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QUALITY CONTROL OF QUANTITATIVE MICROANALYSIS AND REFERENCE MATERIALS

Emma S. Bullock

Carnegie Institution for Science, Earth and Planets Laboratory
5241 Broad Branch Road NW, US-20015 Washington DC, U.S.A.
e-mail: ebullock@carnegiescience.edu

Emma Bullock is the Electron Probe Laboratory Manager at the Department of Earth and Planetary Sciences at the Carnegie Institution for Science in Washington DC. She runs the JEOL 8530F electron microprobe (5 WDS detectors; 2 EDS detectors and CL capability) and the Zeiss Auriga scanning electron microscope (EDS and STEM capability).

Emma obtained her BSc in Geochemistry from the University of Manchester (2001), followed by a PhD in Meteoritics at the Natural History Museum in London and the Open University in Milton Keynes, UK (2005). She studied as a post-doctoral fellow at the National Museum of Natural History, Smithsonian Institution, using mineralogy, petrology and isotope systematics to study calcium-aluminium-rich inclusions (CAIs), the oldest objects preserved from the beginnings of our Solar System. She continued her research into the isotopic systematics and petrology of CAIs at the University of Chicago, before returning to the Smithsonian to take up a position as a Geologist. In 2015, she moved to the Carnegie Institution for Science to operate the electron microprobe and scanning electron microscope. Her current research activities include collaborations with scientists studying samples from the Moon and asteroid belt; high pressure samples that simulate the interiors of planets; novel materials; and geological materials. She is heavily involved in the microscopy community and has served terms in the Microanalysis Society (MAS), the local Chesapeake Microscopy and Microanalysis Society (CMMS), and the Focussed Interest Group on Microanalytical Standards (FIGMAS).

1. ABSTRACT

Electron microscopy is a widely used tool for the imaging and analysis of different types of material, from biological samples to metals to geological samples, and many more. Advances in instrument technology, such as field emission electron sources, have vastly improved the stability and capability of electron-beam instruments and allow analysis of smaller volumes of material and lower abundances of elements than ever before. Improvements in computing power allow faster data collection and more options for data processing, and have in many ways simplified the method of analysing a sample and obtaining its composition. There are still many important aspects to consider in order to collect the best data, and users should take care to think about their sample and the type of data they wish to obtain. In this paper, we will look at methods that can help you to obtain high-quality microanalytical data using energy-dispersive X-ray spectrometry (EDS) and wavelength-dispersive X-ray spectrometry (WDS), and ways to identify good standards and reference materials for your work. We will cover the topics of sample preparation, calibrating your EDS and WDS detectors, choosing your analytical conditions, and selecting and maintaining appropriate standard and reference materials.

2. QUANTITATIVE VERSUS QUALITATIVE ANALYSIS

We should first start out by specifying what we mean when we discuss quantitative analysis. In this work, we are referring to quantitative analysis as that in which the X-ray intensities in known materials (standards) are measured and compared to the intensities obtained from our unknown material. Standardised (also known as quantitative) analysis measures the intensities obtained in your unknown material on the same instrument and under the same conditions as well-characterised reference materials, allowing a thorough understanding of your material. Quantitative microanalysis assumes that the sample and standard are both homogeneous on the scale of the interaction volume of the electron beam, and that your material does not include voids or pore spaces. Totals that sum to less than 100 % indicate problems with the analysis, and the stoichiometry of crystalline materials can be checked once the user is satisfied that all elements present in the sample have been accounted for and the correct valence states applied. In comparison, many vendors of EDS systems offer a "qualitative" or "standards-free" mode of quantification that utilises an inbuilt factory database of materials against which the X-ray intensities of your unknown can be compared, correcting for matrix effects and normalising to 100 % to account for the loss of crucial electron dose information in the factory standards. However, this data can be misleading – because the totals are normalized to 100 %, potential problems such as missing elements may be overlooked, or incorrect element ratios may be given if the valence states of elements are not properly attributed. Standardless EDS is a useful tool for doing a quick check of your sample but is not a substitute for rigorous quantitative analysis to truly determine the composition of your sample.

3. ACCURACY VERSUS PRECISION

We should also mention accuracy and precision in quantitative microanalysis. Accuracy is the measure of how close the analysis is to the "true" or "real" concentration of the element in the sample – in an analogy with a target, it is a measure of how close your arrow hit to the centre of the target (Fig. 1). Precision is a measure of how reproducible your analyses are – in the analogy with a target, the precision provides information on how closely spaced your arrows are to one another. In a perfect world, we will strive to achieve the best accuracy and precision possible in our analysis by controlling as many of the sources of error as we can. In the rest of this paper, we go over some of the factors you should consider when performing quantitative microanalysis.

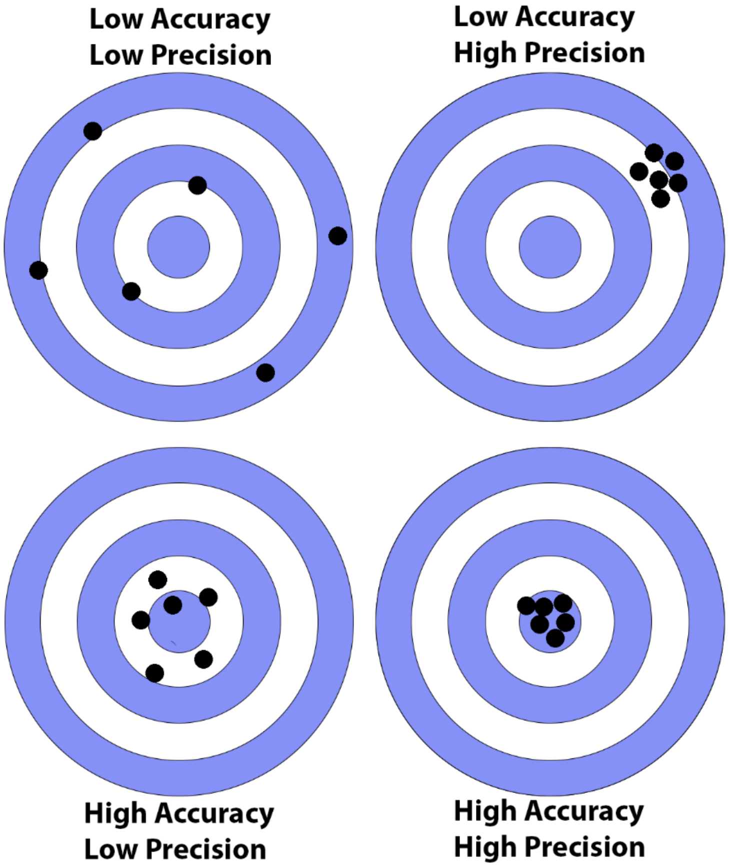

Figure 1. Accuracy and precision can be visualised using a target. Where you have low precision and low accuracy, the shots are far from the centre of the target and are not closely grouped. Shots with high precision and low accuracy are closely grouped but not close to the centre; conversely, shots with high accuracy and low precision cluster around the centre but are still not close to one another. In quantitative microanalysis, we are seeking both high precision and high accuracy: reproducible results that are close to the centre of the target (i.e., close to the "true" composition of our sample).

4. SAMPLE PREPARATION

4.1. Sample surface

Appropriate sample preparation is crucial to obtaining high quality quantitative EDS or WDS data. There is no single recipe that works for every material, and therefore some trial and error in sample preparation may be necessary to produce a result that works for your material. The prepared sample should have a flat, polished surface that is free of surface roughness, scratches, or topography. Ideally, samples will have a "mirror-like" finish, with no relief between neighbouring grains. This will require multiple steps using progressively finer polishing compounds, ending with a sub-micrometre final polishing step. If grains of differing hardness are present, excessive polishing may introduce relief. If this occurs, the sample should be taken back to a rougher grinding step until the topography is removed, before repolishing commences. If feasible, samples should be cleaned in an ultrasonic cleaner or using a soft toothbrush and a water-soap (alconox) solution to remove polishing debris in between polishing steps, to prevent additional X-ray generation by residual polishing compounds from interfering with the analysis.

4.2. Sample coating

Samples should be coated with a conductive coating in order to prevent "charging". Charging is the buildup of electrons at the sample surface which results in a deceleration of the beam at the surface of the sample and the generation of fewer characteristic X-rays. There are many conductive coating materials available, but carbon is one of the most widely used in the geological sciences. Carbon is cheap, provides an even coat that does not interfere with imaging of samples, and emits low-energy X-ray lines that generally do not interfere with the analysis of other elements of interest. If carbon is an element of interest within the sample, then a metal such as iridium or gold may be used instead [1, 2]. Iridium provides a smooth coat with a very thin layer, which makes it suitable for high-resolution imaging, whereas gold coats may show a cracked texture at high magnification. If a heavy metal coating material is chosen, remember that the coating may produce characteristic X-rays near peaks of interest for elements within the sample (e.g., in an EDS spectra, the iridium Mα- and Mβ-peaks overlap with the phosphorous Kα-peak) and this should be taken into consideration.

The coating material and thickness should be the same between the standard and the unknown material. Ideally, they should be coated at the same time to ensure consistent thickness, but in practice this may not be possible. Instead, a thickness monitor, calibrated for the density of the coating material, may be used. If coating with carbon, the change in colour of a clean brass disk or aluminium stub with increasing carbon coat thickness may be used. With increasing carbon deposition, there is a noticeable colour change, especially between 20 nm and 25 nm carbon thickness (e.g. [3]; see Fig. 2).

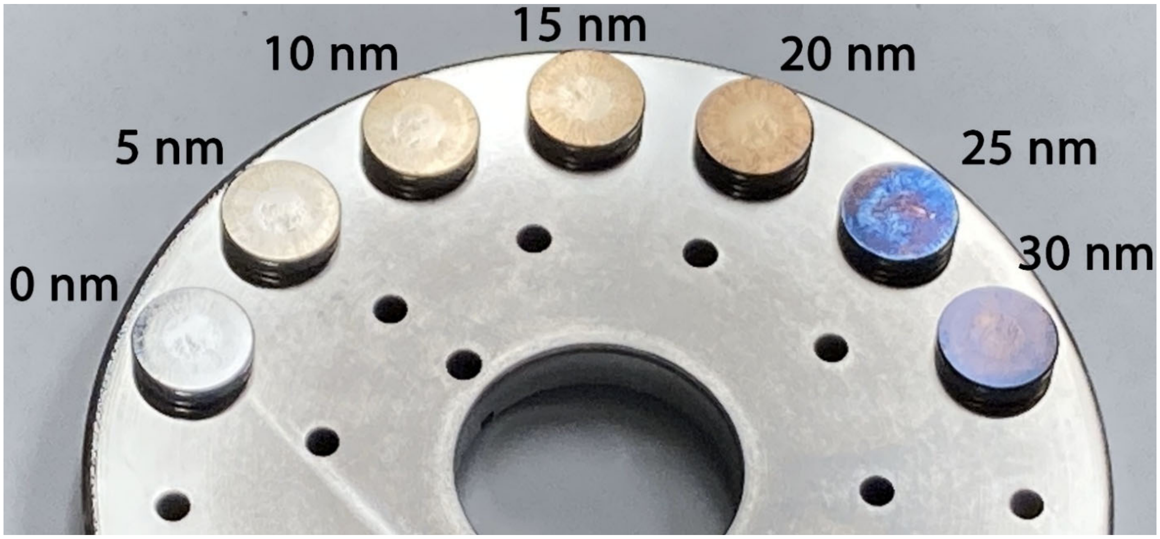

Figure 2. In the absence of a thickness monitor, a clean brass or aluminium stub can be used to monitor carbon coat thickness. Here, a polished aluminium stub shows a change in colour as the carbon layer increases from 0 to 30 nm, with a noticeable jump between 20 and 25 nm thickness. Photo credit: Rob Wardell.

There is an easy test that can be performed with an EDS detector to see if material is charging. A spectrum is collected, and when viewed in log-scale, it should show a sharp drop-off that corresponds to the accelerating voltage being used (Fig. 3). This is known as the Duane-Hunt limit. There may be a few stray counts above the cutoff due to pulse pileup, but if the cutoff is below the accelerating voltage value then this is a sign that the sample is charging, and should be recoated.

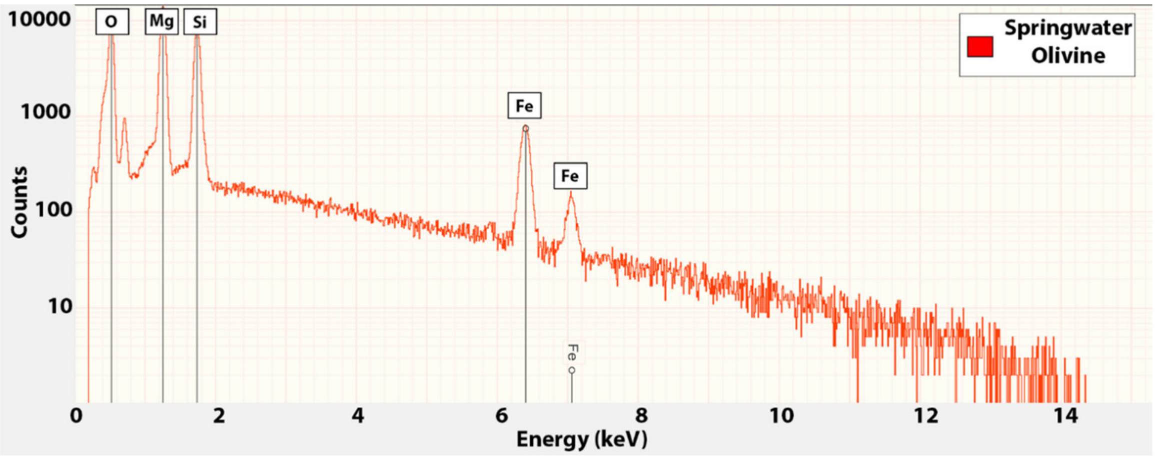

Figure 3. An EDS spectrum of Springwater olivine, shown in log view. Log view allows you to easily see where the continuum drops to zero (the Duane-Hunt limit) and test for charging of your sample. In this case, although the accelerating voltage was set to 15 kV, the Duane-Hunt limit shows a drop-off around 14.5 kV, indicating that the sample is charging and should be recoated.

5. CHECKING YOUR INSTRUMENT

Before you start collecting data on your standards and samples, you should make sure that the instrument is in proper working order, and that the detectors are working efficiently. Individual manufacturers provide documentation with their instruments on how to measure the beam current, so the guidelines below are general: Refer to your specific user manual for details on your particular system. There are also several references available that provide invaluable guides to ensure that your instrument is optimised (e.g., [3-8]). Instruments should be housed in a facility with a stable temperature control system (ideally +/- 0.5 ºC), free of stray electrical and magnetic fields. The take-off angle between the detector and the sample surface (i.e., the angle at which characteristic X-rays emitted from the sample surface are accepted by the EDS or WDS detector) should be known and input into the instrument software, to allow for appropriate absorption calculations during the matrix correction routine.

5.1. Calibrating an EDS system

If your instrument has a retractable EDS detector, make sure that it is inserted before performing any calibrations! For quantitative analysis, the long-term stability of the electron beam should be determined, and the current should also be measured before and after analyses to determine that beam current has not drifted during the course of a session. How often you need to do this will depend on the type of emission source in your instrument and the stability of the laboratory environment in which the instrument is housed. For long-term beam stability testing in our SEM, we place a piece of conductive copper tape, mounted between the sample and the sample holder, and check the count rate compared to the previous measurement, collected under the same conditions. For the geological materials that we most routinely analyse, we set the SEM to 15 kV and 1 nA. We bring the stage up to the appropriate working distance, checking the focus and adjusting the physical height of the stage until the correct working distance is achieved. We then run the beam measurement tool and see how much drift there has been since the previous measurement. Using the same technique each time allows us to see if there is a drift in the beam current over time. Thermal field emission instruments are generally stable over the long term, but cold field emitter instruments may show some variation [4].

Instruments equipped with WDS will check the beam current before and after each analysis, whereas EDS systems might require the user to periodically check the beam current manually before and after collecting data. Electron microprobes have a built in Faraday cup or probe current detector (PCD) – inserting the PCD allows the beam current to be read out easily, and the beam current is checked before and after each analytical point during a WDS measurement. EDS systems mounted on an electron probe may also have the capability to automate this step. On instruments that do not have a built-in Faraday cup, one can be mounted into a sample holder or stage and inserted for use at the same time as the quantitative measurements are to be made.

Performing an energy calibration to make sure that the peaks are generated at the appropriate energy is also important. Again, how often you need to do this will depend on the stability of your system. While factors such as the temperature fluctuation in the room may only cause a slight shift in the peak position, if you want to resolve closely separated peaks in an EDS spectrum then it is a good idea to perform an energy calibration. For example, the mineral galena (PbS) has a Pb-Mα peak within a few eV of the S-Kα peak (Fig. 4). If the energy calibration is not performed, these peaks may be misidentified, leading to incorrect microanalytical results.

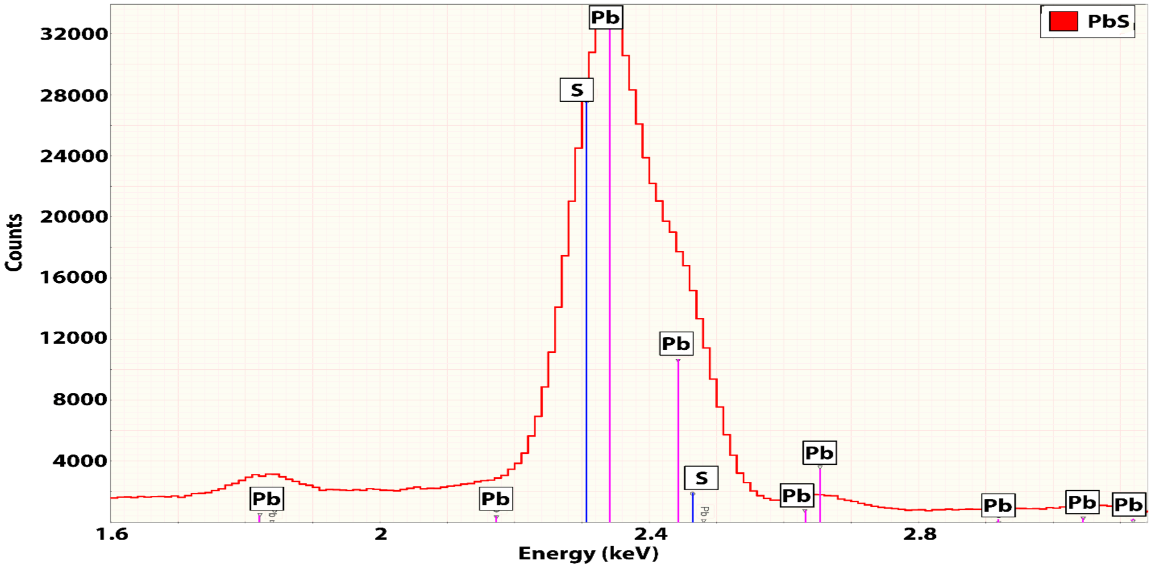

Figure 4. This EDS spectrum of galena (PbS) shows the problem with peak separation for EDS systems when samples contain elements that emit X-rays at similar energies. The blue lines show the emission energies of sulphur, while the pink lines show the emission energies of different lead X-rays. Miscalibration of the system may lead to incorrect identification of the elements present.

The energy calibration process involves verifying the accurate measurement of X-ray energy of an element that has X-ray peaks at the upper and lower end of the energy range such as Cu or Co. An easy method is to use some copper tape on your sample and measure the Cu-Kα and Cu-Lα peak energies and verify their position. If there is a significant mismatch between the measured and expected peak energy, this will contribute to peak misidentification, and the system should be recalibrated. This should be done for each processing time/time constant setting that is used for data acquisition. A pure element standard that does not oxidise easily is recommended, since there may be a slight energy shift in peak position between pure elements and compounds.

5.2. Choosing analytical conditions

An important aspect for quantitative analysis by both EDS and WDS will be your analytical conditions: the accelerating voltage, beam current, and the field of view (or beam diameter) of your measurement.

For selecting the accelerating voltage, the overvoltage should be considered (Eq. 1). This is the ratio between the accelerating voltage and the "critical excitation energy" of the X-ray line, where the critical excitation energy is the minimum amount of energy needed to create a vacancy in the electron shell:

$$U = E/Ec \tag{1}$$

where U is the overvoltage, E is the accelerating voltage, and Ec is the critical excitation energy of the highest energy X-ray of interest emitted by an element within your sample.

During bombardment of the atoms in a sample by the primary electron beam, an inner shell electron may be ejected, with an outer shell electron dropping in to replace it, and a characteristic X-ray is then emitted. To achieve an optimal X-ray yield, an overvoltage of 2 - 3 times the critical excitation energy should be used. At higher overvoltage values, the emitted X-ray intensities decrease as they are being generated deeper in the sample and are more heavily absorbed as a result.

For example, in a silicate mineral such as olivine, an accelerating voltage of 15 kV will excite the most common X-ray lines of interest up to iron. To excite the Fe-Kα line (which has a critical excitation energy of 7.11 keV), an overvoltage of 2 - 3× that amount of energy (~ 14 - 21 kV) is needed. The analysis of Si-Kα and Mg-Kα (Kα critical excitation energy of 1.84 keV and 1.30 keV respectively) requires a lower accelerating voltage (for example 5 kV) but this would not provide enough energy to excite the Fe-Kα line and only the lower-energy Fe-Lα line at 0.71 keV would be present. Prior knowledge of the elements in your sample will allow you to determine an appropriate accelerating voltage with which to analyse your unknown material.

The next consideration will be the beam current. This will depend on the type of instrument and EDS system you are using. A beam current that allows a sufficient count rate while not damaging the sample is recommended. EDS systems mounted on an SEM often have a large cross-section in order to catch as many X-rays as possible since many SEMs operate at lower beam currents. EDS systems on electron microprobes often have a smaller cross-section since they run at higher beam currents, which can lead to the EDS detector potentially becoming saturated.

The optimal working distance (the distance between the objective lens and the sample surface) is crucial for quantitative analysis. The working distance varies based on the models of instrument and EDS system used, and the manufacturers manual should give a recommendation.

In an electron microprobe, the image should appear in focus on the reflected light microscope image. In an SEM, the stage should be brought up and down by moving in the Z-direction until the sample is in focus. If you are unsure of the appropriate working distance, it can be measured by monitoring the count rate as you move the stage up and down in Z. A peak in counts indicates the optimal distance [6].

After setting your accelerating voltage, beam current, and working distance, the next step is to consider the EDS spectrum collection parameters in the software. The collection time varies depending on the data target. For a quick absence/presence determination of an element, a few seconds may suffice, whereas for trace quantities of an element, a longer count is necessary to identify the peak above the background counts. There is also "dead time" to consider – this is the time it takes for the EDS detector to process X-rays. Different manufacturers allow users to modify this time, by adjusting the "processing time" or "time constant". Adjusting this setting affects count rates and peak resolution, and ideally one will keep the settings the same between standards and unknowns in order to keep the peak shapes the same and aid in spectral deconvolution. EDS standardisation uses the area under the peak, instead of the intensity at a single peak position (as is the case for WDS analysis). Some software manufacturers allow you to store your own peak shapes, generated from your material, but there will also be a built-in reference library of peak shapes for each element. Decreasing the time constant may reduce peak resolution and make peak overlaps harder to distinguish. For single point analyses, it is better to count for longer with a resolution-focused setting.

6. *STANDARDS-BASED EDS STANDARDISATION*

Once the EDS system has been calibrated and your analytical conditions selected, it is time to collect data on your standards. EDS manufacturers will provide guidelines about the steps to standardise your particular system, either in the manual or in a guided walkthrough in the software, therefore, the information provided here should be considered a general guideline. For standardisation on our EDS system, we use simple materials where possible – binary compounds or simple silicates, in order to minimise potential issues arising from overlapping peaks. A typical acquisition time for each spectrum in our lab is around 60 seconds, operating with around 10 - 15 % deadtime, with the aim of getting several thousand counts in our peak of interest (although this will depend on the concentration of the element in the standard. For low concentrations, we count for longer. Most EDS systems will allow you to terminate collection when a certain threshold of counts within a peak is reached, rather than based on time). On our system we typically collect three different spectra on each standard and overlap them to compare them, to ensure that our standard is homogenous. We choose the spectrum with the lowest carbon peak to act as our reference spectra. We go through and collect spectra on every standard necessary to cover all the elements that will be present in our unknown, and create our database of standard intensities.

Once the standardisation is complete, it is good practice to analyse a "secondary standard" or a "standard as an unknown" – namely a material of known composition and stoichiometry, to confirm that your standardisation has been performed correctly. The same conditions – beam current, working distance, accelerating voltage – should be used as for the standardisation, and the result should be processed through the matrix correction algorithm using your standard database. If the chemistry and stoichiometry of the standard-as-unknown is acceptable, you can analyse your unknown samples with confidence.

You should strive to account for all major and minor elements present within your unknown material, in order to perform the appropriate matrix corrections [9-12]. For geological materials there may be some components which can either be calculated by stoichiometry (e.g., O, CO_2), or can be specified. Some components, such as OH or H_2O (for example in hydrated mineral such as an amphibole) cannot be directly analysed (as hydrogen does not generate X-rays) and must be specified, either by difference from 100 % or through concentrations established by a different analytical technique.

If we get poor totals on our unknown, we check the peak residuals to make sure we are not missing any elements, check to make sure the appropriate valences are being used, and check for charging. We periodically check the standard-as-unknown to make sure that the calibration has not drifted during the course of an analytical session.

6.1. Setting up the instrument for WDS analysis

Some of the steps for setting up standardised EDS will also apply to WDS quantitative analysis. For WDS analysis, you should know which elements are present in your sample, so they can all be accounted for. As with quantitative EDS analysis, collecting a quick qualitative EDS spectrum and determining all of the elements present in your material before you begin calibration can save a lot of time later on.

As with EDS systems, the instrument should be set up with the appropriate accelerating voltage, beam current, working distance, and spot size. Again, the critical excitation energy of the highest-energy X-ray line you wish to measure should be determined, and the accelerating voltage set to 2 - 3× that value. Increasing the beam current will increase the count rate, which in turn improves analytical errors and detection limits, but some materials are susceptible to damage at higher doses. You may wish to test your unknown material to see how stable it is under the beam – the count rate can be monitored to see if it drops off over time, or if surface damage becomes visible on your material. If this occurs, you can consider lowering the beam current, or slightly broadening the beam. Alternatively, some software packages allow you to monitor the change in count rate during the course of an analysis and correct for loss of elements.

6.2. Calibrating a WDS system

WDS systems utilise diffracting crystals to diffract X-rays of a specific wavelength towards a detector. Each diffracting crystal covers a specific range of wavelengths. Prior knowledge of the elements in your sample and the X-ray lines you wish to measure will allow you to efficiently assign elements to different crystals in instruments that utilise multiple WDS spectrometers and avoid the need to flip the crystal during the analysis. For many geological samples, it is routine to measure the Kα-line of the most common elements present (Si, Mg, Al, Na, Ca, Ti, Fe, Mn, K, Cr) and to calculate O by stoichiometry. However, there may be cases where heavier elements (such as Zn or Pt) are to be measured, which will necessitate measuring the Lα- or Mα-lines at 15 kV, or choosing a higher accelerating voltage. Conversely, if grains of a couple of micrometres in diameter or less are to be analysed, it may be necessary to reduce the accelerating voltage in order to reduce the interaction volume and prevent overlapping with the surrounding material. This may result in the need to analyse unconventional X-ray lines, such as the Fe-Lα or -Ll lines [13-15].

Once elements have been assigned to spectrometers, it is time to find the peak position for each element – i.e., the spectrometer position at which the maximum number of counts are achieved. Using a material that contains a high quantity of the element of interest is important, in order to be able to distinguish the peak from the background. It is also important to choose an element that is in a similar bonding environment to your standard and unknown materials, especially in the case of light elements, as there can be a noticeable peak shift depending on bonding environment (e.g., [17]). For example, in the case of sulphur, there is a noticeable peak shift between S bonded with iron in a sulphide, and sulphur bonded with oxygen in a sulphate (Fig. 5).

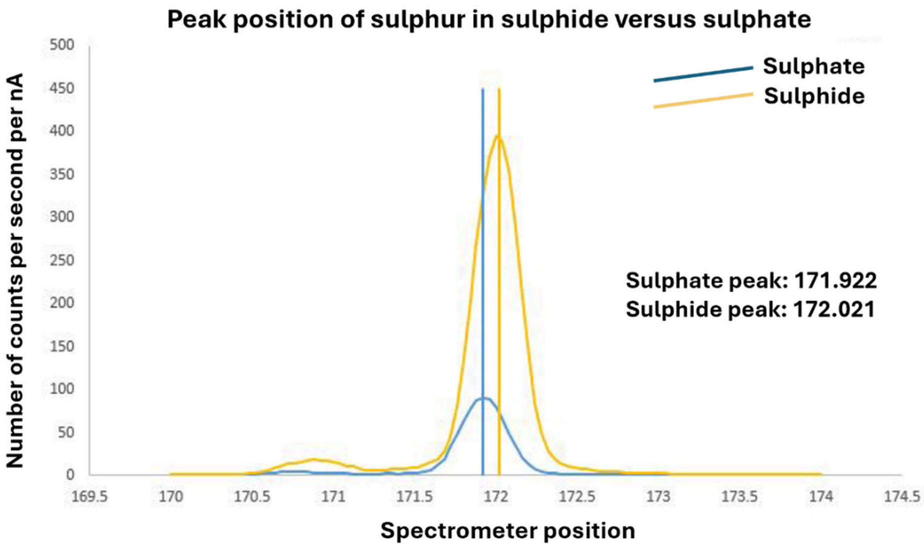

Figure 5. Some elements may show a shift in their peak position, depending on the bonding environment. In this case, the peak position recorded for sulphur shifts depending on whether it is bonded with oxygen in a sulphate or iron in a sulphide.

In order to determine the number of counts attributable to the element of interest, the contribution of continuum X-rays (the "background") must be subtracted from the peak intensity. In traditional WDS measurements, the intensity on both the upper and lower sides of the peak are measured, and the count rate between these positions is interpolated (Fig. 6). Care must be taken that no characteristic X-rays emitted by other elements are present at the chosen off-peak locations as that could produce extraneous counts and would cause an incorrect background value to be subtracted. For some materials that contain a large suite of elements (such as rare earth element phosphates), finding background regions that are free of interferences can be problematic. Some software packages allow alternative approaches to establish background counts, such as multi-point or mean-atomic number background methods [18, 19]. An additional complication is that the X-ray spectrum can show a pronounced curvature depending on the X-ray line, WDS crystal and spectrometer position for certain elements. Some software packages only model a linear geometry between the two background locations, while other software packages allow you to model curved backgrounds – wherever possible, the background model should be carefully chosen.

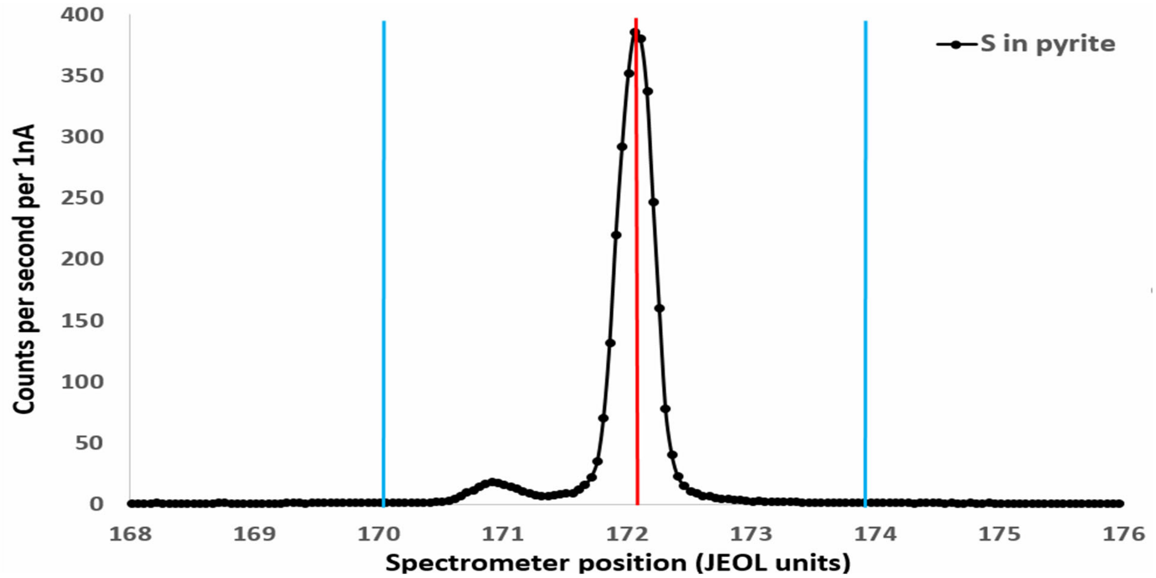

Figure 6. This scan on pyrite shows the location of the sulphur peak on the PETL crystal (red line) on a WDS spectrometer. The background positions are shown by the blue vertical lines. Background positions far enough away from the main peak are chosen; depending on the elements in your sample it may also be necessary to check there are no elements present with peaks that could interfere with your chosen background positions.

Another important step in addition to determining the peak position is to optimize the detector settings as part of the initial tuning. This is known as checking the pulse height analysis (PHA) settings, and neglecting this step and relying on default settings can produce suboptimal instrument performance. As the detector ages over time, there may be shifts in PHA setting values, while short term environmental changes may also have an impact. The PHA is tuned by performing scans at the bias voltage or detector gain settings for each element to visualise the pulse within the voltage range of the detector. Different approaches are applied to re-centre the pulse if needed depending on the instrument maker. On JEOL instruments the gain has a series of fixed values and the bias value is varied to centre the pulse at around 4 V, whereas both bias and gain can be adjusted on Cameca instruments and the peak centred around 2 V. In addition to PHA gain and bias values, a "baseline" voltage has to be defined to exclude low-amplitude noise. For certain purposes, an energy discrimination "window" can be set where only pulses within the window are counted ("differential" mode, in contrast to "integral" mode in which all pulses above the baseline are counted). It is important to note that the position of the pulse in the PHA window can shift by several volts ("pulse height depression", i.e., shifted to the left) with increasing count rates. Therefore, it is important to obtain the PHA values on a material with similar or higher element concentrations than your unknown so that the pulse does not move below the baseline.

As with EDS analyses, the length of time spent measuring the intensity of the peak and background positions will determine the detection limit and precision of your analysis. Longer count times will improve your precision and reduce your detection limit, but may result in sample damage, and fewer analytical points collected within a session. Therefore, the amount of time spent counting on each element will be a function of the type of data you are trying to obtain.

Once the elements and analytical conditions have been determined, and the instrument has been optimised, it is time to collect intensity data on your standards. For WDS analysis, multiple points are collected on each standard material, any outliers are discarded, and good points are averaged to obtain an intensity for each element.

The choice of standards for WDS analysis is an ongoing topic of conversation. Traditionally, in geological analyses standards would be "matrix-matched" – that is, a material of a known composition as similar as possible to your unknown sample would be measured, in order to minimise matrix corrections. Advances in computing power and software developments have led to vastly improved matrix correction algorithms, which in some cases has led to a wider range of standards being available for use. Not all software has these advanced routines though, and so matrix matching may still be preferable. Care should be taken that the standard chosen has a sufficient concentration of the element in question though – just because you're looking for a trace amount of an element in your unknown, it does not mean you should use a standard that has a trace amount of the element present!

As with EDS standardisation, checking secondary standards for the correct abundance of each element and stoichiometry (of crystalline materials) will allow you to test the robustness of your calibration. If every element is appropriately accounted for, you should obtain results of 100 wt% and can move on to analysing your unknown material. Periodic checks on your secondary standards will allow you to ensure that the calibration has not drifted during an analytical session.

7. STANDARDS

7.1. What makes a good standard?

As mentioned above, standards for use in quantitative microanalysis may be pure elements, binary oxides, or complex minerals, depending on your needs and the materials available. All materials that will be used as standards should show a common set of important features:

- They should be compositionally homogeneous, and free of inclusions or zoning at the scale of the analysis (typically 1 - 2 µm). While some natural minerals are suitable for use as standards, many will display compositional zoning or abundant inclusions, which means the measured composition will vary across the grain.
- Samples should be stable, both under vacuum and under the electron beam. Samples should be chemically stable and not degrade over time. Some elements are difficult to measure because they migrate under the beam (particularly volatile elements such as Na and K), and, therefore, care should be taken to use gentle analytical conditions wherever possible to minimize their migration. Similarly, some materials are susceptible to oxidation and should be kept dry and under vacuum as much as possible.
- Standards should be well-characterised, ideally using an independent technique such as wet chemistry or laser ablation. Some standard materials are provided with an unstandardised EDS analysis as proof of their "composition", which can obviously cause problems if minor elements, inclusions, or zoning are present but not reported.
- Standard materials should be easy to mount, polish, and coat. Periodic maintenance of a standard block will require repolishing it to remove any surface damage or contamination, and the repolished surface will need to be free of polishing scratches and relief. Mounting materials of a similar hardness within a standard block can help make repolishing a much simpler task.
- Ideally, standards should be available in large enough quantities that they can be distributed widely. Many labs have relied on home-grown standards that are only available at that institution, which makes intra-laboratory comparisons difficult. Initiatives are underway to source materials that would be suitable for use as standards, and that can be made available to the community as a whole.

7.2. Where to obtain standards?

This is a common question from people who are venturing out to set up their own labs, and from established labs alike. There are several commercial vendors who sell loose material or pre-made standard mounts, or who offer services to prepare and polish custom standard mounts. Customisable standard blocks have the advantage of allowing you to choose materials that will best reflect the specific needs of your lab. Whether you choose a pre-made block, or loose grains in order to make your own standard mount, it is critically important to make sure that they have a flat, mirror-like polish for quantitative analysis, just as you do for your unknown materials.

It is also vital to make sure that the composition of your standard materials has been independently verified and evaluated before including it in your analytical routine. For example, a significant number of laboratories use San Carlos Olivine from the Smithsonian Museum of Natural History (USNM 111312), which has been shown to be an excellent, homogenous standard (it was sourced from one large crystal). However, a variety of alternative sources also provide "San Carlos Olivine" but with discernibly diverse compositions [20], unlike the material distributed by the Smithsonian. Furthermore, standards sourced from natural materials may show inter-grain or intra-grain compositional variation, or may contain inclusions of other materials [21-23]. An evaluation of the Smithsonian pyroxenes showed some evidence of inter-grain variability [24].

Efforts are underway to identify new candidate materials that can be distributed to the community at minimal cost. The Focussed Interest Group on Microanalytical Standards (FIGMAS) was founded in 2016 as a joint project between the Microanalysis Society (MAS) and the Microscopy Society of America (MSA) to create a centralised location to provide information about standards that is available to the global community. The FIGMAS website hosts an online database [25] of existing standards in use, which will be updated over time to reflect developments in standard availability and quality. There are groups in the US that are working to identify easily synthesisable materials which will meet the criteria given above, and to evaluate their potential use as standard materials [26]. Additionally, microanalysts continue to identify natural materials that can be made available for use [27, 28]. We encourage all interested members of the microanalysis community to consider joining FIGMAS, and to take part in the endeavour to make standards available to everyone.

8. REFERENCES

[1] Kearns S, *et al.* 2014 *Microsc. Microanal.* **20** 740-741

[2] Smith M P 1986 *J. Sedimentary Petrol*. **56** 560-561

[3] Kerrick D M, *et al.* 1973 *Amer. Mineralogist* **58** 920-925

[4] Goldstein J, *et al.* 2018 Energy dispersive X-ray microanalysis checklist. in: *Scanning electron microscopy and X-ray microanalysis. 4th Edition*. (Goldstein J, *et al.*; Eds.) [New York, NY: Springer] 461-470

[5] Newbury D E and N W M Ritchie 2015 *J. Mater. Sci.* **50** 493-518

[6] Ritchie N W M, *et al.* 2020 *Forensic Chem.* **20** 100252

[7] Seddio S 2022 *An exhaustive procedural guide for doing standards-based quantitative analysis with EDS and/or WDS using the Thermo ScientificTM PathfinderTM microanalysis software platform*. Personal Communication.

[8] Bullock E S, *et al.* 2024 *Treatise on Geochemistry (Third Edition)* **8** 789-828

[9] Bullock E S, *et al.* 2020 *Microsc. Microanal.* **26** 1876-1877

[10] Fournelle J, *et al.* 2020 *Microsc. Microanal.* **26** 58-59

[11] Dungan M A, *et al.* 2023 *Amer. Mineralogist* **108** 978-986

[12] Moy A, *et al.* 2023 *Microsc. Microanal.* **29** 855-856

[13] Henderson C, *et al.* 2016 *Low beam energy EPMA quantification of transition metals using Ll emission lines*. in: EPMA 2016 Conference 44-45

[14] Fialin M, *et al.* 1998 *X-ray emission valence band spectrometry: application to Cu and Fe L-series*. in: Proc. EMAS '98 Regional Workshop "Electron Probe Microanalysis Today - Practical Aspects" . (Llovet X, Merlet C and Salvat F; Eds.) [Antwerp, Belgium: EMAS]

[15] Gopon P, *et al.* 2014 *Soft X-ray EPMA analyses of nanophase lunar Fe-Si compounds*. in: Proc. Wisconsin Space Conference.

[17] Fournelle J 2006 *Microsc. Microanal.* **12** 822-823

[18] Allaz J M, *et al.* 2019 *Microsc. Microanal.* **25** 30-46

[19] Donovan J J and Tingle T N 1996 *J. Microscopy* **2** 1-7

[20] Fournelle J 2011 *Microsc. Microanal.* **17** 842-843

[21] Jarosewich 1980 *Geostand. Newslett.* **4** 43-47

[22] Rose T R 2008 *Microsc. Microanal.* **14** 528-529

[23] Lambert S, *et al.* 2022 *Chem. Geol.* **605** 120968

[24] Fournelle J 2012 Complications with using natural minerals as microbeam standards: Pyroxenes. in: *American Geophysical Union, Fall Meeting 2012*, abstract id. V23C-2827

[25] Allaz J M 2024 *Microsc. Microanal.* **30** 489-500

[26] Nachlas W, *et al.* 2023 *Microsc. Microanal.* **29** (Suppl. 1) 225-226

[27] von der Handt A, *et al.* 2025 *Microsc. Microanal.* **31** submitted

[28] Allaz J M, *et al.* 2023 *Geostand. Geoanal. Res.* **47** 907-929