accelerating voltage of 25kV
- Knowing the amount of an element in a material this method can also be used to find the conditions at which this element can be detected most quickly
  - by determining the most efficient accelerating voltage
  - by calculating the count time that will be required to detect the element successfully. Why count for 100s if 50s would be sufficient?

Conclusion

- Limits of detection in real samples can vary widely due to the large number of parameters that can effect them
- Absorption is sometimes counter-intuitive because of the sudden changes across absorption edges
- Rule of thumb extrapolations from calculations based on data collected from real samples can be misleading
- Accurate estimates of detection limits which account for all effects can be easily calculated using Spectrum Synthesis, allowing reliable determination of the presence or absence of trace elements
- Spectrum Synthesis can also be used to optimize the detection of trace elements, so that low concentrations can be detected most efficiently

- For further information, please request a copy of Duncumb, P., Barkshire, I.R., Statham, P.J. (2001) Improved X-ray Spectrum Simulation of Electron Microprobe Analysis. Microscopy & Microanalysis 7, pp 341-355.

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