Energy Dispersive X-Ray Microanalysis Checklist

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Overview

This section is intended to take you step-by-step through the process of making a careful standards-based quantitative measure of composition. It discusses the instrumentation, preparation, data acquisition, data analysis, reliability checks, and data reporting—all the steps an expert takes to ensure a high-quality, reliable measurement. It is intended to be a golden path which if followed carefully will take the reader to the intended outcome with the minimum of diversions. As such, it only covers measurements of bulk, homogeneous, carefully prepared samples and avoids consideration of special cases like particles, fibers, or thin films.

26.1 Instrumentation

What you will need to prepare.

26.1.1 SEM

The starting point is a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer. A good and useful measurement doesn't necessarily require a fancy SEM. Almost any functional SEM will do. However, there are a handful of basic requirements.

- The SEM should be capable of beam energies of at least 15 keV (20–30 keV maximum is better). While it is possible to make many measurements at lower voltages, 15 keV is a useful practical minimum to begin an analytical measurement campaign.
- The probe current must remain stable to within a percent or better for minutes or hours. Most thermal sources (tungsten filament, LaB_6 or Schottky field-emitters) will work fine. Cold field emitters can be problematic due to current drift issues. The more stable the probe current the easier and the more accurate standards-based measurements will be. Note that "standardless" analysis methods do not require a stable beam current or knowledge of the value of the beam current. While convenient, this is bought at the price of losing the analytical total, which has considerable value.

26.1.2 EDS Detector

Any functional EDS detector/pulse processor system is likely to be adequate. Older Si(Li)-EDS detectors with poorer resolution and less throughput may require patience and may produce slightly less good results. The one caveat is that some older detectors utilize thick beryllium windows that absorb virtually all X-rays below 1-keV photon energy. These detectors will not be able to measure X-rays from C, O, F, and other light elements. If you need to measure these elements you will need a detector with a thin polymer ("Moxtek") or other high-transparency window. In the end, patience and care is more important than owning the latest equipment.

- Resolution at Mn K-$L_{2,3}$ of 150 eV or better
- Throughput of 1,000 cps second or better on bulk Cu
- A "light element" window capable of seeing C
- Software to acquire spectra and export the spectra in the msa (ISO-22029, 2012) format

26.1.3 Probe Current Measurement Device

You will need a mechanism to measure the probe current—a measure of the number of electrons striking the sample. There are two ways to measure the probe current. You can measure the probe current directly using a Faraday cup and picoammeter. Alternatively, you can monitor the probe current indirectly by measuring an X-ray spectrum of a specific element, for example, Cu, obtain the integrated spectrum count, e.g., from 0.1 keV to E_0, and then use the proportionality between probe current and X-ray emission to calibrate the probe current over the course of a measurement campaign.

Direct Measurement: Using a Faraday Cup and Picoammeter

The classic procedure to measure the probe current is with a Faraday cup and a picoammeter. Some instruments integrate a Faraday cup into the stage. A few instruments implement a Faraday cup as a retractable device within the optics column. Most SEMs require a user-provided Faraday cup.

To perform a beam current measurement you will need the following:

A Faraday Cup

A Faraday cup is essentially a hole which electrons enter but never leave. It consists of a metal aperture with a 10–100-μm diameter orifice mounted over a millimeter-diameter void, for example, a blind hole drilled in a block. Carbon is an excellent material for the block because its low backscattered electron (BSE) coefficient minimizes re-backscattering from the walls of the hole. For a metal block, the interior of the void can be coated in a material with a low backscatter coefficient (such as carbon dag) to minimize possible loss through multiple backscatter events. The Faraday cup should be accessible on the SEM stage simultaneously with the specimen so it just a matter of driving the stage to the appropriate locations, which is usually an automatable function. It should NOT be necessary to break the vacuum and interrupt the specimen measurements to insert the Faraday cup.

Electrically Isolated Stage

The stage should be electrically isolated from the instrument ground. The electrically isolated stage is connected by a single wire to a vacuum electrical feed-through so that the only path to ground passes through the connected picoammeter.

- A picoammeter—A current meter capable of measuring currents between picoamps and hundreds of nanoamps.
- A cable to connect the vacuum feed-through to the picoammeter.

Procedure:

- Drive the SEM stage to the location of the Faraday cup, and center the aperture in the SEM image. Zoom up in magnification until the aperture fills the screen, and then further increase the magnification so the scanned field is well within the aperture. Choose the appropriate current range on the picoammeter and read the current.
- Note: When the beam is not within the Faraday cup, the current flowing to the picoammeter will represent the "specimen current," which is the beam current minus the backscattered electron and secondary electron emission. Because η and δ change with composition, specimen current is NOT a useful measure of absolute beam current or of stability.

Indirect Measurement: Using a Calibration Spectrum

A carefully collected spectrum can be used as an alternative to a Faraday cup and picoammeter. Ultimately, the probe current always appears in formulas for standards-based quantitative analysis as a ratio. We can therefore replace the probe current with any quantity which is proportional to the probe current, even if we don't know the proportionality constant. A carefully collected spectrum can provide such a metric.

The calibration spectrum must be collected—

1. At a consistent beam energy
2. At a consistent working distance (The same working distance that the unknown and standard spectra are collected)
3. On a consistent material (flat, polished)
4. For a consistent live-time (acquisition duration)

Typically, a pure metal such as copper, nickel, aluminum, silicon, among others, is used and the number of counts in the range of energies around the K characteristic lines is used as the proxy for the probe current, or the entire spectrum can be integrated from a threshold, for example, 0.1 keV to E_0.

Precise calibration of the probe current using a spectrum takes patience. For 0.1 % precision, you will need to integrate at least 1,000,000 counts in the range of energies used for the calibration.

Disadvantages:

1. It takes longer to acquire a calibration spectrum of equivalent precision than it takes to measure the probe current with a picoammeter.

Advantages:

1. The polished standard used for calibration can be a member of the set being used for the analysis so that no extra material or preparation needed.
2. A calibration spectrum can compensate for slight differences in measurement geometry.
3. A Faraday cup and picoammeter aren't necessary.
4. The calibration spectrum can also be used for quality control purposes.

26.1.4 Conductive Coating

Many samples and standard materials are non-conductive and need to be coated with a nanoscale coating of a conductive material. Typical equipment used includes—

1. Carbon coater (usually the best choice for X-ray microanalysis unless C, N, or O must be optimized in the analysis)
2. AuPd or other heavy metal/metal alloy coater (usually chosen when secondary electron image performance is important)

The coater should be capable of laying a controlled thickness of a conductive film over the sample. Most coaters rotate to ensure that all sides of the sample are coated. Use the thinnest coating that discharges the specimen, for example, 5–10 nm of carbon should be sufficient, or 1–3 nm of a high Z coating such as Au or Au-Pd.

CRITICAL: The applied coating must actually be connected to electrical ground. Do not assume that an electrical path is automatically established by the coating. The sides of a tall insulating specimen may not actually become adequately coated. Use a strip of conducting adhesive tape from the coated surface to the conducting support stub to ensure the electrical path.

26.2 Sample Preparation

Regardless of whether you are performing standards-based or standardless quantitative analysis, you will need to ensure that your unknowns and standards, if used, are prepared in a suitable fashion for analysis. How you prepare your samples will depend very much on the type of samples that you analyze. For the most accurate analysis of bulk materials, including that utilizing the standardless protocol, the specimen must be prepared with a flat surface, with the degree of flatness becoming increasingly critical for measurements with X-rays having energies below 1 keV—e.g., Be, B, C, N, O, F—where the surface roughness should be reduced below 50 nm root mean square. Some samples require very little preparation (e.g., a silicon wafer) and others (anything that isn't flat) require a lot. You may need to embed the samples and standards in epoxy mounting medium (preferably conductive) and use suitable equipment to grind and polish the samples. Appropriate preparation protocols are so specialized that rather than provide an exhaustive list of possible procedures, the analyst is referred to the rich literature on sample preparation:

- Echlin, P., Handbook of Sample Preparation for Scanning Electron Microscopy and X-ray Microanalysis (Springer, New York, 2009)
- Geels, K., Metallographic and Materialographic Specimen Preparation, Light Microscopy, Image Analysis, and Hardness Testing (ASTM, West Conshohocken, PA, 2006)
- McCall, J., Metallographic Specimen Preparation: Optical and Electron Microscopy (Springer, New York, 2012).
- Vander Voort, G., Metallography, Principles and Practice (ASM International, Materials Park, OH, 1999)

26.2.1 Standard Materials

Standards are specially prepared materials that serve to provide X-ray data for the elements present in the unknown. You will need a standard for each element in the unknown material. Note that some standards can serve for two or more elements, for example, FeS2.

To be useful, a standard must be—

1. Suitably sized—Practically speaking, most standards range in size from tens of micrometers to a tens of millimeters
2. Polished to a smooth, flat surface with surface texture of less than 100 nm (50 nm for low energy X-rays like oxygen)
3. Mounted in a manner that facilitates placement on the stage perpendicular to the beam
4. Conductive or coated with a conductive material
5. There are several different classes of standards, in order of the ease of use:
   (i) Pure element standards:
   The easiest standards to use are pure elements and this is where a novice should start whenever possible.
   (ii) Simple compound standards:
   Some elements are not stable as pure elements—N, O, F, Cl, Br, S—and must be provided as compounds. The easiest to use are typically stable, stoichiometric compounds like alumina (Al_2O_3) or calcium fluoride (CaF_2). With stable stoichiometric compounds, the true composition of the standard is unambiguous. Ideally, the compound is chosen so that there are no interferences between the element's characteristic peaks.
   (iii) Complex standards:
   In many cases, complex standards similar to the unknown sample will produce the most accurate results. However, complex standards often are more difficult to work with and it is often hard to find reliable compositional data. Use of complex standards is an advanced topic and rarely justified unless suitable pure element and simple compound standards are not available.

26.2.2 Peak Reference Materials

Peak reference spectra serve as examples of the shape of an element's characteristic peaks. A peak reference can serve as a reference for one or more families. Standards materials can be used as references if there are no interferences for that element. Paradoxically, some materials suitable to serve as peak references are not suitable for use as standards, generally due to instability under the electron beam; for example, $BaCl_2$ provides an excellent peak reference for the Ba M-family, but it is unstable under electron bombardment and thus cannot serve as a standard.

26.3 Initial Set-Up

26.3.1 Calibrating the EDS Detector

Most EDS detectors allow you to configure two different characteristics of the detector—the pulse process time and the energy calibration. Some detectors provide other more advanced options. You will need to consult the manufacturer's documentation to determine the optimal setting for these parameters. In general, the goal should be to ensure that the detector is configured the same way day-in/day-out even if it means making small compromises to the ultimate performance.

Selecting a Pulse Process Time Constant

1. Most EDS detectors will allow you to make a trade-off between X-ray throughput and detector resolution. Higher throughput comes at the price of poorer detector resolution. This setting is called different things by various vendors—throughput, pulse processor setting, shaping time, or time-constant.
2. Typically, a pulse processor time constant selected in the middle of the allowed range represents the best trade-off. Despite common belief, the highest resolution setting is rarely the optimal choice as this setting is usually accompanied by severe throughput limitations. Usually, it is better to select a moderate resolution and obtain a moderate throughput.
3. On a modern silicon drift detector (SDD), throughput is typically not limited by the pulse-process time but rather through pulse pile-up (coincidence) events. Selecting a very fast process time won't actually improve usable throughput.

4. Be sure to turn off "adaptive shaping" or other mechanisms that adapt the process time dynamically depending upon X-ray flux. Adaptive shaping changes the shape of the characteristic peaks as the count rate varies due to variations in local composition and makes linear peak fitting less accurate.

Energy Calibration

1. Select one material that you will always use to calibrate your detector. Mount a piece of it near your Faraday cup. Copper is a good choice but there are other materials that have both low energy and higher energy X-ray peaks that can be used for calibration.
2. Select a channel width and channel count that fully covers the range of beam energies that you may use. A width of 10 eV/channel and 2,048 channels is a good choice for a 20-keV beam energy. A width of 10 eV/channel and 4,096 channels is suitable for higher-energy work. Since EDS spectra comprise relatively small size files and computer storage is inexpensive, consider 5 eV per channel, especially for low photon energy work to provide adequate channels to describe the peak. Whatever choice is made, it is important to consistently use that choice.
3. Each day before you start collecting data, collect and store an initial spectrum from your selected calibration material, for example, Cu. Use this spectrum and your vendor's software to calibrate the energy axis. Usually this involves adjusting the electronics to ensure that the measured peaks are centered around the correct channels. Most modern detectors automatically and dynamically adjust the zero offset and the calibration is just a matter of the software automatically selecting a gain that produces the desired number of eV/channel. Older detectors may require a manual gain and zero offset adjustment using external potentiometers. Regardless of the mechanism, at 10 eV/channel a 0.1 % mis-calibration will correspond to a single channel error in the position of a peak at 10 keV, so the detector calibration should ideally be maintained to better than 0.1 %. Fortunately, modern detectors are able to hold this precision of calibration for days or weeks.
4. Once the detector is calibrated, set the beam energy and probe current to established nominal values and collect a spectrum for a established live time. Save this spectrum as a demonstration that your detector is performing correctly. DTSA-II provides tools to extract and track performance metrics and then plot the results over time as a control chart.

Quality Control

Sooner or later, you will be asked by a client to demonstrate that your instrument was performing correctly when their data was collected. The easiest way to satisfy this requirement and to impress the client is to keep a long term record and present the data as a control chart. DTSA-II provides functionality which permits you to archive the spectra you just used to calibrate your detector as a record of the detectors performance. The program extracts efficiency, calibration and other pieces of instrumental data and records them in a database. This database can then be exported as control charts or tabulations. It is a nice way to make the most of the calibration data you have already spent the time to collect.

Maintaining the Working Distance/Specimen-to-EDS Distance

Maintaining consistent experimental conditions is critical for achieving rigorous quantitative microanalysis. A critical parameter is the specimen-to-EDS distance, S_{EDS}, since the solid angle of the EDS varies as $1/S_{EDS}^2$. The SEM and/or EDS manufacturer(s) will have specified the ideal SEM working distance (WD) at which the EDS central axis intersects the SEM optic axis. An electron probe microanalyzer uses a fixed-focus optical microscope with a very shallow depth-of-focus to bring the specimen to this ideal WD position (to which the wavelength dispersive spectrometers are also focused) on a consistent basis. While very useful, such an optical microscope is rarely available on an analytical SEM, so that another method must be used to select the working distance properly and consistently. The following procedure assumes the use of a flat polished specimen.

1. Load the specimen so that its Z-height is approximately correct for the ideal working distance specified by the manufacturer. Most SEMs provide a mechanical mounting reference frame to approximately set this initial specimen altitude.
2. Using the manufacturer's specified value of the ideal SEM working distance for EDS (e.g., 10 mm), set the SEM objective lens strength to focus at this optimal working distance, making use of whatever objective lens meter reading is available to monitor this adjustment.
3. Select a low magnification to begin (e.g., 100×). Despite care in polishing, there are almost always a few fine scale scratches or other irregularities to be found. Locate one, and use the stage Z-motion (i.e., motion along the optic axis of the SEM) to bring this scratch into approximate focus, without adjusting the objective lens strength. Increase the magnification in stages to 5000× and refine the focus with the Z-axis motion, not by changing the objective lens strength. If the SEM stage automation system permits, save this Z-parameter.
4. This procedure is likely to be more reproducible at lower probe currents where the convergence angle is larger and depth-of-focus is smaller.
5. Consistency is critical. Always collect your spectra at this ideal working distance. Before collecting each spectrum ensure that the sample surface is at the optimal working distance by setting the objective lens/working distance and bringing the sample into focus using the vertical stage axis.

Sample Orientation

Sample orientation is also a critical parameter to hold constant.

1. The ideal sample orientation has the sample perpendicular to the electron column's optical axis. The electrons strike the sample normal to the surface and their behavior in the sample is best understood.
2. Tilts of a few degrees from the ideal perpendicular orientation can significantly degrade the accuracy of quantitative measurements for highly absorbed X-rays, such as low energy photons below 1 keV.
3. The best way to ensure that the samples are oriented correctly is by checking the orientation of the stage using a spirit level and then ensuring that the sample's surface is parallel to the stage datum. Check both orientations as a stage may be perpendicular to the optic axis in one direction (x or y) and tilted on the other (y or x).
4. Sometimes it is not possible to use a level to ensure orientation, in these cases you may be able to use a flat portion of the sample and the image focus to ensure that the sample maintains focus as the stage moves. A 1° tilt corresponds to a change of working distance of 17 µm over a travel of 1 mm.

Detector Position

Maintaining the position of the detector relative to the sample is critical. The sample position aspect of this has been discussed above in terms of setting the proper working distance. On some instruments, it is also possible to position the X-ray detector along a slide mount with a screw drive (manual or motor driven) that moves the detector along its central axis out of the chamber and away from the sample.

1. Usually, the optimal location for the detector is as close to the sample as possible without obstruction or collision.
2. The detector snout should not touch anything inside the chamber. The snout should be electrically isolated from the chamber.
3. The position of the detector should be maintained by setting a stop that ensures that the detector is returned to precisely the same position each time it is removed and returned.
4. The solid angle and therefore also the throughput is a function of the distance of the detector to the sample squared. Thus small variations in this distance can contribute to large differences in measured X-ray intensities. A 1 % error in distance leads to a 2 % error in intensity.
5. On a few instruments, the take-off angle can be varied. A single take-off angle should be selected and maintained. All else remaining the same, higher take-off angles are better than lower ones.

Probe Current

1. It is not necessary to maintain exactly the same probe current throughout the entire measurement process but it is beneficial to try to maintain the probe current to a narrow range because this minimizes errors resulting from non-linearities in the picoammeter.
2. Typically, the probe current is selected to maximize the X-ray throughput on a selected material (e.g., Cu), while simultaneously maintaining a low rate of coincidence events (pulse pile-up).
3. Coincidence events occur at all throughputs but become much more common at higher throughputs (scaling roughly as the square of the throughput). The acceptable coincidence rate is composition dependent. Lower probe currents and lower coincidence rates are required for trace element analysis and when a coincidence event occurs at the same energy as a minor elemental peak.
4. Older Si(Li) detectors with lower throughputs typically had less of an issue with coincidence events and maintaining a dead time of 30 % was close to optimal for all vendors and most samples.
5. Silicon drift detectors are capable of higher throughput but are also more susceptible to coincidence events so an acceptable coincidence rate, rather than a specific dead time, should be used as a metric to select the probe current. Note that coincidence depends strongly on how many high-count-rate peaks are present in the spectrum, so the degree of coincidence will vary with composition.
6. A good starting point is to observe the coincidence events that occur with alumina (Al_2O_3). Adjust the probe current to maintain the amplitude of the largest coincidence peak on this challenging sample as less than 1 % of the amplitude of the parent peak.

26.4 Collecting Data

26.4.1 Exploratory Spectrum

1. Before proceeding to collect final data on a sample, it is generally a good idea to collect an exploratory spectrum. This exploratory spectrum should be collected for sufficiently long to ensure that all the elements (major, minor, and trace) present in specimen can be identified. This exploratory spectrum can also be used to determine how long an acquisition will be necessary to get the precision you desire for each element in the spectrum.
2. Subject the exploratory spectrum to qualitative analysis using the vendor-supplied automatic peak identification tool but always follow with manual inspection of the suggested elemental identifications to determine validity. The elements identified will determine the standards that will be necessary for the analysis.
3. If you suspect that an element may also be present but is obscured by another element, a standard should be collected for that element too.
4. It may be beneficial to perform a standardless analysis on the exploratory spectrum to get a rough idea of the composition of the unknown (Be sure that the manually confirmed element list, not the raw automatic peak identification list, is used for the standardless analysis.)

26.4.2 Experiment Optimization

Determining the peak fitting reference requirements and the optimal acquisition times can be a challenge. DTSA-II provides a tool to help. The user provides an estimate of the composition of the unknown (crude estimates are fine), the standards you are going to use and the desired measurement precision and the tool will tell you when references are required and suggest approximately how long to acquire each standard, reference and unknown spectrum.

26.4.3 Selecting Standards

1. Select a standard for each element that you believe is present in the unknown.
2. In certain problem domains, you may be able to omit a standard if you calculate oxygen by assumed stoichiometry or assume an element by difference from an analytical total of one.
3. It's generally best to assume that you will measure every element and collect a standard for each. You can always change your mind later.
4. Initially, it is probably best to select a simple standard (one for which no peak shape references are required)

26.4.4 Reference Spectra

References serve two purposes:

1. To resolve interferences in multi-element standards
   - Example: In BaF_2, the Ba M lines interfere with the F K lines. To use BaF_2 as a standard for Ba, two references (e.g., $BaCl_2$ for Ba and CaF_2 for F) are required to provide clear, interference-free views of the Ba M-family peaks and the F K-family peaks in the range of energies in which the Ba M lines interfere with the F K lines.
2. To strip elements which are known to contribute to the unknown spectrum but are not really present in the material
   - Example: A reference to strip a thin conductive coating of Au, Pt, or C.

26.4.5 Collecting Standards

1. Since standards will typically contribute to many measurements, it is generally a good idea to spend extra time to ensure that standards are of high quality.
2. The total acquisition time necessary depends upon the measurement goals and can be determined by examining the intensity in an element's characteristic peaks. In particular, you should examine the characteristic peaks that will be used to perform the quantification. The background corrected peak integral should contain at least 10,000 counts for approximately 1 % precision or 160,000 counts for 0.25 % precision.
3. It is generally better to collect multiple shorter acquisition spectra from multiple points on the standard and build a single high-quality standard spectrum from the best of these. Collecting multiple spectra allows you to discern problems with individual spectra that may otherwise go unnoticed.
4. Collect N where $N > 2$ spectra from various different points on the standard.
   - Measure and record the probe current before collecting each spectrum and after the last.
   - Note any significant changes in probe current where "significant" is determined by the desired measurement precision.
5. Compare the N spectra but plotting them simultaneously using the same vertical scale for all. Examine carefully the intensity in the characteristic peak of choice. Discard any spectra which differ systematically by more than counting statistics. Sum the remaining spectra together to form a single spectrum.
6. Ensure the following properties are assigned to the standard spectrum.
   (i) Beam energy
   (ii) Probe current
   (iii) Live-time
   (iv) Composition of the standard
7. Save the standard to disk.
8. Repeat for each required standard.

26.4.6 Collecting Peak-Fitting References

References serve as examples of an element's characteristic peak shapes. The factors that make for a good reference are different from those that make a good standard.

1. A good material for a reference need not be as carefully mounted and prepared as a standard or unknown.
2. Particles or rougher surfaces can serve as adequate reference materials.
3. You don't need to know the probe current or live-time.
4. While it is generally a good idea to collect the reference at the same beam energy (particularly for lower overvoltages on the L and M lines), it is not always necessary.
5. References should be high count spectra but are less susceptible to count statistics than the standards. In general, a reference should have significantly more than 10,000 counts in the element's useful characteristic peak to provide an adequate perspective of the peak shape.
6. Simple elemental standards can always be reused as references.
7. Save the references to disk.

26.4.7 Collecting Spectra From the Unknown

1. Examine the exploratory spectrum to determine how long an acquisition time to use for the unknown

2. Examine the intensity in the measured characteristic peak for each element in the unknown to make realistic precision goals for each element:
   - 1 % or better precision is realistic for major elements ($C > 0.1$ mass fraction)
     - 1 % precision requires at least 10,000 counts in the unknown's quantified characteristic peak
   - 3–1 % is realistic for minor elements ($0.01 \leq C \leq 0.1$ mass fraction)
     - 3 % precision requires at least 1,000 counts in the unknown's quantified characteristic peak
3. Each element is likely to require a different acquisition time. Select the longest.
4. Collect multiple spectra from different positions on the unknown as you did with the standards, compare the unknown spectra looking for differences. If one or more spectra are different, try to identify the source of the differences. The differences may reflect real inhomogeneities or they may represent measurement artifacts like surface contamination, roughness, voids, or probe instability.
5. Collect an image with the spectrum so that if there is a problem with a particular spectrum, you can assess whether there may be a sample-related problem.
6. You may reasonably eliminate (and potentially recollect) spectra that differ due to recognized measurement artifacts. However, unexpected differences may be important clues that the specimen is locally different in some unexpected manner that this difference comprises real information that you do not want to ignore. Reality on the micrometer-scale is often more complex than we expect.
7. Identify the subset of the acquired unknown spectra that you are going to quantify. Ensure each spectrum from the unknown contains the following data items:
   (i) Beam energy
   (ii) Probe current
   (iii) Live-time

26.5 Data Analysis

26.5.1 Organizing the Data

By this point, you should have collected all the pieces of data you need to perform the quantification:

1. Standard spectra—One high-quality standard for each element in the unknown
2. Reference spectra—For each standard with an interference and for each element to strip
3. Unknown spectra

26.5.2 Quantification

DTSA-II quantification proceeds as follows:

1. Select the unknown spectrum or group of spectra to quantify.
2. Select the standards. If a standard has two or more elements, you will be asked which of the elements are to be considered for this analysis: for example, if FeS_2 is selected, you will can select Fe and/or S. Only one standard can be selected per element. If an element present in the standard has already been selected, it will be grayed out.
3. Select the references. DTSA-II will inform you if a standard cannot serve as a reference due to a conflict from interfering peaks; for example, for BaF_2, the Ba M-family and F K-peak mutually interfere. If a reference is needed that is different from the standard, then select the element in dispute (which appears in red) from the list and select an appropriate spectrum to serve as a reference, for example, CaF_2 for F and $BaCl_2$ for Ba M-family.
4. DTSA-II will then execute and return a report with the k-ratios measured, the elemental concentrations calculated, the residual spectrum after peak fitting, and the uncertainty budget consisting of the uncertainties due to counting statistics of the unknown and standard, the atomic number correction, and the absorption correction.

26.6 Quality Check

26.6.1 Check the Residual Spectrum After Peak Fitting

You aren't done until you've checked for blunders, mistakes, and surprises. Two of the most common mistakes are missed elements and misidentified elements. Both of these mistakes can be identified using the residual spectrum. The residual spectrum is a derived spectrum computed from the unknown spectrum in which all the quantified characteristic peaks are removed.

1. Missed element: One of the most common surprises is a missed element. Sometimes, the element is hiding under the characteristic lines for another element. You won't know about the other element until you've performed peak fitting for the intensity contributions from the elements that you already know about. A missed element will show up as a peak in the residual. If you have missed an element, you will need to add an appropriate standard for that element (and possibly a reference) and re-quantify the data.

2. Misidentified element: Many characteristic peaks can be mistaken for another element. A peak may be at the correct energy for another element but the residual will reveal the mistake. The shape of peaks will be different and the residual will appear irregular and non-physical. Alternatively, there may be other peaks that remain in the residual unaccounted for by your initial choice of standards. To fix this problem you should replace the standard for the misidentified element with one for the correct element and re-quantify the data.

26.6.2 Check the Analytic Total

The analytic total is the sum of the mass fractions measured for each element in the unknown. The analytic total should be close to unity if all elements have been recognized and included in quantitative calculations. When a typical material is analyzed under typical conditions, the analytical total may reasonably vary 1 % or 2 % from unity due to measurement uncertainties. Simple measurements based on energetic K peak transitions can be reliably measured to better than a percent. More complex measurements involving low energy X-rays (like carbides and oxides) are likely to have larger deviations. A deviation of more than a percent or two should inspire you to start asking questions.

1. Have I missed an element?
   (i) Check the residual. Is there a peak that hasn't been quantified?
   (ii) Is it possible that there is an unmeasurable element like H, He, or Li in the unknown?
2. Is there a problem with the measurement process?
   (i) Is the sample preparation adequate?
   (ii) Is the sample tilted?
   (iii) Is the sample at the correct working distance?
   (iv) Is the probe current being measured accurately?
   (v) Did the probe current drift?
   (vi) Did the specimen charge?

26.6.3 Intercompare the Measurements

Whenever feasible you should make multiple measurements of each material. As part of the quality control process, you should compare these measurements.

1. How do the measurements vary among themselves?
2. How does the variance calculated from the measured values compare with the estimated uncertainties (particularly the uncertainties due to precision)?
3. Do the measured variances suggest that the material is homogeneous or inhomogeneous?
4. Is there an outlier? Can you explain the outlier? Examine the SEM image of the region. Is there any obvious difference in the image compared to other areas? If there is no obvious reason for the outlier, does it suggest something about the sample or does it says something about the measurement process? Can you reproduce the outlier by re-measuring the spectrum at the same location?

Report the Results

- What to Report

The analytical report should be a concise description of what request was made to the analyst, what analytical strategy was developed, how the measurement was performed and the results.

- Analytical Procedure

The analytical procedure should provide sufficient detail that you or someone else with the correct instrumentation could replicate the measurement.

1. Scanning electron microscope
   - Manufacturer and model
   - Beam energy
   - Nominal probe current
2. X-ray detector
   - Manufacturer and model
   - Configuration settings
3. Other aspects
   - Picoammeter
   - Software
4. Standards
   - Identity, composition, source, live time, probe current, sample preparation, coating
5. References
   - Identity, composition, characteristic line assignment, sample preparation, coating
6. Unknown
   - Identity, sample preparation, coating
7. How the locations for analysis were selected. Was it based on the customer's directions or if the analyst selected the locations, what criteria were used?

- Results

Each spectrum should be reported independently. For multiple spectra, tabular form works well.

1. Reporting the elemental data
   - It is generally best to report the non-normalized mass-fraction unless there is precedent for using an alternative format. It is only acceptable to report the normalized mass-fraction if the analytical total is also reported.
2. If you report in oxide fraction or atom fraction be sure to include the analytical total since the act of converting

from mass concentration (weight fraction) to atomic fraction or oxide fraction includes normalization.

3. DTSA-II provides an estimate of the measurement uncertainty for each element. The estimate should make clear which factors were considered and whether the estimate should be considered an estimate of accuracy or just an estimate of precision. A measurement without an uncertainty estimate is open to misuse. The client may assume that the result is more accurate than it really is and draw conclusions that cannot be justified by the data. Alternatively, the client may not trust the data or may assume that it is less accurate than it is and fail to draw conclusions that are justified. Either way, data presented without uncertainties is of limited utility.
4. If the spectra represent a nominally homogeneous region (or one you suspect to be), add descriptive statistics (mean, standard deviation) summarizing the variation between locations for each element. Compare this value with the uncertainty estimate for a single measurement to detect heterogeneity.

- Conclusions

Conclusions should be pithy. You should be very careful only to report that which is directly supported by the measurement results. In other words, stick to the facts and avoid conjecture. Don't answer questions that go beyond the data and your personal expertise.

Reference

International Organization for Standardization (2012) Standard file format for spectral data exchange ISO 22029:2012. ► https://www.iso.org/standard/56211.html