

5 Guidelines for Quantitative (Standards-Based) EDS Analysis of Minerals

WWDD? (What would Dave do?)

David Mogk, Asst. Director ICAL

October 10, 2025

Careful planning and execution of established protocols are needed to obtain accurate EDS elemental data. The following guidelines will help ensure that your session on the ICAL FESEM/ICAL instruments will be efficient, productive and produce meaningful results.

Think through your analytical session BEFORE you start work on the FESEM—there are many decisions to be made that will optimize the quality of your results.

Preparation for Your SEM/EDS Session

- **Clearly define the research questions** you are addressing, and **how these data will be interpreted and used.**
 - What can be learned from EDS elemental analysis, e.g., phase identification based on composition, evidence of compositional zoning, EDS maps to locate trace phases defined by specific elements in a matrix, etc.
 - How can the EDS data be integrated with other SEM imaging such as secondary electron imaging that defines particle size, shape, morphology, distribution; and back-scattered electron (BSE) that discriminates phases based on mean atomic number (roughly proportional to relative density)?
 - How will the data be used: compositional zoning to document history and process of crystallization; alteration and replacement textures; mineral reactions; geothermobarometry, etc.?
 - Use geological context and insights to inform your analytical strategy: what is the rock type, what geochemical system was sampled, what prior information is available from the literature or from earlier work? This geological context will place constraints on what is expected, permitted to occur (or not) in nature, associated with related minerals, etc. and will greatly increase the likelihood of successful experiments and correct interpretations.
- **Sample preparation**
 - In general, **polished thin sections or circular probe mounts are preferred for BSE imaging and EDS mapping and analysis.** This allows you to do optical petrographic analyses prior to SEM/EDS work. Flat samples minimize issues related to take-off angle of secondary X-rays, shielding or screening of X-rays from the flight path to detectors due to morphologic features, and to address charging problems associated with irregular samples.
 - Grain mounts can be used to obtain EDS data, but grain morphology can introduce issues described above. In addition grains may overlap that will result in a “hybrid” analysis as the excitation volume may be as deep as 3 microns, generating secondary X-rays from more than 1 grain and thus making quantitative analysis impossible. Grains mounted in an epoxy puck

and then polished work quite well for imaging (BSE), elemental mapping and spot analyses (EDS). Cathodoluminescence (CL) imaging may also provide good spatial maps to select areas for spot analysis.

- **Document and map key features of interest on the sample prior to introduction into the SEM.** Reference marks can be used to identify minerals or textures of interest. I use India ink with a quill point pen, but Sharpie marks can also be used. Draw a map with features such as distinct grains, fractures, veins, etc. or simply take a photo with your cell phone or photomicrographs with a petrographic microscope. PLEASE CHECK that your photomicrographs are not mirror images of what will be seen in the SEM. This confusion can cause much wasted time trying to find areas of interest. *It is extremely difficult to navigate on the micro-scale fields of view inherent in SEM imaging so anything you can do to locate interesting features ahead of time will help you to effectively obtain the data you need to address your research question.*
- **Sample coating: Carbon coats are preferred for EDS analysis to address charging issues on insulating rocks or fossils.** Carbon has a smaller atomic cross-section that allows a higher yield of secondary X-rays to reach the detector. In some cases, the choice of a metal coating medium may produce peak interferences with elements of interest, e.g., Ir has significant peak overlap with P. **Be sure to apply the coat at roughly the same thickness as the EDS standards used, ~20 microns** (use the thickness monitor on the carbon coater). Other metal coats such as Au, Au/Pd, Ir etc. can still be used for EDS, but the X-ray flux will be a bit diminished, and elemental peaks of the coating material will be part of the overall EDS spectrum. These metal coats are typically used to obtain optimal high-resolution imaging. The type and thickness of the conducting coat must be entered into the software prior to acquisition of EDS data.

Instrument Set-Up

For best elemental analysis using EDS, these factors should be considered (and note, instrument parameters that produce the best EDS results are not those that will produce the highest resolution images). Directions for the Standards of Practice are written in detail in the FESEM lab manual, but here is an overview that includes the rationale for these selections.

- **Beam Voltage:** The energy of secondary X-rays produced by the e-beam will be about 2/3 of the energy input from the beam voltage. The X-ray spectrum for most elements (K-alpha, or L-alpha) is covered in the interval of 0–10 KeV so a beam voltage of 15 KeV is usually sufficient.
 - However, there are a number of peak overlaps in this range that require confirmation of other peaks that may be >10 KeV; e.g., S and Pb have significant peak overlaps, but a diagnostic Pb peak at ~10.8 KeV can unequivocally confirm if Pb is present, so a beam voltage of 20 KeV is

recommended. Similarly, confirmation of As can be documented in this range.

- Be aware that some elements may volatilize under the e-beam (due to thermal ionic diffusion). Na is known to devolatilize in feldspars. The solution can be to a) decrease the beam voltage to 10 KeV, or b) widen the analysis region to analyze an area rather than a single spot.
- **Apertures:** maximum signal is needed for both BSE imaging and EDS analysis, so be sure to **pick the 60-micron aperture** (smaller apertures will produce higher resolution images). **Select the High Current option.**
- **Counts:** The Oxford EDS detectors are quite efficient. **Set the Spectra Acquisition Settings to acquire at least 1,000,000 counts.** Under “Point and ID”, “Acquire Spectra” choose Settings and instead of a timed spectrum acquisition choose for a specified number of counts and set the threshold for >1 million counts. This will optimize the signal-to-background ratio and will provide enough counts to a) help resolve peak overlaps, and b) to allow peaks of trace elements to emerge from the background.
- **Beam Measurement is critical.** To optimize, *before inserting your sample into the chamber*, place a piece of copper tape on your sample off to the side without obscuring the areas of interest. Before any other spectral measurement on your sample, navigate to the Cu tape and choose “Optimize” and “Beam Measurement” while placing the beam on the tape. The software will automatically calibrate the beam intensity to the standards, whereby the count rates for all following analyses will be referenced to this beam measurement on Cu.
- **Working distance (pole piece of column to sample) should be ~8.5 mm.** For grain mounts or other samples with topography, be careful to avoid driving the sample and stage into the pole piece. (Working distance can be smaller for high-resolution imaging).
- **Be sure to acquire a well-focused image of the sample.** Out-of-focus fields of view will result in incorrect production and detection of the secondary X-rays.
- **Don’t forget to physically insert the EDS detector** (a surprisingly common oversight).
- **Data acquisition is straightforward and intuitive in the Oxford Aztec software.** (Scan image, Acquire Map or select “Point and ID”, be sure to access settings, acquisition mode and select counts—confirm >1 million).
- **Make sure that all peaks are identified!** The quantitative analysis routine will expect that all major elements are included.
 - **Look for possible peak overlaps (S-Mo-Pb for example or Ti-Ba).**
 - **Particularly for the transition metals, some of the K-beta peaks may overlap with the K-alpha peaks of adjacent elements.**
- **Calculate Composition; select standards:** under Advanced, choose User Identified and select from the pre-set list of recommended standards (see tables at the end of this report).
- **Process the Data:**

- If you ran the Beam Measurement at the beginning of your session, do not normalize the data to 100%! A good analysis should be +/-1%, but there are many reasons why a 100% analysis is not obtained: hydroxyl (not measured) in the structural formula of the mineral (2.5% for amphibole 2–4% for biotite, up to 12% for chlorite). Or you could have excess Oxygen related to ferric iron (vs ferrous iron) in the sample. Or one of the elemental analyses could be erroneous due to low secondary Xray production, matrix effects, etc.
Bottom line: when you normalize to 100% you are distributing this error equally among the measured components and this will lead to an inaccurate result.
- **For geologic materials, the elements are typically reported as wt% oxide; you can choose this option if analyzing most minerals. Or you can select data output as wt% or at%.**

Selection and Use of Standards

Standards-based analyses are superior to analyses reported from the Oxford Aztec software that uses “internal” or “factory” standards. Analytical results that are produced using these internal standards are good for rapid identification of elements present and to determine relative elemental abundances, but are considered to be ‘semi-quantitative’ at best. Recent tests by ICAL staff indicate that the factory standards are probably pretty close, to within a few relative wt%. In most cases, these results are “close enough”. But if you plan to do thermodynamic modeling (e.g., determining activities of components; use in geothermobarometry; use in elemental partitioning experiments, etc.), you will want to go a step further and apply standards-based analyses.

ICAL uses a certified block of 53 mineral standards from Astimex that will cover most compositions of minerals that occur in nature. Consider the following when selecting standards:

- Standards should be selected according to the mineral group to be analyzed; e.g., feldspar standards for feldspar unknowns.
- Standards should approximate the mean atomic number of the unknowns; this is why the factory-based internal EDS standards which are typically pure metals or alloys are not appropriate for analysis of silicate, carbonate, etc. minerals.
- It is usually better to pick standards with somewhat higher concentrations than the unknown; i.e., it’s better to interpolate counting statistics rather than extrapolate, as the X-ray yield becomes non-linear at greater and greater concentrations.
- Recommended standard blocks used for different mineral groups such as feldspars, pyroxenes, carbonates, etc. are compiled at the end of this report. These are recommended selections of standards that will provide a good place to start.
 - You should feel free to substitute a different standard for select elements if you are not getting good analyses for that element, following the recommendations above.

- We may not have all elements represented in our standard collection or the standards may not have appropriate concentrations; e.g., we do not have a V standard that might be needed for magnetite analysis; our Co standard may be too low concentration for some applications.
- For some unusual compositions, you may need to either make or acquire your own standards. Sources include the Smithsonian, NIST, USGS and corporate vendors.

EDS Analysis

BE CRITICAL OF YOUR EDS RESULTS! DON'T ASSUME THE NUMBERS THAT ARE COMPILED AUTOMATICALLY BY THE AZTEC SOFTWARE ARE RELIABLE DATA. THERE ARE MANY POTENTIAL PITFALLS. So, consider the following:

- The concentrations and counts for each standard are stored in the Aztec software and can readily be accessed and applied using the Quantitative Analysis routine. The FESEM is fairly stable over weeks to months, and the standard counts should be pretty reliable. Still, it would be good practice to recollect counts on the standards you select to use and update the standards database. **Best practice: restandardize to get the best results.**
- Keep in mind that the **detection limits for EDS are ~0.1 wt%**. So, trace elements will most likely be “lost in the background”.
- Also keep in mind that the penetration of the e-beam (i.e., **the excitation volume**) is **on the order of 2–3 microns** depending on beam voltage and nature of the matrix material.
- This means you have to **pick your analytical spots carefully. Use SEI or BSE imaging or an EDS Elemental map to identify areas that are relatively homogeneous and to document areas with any morphologic or compositional irregularities on the sample. Avoid cracks, veins, and obvious alteration.** Grain rims may be problematic if they are tapered, as you may get an aggregate signal from one or more grains that will yield a “mixed” analysis that is meaningless (of course you may be looking for grain rim compositions to demonstrate chemical zonation of minerals such as feldspars or garnets).
 - If you are looking at **minerals that decorate the surfaces of other minerals**, or perhaps micron-scale inclusions, **just be aware that you may get a mixed analysis**, and you will possibly need to subtract the contribution of the underlying grain.
 - **If you are looking at grain mounts, try to find isolated grains to analyze;** a little sand pile of grains most likely will yield a mixed analysis from 2 or more grains.

- **Be aware of peak overlaps that must be resolved.** EDS quantitative routines can only measure the area under each peak, so if there are overlapping peaks this will give erroneous results.
 - For sulfides, peak overlaps of S, Pb and Mo are well known.
 - Similarly, for the transition metals there may be peak overlaps of K-alpha X-rays of one element and K-beta X-ray peaks of another element.
- **Analyze for the full suite of elements expected to be in your mineral unknown.** As a guide, look for published analyses in any Mineralogy text, a mineral atlas such as Deer, Howie and Zussman, or use the MINDAT database <https://www.mindat.org/>
 - **It's important to have a sum near 100% for each analysis to be able to calculate a stoichiometric mineral structural formula.** For example, for alkali feldspars the major elements that might be expected are K, Na, Ca, Al, and Si; however, alkali feldspars may also have significant concentrations of Ba (celsian component) and even Pb (amazonite) and in some cases, ferric iron may substitute for Al.
 - **In reporting your results it's a much stronger statement to report "we looked for Ba in microcline and didn't find it" (reported as n.d., not detected) rather than reporting nothing and leaving to doubt whether it's there or not and you didn't bother to look.**
 - **For hydrous minerals** (micas, amphiboles), it's best to also **analyze for halogens (F, Cl)** as there may be significant substitution in the hydroxyl site.

EDS Data Reduction and Evaluation

Once you've obtained your EDS data, you have to do something with it. Careful inspection of your data is critical, and there are some QA/QC procedures you can use to confirm the quality of your data:

- **Direct analysis of the light elements (C, N, O) is always suspect** due to their relatively low X-ray yield under the e-beam. Don't believe quantitative analyses for these elements.
- **Mineral compositional data are typically reported as wt% oxide** rather than wt% element (for historical and practical reasons going back to Goldschmidt). Be sure to select this option in the Aztec software.
 - If you get your analyses in wt% element, to **convert wt% element to wt% oxide**: Divide by the molar mass of the element, and multiply by the molar mass of the oxide. For example, molar mass of silicon is 28.085, and of the oxide is $28.085 + 2 \times 15.999 = 60.08$. Note that you need this to be on a single cation basis. For oxides like Na_2O or Al_2O_3 , you actually need the molar mass of $\text{NaO}_{0.5}$ and $\text{AlO}_{1.5}$.
 - You have to be careful about how you handle Fe. **EDS does not discriminate between ferrous (Fe^{+2}) and ferric (Fe^{+3}) iron—what you get is Fe(total). So, depending on what you know about the mineral unknown, the**

geochemical environment, etc., you'll have to report Fe as one or the other—typically this will be ferrous iron to represent Fe(total).

- For anhydrous minerals, the sum of the oxides should total 100%, $\pm 1\%$.
- You can apply the same type of **recalculation for carbonates and sulfates by casting the cations as a wt% of carbonate or sulfate**.
- **For hydrous minerals, recognize that amphiboles will have 2–2.5 wt% hydroxyl; micas ~4% hydroxyl; chlorites 10–12% hydroxyl**, etc. This is why it's also important to analyze halogens (F, Cl) as they will occupy some of this hydroxyl site in these hydrous minerals.
- **Also, for ferric iron there will be excess oxygen to account for if iron is reported as Fe_2O_3 rather than FeO.**

Critical Review of EDS Data

It is essential to review the quality of your EDS data—don't just accept the numbers as they come off the computer screen and dumped into a report data table. Three simple tests will give you confidence in the quality of your data:

- **First inspection: did you obtain a close to 100% analysis?** Typically, $\pm 1\%$ is good. Amphibole will be 97.5–98.0; micas ~96%; chlorites ~88%, etc. If not, could there be elements missing from your analysis?
 - **Do not let the program renormalize the data to automatically sum to 100%!** This assumes the analytical error is equally distributed among all the elements and this is a dangerous assumption. You could have simply not analyzed for an element that is important to the composition of the mineral. You could have unresolved peak overlaps. You could have loss of an element such as Na due to devolatilization under the beam. **Use the sum of the oxide components (with water as needed) to determine if you have a complete analysis.**
- **Stable minerals must be stoichiometric, and all crystallographic sites must be filled.** Refer to the website: *Mineral Formulae Recalculations* <https://serc.carleton.edu/18592> where there are numerous spreadsheets available to recalculate mineral structural formulae for different mineral groups. The output of these spreadsheets will be the number of atoms per formula unit for each element in a given mineral type.
 - These programs convert wt% to atomic proportions (divide wt% by atomic mass), and then normalize to a fixed number of oxygen (for silicate minerals): feldspars have 8 oxygen per formula unit; pyroxenes 6 p.f.u., garnets 12 p.f.u., olivine 4 p.f.u., and the hydrous minerals get more complex with amphiboles normalized to 23 oxygen p.f.u.
 - The molecular proportions of the elements are then assigned to appropriate crystallographic sites: Si, Al—tetrahedral; Fe, Mn, Mg—octahedral; Ca—cubic; Na, K—12-fold sites. This should result in a complete structural formula.

- For example, the generic formula for microcline is KAlSi_3O_8 . After the recalculation, normalized to 8 oxygen, there should be one atom K, one atom Al, and 3 atoms Si per formula unit. In detail, minerals in nature have complex compositions and an actual formula might be something like $(\text{K}_{0.9}\text{Na}_{0.1})\text{Al}(\text{Si}_{0.95}\text{Ti}_{0.05})_8$. The point being that there must be 1 atom equivalent in the large alkali site, one Al in one tetrahedral site, and another three (Si+Ti) in the remaining 3 tetrahedral sites. **You can't have holes in the crystal structure — all sites must be fully occupied by elements of appropriate charge and ionic radius. Are all elements accounted for in appropriate stoichiometric proportions in your sample analysis?**
- **Stable minerals must have a neutral charge.** With reference to the structural formula determined above, determine the sum of charges attributed to each element in its stoichiometric proportions. **If you've demonstrated charge balance, this is a good check on the quality of the analysis.**
 - For example, microcline has a structural formula of KAlSi_3O_8 . In terms of charge balance: $\text{K} (+1) + \text{Al} (+3) + 3\text{Si} (+4)$ is a net cation charge of +16 and this exactly balances the net negative charge of $8 \text{ O} (-2) = -16$.
 - For iron with variable +2 and +3 valence state, IF you have a complete analysis that accounts for all elements present (i.e., all charge is accounted for), you can use this charge balance argument to calculate the ferric/ferrous iron ratio of a mineral. The spreadsheets will iteratively calculate the amount of Fe that must be represented as ferrous and ferric iron to satisfy the requirements of stoichiometry and charge balance.

A Recommended Flow Chart for Mineral Analysis Using FESEM/EDS Aztec Software

1. **Define research objective:** e.g., obtain compositional data on garnet, hornblende and plagioclase in a garnet amphibolite for geothermobarometry.
2. **Prior to Analysis**, map (optically in thin section) sample with fiducial markers to aid in navigation to find grains of interest. Identify non-altered grains with straight grain boundaries and no evidence of alteration, veins or cracks.
3. **Carbon coat, 20 microns. Attach a small strip of Cu tape.**
4. **Select operating conditions;** 15 KeV beam voltage, 60-micron aperture, acquisition terminates at 1,000,000 counts. **Select standard sets for minerals to be analyzed. Restandardize if necessary.**
5. **Navigate to Cu tape and run Beam Measurement calibration.**
6. **Navigate to region of interest (ROI)1.**
7. **Obtain large format (wide field of view, low magnification) BSE image of ROI.** Use this "reconnaissance" view to check for heterogeneity of the sample, to identify locations of different minerals of interest. For example, garnets will be bright, amphiboles will have lower intensity gray levels, plagioclase less, quartz dark gray; other accessory minerals such as apatite, oxides (ilmenite, rutile) or sulfides may become evident.

- a. **Obtain EDS elemental map of same area**—elemental maps will be a good indicator of the location of different mineral species: high Al = garnet; Na, Ca = plagioclase; complex Na, Mg, Al, Si, Ti, Fe spectrum = hornblende, etc.)
- 8. Use these recon BSE and EDS maps to define specific areas of interest for detailed EDS analysis.**
 - a. **Obtain finer scale BSE image and EDS maps** of inset area.
 - b. **For spot analyses, select spots for specific purposes** such as compare core to rim compositions; identify any inclusions in the host mineral; analyze phases that might be involved in reactions...For solid solution minerals, you might want to obtain a linescan core-to-rim within a grain, or across a grain boundary, etc.
- 9. Repeat as many times as is representative, statistically significant, etc.**
- 10. Prepare EDS report in Aztec software.**
 - a. **Report data to Excel spread sheet**, and as wt% oxide of each element.
- 11. Test data to confirm that a) they produce stoichiometric mineral formulae and b) they are charge balanced.**

Pyroxene		Major Elements								Tr El
OPX: enstatite, hypersthene,		Si	Al	Ti	Fe+2	Mn	Mg	Ca	Na	Cr
34	Olivine (or Diopside) for Mg				x		x			
21	Diopside	x					x	x		
28	Jadeite		x						x	
39	Rhodenite					x				
29	Kaersutite (or Bustamite for Fe)			x	x					
16	Cr-Diopside									x
Notes: For very Mg rich use Olivine for Mg and Fe; Kaersutite will probably be better for Fe for most intermediate compositions										

Garnets		Major Elements								Tr El
Almandine, pyrope, grossular		Si	Al	Ti	Fe+2	Mn	Mg	Ca		Cr
2	Almandine	x	x		x			x		
37	Pyrope	x	x				x	x		
6	Benitoite			x						
10	Bustamite (or 39 rhohdonite)					x				
16	Cr-Diopside									x

Notes: Alm or Py will work for most elements, Alm is best for Fe, Py is best for Mg; Ti will be trace, Cr is also trace except for variety uvarovite. Pyrope (Mg₃Al₂), Almandine (Fe₃Al₂) Grossular (Ca₃Al₂) and Spessaertine (Mn₃Al) garnets will have most of their Fe as Fe+2. Andradite (Ca₃Fe₂) and Uvarovite Ca₃Cr₂) formulae should be recalculated with iron as Fe+3. Normalize to 12 oxygen for structural formulae.

Chlorite	Clinochlore	Major Elements										Halogens	Tr El	
	Talc, Serpentine, Chrysotile	Si	Al	Ti	Fe+2	Mn	Mg	Ca	Na	K	F	Cl	Ni	Cr
15	Chlorite	x	x		x		x							
29	Kaersutite			x	x			x	x					
7	Biotite									x				
10	Bustamite					x								
4	Apatite										x			
45	Tugtupite OR 33 Obsidian for small#													
16	Cr Diopside													x
34	Olivine												x	
Notes: Chlorite standard will be good for most chlorites, talc, and serpentine minerals; for Fe-rich chlorites may need Kaers for Fe; halogens are not important to analyze; Ca, Na, K are minimal and can mostly be ignored; oxide totals should be 88-90-% to account for 12-10% structural water														

Carbonates	Calcite, Dolomite, Rhodochrosite	Major Elements				Tr El
	Siderite Magnesite Aragonite	Ca	Mg	Fe	Mn	Sr
11	Calcite	x				
22	Dolomite		x			
10	Bustamite			x	x	
13	Celestite					x
Note: recalculate wt% element as wt% carbonate; should total to 100%						

Phosphate	Apatite	Major Elements			Trace Elements
		Ca	P	F	REE, La, Ce, Y
4	Apatite	x	x	x	
32	Monazite		x		x
Note: Apatite may have abundant REEs, use 32 Monazite standard; may also have Cl use 45 tugtupite or 33 obsidian; may also have sulfate use a sulfate standard.					

Sulfates	Gypsum, anhydrite, barite....	Major Elements					Tr El
		S	Ca	Mg	Fe	Ba	Sr
5	Barite	x				x	
13	Celestite	x					x
11	Calcite		x				
22	Dolomite			x	n.d.		

Oxides	Magnetite, hematite, rutile, cuprite....	Major Elements							
		Fe+3	Ti	Mg	Cu	Cr	Sn	Pb	Zr
25	Hematite	x							
26	Magnetite	x							
40	Rutile		x						
27	Periclase			x					
14	Cuprite				x				
17	Chromium oxide Cr2O3					x			
12	Cassiterite						x		
20	Crocoite PbCrO4					x		x	
47	Zirconia ZrO2								x

Notes: user will have to make informed decision if Fe is used as a standard as Fe+3 or Fe+2; important for calculating stoichiometry.

Notes: May have to combine sulfide and sulfosalt standards for complete analysis of some compounds; Co uses pentlandite but is only 0.43 wt%, best we can do; Cu use oxide cuprite

Notes: May have to combine sulfide and sulfosalt standards for complete analysis of some compounds; Co use pentlandite but only has 0.43 wt%