

## Quantitative Analysis: EDS: Standardless, or with Standards?

Our goal is to test out the ability of the Oxford Aztec EDS software to provide a reliable quantitative analysis, without explicitly acquiring counts on standards. We will follow Oxford's instructions, and acquire reference counts on a piece of Co (they recommend Co as it is more resistant to oxidation than other metals). This then allows the software to recast the user's measured counts to some normalized current setting, so that "true analytical totals" can be determined, as one measure of the trustworthiness of the "standardless" analysis.

Today we are using two mounts: a Co mount, and a stainless steel mount with ~13 minerals and glasses, for which we may know "representative compositions" --this mount is going to be evaluated by us also with WDS, and by others, as a "round robin" exercise (See Appendix 2).

This stainless steel mount has 13 positions which are filled with 3 synthetic glasses and the remainder natural minerals. Some of these are potential EPMA standards, assuming they are homogenous (does it matter if there are easily avoided inclusions???) and their chemical composition is certain. So there are many, many "targets" for us to evaluate using EDS and later WDS.

➔ The first goal being to see how well we can get EDS compositions to match WDS compositions, first EDS "standardless". The second goal being to see how many (some I hope) are homogeneous enough to be considered EPMA standard material.

1. Measure and then place both mounts should be in the SEM. We will use 15 kV. Set the working distance to 10 mm. Set Probe current initially to 90 (will change it later based upon deadtime). Turn on the Aztec software, sign in to the appropriate folder and project.

2. Drive to the KK2 sample in the sample mount (we use it to start with as it has a wide range of elements) and set the deadtime to ~35%. (Note: once we set probe current, we use that same value throughout; **also do not change the stage Z working distance—ADJUST THE OBJECTIVE LENS FOCUS**). Store the position in the Hitachi software (if not already). Having verified that, then drive to the Co metal. Focus, then zoom in so whole field of view filled, high mag.

3. Be in EDS-SEM. Instead of Point & ID, select Optimize.

Routine= Beam Measurement

Element=Cobalt

Settings: 15 keV; 2048 channels; Process Time 4; Total counts in spectrum=2,000,000

Click Start, wait until finished.

4. Drive to NIST K530 glass. This is a Mg-Al-Si-Ca-Fe-O glass which should be close to the published K412 composition (that was the intention). We'll see how AZtec quantifies it. Appendix 2 lists some "reference" and "nominal" compositions.

5. Switch to Point & ID.

6. Scan Image. New Site. Start.

7. Acquire Spectra. 15 kV, 2048 channels, 4=process time, 60 sec live; pulse pile up corr on. It will run for 60 sec. We will spend 10-15 minutes on K530 ("like K412"), using it as a test platform to understand how AZtec "does" quantitative analysis. Eventually acquire 5 spectra—but first, let's look at the first spectrum when it is completed...

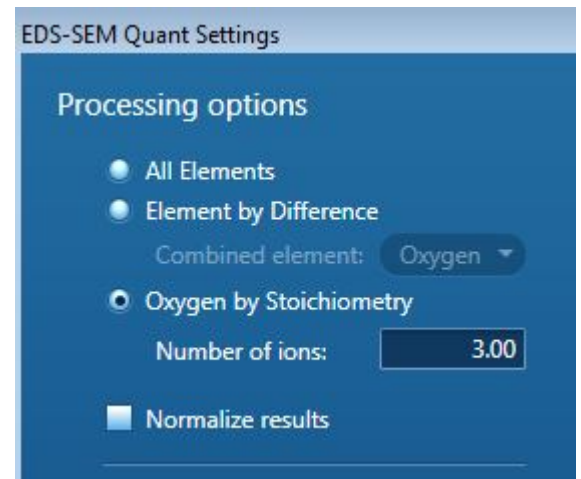
8. But first, we need to do some preliminary setup: Jump ahead to Calculate Composition chevron, and click Settings.



There are 4 options for samples with oxygen present (most materials we will look at today in lab):

- (1) All elements – normalized
- (2) All elements – not normalized
- (3) Oxygen by stoichiometry – normalized
- (4) Oxygen by stoichiometry – not normalized

We will play with these four options. But let's start with All elements – normalize results. Click Apply and Save at bottom right.



9. Go to the Confirm Elements chevron; click Settings. Then click Fitted Spectrum.

First, a bit of explanation about useful features:

**Show Fitted Spectrum:** overlays pink "Fitted Spectrum" onto actual. A theoretical Background curve has been fitted to the obvious background regions, and "auto ID'd" peaks are shown. If a peak shows up (yellow) and is missing from the pink Fitted Spectrum, use the orange "?" tool to double click the peak, and possible choices are shown to the right. If one matches, add it to the Periodic Table (update). "The Fitted Spectrum shows whether the fitted peak areas are accurate, but does **not** give any indication of any errors in the conversion of areas to elemental composition."



Do you see any spectral features (peaks) that are not accounted for with the auto-ID'd elements? Probably yes... If so, then first expand the area of interest (mouse scroll wheel) and then point at the questionable peak and double click, and now "Candidate Elements" pop up to the right. If you see one you think fits, double click on it, and it is added. If the pink Fitted Spectrum gives a better fit, it might be a missing element; but also use common sense.

When you are satisfied, go back to Settings and select Theoretical Spectrum.

First, some explanation of this feature.

**Show Theoretical Spectrum:** overlays a blue-green "Theoretical Spectrum" onto actual. "The Theoretical Spectrum shows the results of a theoretical calculation that simulates the

spectrum for a specimen with the elemental composition given in the analysis results. A theoretical overlay that looks similar to the measure spectrum gives some confidence that the overall analysis is reliable.”

10. When you are satisfied with the Theoretical Spectrum, click Calculate Composition. Top Left: Available Templates; select Summary Table-multiple spectra (can change). If data in table left over from previous work, click :”Clear all Spectra” on bottom left. Back to right, Data Tree, select the specimen and Spectrum, then click “Add Selected Spectra” button and it will put it in the table. Look at the total: a perfect 100 wt%! Magic! Do you necessarily believe it? \_\_\_\_\_ Compare with the “book values” in attached spreadsheet.

One way available to evaluate it for accuracy is to turn off the “normalize” option. Back to Settings, uncheck the Normalize results button, and click the Apply and Save button on bottom. What’s the unnormalized analytical total? \_\_\_\_\_ wt%

Recall that you had selected the “All elements” button in the Processing options. Now go and rerun with Oxygen by stoichiometry. For both normalized and non-normalized? Is there any difference? \_\_\_\_\_ If so, what might be the explanation? \_\_\_\_\_ (Don’t record these 4 numbers for the one spectrum; you will record the averages for 5 spot analyses.)\

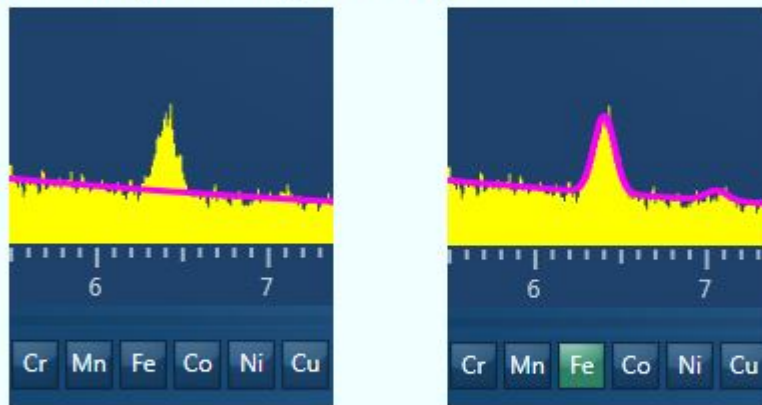
Write short evaluation of “standardless” and “sort of with-standards” EPMA with the Oxford AZtec software and the difference between explicitly measuring oxygen and using oxygen by stoichiometry.

Appendix I

### Show Fitted Spectrum

You can overlay the Fitted Spectrum on your measured spectrum to help you to validate the accuracy of spectrum processing. Peaks that have been fitted to the underlying spectrum data are added to a theoretical background curve that has been fitted to background regions in the spectrum, and the result is displayed as the “Fitted Spectrum”.

If you omit or incorrectly assign any elements, the overlay is likely to differ from the measured spectrum. As you add or remove elements from the element list, the fitted spectrum changes accordingly, and thus you obtain a better fit.



When you add an element, the software adds peak shapes for all excited line series (K,L,M) to the fit. Adding peak shapes will usually improve the fit but the “Fitted Spectrum” will not indicate whether the relative line intensities and background level are realistic and consistent with the analysis result. When you have achieved a good fit for the “Fitted Spectrum”, you can use the “Theoretical Spectrum” overlay to check whether the analysis results are realistic and consistent with the measured spectrum.



## Show Theoretical Spectrum

You can overlay the Theoretical Spectrum on your measured spectrum to help you to determine whether your elemental composition (weight % or atomic% ) analysis is realistic.

Analysis errors can occur if any of these conditions arise:

- The geometry is incorrect.
- The specimen surface is not flat over the region where any X-rays exit towards the detector
- The beam penetrates to layers of different composition or scatters sideways into different materials. The region of the specimen that is excited by the electron beam must be homogeneous.
- Any elements are misidentified or omitted. This might occur if there is no excited line suitable for analysis.
- The beam energy is incorrect or the specimen is charging.

The Fitted Spectrum shows whether the fitted peak areas are accurate but does not give any indication of any errors in the conversion of areas to elemental composition.

The Theoretical Spectrum shows the result of a theoretical calculation that simulates the spectrum for a specimen with the elemental composition given in the analysis result. A theoretical overlay that looks similar to the measured spectrum gives some confidence that the overall analysis is reliable. If you are not sure about any peak in the spectrum, you can change the elements in the "Confirm Elements" periodic table to obtain a better fit. If several alternatives seem equally likely, you can often decide by overlaying your spectrum with the Theoretical Spectrum. For example, if you see a small peak that seems a good match for the K line of an element (such as Zn K), you expect to see a peak from Zn L. The Theoretical Spectrum shows you whether the Zn L line has the right intensity. If you see a small peak at low energy (such as V L), the Theoretical Spectrum shows you whether the higher energy peak from that element (such as V K) should also be visible for a specimen with the composition given by the analysis result.

The theoretical simulation calculates the expected ratios between K, L and M peaks, and includes effects (differential excitation and absorption of individual X-ray line emissions) that can change the peak shape based on the composition of the specimen. For example, the peak shape for Fe L is different in FeS<sub>2</sub> and in pure Fe.

If the specimen is coated with Carbon, the calculation includes the effect of the coating, and also simulates a corresponding carbon peak. If you selected "Normalize Results" in the Quant Settings, the software normalizes the Theoretical Spectrum to match the area of the measured spectrum. Otherwise, the software uses the beam-calibration measurement to simulate a spectrum that is obtained at the same beam current. The simulation has been tested on a wide range of materials at 5kV and 20kV where simulation errors are typically less than 10%, and it is suitable for any accelerating voltage between 0.5 and 30kV.

## Appendix 2

This stainless steel mount has 13 positions which are filled with 3 synthetic glasses and the remainder natural minerals. Some of these are potential EPMA standards, assuming they are homogenous (does it matter if there are easily avoided inclusions???) and their chemical composition is certain.

There are 3 silicate glasses: an experimental NIST glass K530 (K412-like), and 2 "andesite glasses", 1 doped with Na and the other with K.

There are 4 minerals from the famous Kakanui site in New Zealand: pyrope, augite, anorthoclase and kaersutite. The augite has a part full of iron oxide and sulfide inclusions.

There are 5 minerals from our UW mineral collection: ankerite (Fe-Mg carbonate), plagioclase (~An78), Hedenbergite (Fe-rich pyroxene), Kilbourne Hole olivine (also Marjahlati olivine), and also fayalite from the Wards Science company (many Mn-rich and quartz inclusions). There "was" a F-rich apatite but it fractured and little remains, and the hole with filled with zircon + monazite sand.

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STILL IN PROCESS OF REVISION....