Guide for Combined EDS/WDS Quantitative Analysis

Requirements:

Standards

Both "Standardless" quantitative analysis and analysis using standards can be performed with EDS. Standards *must* be collected for WDS quantitative analysis. It is recommended that for combined EDS/WDS quantitative analysis, standard data should also be collected for EDS.

Faraday Cup

A faraday cup is required for measuring the electron beam prior to collecting WDS standard data. If the results are to be presented as unnormalized, then the beam current *must* be measured prior to analyzing the unknown. The Faraday cup is typically found on the standard block or on a modified sample holder dedicated to quantitative analysis.

P10 Gas

If the P10 gas is tank is closed. Open the value and adjust the regulator until 10 psi is reached and maintained. This may require small adjustments of the regulator until the gas flow becomes stable at 10 psi. The analyst should wait an hour to allow the flow to stabilize before collecting standard data or analyzing their samples.

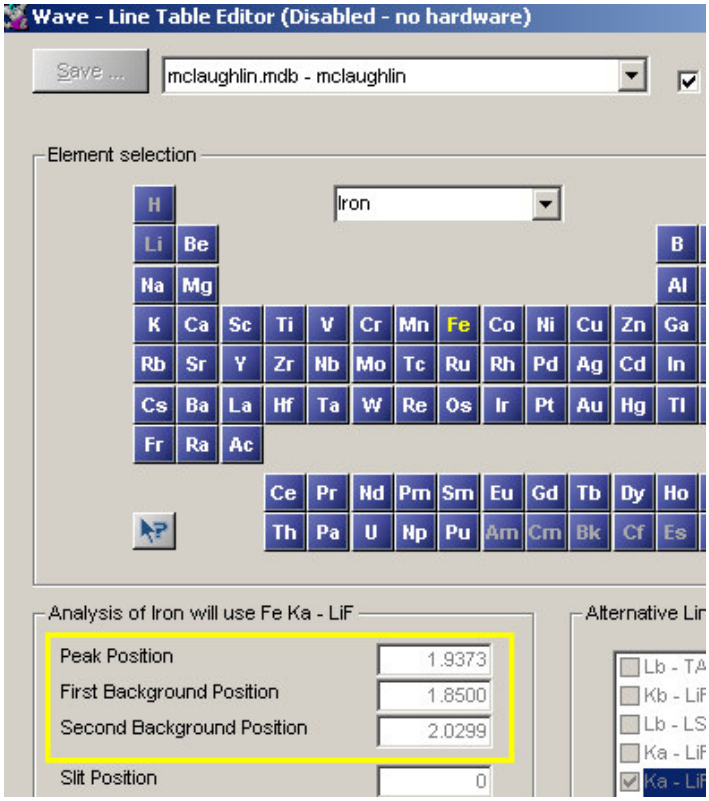
Step 1: Know Your Sample.

Prior to analyzing your sample, a list of all elements known to be in the sample and those elements that may or may not be in the sample should be made. From the list, the user should determine the most suitable detector for each element. Typically, minor and major elements (> 5.0 wt%) will be analyzed using the ED detector and elements < 5.0 wt% will be analyzed using the WD detector. However with severe overlaps the user may elect to use the WD spectrometer for minor or major elements as well.

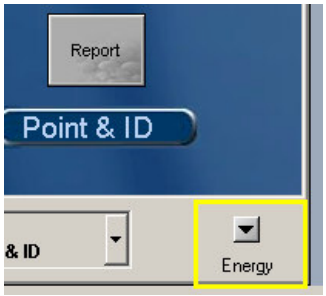
WD preparation

Wavelength dispersive quantitative analysis requires that X-ray counts be measured at two background positions for each element. Typically, the background positions are located on either side of the element peak to be measured and are located the same distance (wavelength range) from the peak. The peak position and background positions are stored in the *Line Table* of INCA Wave. The Line Table can be accessed by going to INCA Point & ID or INCA Analyzer, going to the menu item Options | Energy + Options…| Line Table Editor. In the Line Table Editor window you will see entries for

Peak Position, First Background Position, and Second Background position. You can change these entries if necessary.



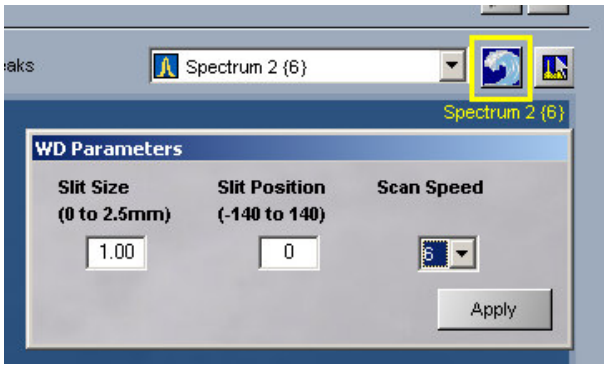
You can also access the Line Table by going to INCA Wave by choosing “Wave” through the detector button. Once in Wave, choose the menu item Options | Wave Options…| Line Table Editor.



The analyst should ensure that there are no general peak overlaps, higher order peak overlaps, or satellite peak overlaps with the elemental peaks chosen for analysis and the background positions. This can be accomplished by performing a preliminary, but thorough WD scan in INCA Energy by covering all the elements to be analyzed.

Go to INCA Analyzer, go to the “Acquire Spectra” window, place beam on the sample of interest, by going to the centre of the sample and setting the microscope magnification to >100,000x (essentially spot mode). Collect a good EDS spectrum

(Process Time 3, deadtime between 40-50 %, 30 second livetime). Once a spectrum has been collected, increase the beam current on the microscope, by using largest aperture and choosing a large spot size. Go to the "Confirm Elements" window click on the "WDS scan parameters" button and choose a relatively fast scan speed (6, 7, or 8).

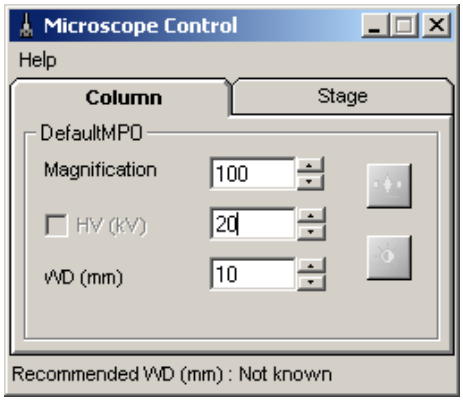


Note that X-ray intensities will increase with energy for each crystal analyzer. After choosing the appropriate scan parameters, choose the region to scan by holding the shift key down on the keyboard and swiping the desired region of the spectrum while holding the left mouse button down. The WD spectrum should appear as the crystal analyzer and the detector assembly move along the Rowland Circle. The analyst may choose to scan over the entire spectrum, but it is more efficient to scan over the element peaks that will be used for the quantitative analysis. After the WD spectrum has been collected, use the spectrum to detect potential overlaps. If overlaps are found then Peak, First, and Second Background Positions must be modified in the Line Table to avoid the overlaps.

Step 2: Analytical Setup

There is a great benefit if standards and specimen can be mounted in the microscope at the same time and is highly recommended even if it requires modifying an existing sample holder or machining a new holder dedicated to quantitative analysis. Swapping standards and specimen increases overall analytical time, increases potential error due to differences in grounding, and possible changes in geometry and microscope column conditions. The standard block and specimen should be mounted so that they are the same height. This will prevent possible shadowing of the detectors and stray X-ray generation from mounts.

Prior to collecting standards, the analytical conditions for analysis (beam current and accelerating voltage) must be chosen. Choose an appropriate accelerating voltage such as 15 kV. Set the WD to exactly 10.0 mm (This is the working distance for ED/WD on a Quanta 250 microscope). The working distance can be set to 10.0 mm WD by going to INCA Energy, choosing the menu item Options | Microscope Control… and then typing 10.0 for the WD parameter in the Microscope Control window.



Once the WD is set, it should never be changed. To focus the specimen/standard, the Z-position of the stage should be used to bring the surface of the specimen or standard to 10.0 mm. This is to ensure that the specimen-crystal analyzer-detector geometry is constant.

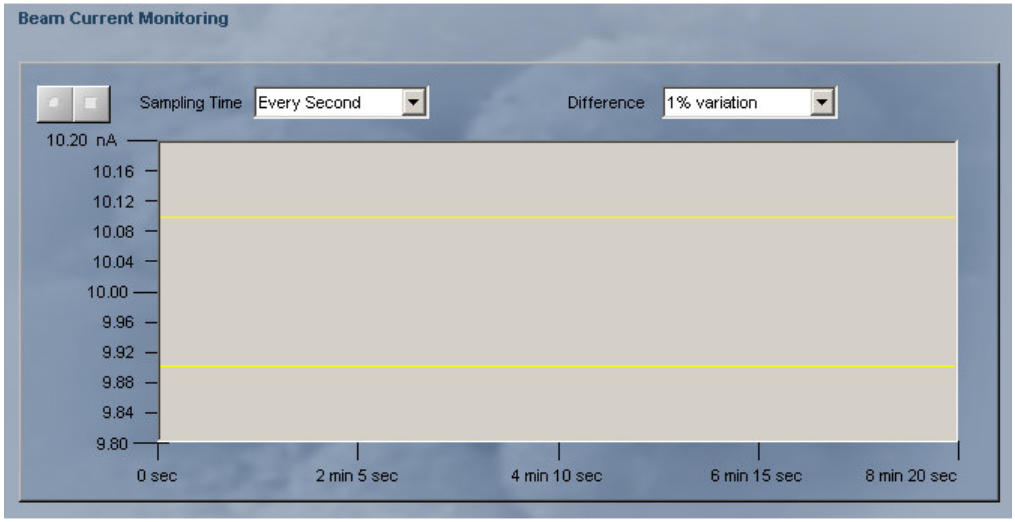
Due to the higher beam current required for WD, the ED detector should be retracted to its maximum position. This is done by going to INCA and Options | Detector Control and then clicking on the Move Out button.

Make sure that Pile-up correction is on. In INCA Analyzer, go to menu item Options | Analyzer Options, go to the "Pile up correction" Tab and check enabled.

Go to the "Microscope Setup" window and choose Process Time 3. With the specimen under the beam (magnification > 100,000x), adjust the beam current (spot size) and/or aperture on the microscope until you obtain a deadtime of approximately 45%. This will be the microscope setup that you will use for your quantitative analysis. To measure the beam current at 45 % deadtime, go to the Faraday cup and place the beam in the hole.

Select menu item Options | Energy + Options… | Display Status Bar. This will show a status bar with the measured beam current. For your quantitative analysis, the beam current will always be near this value. *For quantitative analysis, it is critical that the beam current on the microscope is stable*. Any error in measuring the beam current prior to collecting a standard or analyzing the specimen will result in errors in the quantitative analysis. This error will be reflected in the atomic proportions and in the total wt% of the analysis. The error in beam current measurement before analyzing the specimen will be directly proportional to the error in the total weight%. One percent error in measuring the beam will result in 1 percent error in the calculated total wt%. This fact will most likely be the largest source of error for both EDS and WDS analysis. To monitor beam stability go to INCA Wave using the detector button (see above). In INCA Wave, go to the "Microscope Setup" window. With the electron beam in the Faraday cup, press the start button for the Beam Current Monitor. This will record the beam current

over time. With proper setup (gun and aperture alignment) the beam current should not vary more than 1% / hour. The yellow lines in the monitor display a user-selected variation range.



A rapidly changing beam current (for example, 1% every 10 minutes) is unsuitable for quantitative analysis and remedies should be taken to stabilize the beam.

Step 3: EDS Standardization

The microscope beam current must be stable for standardization. Before collecting spectra used for standards, a "Quant Optimization" must be performed. The analyst can choose what pure element to use for quant optimization, however, once chosen the same element must be used for all standards and for quant optimization before analyzing the specimen. Quant Optimization provides two features:

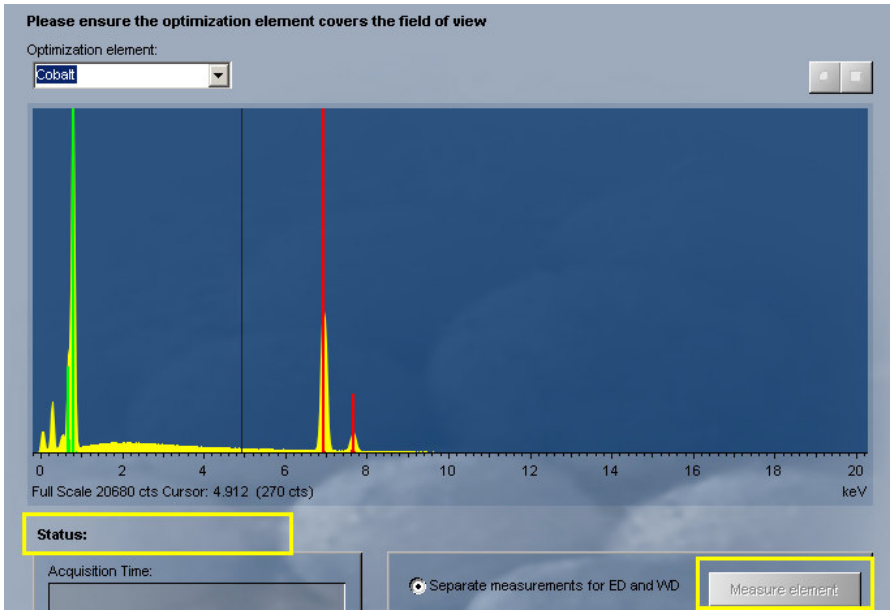
i) It ensures that all elemental peaks are located at their proper positions in the spectrum.

ii) It measures the beam current indirectly by measuring and recording the x-ray generation rate of the element peak. This information is saved with every subsequent spectrum and is a record of the beam current at which the spectrum was collected.

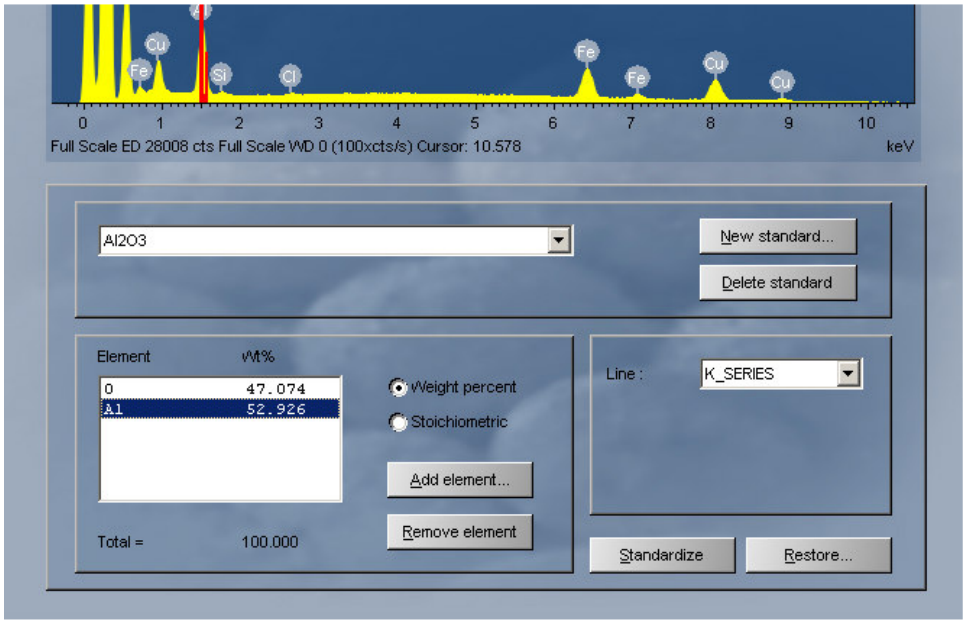
As can be seen with item ii, if the quant optimization was performed at a certain beam current and the beam current changed prior to collecting a spectrum, the incorrect beam current would be stored with the spectrum. This will result in errors in the quantitative analysis whether the spectrum is used as a standard or is collected from the unknown specimen. No change in beam current must occur between the last Quant Optimization and the collection of spectra. If the beam current changes due to user error or by beam current drift, another Quant Optimization must be performed.

Once quant optimization has been performed, as quickly as possible, go to each standard and collect a high quality spectrum (remember that you are at Process time 3

and the EDS detector is retracted). After collecting the standards go back to the Faraday Cup and measure the beam current. If the measured beam current has drifted substantially (> 0.5 %) the standard spectra should be reacquired. You can also measure the change in beam current since the last quant optimization by performing another quant optimization. When the “Measure element” button is pressed the change in beam current is shown below the quant optimization spectrum.



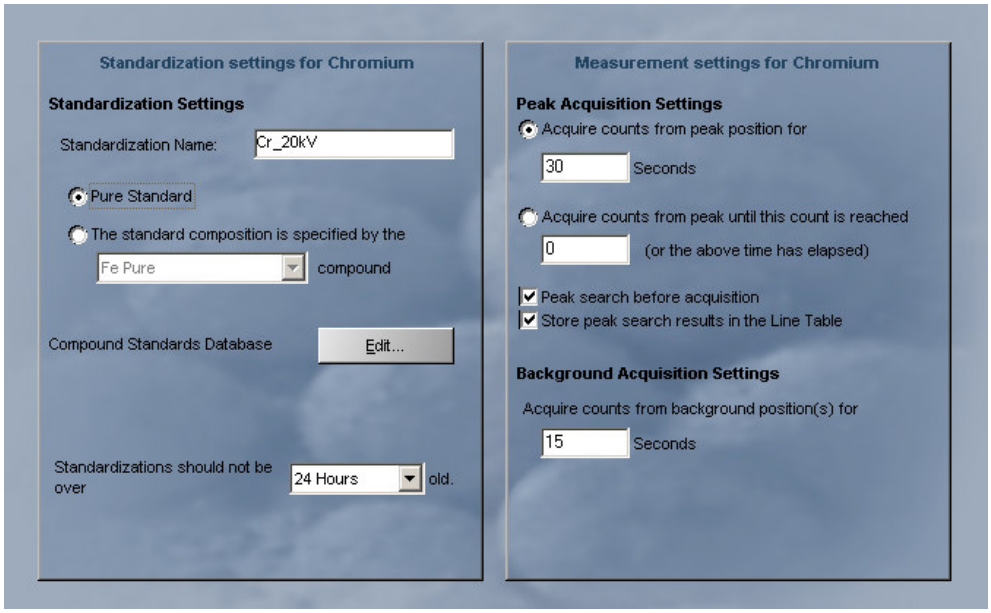
When you finish collecting all spectra you must then standardize using the collected spectra. Go to INCA Analyzer and the “Standardize” window. Display each standard spectrum in turn and standardize the desired element.



To Standardize, you must list all elements in the standard material and their weight percents. To standardize a particular element, highlight the element of interest and choose the line series to standardize then press the “Standardize” button. From then on, INCA will use the standards that you created. Remember to save the INCA project that contains the standard spectra, you may want to use them later on to restandardize.

Step 3: WDS Standardization

WDS standardization is performed in the INCA Wave portion of the software. Go to INCA Wave by clicking on the detector button. Choose the “Standardize” Navigator and then go to the “Choose Elements” window. Select the elements to be standardized by clicking on the periodic table. Go to the “Standards Setup” window and for each element, adjust Peak Acquisition settings and Standardization settings. For simplicity, set the Acquisition time for each elemental peak to 30 seconds and Background acquisition time to 15 seconds. Check “Peak search before acquisition” and “Store peak search results in the Line table”. If needed create the needed standard composition by clicking on the “Edit…” button.



Once the Standard Setup is finished go to the Faraday cup and place the electron beam in the hole. Go to “Microscope Setup” window and press the “Measure” button beside the “Beam Current (nA)” entry. This will record the beam current in nA. Alternatively, you can measure the beam current by right mouse clicking on the Status Bar and then choosing “Measure Beam Current”. No change in beam current must occur between the last beam current measurement and the collection of WD data.

Go to the “Measure Standards” window and press the start button. A series of popup windows will appear telling which standard will be collected next. Make sure you move to the proper standard and bring it into focus using the Z-position of the stage, before pressing the “OK” button in popup window.

After the standards have been collected, go back to the Faraday Cup and measure the beam current. If the measured beam current has drifted substantially (> 0.5 %) the standard data should be reacquired. From now on, the WD standards collected in INCA Wave will be used for quantitative analysis if WD data is collected from the specimen.

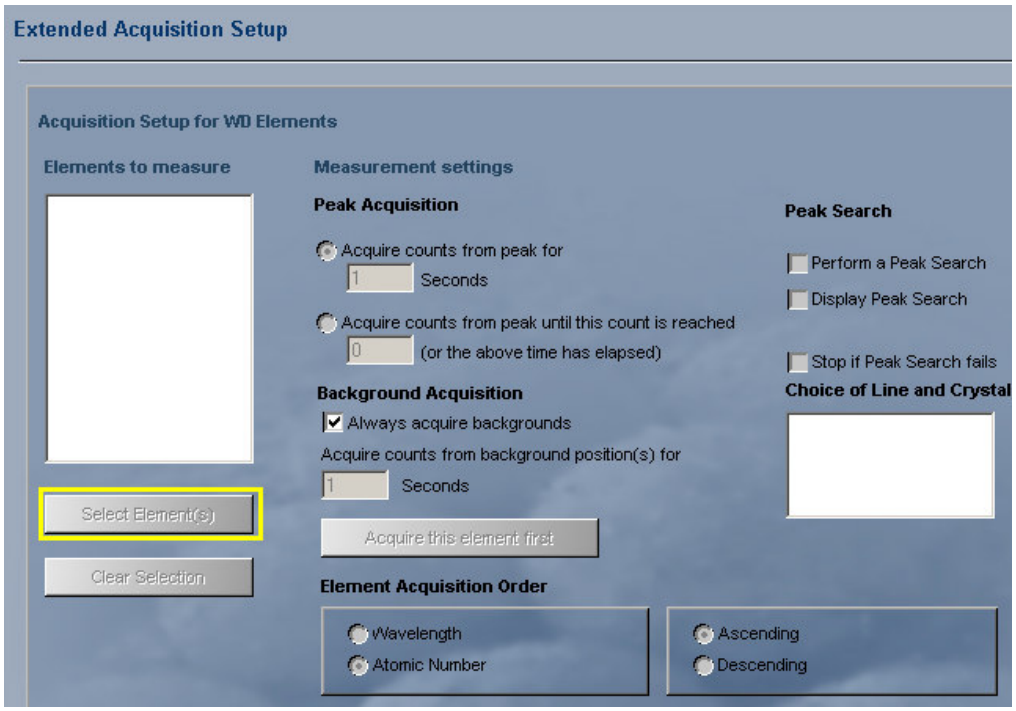
All standardization has been performed and one more step is required before analyzing the unknown specimen. In setting up standards, the beam current was measured by two different methods. For ED standardization, quant optimization was used for beam current measurement and in WD standardization, the Faraday cup was used. INCA allows you to associate measured values from these two methods allowing one method to be used for both ED and WD acquisition. Return to INCA Energy and the "Quant Optimization" window. Perform a quant optimization on the Quant Optimization element by collecting a new spectrum and pressing the "Measure element" button. Immediately go to the Faraday cup, place the beam in the hole and measure the beam current by clicking on the "Measure beam" button. Choose option "Beam current for ED and WD" or "Element optimization for ED and WD". Press the "Associate" button. Depending on the option you chose, you will only need to measure the beam current using the Faraday cup or the quant optimization element. Remember, if the beam current changes between the Quant optimization and measurement using the Faraday cup, then errors will occur in the quantitative analysis.

Step 4: Analyzing the Specimen

Before running a complex multi spectra automated run, the analytical setup should be verified by performing individual analyses on the sample. This will reveal any errors in standardization or analytical setup (for example, using the wrong peaks for quant or missed overlaps). Secondly, the true time of acquisition for a single analysis can be determined.

Setting up for Analysis

Go to the Analyzer Navigator in INCA Energy. Go to Acquisition Setup and then press the "Select Element(s)" button. Select all elements that will be analyzed using the WD spectrometer.



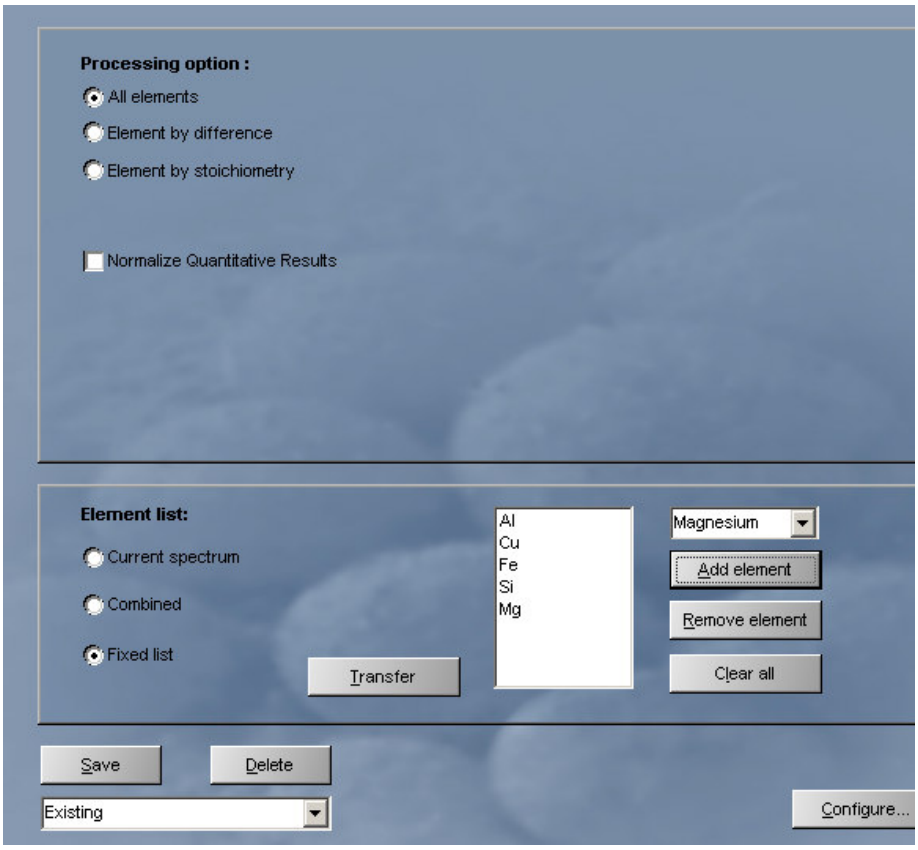
For each element in the list, you must select the element from the "Elements to measure" list and then enter the amount of time for Peak acquisition and Background acquisition. For trace elements set the Peak acquisition time to 100 secs and the Background acquisition time to 50 seconds. Note that this means that each element will require approximately 3 ½ minutes to analyze. If 10 trace elements are to be analyzed, then each data point will take approximately 35 minutes to collect. It is possible to save representative Background counts for each element and save them in the Line Table. This will greatly speed up the acquisition by shortening the acquisition time for each element to 1 min and 40 seconds and the acquisition of the data point to approximately 17 minutes. However, you must be completely confident that the beam current will not vary over the complete run.

You should not enable "Peak Search" and you should adjust the "Element Acquisition Order" so that the light elements are analyzed first.

Go to the "Acquire Spectra" window and enter a livetime of 200 seconds. This will control how long the EDS spectrum will be acquired for. Before analyzing the specimen, it would be wise to monitor the beam current by going to the Faraday Cup and displaying the WD Status Bar. You can display the WD Status Bar in INCA Energy by going to menu item Options | Energy + Options…| Display Status Bar. If the beam current has drifted significantly from the "Ideal" beam current, then you may want to adjust the spot size on the microscope to return the current to its initial value. Depending on what option you chose for measuring the beam current, go to the Quant Optimization element and perform a quant optimization or go to the Faraday Cup and measure the beam current.

Go to a clean place on the specimen and if necessary, bring the specimen into focus, by adjusting the Z-position of the stage. Go to high magnification (>x100,000) so that the microscope is essentially in spot mode. In the "Acquire Spectra" window press

the start button and collect the data. At the end of the analysis, you should have both an ED spectrum and WD data. If possible, be present when the analysis is finished so that you can immediately, return to the Faraday cup and measure the beam current. If the beam current has drifted during the run, then this will be a source of error and should be used to interpret the quant results



In the “Quant Setup” window choose processing option “All elements”, uncheck the “Normalize Quantitative Results” option. Choose “Fixed list” and add all elements that will be quantified to the list. You can save this list by typing in a name in the dropdown box and then pressing the “Save” button.

Go to the “Quant” window and the “Summary” tab. The quant results should be displayed here showing which elements were analyzed by ED and WD. Make sure that each element was analyzed using the desired detector. If the analysis was successful then the weight% total should be close to 100 %. If the total deviates substantially from 100 % then the problem must be found. The problem may be caused by beam current drift or incorrect standardization. Note that that it is unlikely that the trace elements will have a large affect on the total weight %, therefore problems are likely a result of incorrect EDS standardization of one or more of the major elements. If the analysis was successful then reanalyzing the sample two more times will give confidence in the reproducibility of the analysis.