

Electron Microprobe Users Manual

Graphical Software for the Cameca SX50

Part 2. Quantitative Analysis using the Quantitool Program.

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INTRODUCTORY NOTE ON STANDARDIZING FOR QUANTITATIVE ANALYSIS.

In very simple terms, the microprobe produces quantitative analyses of elements in an unknown sample by measuring the intensity of an X-ray line that is characteristic of that element. It compares this intensity with an intensity previously stored in memory of the same X-ray line measured under the same conditions on a standard containing a known concentration of that element. To a first approximation, the microprobe assumes that the ratio of these measured intensities (I_{unk}/I_{std}) is equal to the ratio of concentrations of this element between the unknown and the standard (C_{unk}/C_{std}) and then solves for the concentration of the element in the unknown (C_{unk}).

However, the situation is somewhat more complicated because in multi-element materials the X-rays produced by a given element (and the electron beam as well) interact with the other elements in the sample. Thus the measured X-ray line intensity produced by a given concentration of an element will partially depend on the identities and concentrations of all the other elements in the sample (i.e. the matrix). The microprobe uses correction routines to try to estimate these matrix effects and adjusts the X-ray intensities it measures accordingly. The concentration number you ultimately get from the microprobe is therefore calculated from the equation $((I_{unk} - \text{corrected})/I_{std} - \text{corrected}) = (C_{unk}/C_{std})$.

Standardizing involves storing corrected X-ray intensities for a known concentration of an element in a standard in the microprobe's memory to use in this calculation. Obviously, it is important that this stored standard intensity be as accurate as possible to achieve good results. It is necessary that the analytical conditions (accelerating voltage, beam current, beam size, spectrometer used, focus, carbon coat thickness, ... even the room temperature) be identical for measuring intensities on the standard and on the unknown. It is because these factors inevitably change over time that it is necessary to re-measure these intensities (i.e. re-standardize) frequently, generally on the order of hours to a few days.

In addition, the corrections the microprobe uses to adjust for matrix effects are not perfect. It is therefore usually best to try to minimize the size of these adjustments in the final calculations. The surest way to do this is use a standard with exactly the same concentration of all elements as the unknown. Of course if you already knew these concentrations you wouldn't be analyzing the sample in the first place, so there is always some degree of guesswork involved in picking standards.

The above considerations generally lead to a tradeoff in the way you standardize and analyze your samples. You can attempt to achieve the maximum accuracy the microprobe is capable of (usually around at ± 0.01 wt under normal conditions) by analyzing only one phase at a time, selecting the best standard(s) possible (those closest in composition to the unknown), and testing and re-calibrating frequently. Alternatively you can analyze the composed of several phases in one session (as you might want to do in analyzing a rock containing several different minerals) at a lower level of accuracy (generally $\pm 1 - 2$ wt%). For this you use standards chosen as "close enough" in composition to the unknown minerals to provide reasonably good analyses for all of them (alternatively you may elect to get good analyses on one or two phases of interest and less accurate analyses on the remainder). The choice of method will depend on the problem

you are working on and the amount of time you have available. However, in either case you should carefully plan in advance what standards you want to use, what level of accuracy you need to achieve, and how much time you are able to spend to accomplish your goal.

TYPOGRAPHIC CONVENTIONS

The following typographic conventions have been used:

BOLD CAPITALIZED - indicates the name of a window or icon.

UNDERLINE CAPITALIZED - indicates a software button, field, or menu choice that the user needs to select or enter data into.

• Message: **Bold** - indicates an instruction that appears on the computer screen

Action: - The response you should make to an instruction from the computer.

R-Click – Indicates that you should click on the Right mouse button

L-Click - Indicates that you should click on the Left mouse button

QUANTITATIVE ANALYSIS

A) OPEN QUANTITOO

- 1) L-Click on the QUANTI icon in the **SX50** icon bar.
- 2) L-Click on the pin of the message screen concerning the layer option to remove it.
- 3) L-Click on the SET CONDITIONS BULK option in the window that appears at the lower left portion of the screen.

The main **QUANTITOO** menu bar should appear along the top of the screen.

B) CALIBRATE ON THE DESIRED STANDARDS (Manual Mode)

- a) L-Click on CALIBRATE in the main **QUANTITOO** menu bar.

The **QUANTITOO CALIBRATION** window should appear

- b) R-Click on STANDARD in the **CALIBRATE** window and R-Click once on BLOCK 0 (for the normal standard block). Select the standard you want to calibrate from the pop-up menu.
- c) L-Click on the MOVE TO STANDARD button.

The stage should move to the desired standard.

- d) Check that the ACC(kv) and CURR(nA) entries are the same as those being used in the analysis. If not R-Click on these and select the appropriate values from the pop-up menus.
- e) Enable the spectrometers to be calibrated by R-Clicking on the SP1, SP2, SP3, and/or SP4 buttons and selecting ENABLE from the pop-up menu (their settings will appear in dark black letters).

- f) Similarly Disable spectrometers that are not to be calibrated by R-Clicking on the SP1, SP2, SP3, and/or SP4 buttons and selecting DISABLE from the pop-up menu (their settings will be grayed out).

Note: L-Clicking these buttons also toggles Spectrometer ENABLE/DISABLE.

- g) Set up the Calibration conditions:

- A) To set up a new Calibration for a given Standard, Spectrometer, Crystal, and X-ray line, Accelerating voltage and Beam current; R-Click on the CONDITIONS button for the spectrometer to be calibrated and select NEW CALIBRATION from the pop-up menu.
- B) If a valid previous calibration exists for this Standard, Spectrometer, Crystal, and X-ray line, Accelerating voltage and Beam current, and you want to reuse these settings; R-Click on the CONDITIONS button for the spectrometer to be calibrated, R-Click NEW CALIBRATION from the pop-up menu, and select the desired calibration from the pull-right menu.

Select the element and X-ray line to be calibrated by R-Clicking on the X-RAY field and selecting the desired line from the pop-up menu.

Set or change the other calibration parameters as desired, either by R-Clicking on them and selecting values from the pop-up menus or by typing in values (always followed by a <return>).

The required parameters and their typical values are:

PEAK SEARCH – Yes

PEAK POSITION – leave blank

AUTO ADJUST PHA – grayed out (not applicable)

TIME (sec) - 10 – 20 sec for major elements for major elements in the standard

PREC (%) – 0.1

Background Offset(s)

FREQUENCY – Once

1st BKG - 500 (LIF), 600 (TAP), 600 (PET), 2500 (PC1, PC2, PC3)

2nd BKG - -500 (LIF), -600 (TAP), -600 (PET), -2500 (PC1, PC2, PC3)

BKG SLOPE - leave blank

Note: Background values and background slope may need to be set to different values depending on the standard used.

- h) When you are done setting up the calibration conditions L-Click APPLY.

The specified conditions will be setup on the microprobe.

- Message: **Calibration Setup Ready**

- i) L-Click ACQUIRE.

The **Calibration Measurement** sub-screen will appear.

- Message: **Adjust column and stage conditions.**

Action: Focus the optical image and move to a good analysis spot. Use the SE electron image to locate spots (SCAN ON, CUP OFF). After selecting a spot to analyze make sure SCAN is off (CUP ON, SCAN OFF) then L-Click READY.

A peak search will be performed for the selected X-ray line(s).

- j) Open the **WDS Display** window to view the peak search results (to do this L-Click WDS in the **SX Setup** window and L-Click XTAL and DISPLAY in the **WDS Setup** window).

- Message: **Verify the peak position.**

Action: Check if the peaks appear centered on in the correct position for that element. Then L-Click OK.

- Message: **Set PHA?**

Action: L-Click NO.

The PHA settings set during column setup will be used.

Brief Note: Setting PHA (Not necessary in most cases).

If there is a high-order interference with the element of interest it may be necessary to set the PHA as follows:

- a) Before answering the **Set PHA** message, change the MODE setting in the **WDS PHA Setup** sub-window to AUTO to find the stored baseline and window settings for this element, X-ray line, and spectrometer.
- b) Change the PHA MODE setting back to DIFF in the **WDS PHA Setup** window. The WINDOW and BASELINE values should stay at the values set by the auto-PHA adjustment.
- c) Answer YES to the **Set PHA** message in the **QUANITOOL** pop-up window and proceed with calibration for this element.

- k) Wait for the message:

- Message: **Adjust stage position for WDS line measurements.**

Action: Move a clean calibration point and focus. Make sure the cup is On and the scan is Off. L-Click OK when done.

The calibration measurement will be performed.

Step k will be repeated until three points have been accumulated

Note: It is usually good practice to view the SE image of the standard in order to select a good spot. To do this:

- a) R-Click on MAG in the **Roller Wheel Control** window and select 1000.
- b) L-Click SCAN ON.
- c) L-Click CUP OFF.
- d) Find a clean spot to analyze.
- e) L-Click CUP ON.
- f) L-Click SCAN OFF.

l) After three points have been accumulated the message will appear:

• **Message: Press [Again] for more Measurements or [Continue] for Background Measurements.**

After three measurements have been made you have the option of collecting more points or using the ones you already have. If you collect more points, you will later have the option of discarding individual measurements that you believe may have been inaccurate for some reason. However, you must always keep at least three points for calibration.

Note: In general it is sufficient to collect 5 to 10 points. However, the exact number of measurements to make will depend on the circumstances. The maximum number of points allowed is 19.

m) To collect another measurement, move to the next calibration point and focus, then repeat step k. Repeat this step for each calibration point you measure. When you are satisfied with the measurements already collected L-Click STOP CALIBRATION.

• **Message: Select/Unselect the measurements you want to keep/ignore ... use STORE to save.**

- n) Always L-Click CONFIRM.
- o) The list of measurements will be displayed at the bottom of the screen (you can only view three measurements at a time, use the scroll bar to move through the list).

Measurements that will be included in the calibration appear on a dark background. Those that will be excluded appear on a light background. You can toggle a measurement between included and excluded by L-Clicking on the line containing it. (Note: If more than one spectrometer was calibrated, the measurements for the other spectrometers displayed on the excluded line will also be ignored).

You should definitely exclude measurements you know to be in error for some reason (scan was on, standard was out of focus, etc.). Alternately, you don't want to bias the results by simply throwing out those you don't like. There are several statistical measures available to assist in making this selection:

- The average peak value in counts/sec and counts/sec/nA. Typically this should not vary much between probe sessions. If it does you should attempt to determine why.
- The percentage deviation of each measurement from the average of all measurements (Sgl.Dev(%)) is shown on each line. In general, excluded measurements will be the ones with the largest Sgl.Dev(%) (i.e. farthest from the average).
- The Measured Standard Deviation of all measurements is shown as (Meas.Dev(%)).
- The Theoretical Standard Deviation of the measurements from counting statistics is labeled (Theo.Dev(%)). Statistically this represents the best standard deviation possible

Good calibrations generally should have Theo.Dev/Meas.Dev of 1 – 1.5. A value < 1 usually means either that there are not enough counts or enough measurements to make a statistically meaningful comparison.

Another rule of thumb is that for most elements Meas.Dev. should typically be < 0.5%. However, this is very approximate and does not hold in all cases.

As always, there will be exceptions to these general guidelines.

p) After excluding anomalous calibration measurements, L-Click CONTINUE.

If backgrounds are being measured only once they will be collected at this time.

q) If you are satisfied with the calibration L-Click STORE to save it.

The calibration will be stored and the **Calibration Measurement** sub-window will close.

r) Repeat steps 1 – 17 for each standard to be calibrated.

C) DEFINE AN ELEMENT LIST FOR ANALYSIS

1) L-Click on DEFINE in the main **QUANTITOO** menu bar.

The **DEFINE** window should open.

2) Type in a label name in the LABEL field or select an existing label name by R-Clicking and selecting a Label from the pop-up menu.

The Label is used as the root filename for all files created for the given set of elements and experimental conditions. The first character must be a letter. Otherwise any unique name can be used.

3) R-Click on TYPE and select the type of analysis from the pop-up menu. By far the most commonly used types are **ALL** (to measure all elements, usually used for metals and sulfides) and **STOICHIOMETRY** to calculate one element, typically O by charge balance (usually used for silicates and oxides).

- 4) If **STOICHIOMETRY** is selected, enter the anion to be measured and its valence (default is O, -2). Cation valences can be modified when elements are selected.
- 5) R-Click on the ACC(kV) and CURR (nA) and select the correct accelerating voltage and beam current from the pop-up menus.

Note: If two different experimental conditions are desired (e.g. different beam currents for major and trace elements, etc.), R-Click on CONDITION and select 2 CONDITION from the pop-up menu. Then fill in the #2 ACC(kV) and CURR (nA) values for the second condition. Note: The first element added to the definition must use condition 1.

• **To select elements for a newly created Label:**

- A) L-Click on the **CALIBRATION** button

The **Append Elements** sub-window will open showing all calibrations made for the desired accelerating voltage(s) and spectrometers in the upper table and any calibrations already selected for this Label in the lower table.

Select the calibration records you want to use.

- B) R-Click on the SORT BY: button at the bottom of the **Append Elements** sub-window and select DATE from the pop-up menu and then R-Click on the THEN BY button and select Z from the pop-up menu.

The calibration records in the upper table will be sorted by Date and Element.

- C) L-Click on the lines in the upper table containing the calibration record to be used for each element (after sorting this will normally be the first entry for this element). The selected line will turn dark in the upper table. Calibrations will be added to the lower table and a button for each element selected will appear in the main **DEFINE** window.
- D) For each spectrometer, the order in which the elements are selected will be the order in which they will be measured during the actual analysis. However, this order can be changed by rearranging order of the buttons in the main **DEFINE** window.

Note: Only one calibration can be selected for a given element.

- E) After selecting all the elements for this label in the **Append Elements** sub-window select DONE at the bottom of the sub-window.

• **To update old calibrations for a previously stored Label:**

- A) Highlight the button of the element to be updated in the main **DEFINE** window by L-Clicking on it.
- B) L-Click on UPDATE.

The **Update Element** sub-window will open. The upper table will show all available calibrations for that element and spectrometer at the appropriate conditions. The

currently selected calibration will appear with a dark background and is also shown in the lower table of the sub-window.

Note: If the calibration you are looking for does not appear on the list, the most common reason is that the element was calibrated on different spectrometer or at a different accelerating voltage than was used the last time the label was stored. Only calibrations made under the exact same conditions are displayed in the **Update Element** sub-window.

C) R-Click on the **SORT BY:** button at the bottom of the **Update Element** sub-window and select **DATE** from the pop-up.

The calibration records in the upper table will be sorted by Date.

D) Select the new calibration by L-Clicking on it in the upper table of the **Update Element** sub-window.

E) Select the next element button in the DEFINE window and perform the same procedure.

F) When you have updated all elements L-Click on **DONE** at the bottom of the **Update Element** sub-window.

G) Make sure the buttons in the DEFINE window are arranged in the order in which you want the elements analyzed. Use the **INSERT** and **DELETE** to change the order of the element buttons if necessary.

To **DELETE** an element button: L-Click on the element button you want to remove (it will turn dark gray) and then L-Click on **DELETE**.

To **INSERT** an element button: L-Click on the element button located after the place you want to insert a new element. Then L-Click on **INSERT** and select the desired calibration record from the upper table of the **Append Elements** sub-window.

Note: It is good practice to use the spectrometers efficiently (i.e. to have multiple spectrometers running simultaneously as much as possible). This will greatly shorten the analysis time. In addition, elements that migrate under the beam (Na, K) or that may be volatile (F, Cl) should usually be placed in the first group of elements to be analyzed.

H) L-Click on each element button and check the associated parameters. These parameters can be modified either by R-Clicking and selecting other values from pop-up menus or typing them in. Typically the only parameter that is changed at this time is **COUNTING TIME (sec)**. However, other parameters such as background offsets may need to be changed in specific cases.

I) When finished R-Click on **SHOW** and select **PRINT ALL** from the pop-up menu. Save this list for future reference.

J) L-Click on **STORE, APPLY**. The experimental conditions and calibrations for this Label will be stored. If the label already exists you will be asked if you want to overwrite the old Label. Note: the data previously collected for this label will be overwritten. If you haven't already save it you show L-Click **CANCEL** and save it now.

• **Message: Make sure now that you have the right conditions on the column: ...**

Action: Make sure that you have set SCAN to OFF in the **Roller Wheel Control Window**. In addition, all of the analytical conditions (beam size, beam current, etc.) should be the same as you want to use during your analyses. When you are ready L-Click CONFIRM.

The **DEFINE** window will close.

K) CHECK THE CALIBRATIONS

- 1) L-Click on CONTROL in the **STAGE** window to open the **Stage Control** sub-window.
- 2) R-Click on NAME in the **Stage Control** sub-window and select the name of the standard you want to analyze as a test from the pop-up menu.
- 3) L-Click on MOVE in the **Stage Control** sub-window to move to the desire standard. Then close the **Stage Control** sub-window by L-Clicking on the CONTOL button in the **STAGE** window.
- 4) Move to a clean spot and focus optically.
- 5) L-Click on the ANALYZE button in the main **QUANTITOO**L menu bar.

The **ANALYSIS** window will appear.

- 6) R-Click on the ACQUIRE button and select SINGLE POINT from the pop-up menu.

The LABEL field will appear.

- 7) R-Click on the LABEL field and select the desired analysis label from the pop-up menu.

After a few seconds the CONTINUE button will appear.

- 8) L-Click on the CONTINUE button.

The CONTINUE button will disappear and then reappear after a few seconds. If there is already analytical data stored for this Label the APPEND button will also appear at this time. If you want to overwrite existing data R-Click on the APPEND button and select OVERWRITE from the pop-up menu.

- 9) L-Click on the CONTINUE button for the second time.

The CONTINUE button will disappear and then reappear after a few seconds.

- 10) Check the focus and L-Click on the CONTINUE button for the third time.

The first analysis will begin. When it is finished the analytical results and other information about the analysis will be displayed

- 11) If desired, move to another point on the standard and L-Click CONTINUE.
- 12) Make sure you are focused and L-Click on the CONTINUE button a second time.
The selected point will be analyzed
- 13) Repeat steps 11 and 12 for each point you want to analyze on this standard.
- 14) After analyzing points on the first standard, move to another standard containing other elements of interest and collect data by repeating steps 11 - 13.
- 15) Repeat step 15 until you have collected data for each element that you consider to be important in your unknown sample.
- 16) To print the analytical results L-Click on PRINT ALL.
- 17) L-Click on DONE when you are finished analyzing the standards.

The analysis window will close.

Check your results. The concentrations of the elements of interest should be close to those shown in the standard book. The acceptable degree of error will depend on the accuracy you require for your analyses, the element being analyzed, and the primary and secondary standards being used, etc. However, for a normal analysis of several different minerals or phases, an acceptable error is generally $< 0.2 - 0.3$ wt%.

If you have analyzed for most of the major elements in the secondary standard you should check the un-normalized total. It should be close to 100 (± 1 wt%). Note this will not be true for hydrous phases or for phases containing significant amounts of elements lighter than F (O in oxides is usually estimated by stoichiometry).

Finally, if the secondary standard is similar in composition to the unknown, look at the correction factors for elements that are present in significant amounts (approximately > 1 wt%). Ideally these should be close to 1 (a number > 2 for example indicates that the intensity of this element has been adjusted for matrix effects by over +100%). The amount of correction applied will be different for different elements in different situations. However, if there is a consistently large correction for an element of interest, you might want to use a standard for that element that is closer in composition to the unknowns you intend to analyze.

Congratulations. You are at last ready to quantitatively analyze your sample.

L) ANALYZE THE SAMPLE

- 1) Remove the standard block and insert a shuttle containing the sample to be analyzed. Follow the directions given in the section Shuttle Exchange Procedures.
- 2) When the Vacuum Ready message appears. Turn the beam on by loading the HV15 setup file.

- 3) L-Click on the STAGE DISPLAY button in the **STAGE** window.

The **Stage Display** sub-window will appear.

- 4) For a normal 6 hole sample block, R-Click on the HOLDER button and select HO6 from the pop-up menu. Then R-Click on BLOCK TYPE and select SAMPLE from the pop-up menu.

A diagram of the sample holder will appear in the **Stage Display** sub-window.

- 5) Make sure to set CUP ON. L-Click once on the approximate location of the first sample you want to analyze.
- 6) Use the X,Y,Z thumbwheels to focus optically and move to the sample.
- 7) R-Click MAG and select MIN. R-Click SCAN ON. R-Click CUP OFF.
- 8) L-Click on VIDEO in the **SETUP** window and make sure AUTO is selected in the **VIDEO SETUP** window.

Wait for a picture to appear on the screen and for the contrast to adjust.

- 9) L-Click on DETEC. OFF to turn off the SE detector.
- 10) L-Click on BSE to turn on the backscattered electron detector.
- 11) L-Click on Q in the **SETUP** window and L-Click on the Light ON button in the **OPTICS SETUP** window. Note: do this even if ON already appears to be selected.
- 12) L-Click on the ROLLER CHOICE button in the **Roller Wheel Control** window to reset the roller wheels to XYZ.

Wait for the contrast to adjust on the TV screen.

- 13). Locate the spot you want to analyze using the video and optical displays.

SINGLE POINT ANALYSIS

For point by point analysis follow the same procedure described in **Checking Calibrations** (Section D, above).

MULTIPOINT ANALYSIS – STAGE MOTION

- 1) L-Click XYZ in the **QUANTITOO** menu bar.

The **XYZ** window will appear.

- 2) R-Click on DELETE and select DELETE ALL to remove old data points.
- 3) R-Click on the LABEL field and select the desire label from the pop-up window.

- 4) L-Click on STAGE to select stage scanning.
- 5) R-Click on AUTOFOCUS and select 1 (i.e. autofocus on every point).
- 6) R-Click on COLUMN SETUP and select 0 (i.e. don't adjust the column settings during the scan).
- 7) L-Click on VIEW

The **XYZ VIEW** window will open below the main **XYZ** window.

SINGLE POINTS

Move to the starting point of the line you want to scan and focus optically.

- a) L-Click on POINT.

Note: The probe marker on the TV screen may disappear. To get it back R-Click on ROLLER CHOICE in **Roller Wheel Control** window and select PROBE MARKER from the pop-up menu. Then immediately L-Click on the ROLLER CHOICE button to return the wheels to stage control. If the Label disappears, enter the Label again.

- b) Enter a comment in the COMMENT field for this point.
- c) L-Click on VALID to set the XYZ coordinates.
- d) L-Click on ADD to add the point to the list to be analyzed.

The points will be added to the list in the **XYZ VIEW** window.

- e) Repeat steps b – h for each point you want to add. The total number of points and the number of scans set up will be shown in the DATA and points fields.

LINE SCANS

- a) L-Click on LINE SCAN.

Note: The probe marker on the TV screen may disappear. To get it back R-Click on ROLLER CHOICE in **Roller Wheel Control** window and select PROBE MARKER from the pop-up menu. Then immediately L-Click on the ROLLER CHOICE button to return the wheels to stage control. If the Label disappears, enter the Label again.

- b) Move to the starting point of the line you want to scan and focus optically.
- c) L-Click on VALID START to set the starting point of the line.
- d) Move to the ending point of the line you want to scan and focus optically.
- e) L-Click on VALID STOP to set the ending point of the line.

- f) Erase the number shown in the POINTS field and enter the number of points you want to analyze on this line (they will be automatically be evenly spaced, the distance between points is shown in the distance field.).
- g) Enter a comment in the COMMENT field for this line.
- h) L-Click on ADD to add the line to the list of lines to be analyzed.

The points for the line scan will be added to the list in the **XYZ VIEW** window.

- i) Repeat steps b – h for each line you want to scan. The total number of points and the number of scans set up will be shown in the DATA and points fields.

Note: You can delete individual points or line scans by selecting the number of the point or scan in the DATA field then R-Clicking DELETE and selecting DELETE CURRENT form the pop-up menu.

Note: You can mix line scans and point analyses in the same automatic run.

- 8) When you are finished entering line scans L-Click DONE.

The XYZ window will close.

- 9) L-Click on the ANALYZE button in the main **QUANTITool** menu bar.

The **ANALYSIS** window will appear.

- 10) R-Click on the ACQUIRE button and select MULTIPOINT from the pop-up menu.
The first line scan will begin immediately.