CalcImage v. 13.7.5
User's Guide

Probe Software

Contents

Introduction

Description
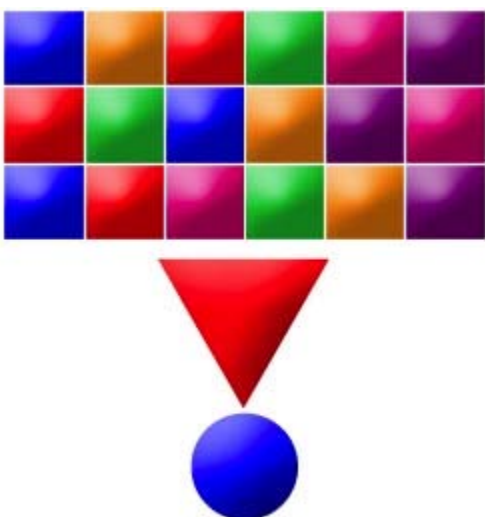
CalcImage is designed for off-line calculation of quantitative images from x-ray maps running under Windows NT, 2000, XP Vista or Win7, on the Intel platform.

CalcImage utilizes standard intensity data from Probe for EPMA database files to convert grid files (.GRD) containing off-peak corrected x-ray intensities (or raw x-ray intensities for use with the MAN background correction) into quantitative maps in elemental weight percent.

These grid files may be from any source but are typically generated in the image acquisition package Probe Image. The intensity data must be stored in counts per second (cps) units. A beam drift correction will be performed by default so the only quantitative parameter necessary for image quantification are the beam energy (keV) and beam current (nA) of the x-ray map acquisitions.

To produce presentation quality output and/or slice, polygon and/or strip extraction methods you will need Golden Software's Surfer application also. For basic output you will need version 7 or higher. The advanced extraction operations require Surfer version 9 or higher.

CalcImage is written primarily in Visual Basic 6.0 (Professional) for Windows.

License

CalcImage has a flexible site license policy. You may install CalcImage on as many computers as you require for the processing of off-line data from your microprobe.

Special Thanks

I would like to give special thanks to my wife Barbara, for her patience and support throughout the development of this program.

Technical Support

Technical support for CalcImage is provided by Probe Software, Inc. Please contact John Donovan at (541) 343-3400 for any questions or difficulties you may have with CalcImage.

If an error message or software bug is seen, please note the exact error message and record as many details of the incident as you can to help us in determining a solution to your problem. Suggestions regarding new features or improvements to CalcImage are always welcome and every effort will be made to incorporate them in future releases. If you have an idea for a new feature, we would like to hear about it. Please write John Donovan at the address below or call anytime.

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Platform Requirements

CalcImage requires a fairly fast computer platform for reasonable calculation and data access times. The following system requirements are the minimum and preferred hardware that can be used to run CalcImage.

Minimum

- Windows XP
- 100 GB hard disk with at least 10 GB free disk space
- 22" color monitor (1024 x 768)

Preferred

- Windows 7
- 500 GB hard disk with at least 200 GB free disk space
- 24" color monitor (1920 x 1200)

Installation

CalcImage is installed along with Probe for EPMA and can be found in the Probe for EPMA application folder (normally C:\Probe Software\Probe for EPMA).

CalcImage

Overview

CalcImage consists of a main MDI (multiple document interface) window that contains the working x-ray images. Any grid file (*.GRD) image may be opened for viewing in CalcImage. To open the log window, click the Window | Log Window menu.
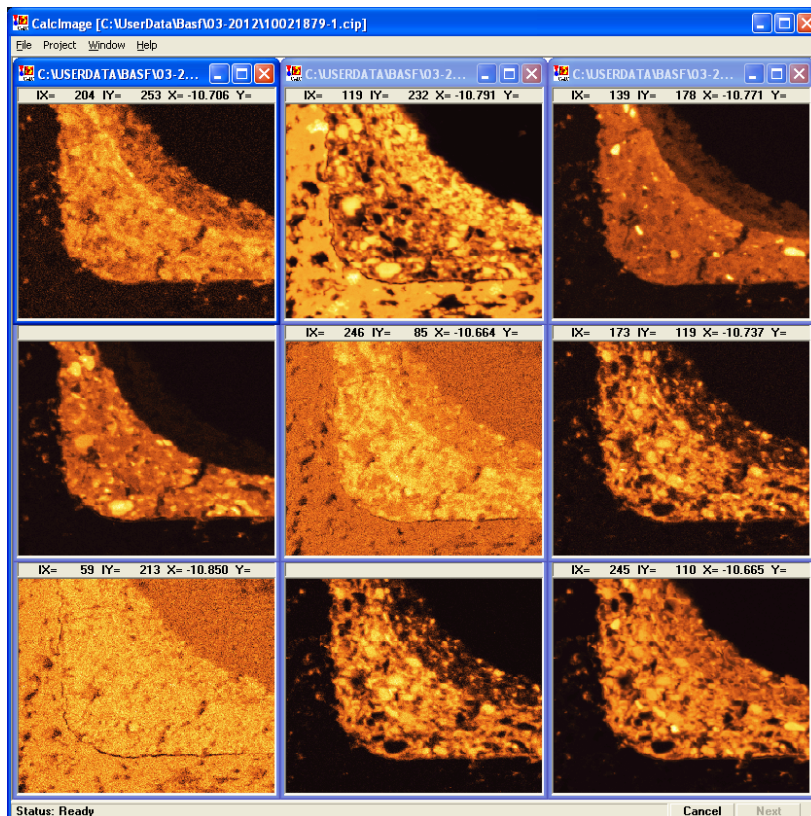
Description

To begin calculating quantitative images, start by opening an existing or creating a new CalcImage project file (*.CIP).

If you select the Project | Create (new) Project Wizard, the software will guide you through the process of creating a new CalcImage project and prompt you to select the Probe for EPMA database containing the sample setup, standard intensities, MAN intensities, interference intensities, etc.

Next the software will prompt you to select the .PRBIMG files exported from ProbeImage for quantification. Note that you only have to select a single file for each acquisition. So if you acquired a single set of elements (one per spectrometer), the software will automatically load in the other element files and convert them into .GRD files which are stored in the same folder. Off-peak .PRBIMG files (if present) are also loaded automatically. If the files are in another folder, the software will automatically copy them for you to the folder containing the selected .MDB file.

If you want to make a new project manually use the Project| New (empty) Project menu. After creating a new CalcImage project file, next select a condition file for specifying the standard intensities. This condition file can be any Probe for EPMA database (*.MDB) file that contains a complete standardization of the standard intensities for the x-ray maps that require to be converted into quantitative images.

> ***Note that the MDB file and GRD files must reside in the same folder as the CIP project file.***

Note that the condition file can contain additional elements that can be ignored during the CalcImage quantification process, as long as each image added to the CalcImage project is assigned as properly standardized element.

Next select a condition sample from the file that most closely matches the analytical conditions of the x-ray maps that are to be converted to quantitative images. The count time and beam current need not be equal as long as the deadtime correction is accurately calibrated.

For example, the standard intensities might have been acquired at 15 KeV, 20 nA using a count time of 20 seconds, while the x-ray maps might have been acquired at 15 KeV, 200 nA and 0.1 seconds (to save time for high resolution maps). As long as the keV (and takeoff) conditions are equal, the software can normalize the standard intensities and x-ray maps to similar counts per second per nanoamp values.

CalcImage .CIP File Format

The CalcImage project file is an ASCII text file with the extension .CIP. An example .CPI file is listed here for reference:

```
8           "CalcImage Quantitative Image Project 2/25/2017 9:46:42 AM"
"PI_Testing_MAN_09-09-2013_MSH4-1_00652_"
"PI_Testing_MAN_09-09-2013.MDB"
 24          10          -1          -1          0           0           0           0           -1          -1
-1           0           0           -1          -1          0           0           0           0
 0           2           .400        29.8089     29.7952     41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP1_Si_PET_.grd"
 0           1           .400        29.8089     29.7952     41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP2_Na_LTAP_.grd"
 0           3           .400        29.8089     29.7952     41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP3_K_LPET_.grd"
 0           4           .400        29.8089     29.7952     41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP4_Al_TAP_.grd"
 0           6           .400        29.8089     29.7952     41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP5_Fe_LIF_.grd"
 0           7           .400        29.7967     29.7784     41527.8630208333        41528.0549189815        "MSH4-
1_00653_SP1_Ca_PET_.grd"
 0           5           .400        29.7967     29.7784     41527.8630208333        41528.0549189815        "MSH4-
1_00653_SP2_Mg_LTAP_.grd"
 0           8           .400        29.7967     29.7784     41527.8630208333        41528.0549189815        "MSH4-
1_00653_SP3_Mn_LPET_.grd"
 0           10          .400        29.7967     29.7784     41527.8630208333        41528.0549189815        "MSH4-
1_00653_SP4_P_TAP_.grd"
 0           9           .400        29.7967     29.7784     41527.8630208333        41528.0549189815        "MSH4-
1_00653_SP5_Ti_LIF_.grd"
 10
 0  0  0  0  0  0  0  0  0  0
 0
-1           0           0           0           0           0           0
 0           ""
 0           0
 0           "SE"        0           "BSE"       0           "CL"
"MSH4-1_00653_VS1.grd"      ""          ""
 0           0
```

The following is a line by line explanation of the various parameters stored in the .CIP project file started with the first line:

Line 1:
```
8          "CalcImage Quantitative Image Project 2/25/2017 9:46:42 AM"
```

This line contain the CIP version number (no version number indicates file version "0"), and a text description with the date and time it was created. The string in double quotes is the name of the project and a time stamp. This title string may be edited as desired by the user.

Line 2:
```
"PI_Testing_MAN_09-09-2013_MSH4-1_00652_"
```

This line contain the project title of the CalcImage project which is normally a combination of the Probe for EPMA MDB file name, and the Probe Image PrbImg x-ray map file basenames.

Line 3:
```
"PI_Testing_MAN_09-09-2013.MDB"
```

This line contain the name of the Probe for EPMA MDB which contains the run, sample and element setups and the standard intensities.

Line 4:
```
24         10         -1         -1         0          0          0          0          -1         -1
-1         0          0          -1         -1         0          0          0          0
```

This line contains a number of important flags which are:
CalcImageProbeDataSample = the row number of the sample containing the element setup utilized for x-ray mapping
CalcImageNumberofImageFiles = the total number of raw intensity x-ray map files contained in the project

The remaining flags indicate calculation of specific data types where 0 = no, -1 = yes. The following flags are listed:
CalcImageCalculateTotalsImageFlag = flag for calculation of the analytical totals image
CalcImageCalculateStoichiometricOxygenImageFlag = flag for calculation of the stoichiometric oxygen image
CalcImageCalculateExcessOxygenImageFlag = flag for calculation of the excess oxygen image
CalcImageCalculateNetIntensitiesFlag = flag for calculation of the net intensity (bgd corrected) images
CalcImageCalculateBgdIntensitiesFlag = flag for calculation of the background intensity images
CalcImageCalculateKratioIntensitiesFlag = flag for calculation of the k-ratio intensity images
CalcImageCalculateQuantPercentsFlag = flag for calculation of the elemental concentration images (always set true)
CalcImageCalculateAtomicPercentsFlag = flag for calculation of the atomic percent images
CalcImageCalculateOxidePercentsFlag = flag for calculation of the oxide concentration images
CalcImageCalculateFormulaBasisFlag = flag for calculation of the formula element images
CalcImageCalculateElementByDiffImageFlag = flag for calculation of the element by difference image
CalcImageCalculateDetectionLimitsFlag = flag for calculation of the detection limit images
CalcImageCalculateAnalyticalSensitivityFlag = flag for calculation of the analytical sensitvity images
CalcImageCalculateLogWeightPercentsFlag = flag for calculation of the log wt.% concentration images
CalcImageCalculateDetectionLimitsBlankingFlag = flag to blank values for concentrations greater than 10 wt.%
CalcImageCalculateAnalyticalSensitivityBlankingFlag = flag to blank values for concentrations less than 1 wt.%

The final flag value is not currently utilized at this time.

Lines 5 to 5 + Number of CalcImageNumberofImageFiles:
```
0          2          .400       29.8089    29.7952    41527.6709143519        41527.8628009259        "MSH4-
1_00652_SP1_Si_PET_.grd"
```

```
    0          1          .400           29.8089        29.7952        41527.6709143519         41527.8628009259         "MSH4-
1_00652_SP2_Na_LTAP_.grd"
    0          3          .400           29.8089        29.7952        41527.6709143519         41527.8628009259         "MSH4-
1_00652_SP3_K_LPET_.grd"
    0          4          .400           29.8089        29.7952        41527.6709143519         41527.8628009259         "MSH4-
1_00652_SP4_Al_TAP_.grd"
    0          6          .400           29.8089        29.7952        41527.6709143519         41527.8628009259         "MSH4-
1_00652_SP5_Fe_LIF_.grd"
    0          7          .400           29.7967        29.7784        41527.8630208333         41528.0549189815         "MSH4-
1_00653_SP1_Ca_PET_.grd"
    0          5          .400           29.7967        29.7784        41527.8630208333         41528.0549189815         "MSH4-
1_00653_SP2_Mg_LTAP_.grd"
    0          8          .400           29.7967        29.7784        41527.8630208333         41528.0549189815         "MSH4-
1_00653_SP3_Mn_LPET_.grd"
    0          10         .400           29.7967        29.7784        41527.8630208333         41528.0549189815         "MSH4-
1_00653_SP4_P_TAP_.grd"
    0          9          .400           29.7967        29.7784        41527.8630208333         41528.0549189815         "MSH4-
1_00653_SP5_Ti_LIF_.grd"
```

Each line corresponds toone raw intensity file. The first parameter is the image type where 0 = on-peak, 1 = high off-peak and 2 = low off-peak. The second parameter is the element channel number in the PFE sample setup that corresponds to the x-ray map. The thrid parameter is the pixel dwell time in seconds and the fourth and fifth parameters are the beam current before and after the map acquisition. The sixth and seventh parameters are the date/time in Microsoft Excel format where 0 is Jan 1, 1900 and the units days elapsed since then. Finally the name of the raw intensity x-ray map in GRD (Surfer GRD format).

The next three lines are reserved for Correlated Pixel Quantification (CPQ) calculations:

```
10
 0  0  0  0  0  0  0  0  0  0
 0
```

Where an x-ray map can be assigned to each element for assigning the standard intensity on a correlated pixel basis as opposed to point intensities from standards in Probe for EPMA. In other words the analytical k-ratio is constructed from the pixel intensity in the unknown x-ray map, divided by the pixel intensity in the standard x-ray map.

Here is an example of CPQ parameters. First is the number of CPQ elements.

The next line contains the CPQ channel flags for each element (0 = do not use CPQ calculations, 1 = use CPQ calculations). This useful so one can toggle the CPQ correction on and off without changing the CPQ assignments.

The next line indicates the number of CPQ standard intensity images. Note that these standard intensity images must be the same number of pixels and stage extents as the unknown images and obviously should also reflect the unknown acquisition sample setup, though one may use different count times and/or beam currents for the standard intensity images.

Followed by (for each standard intensity image), the CPQ image type (0=on, 1=hi or 2=lo), element channel, MAN or interference index number, pixel count time (sec), beam current (nA) and image name (.GRD file).

```
 2
-1 -1
 9
 3   1   1   0    30.0393    "CPQ_Test_Si_1300x_00516_SP3_Fe_LLIF_.grd"
 3   1   2   0    30.0393    "CPQ_Test_Ti_1300x_00517_SP3_Fe_LLIF_.grd"
 3   1   3   0    30.0393    "CPQ_Test_Cu_1300x_00519_SP3_Fe_LLIF_.grd"
 3   2   1   0    30.0393    "CPQ_Test_Si_1300x_00516_SP2_S_LPET_.grd"
 3   2   2   0    30.0393    "CPQ_Test_Ti_1300x_00517_SP2_S_LPET_.grd"
 3   2   3   0    30.0393    "CPQ_Test_Fe_1300x_00518_SP2_S_LPET_.grd"
 3   2   4   0    30.0393    "CPQ_Test_Cu_1300x_00519_SP2_S_LPET_.grd"
 0   2   0   0    30.0393    "CPQ_Test_FeS2_1300x_00520_SP2_S_LPET_.grd"
 0   1   0   0    30.0393    "CPQ_Test_Fe_1300x_00518_SP3_Fe_LLIF_.grd"
```

Normally these three lines are just as they are shown as three lines with the number of acquired elements and zeros for the flags and zero for the number of CPQ standard intensity maps. If you would like to obtain more information on the CPQ calculations in CalcImage please contact Probe Software.

The next line is for miscellaneous quantification flags.

```
-1          0          0          0          0          0          0
```

These flags are:
CalcImageTitleAppendDataFlag = this flag indicates to append the user provided text to the output data type
CalcImageSurferOutputTemplateFlag = this flag indicates the custom template number for normal quant output
CalcImageSurferSliceTemplateFlag = this flag indicates the custom template number for slice output
CalcImageSurferPolygonTemplateFlag = this flag indicates the custom template number for polygon output
CalcImageSurferStripTemplateFlag = this flag indicates the custom template number for strip output

The final two flags value are not currently utilized at this time.

The next line contains flags for EDS spectrum image quantification:

```
0          ""
```

The first flag indicates that an EDS spectrum image should be utilized for quantification, the second value is the EDS spectrum image file name. These parameters are not currently available at this time.

The next line contains the scan type and stage scan polarity:

```
0          0
```

The first flag is the scan type where 0 = beam scan and 1 = stage scan. The second flag indicates the stage scan polarity where 0 = cartesian orientation (Cameca) and 1 = anti-cartesian (JEOL).

The next line contains flags for output of analog signal images:

```
0          "SE"       0          "BSE"      0          "CL"
"MSH4-1_00653_VS1.grd"   ""        ""
```

It's pretty self explanatory

The final lines are reserved for scanning TDI corrections for beam sensitive samples.

```
0          0
```

The first value is the total number of TDI x-ray maps loaded, and the second value is the number of TDI intervals. If you would like to obtain more information on the TDI calculations in CalcImage please contact Probe Software.

CalcImage Menus

File

The File menu can be used to open or close an existing x-ray map file, save a currently open x-ray map, print the current log window contents or x-ray map or exit the program.

Select Standard Database

The Select Standard Database menu allows the user to select a standard database other than the default STANDARD.MDB. This is usually only necessary when processing data for a set of x-ray maps that were acquired on another instrument that utilized a different default standard database.

Import PrbImg File

This menu allows to import a Probe Image image file (.PRBIMG). If a CalcImage project is open, a dialog window is displayed after import where the user can choose to save the imported image in the project folder:
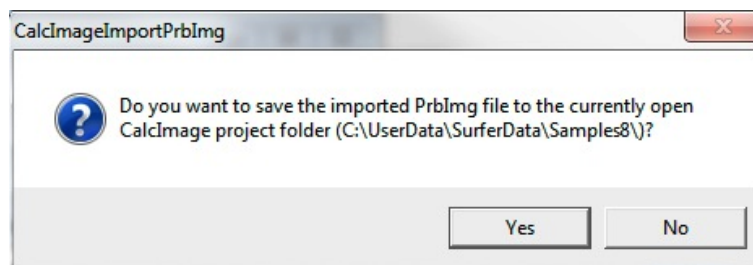
Open GRD

The Open GRD menu allows the user to open an existing CalcImage x-ray map (or quantitative image). All CalcImage images are grid files (*.GRD) created by MicroImage or exported from ProbeImage that use floating point data values for high precision calculations. Note that .GRD files can also be opened by drag & drop onto CalcImage.

Close GRD

The Close GRD menu allows the user to close a currently open x-ray map file.

Save GRD

The Save GRD menu allows the user to save a currently open x-ray map or quantitative image, if it has been modified.

Save As GRD

The Save As GRD menu allows the user to save a currently open x-ray map or quantitative image to another file name.

Save As BMP

The Save As BMP menu allows the user to save a currently open x-ray map or quantitative image as a BMP bitmap file.

Close All Images

This menu closes all images which are currently open.

Close Off Peak Images

This menu allows the user to close only the off peak images.

Print Log

This menu allows the user to print the entire contents of the log window or selected portions of the log window. Be sure to click the Selection field if only a text selection is to be printed, otherwise the program will print the entire log window text.

Print Image

This menu will print the image and cursor coordinate field of the current x-ray map or quantitative image to the default printer.

Print Setup

This menu allows the user to change the default printer or printer setup options for the currently selected printer.

Exit

This menu exits the program.

Project

Create (new) Project Wizard

Use the CalcImage Create Project Wizard to quickly create a new CalcImage project. The software will prompt you to select your Probe for EPMA .MDB file, sample setup and .PRBIMG image files.

The wizard combines the operations New (empty) Project, Add (or change) Probe Data File To Project (*.MDB), and Add (or change) Probe Sample Setup To Project, and adds an additional .PRBIMG import routine, which will automatically generate .GRD from .PRBIMG files and assign images to elements.
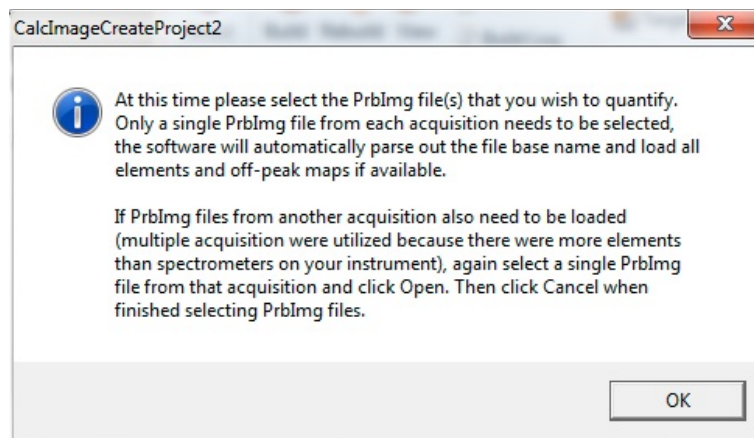
Note that you only have to select a single .PRBIMG file for each acquisition. So if you acquired a single set of elements (one per spectrometer), the software will automatically load in the other element image files. Off-peak image files (if present) are also loaded automatically. If the files are in another folder, the software will automatically copy them for you to the folder containing the selected .MDB file. Once you have selected one image for each acquisition, click cancel in the import dialog to exit the import routine.
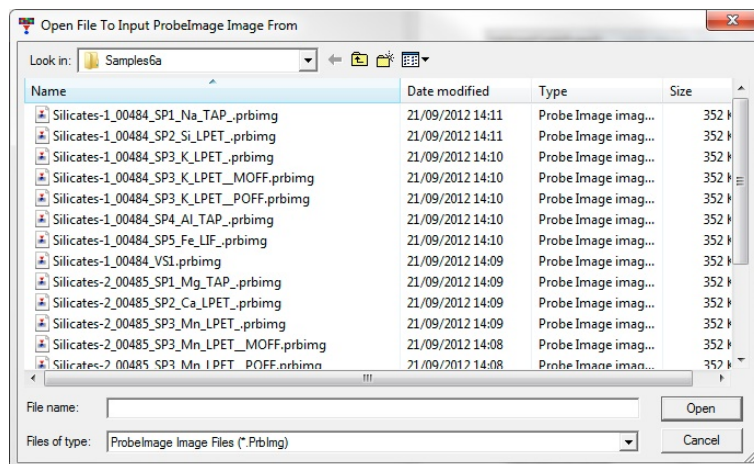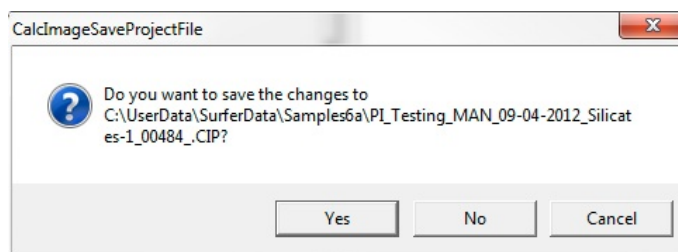

Once the wizard is completed, it will ask if you want to save the new project file. The .CIP project file is an ASCII file which can be read with a text editor.

The software will also create a GRDInfo.INI file which contains a few global parameters for the .GRD files. Finally the software will display a message box with information what to do next.
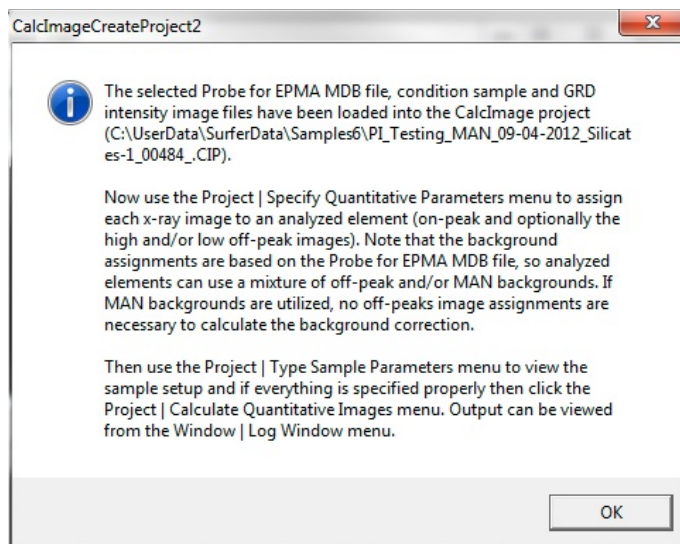
Open (existing) Project

Open an existing CalcImage project file (*.CIP). The menu will read the .CIP files, then load the standard intensity data from the condition file and finally open and load each x-ray map specified in the .CIP file.

Close (current) Project

Close the current CalcImage project file (*.CIP). The program will prompt the user whether to save any changes to the CalcImage parameters.

New (empty) Project

Open a new CalcImage project file (*.CIP) for manual loading of x-ray maps in GRD format.

Save (current) Project

Save any changes to the current CalcImage project file (*.CIP).

Note that some changes to the CIP project as automatically saved back to the Probe for EPMA MDB files, for example, stoichiometric element, analysis options, etc.

Save (current) Project As

Save the current CalcImage project file (*.CIP) to another name.

Add (or change) Probe Data File To Project (*.MDB)

Add (specify) a condition file for the CalcImage project. This file is a Probe for EPMA .MDB database which contains appropriate standard intensities for use in quantifying the specified set of x-ray maps.
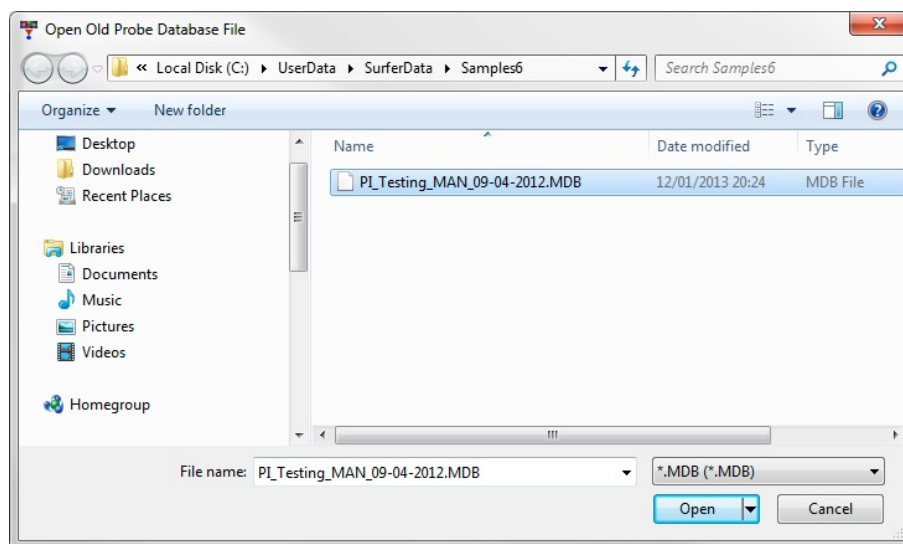
Note that the condition file can contain additional analyzed elements that can be ignored during the CalcImage quantification process, as long as each image added to the CalcImage project is assigned as properly standardized element in the condition file. In other words an x-ray map for each analyzed element is not necessary. Analyzed elements that have not had an x-ray map assigned to them will be set to zero intensity for the quantitative calculation.

Add (or change) Probe Sample Setup To Project

Add (specify) a condition sample for the CalcImage project from the list of analyzed samples in the assigned .MDB file. Standard assignments, interference corrections, and off-peak correction type will be retrieved from this sample. To calculate standard intensities with a proper drift correction select a sample that is closest in time to the x-ray map acquisition. This sample must contain at least the elements representing each x-ray map in the project, although it may contain other elements not assigned to x-ray maps (for example minor or trace elements).
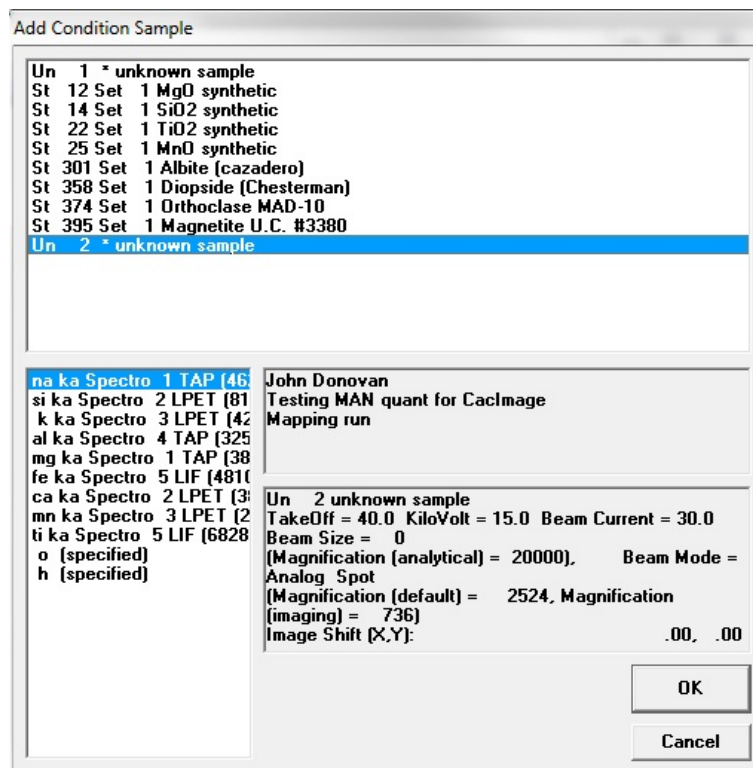
Add Image Files To Project (*.GRD)

Add each x-ray map that is to be converted to a quantitative image to the CalcImage project. On-Peak, High Off-Peak, and Low Off-Peak images can be added.

The maps should represent approximately 90% or more of the total elements present in the physical sample in order for the software to calculate an accurate matrix correction. However, elements may be calculated by stoichiometry (oxygen), difference, by stoichiometry to stoichiometric oxygen or by stoichiometry to another analyzed element.

Note that CalcImage provides considerable image math capabilities for this and other image processing purposes.

If the element assigned to the x-ray map is off-peak corrected, then for best results (especially for minor and trace element images), the image should also be off-peak corrected. This is normally done by acquiring a second x-ray at the same sample coordinates (and at the same sample conditions) but with the spectrometers move to an off-peak position. This second image is then simply subtracted from the on-peak image. For greater accuracy, an off-peak image can be acquired on each side of the peak, then the two images can be added together and then subtracted from the on-peak image.

Elements that are MAN corrected can be simply assigned to raw x-ray maps without the necessity of acquiring an off-peak x-ray map. This may not be accurate enough for trace element imaging.

If an image is to be off-peak background corrected, then either or both high off-peak (_POFF) and low off-peak x-ray maps (_MOFF) may be added to the project. If the off-peak background correction requires both a high and low off-peak measurement then images containing both data should be acquired and specified. Here is a list of the off-peak background correction types and what off-peak data is required for each background correction:

1= linear slope interpolation or extrapolation	high and low off-peak
2= average of both high and low off-peak counts	high and low off-peak
3= use only the high off-peak counts	high off-peak only

4= use only the low off-peak counts	low off-peak only	
5= use exponential off-peak calculation (based on exponent)	high and low off-peak	
6= slope-high (based on high off-peak and slope coefficient)	high off-peak only	
7= slope-low (based on low off-peak and slope coefficient)	low off-peak only	
8= polynomial (based on high and low off-peak and three coefficients)	high and low off-peak	

Specify Quantitative Parameters

This dialog allows the user to assign analyzed elements to x-ray maps and specify a beam current individually for each on and off peak x-ray image. Calculation options and specified concentrations may also be changed. Further analysis options are available in the Analytical menu.
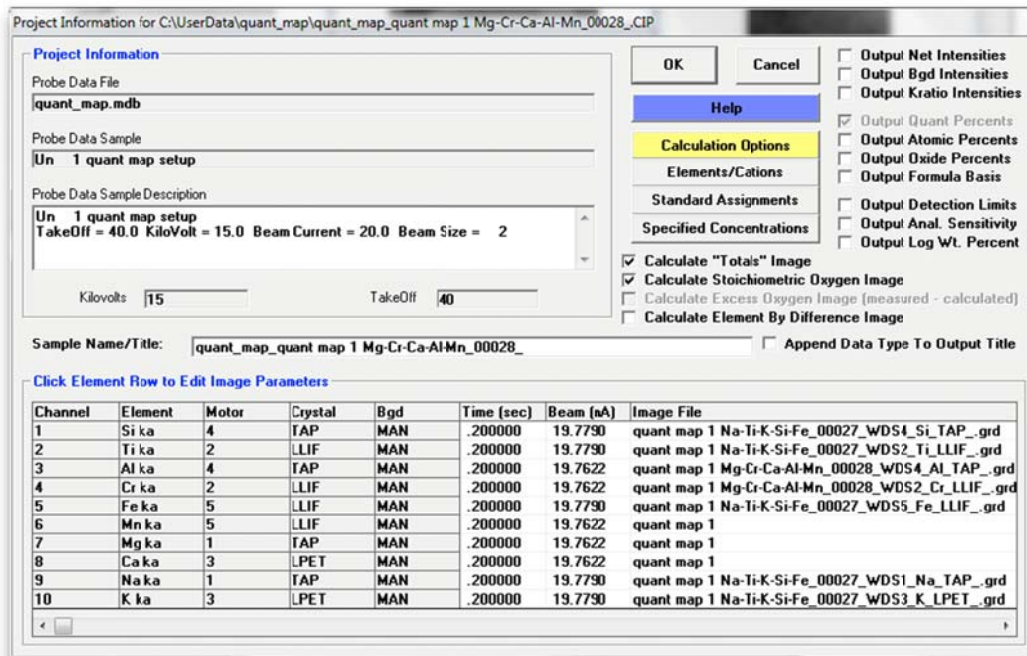
Various options are offered for calculation of quantitative images which can be selected by tick boxes. For example, the first option will have the program calculate a "totals" image along with the other quantitative images. This is useful in order to ensure that a majority of the elements present were analyzed in all visible phases. The second is an option to have the program calculate an image based on the calculation of stoichiometric oxygen. This is usually done to calculate oxygen in oxide samples where a fixed cation to oxygen ratio can be assumed. The image files will be named <project file name>_Total_Quant.GRD and <project file name>_Oxygen_Quant.GRD, respectively.

Clicking on a channel row opens the corresponding Image Parameters window. Here, the correct .GRD image files can be selected from a drop-down list for the on-peak and both off-peak images. The beam current can be specified individually as well. The Remove button clears the image file selection:
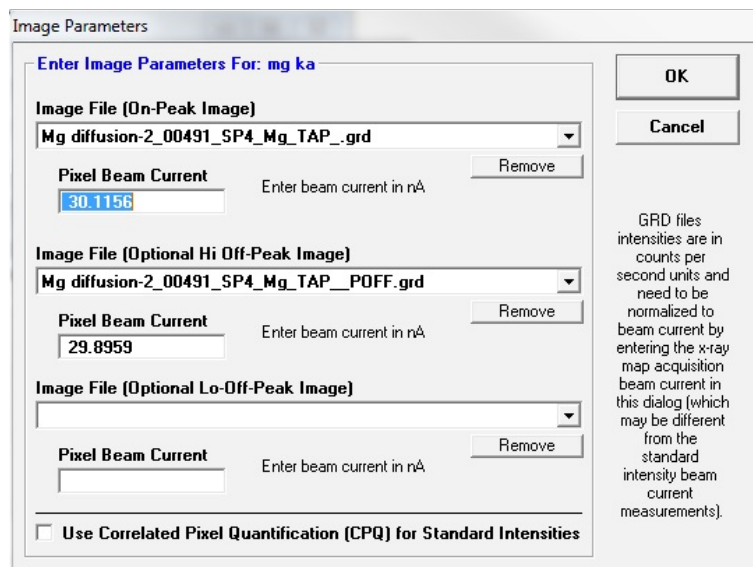
Use Correlated Pixel Quantification (CPQ) for Standard Intensities

Correlated Pixel Quantification (CPQ) allows to use x-ray maps acquired on standards under the same conditions as the unknowns to be used for map quantification, instead of using conventional point measurements on standards. Each pixel in the unknown map will be quantified using the corresponding pixel in the standard map. If exactly the same conditions are used for standard and unknown map acquisition, this technique can assist in reducing acquisition issues like contamination or defocussing, for example carbon contamination build up when mapping carbon in steel. This requires that unknown and standard behave in a similar way.

Ticking the "Use Correlated Pixel Quantification (CPQ) for Standard Intensities" box expands the Image Parameters window. Three new sections become available. The Browse buttons in the top section "Enter Image Parameters for Correlated Pixel Intensity Calculations For Standards" is used to specify the .PRBIMG file for the on-peak image of the calibration standard, and, if off-peak background correction is used, the corresponding high and low off-peak images. Note that the standard number refers to the standard assignments performed using the Project | Add (or change) Probe Sample Setup To Project menu.

If MAN background correction is utilized, the Browse Selected Row button in the section "Enter Image Parameters For Correlated Pixel Intensity Calculations for MAN Standards" can be used to specify a .PRBIMG image file for every standard in the list which again refers to the .MDB file. Finally, if interference corrections are specified, corresponding on-peak and off-peak images for the interference standards can be loaded in the section "Enter Image Parameters For CPQ Calculations For On-Peak Interf Standards".
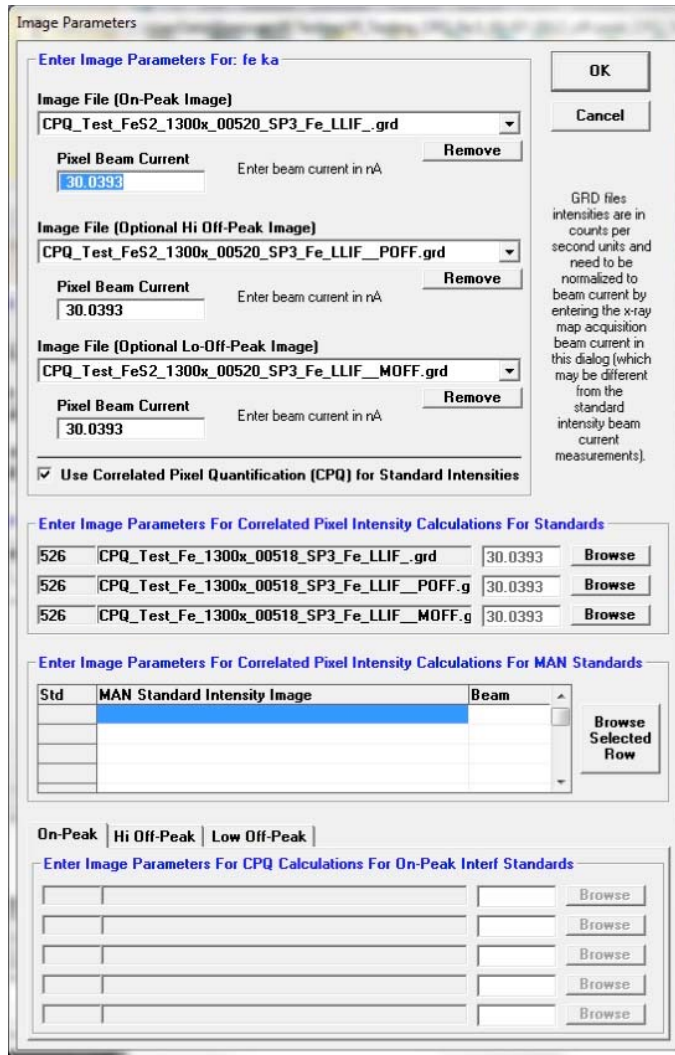
Calculation Options

This menu provides a range of options for quantification, including calculation of oxygen by stoichiometry, other elements by difference or stoichiometry to oxygen, and coating thickness.

Display Results As Oxide Formulas / Calculate With Stoichiometric Oxygen

CalcImage allows the user to display the results of an analysis in oxide weight percent based on the cation ratios defined for each element. In addition the user may select to calculate oxygen by stoichiometry if oxygen is not an analyzed element. If oxygen is measured or calculated by stoichiometry, the program will automatically calculate the actual excess or deficit oxygen in the analysis if the Display As Oxide option is selected.

If the element to be calculated by formula basis, difference or stoichiometry is not already in the sample setup, it must be added as a "not analyzed" element using the Elements/Cations button first, by simply clicking any empty row in the element list and typing in an element symbol with a blank x-ray line.

Note that if the sample being analyzed is a standard and oxygen is not measured, then the program will automatically specify any oxygen from the standard database. However, if the sample is an unknown, then the program will add in any specified oxygen as "excess" oxygen into the matrix correction, if the user has specified any element concentrations.

Use Oxygen From Halogens Correction

If oxygen is calculated by stoichiometry (based on the cation ratios defined for each element) and halogen elements such as fluorine or chlorine are analyzed, this option will correct for cation compensation by halogen anions, i.e. reduce the amount of calculated oxygen accordingly.

Calculate As Elemental

This option calculates all elements as pure elements without the addition of stoichiometric oxygen in the matrix correction calculation.

Element by Difference

An element by difference can be included in this way also to account for their effect on the x-ray intensities. The element by difference must be one of the specified elements in the sample setup. Note that the this option should be utilized carefully, because the calculation will always result in a 100% total which could mask the results of a bad acquisition.

Stoichiometry to Oxygen

Another useful feature for the analysis of carbonate or borate samples in an oxide run is the use of the "element by stoichiometry to the stoichiometric element (oxygen)" option. With this feature the analyst can analyze just the cations (Fe, Mg, Ca, etc.) in a sample and have the oxygen calculated by stoichiometry and another specified element (usually C for carbonates or B for borates) calculated relative to oxygen. In the case of carbonates, for example $CaCO_3$, carbon is always in the ratio 1 to 3 to oxygen.

Therefore by simply specifying C by stoichiometry relative to the stoichiometric element (oxygen) at 0.333 (1 divided by 3) the correct amount of both oxygen and carbon will be incorporated into the ZAF matrix correction and totals without analyzing for either. This calculation should only be used with compounds where the ratio to oxygen is both known and unchanging.

Note that oxygen must be an analyzed or specified element before this calculation can be applied. One more point about element by stoichiometry to oxygen. Consider the example of a trace element analysis of several metals in an alumina (Al_2O_3) matrix. If Al and O are not to be analyzed, yet the user desires to have Al_2O_3 added to the matrix correction, how can this be accomplished?

There are two ways this can be achieved. One way would be to simply specify Al by difference and calculate oxygen by stoichiometry. The program will then correctly add in the proper amount of stoichiometric Al_2O_3 to the matrix correction for each analysis line. The other way is to use the element by stoichiometry to oxygen calculation as discussed below.

Adjust the cation ratios of the metals to elemental stoichiometries (one cation and zero anions). Next, select "element by stoichiometry to oxygen" and (in this example) select "al" as the element by stoichiometry. To achieve a 2 to 3 ratio, next enter "0.666" Al atoms per O atom. Run the calculation and note that Al_2O_3 was not added to the matrix calculation! What happened? In this example, the user had selected a cation ratio for the analyzed elements of all elemental atoms, and since there was zero oxygen to begin the iteration, the program never got to add the Al which then never added the stoichiometric oxygen! How can this be avoided? Simply specify some small concentration of an oxide element (for instance SiO_2) in the specified element concentration, say 0.05 %. This will give the iteration a chance to get started, and allow it to converge on a very close approximation of the Al_2O_3 by difference!

Stoichiometry to Another Element

Yet another option for recalculation is the element relative to another element (by stoichiometry). This calculation is similar to the "element by stoichiometry to oxygen" as described below, however the user may select any other analyzed or specified element as the stoichiometric basis element.

Sample Conductive Coating

This section can be used to specify type, density, and thickness of conductive coating. To activate the coating correction for quantification, tick "Use Conductive Coating Correction For Beam Energy Loss" and/or "Use Conductive Coating Correction For X-Ray Absorption" in the Analysis Options dialogue.

Elements/Cations

The Elements/Cations dialog provides the same functionality as in Probe For EPMA | Analyze!.

Standard Assigments

The Standard Assignments dialog provides the same functionality as in Probe For EPMA | Analyze!.

Specified Concentrations

CalcImage allows the user to specify concentrations of elements not analyzed for. Consider that in order for the program to compute matrix corrections properly, the program must know the concentration of all significant element concentrations. This means that the program should be able to compute a total of at least 90-95% to calculate matrix effects properly. Element concentrations which you have previously measured or estimated but are not analyzing for, can be manually specified.

This feature is especially useful when adding excess oxygen from oxide (T-fO2) ferrous-ferric calculations or H2O for hydrous phases. The effect of absorption by oxygen upon Si and Al x-rays is not insignificant and must be considered for the most accurate results.

First make sure the element(s) to be calculated as a specified element is/are in the sample setup by clicking the Elements/Cations button in Probe For EPMA. If the element is not in the sample element list, add it as a specified element by clicking any empty element row and typing the element in the element field. Be sure to select an x-ray line of none by clicking a blank x-ray line. Then click OK or type <enter> to accept the element.

Then return to the Specified Concentrations window in CalcImage. Specify if you want to enter the composition in oxide or elemental percent by clicking the corresponding radio button (top right of window). Then click the respective element. Enter the composition and click OK or type <enter>.

Specified concentrations can be cleared by clicking Clear Concentrations (top right of window).

Specify By Standard

This option allows the user to select a standard composition from the standard database for loading of specified element concentrations. For example, if the sample was a standard but acquired as an unknown.

Specify By Formula

This options allows the user to specify a formula for the specified elements. For example if one is analyzing Ti in quartz, but not analyzing Si, the user can specify SiO2 as the matrix for the specified elements.

Specify By Text File Input

This button allows the user to select a tab delimited text file to load specified concentrations, for example from ICP-MS analyses. The user can then select the sample line from the text file and the program will automatically load all the element concentrations (in elemental weight percent only).

A sample tab delimited file for loading specified concentrations is shown here.

%	Si	As	La	Ce	Pr
NYPK6-1.1	0.2308	0.0000	0.0112	0.1193	0.0506
NYPK6-1.2	0.2784	0.0000	0.0078	0.0822	0.0343
NYPK6-10.1	0.2285	0.0000	0.0131	0.1216	0.0474
NYPK6-10.2	0.2950	0.0000	0.0080	0.0826	0.0354
NYPK6-2.1	0.2499	0.0000	0.0070	0.0760	0.0329
NYPK6-2.2	0.3949	0.0002	0.0161	0.1672	0.0621
NYPK6-3.1	0.2743	0.0001	0.0069	0.0756	0.0323
NYPK6-4.1	0.2189	0.0000	0.0129	0.1334	0.0504
NYPK6-4.2	0.2409	0.0000	0.0102	0.1117	0.0469
NYPK6-4.3	0.2423	0.0000	0.0169	0.1679	0.0649
NYPK6-5.1	0.2540	0.0000	0.0077	0.0822	0.0352
NYPK6-5.2	0.2525	0.0000	0.0118	0.1097	0.0426

Note that the elements can be in any order, but the first column must contain the sample names, and the first row of the file must contain the element symbols.

Specify By Analysis

The option allows the user to specify a sample to load the specified concentrations from. The specified element concentrations are loaded based on the current specified concentrations already specified in the selected sample.

Specify By Unknown Sample

This option allows the user to specify an unknown sample in the run to load the specified concentrations from. The program will automatically update the specified concentrations in the selected unknown each time the sample analysis is performed. This is useful if the specified concentrations are calculated during the analysis, for example an element calculated by stoichiometry.

Type Sample Parameters

This menu will write all sample parameters to the "CalcImage Calculation" log window, including standards, beam conditions, counting times, and spectrometer and PHA parameters. These parameters can then be copied or saved to disk.

Calculate Quantitative Images!

This menu will check that all quantitative parameters are properly specified and begin the quantitative calculation for each pixel in the images. Note this may take considerable time depending on the matrix correction methods selected, the speed of the computer and the number of pixels in the image. The number of quantified pixels and the estimated time to

completion are displayed in the status bar at the bottom of the main CalcImage window. The calculation creates a quantitative .GRD image file for each element, adding "_Quant" to the original .GRD file names.
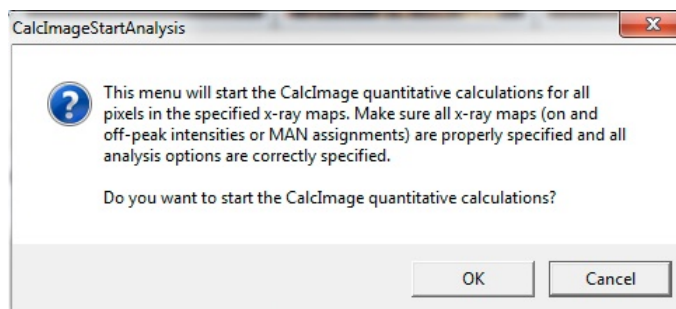
For faster results, select Bence-Albee methods, for more accurate corrections, especially for highly absorbing or fluorescing matrices, select ZAF or $\phi(\rho z)$ methods.

Note that the user can observe the matrix correction calculations as they are calculated by opening the Log Window. Also the calculation can be paused and started by the Pause button in the lower right of the Log Window. Use Cancel to stop the quantitative matrix correction calculations.

On completion of the calculations, the user is prompted to save the data into a tab-delimited ASCII file for further processing. As default for the name of this file "_Quant_Image_Classify" is added to the project file name, the default extension is .DAT. The format of this file is given below:

1st line = (number of x pixels), (number of y pixels), (total number of pixels), (number of columns: K+X+Y+N+ data...)
2nd line = column labels
1st column = K (zero placeholder for cluster number)
2nd column = X pixel number index
3rd column = Y pixel number index
4th column = data row/pixel number index
5th column = channel 1 data value
6th column = channel 2 data value...

This file can be used as input file for the classification operations available in the Processing Menu.

Output Image Statistics For

This menu can be used to calculate statistics for different images (quantitative, net intensity, oxides,… as available) and output to Excel.

Convert Quantitative Images

This menu can be used to convert quantitative wt% images into either atomic %, or log scale wt%.

Open Images For Current Project

This menu will open images in the project which is currently open. Depending on availability, the user can choose to open net intensity images (background corrected), quant images, or atomic percent images.

Export the Project Quant Grid Files For Presentation Output

This menu will create a Golden Software Surfer .BAS script that can be run in the Scripter application to automatically create presentation quality color image maps. Net intensity maps, quant images, or atomic percent maps can be exported, if they exist. The following message is displayed:
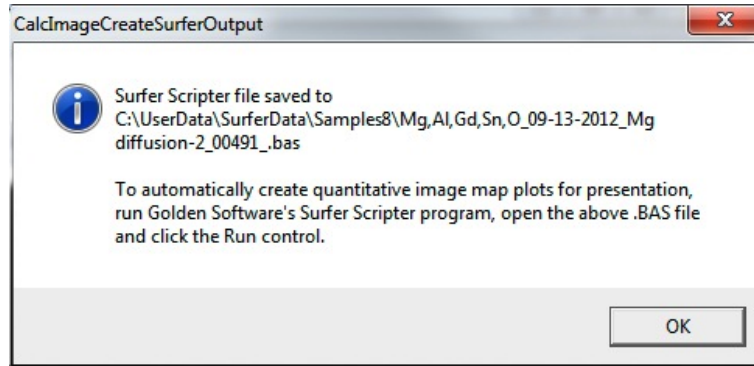
In the following dialog box, the user can choose to call Scripter directly to run the script that was generated:
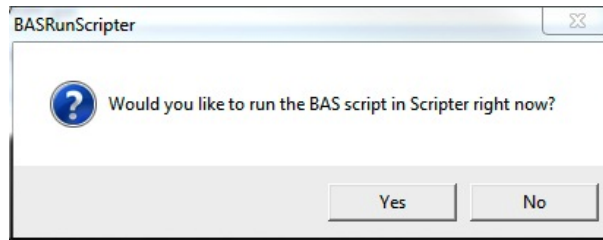
This requires Golden Software Surfer and Scripter to be installed. An example of quantitative images is shown below:
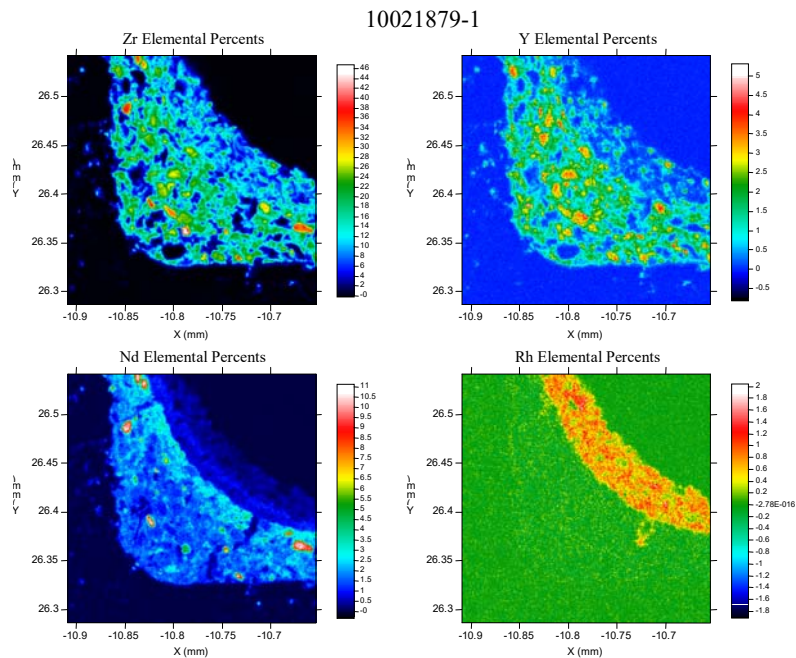
Export the Project Grid Files To Surfer For "Slice" Cross Section Output

This menu allows the user to create a Surfer (Golden Software) script to allow an interactive session for defining a cross section of a previously saved or exported GRD file for display of the intensity or quantitative data using arbitrary selected points for the cross section.
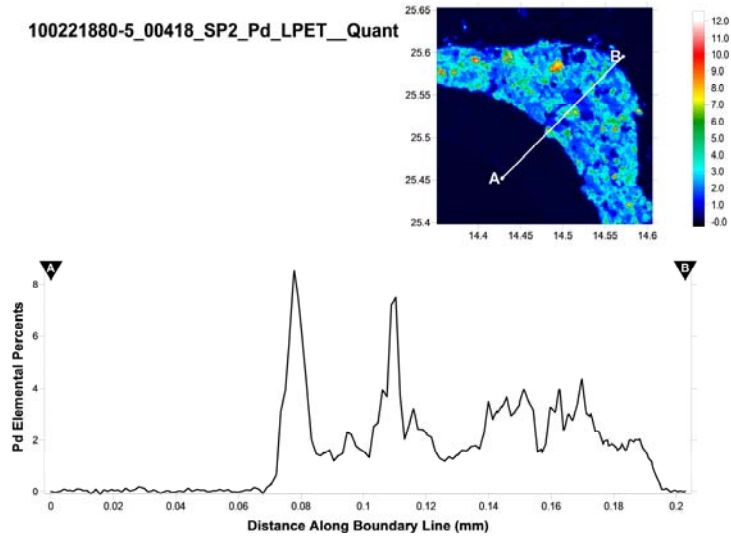
Simply open the generated .BAS file in the Surfer Scripter application and click the Run button. The interactive script will start and prompt you with instructions. Note the script also supports multiple line segments as shown here:
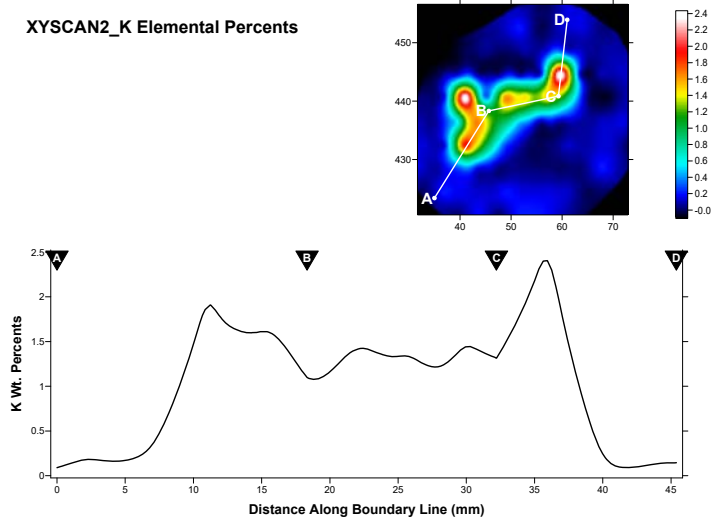
The user may select up to 26 points for generating the cross section boundary file.

The script created for Surfer Scripter.exe will automatically save all maps to JPG. If the resolution of the JPG files is insufficient, simply open one of the SRF files created by the script and use the File | Export menu to save again JPG, but this time enter a larger default value to the number of pixels in the image width. Typically 2048 pixels wide is reasonable.

Export the Project Grid Files To Surfer For "Polygon" Extraction Output

This menu allows the user to specify a polygon shape in the first GRD image and then calculates the average concentration (or intensity) and variance for the selected pixels. See below for example output:
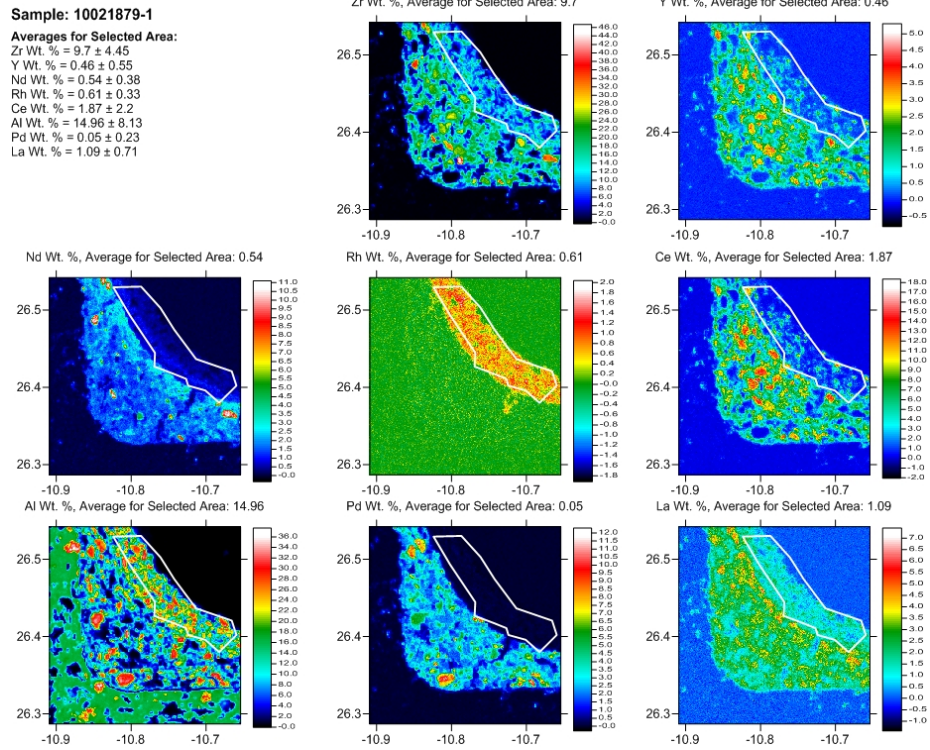
The script created for Surfer Scripter.exe will automatically save all maps to JPG. If the resolution of the JPG files is insufficient, simply open one of the SRF files created by the script and use the File | Export menu to save again JPG, but this time enter a larger default value to the number of pixels in the image width. Typically 2048 pixels wide is reasonable.

Export the Project Grid Files To Surfer For "Multiple Strip" Extraction Output

This menu allows the user to calculate average compositions in a heterogeneous material by averaging the concentrations instead of the raw intensities. This will eliminate matrix correction errors for those interested in the true average composition as a function of either X or Y distance. See below for an example:

The script created for Surfer Scripter.exe will automatically save all maps to JPG. If the resolution of the JPG files is insufficient, simply open one of the SRF files created by the script and use the File | Export menu to save again JPG, but this time enter a larger default value to the number of pixels in the image width. Typically 2048 pixels wide is reasonable.

Sample: Mg diffusion

File: Mg diffusion_00482_SP4_Mg_TAP__Quant
Element: Mg Wt. %
Strip Direction: Horizontal
Strip Increment: 8 µm
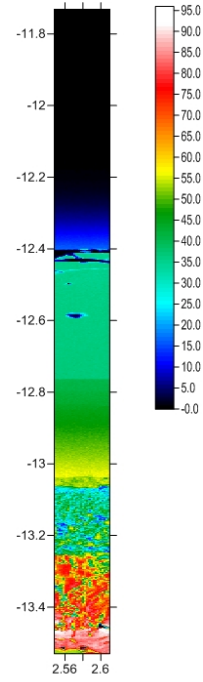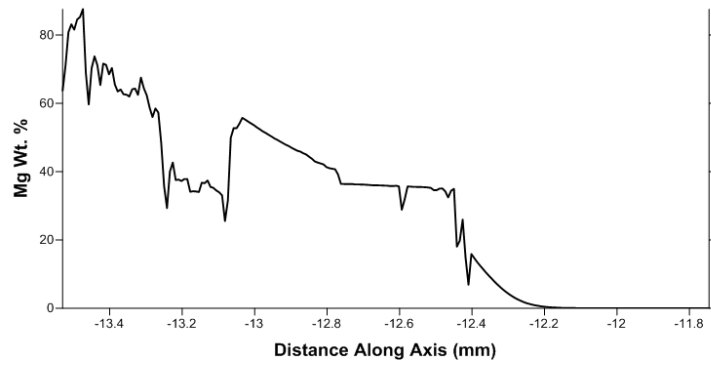
Analytical

Analysis Options

The Analysis Options dialog is similar to the corresponding window in Probe For EPMA, but some features are not available in CalcImage due to the particularities of x-ray mapping. It enables the user to turn on or off a number of analytical options. This allows for greater flexibility in the quantitative analysis of unusual samples or to pinpoint problems in the analysis.
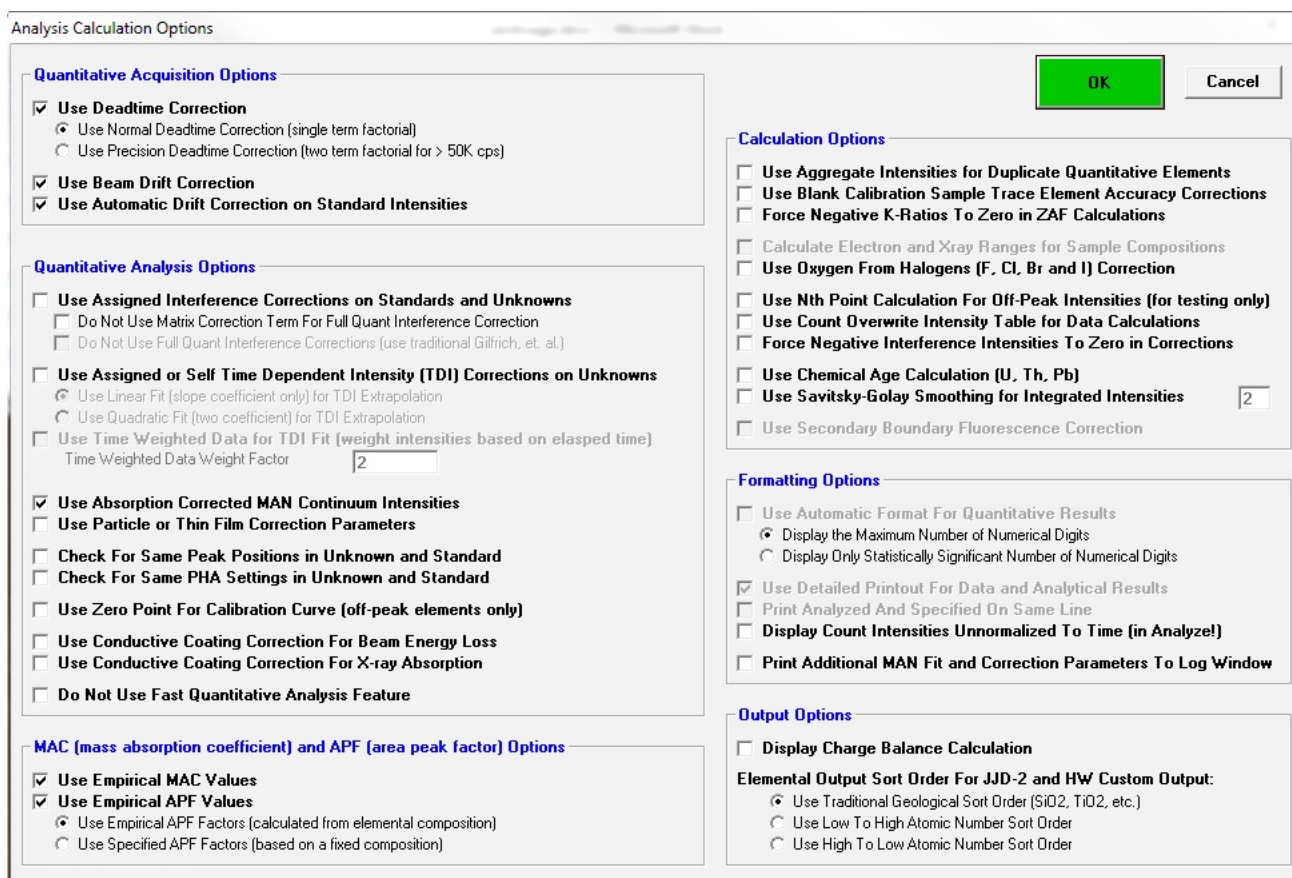
Use Deadtime Correction

The deadtime correction can be disabled for use in certain unusual analytical situations. The program will type a warning to the log window during a quantitative analysis if the deadtime correction is disabled. Two deadtime correction options are available, the normal expression shown here :

Expression # 1 :
$$I = \frac{i}{1.0 - i\tau}$$

Where :
- i is the raw measured counts in cps
- τ is the deadtime constant in seconds
- I is the deadtime corrected counts in cps

and a high precision expression (Willis, 1993) for use with very high count rates (> 50K cps) shown here :

Expression #2 :

$$I = \frac{i}{1.0 - \left(i\,\tau + i^2\,\dfrac{\tau^2}{2} \right)}$$

This high precision expression differs from the normal expression only at very high count rates. The following table shows the difference between the two expressions at various count rates :

CPS	#1 @ 1 us	#2 @ 1 us	#1 @ 2 us	#2 @ 2 us	#1 @ 4 us	#2 @ 4 us
5K	.995	.9950125	.99	.99005	.98	.9802
10K	.99	.99005	.98	.9802	.96	.9608
50K	.95	.95125	.9	.905	.8	.82
100K	.9	.905	.8	.82	.6	.68
200K	.8	.82	.6	.68	.2	.52
400K	.6	.68	.2	.52	--	--

Use Beam Drift Correction

The beam drift correction can be disabled for use in certain unusual analytical situations. The program will type a warning to the log window if the beam drift correction is disabled.

The beam drift correction calculation is shown here :

$$I_C \;=\; I_U \; \frac{B_N\,\dfrac{T_U}{T_N}}{B_U}$$

Where : I_C is the beam drift corrected unknown intensity

I_U is the uncorrected unknown intensity

B_N is the nominal beam current

T_U is the count time for the unknown intensity

T_N is the count time for the nominal beam current measurement

B_U is the beam current for the unknown intensity

Use Automatic Drift Correction on Standard Intensities

CalcImage uses a sophisticated automatic drift correction to correct the counts on the standard, interference and MAN standard intensities based on the acquisition time and date of the first data point in the selected "Condition Sample". If the selected "Condition sample" does not contain intensity data, then the program will utilize the last standard data for the x-ray map quantification.

This standard drift correction should not be confused with the beam drift correction described previously. With the automatic standard drift correction, when CalcImage loads the unknown count data to analyze a sample data point, the program will automatically check each element to see if the standard for that channel was measured both before and after the data on the unknown. If there exist sufficient standard sets, the program will automatically compute a linear interpolated drift corrected analysis.

If there is only a single standard data set, the program will simply use the set of counts on that standard which occurred closest in time prior to the unknown. Thus it is possible to perform analyses of unknowns as they are acquired, although they will not be corrected for drift. Later, when the standards have been run again, the program can recalculate all the analyses, and they will be corrected for standard count drift in real time.

The user may go back and acquire each standard up to 20 times during a run (20 "sets" of counts on the standard) and the program will determine which two sets, if any, were made closest, before and after, the counts on the unknown. The form of the standard drift correction is shown below :

$$ I_S \ = \ I'_S \ + \ (I''_S \ - \ I'_S) \ \frac{(T_U \ - \ T'_S)}{(T''_S \ - \ T'_S)} $$

Where : I_S is the drift corrected standard intensity

I'_S is the standard intensity from the preceding standardization

I''_S is the standard intensity from the following standardization

T_U is the real time of the unknown analysis

T'_S is the real time of the preceding standardization

T''_S is the real time of the following standardization

The following explanation will demonstrate how the standard drift correction is actually implemented in CalcImage. The example data shown here consists of four standard data points (set 1), followed by three unknown data points (points 5, 6 and 7), followed by four more standard data points (set 2), followed by three more unknown data points (points 12, 13, and 14), followed by a final four standard data points (set 3).

The first graph shows the standard intensities and how they are applied to unknown data *without* the use of a standard drift correction. The stepped horizontal lines drawn between the standard sets represents the standardization intensities. Note that each unknown data point uses the average intensity of the previous standardization. In a situation where drift has occurred, significant errors will result for the unknown analyses.
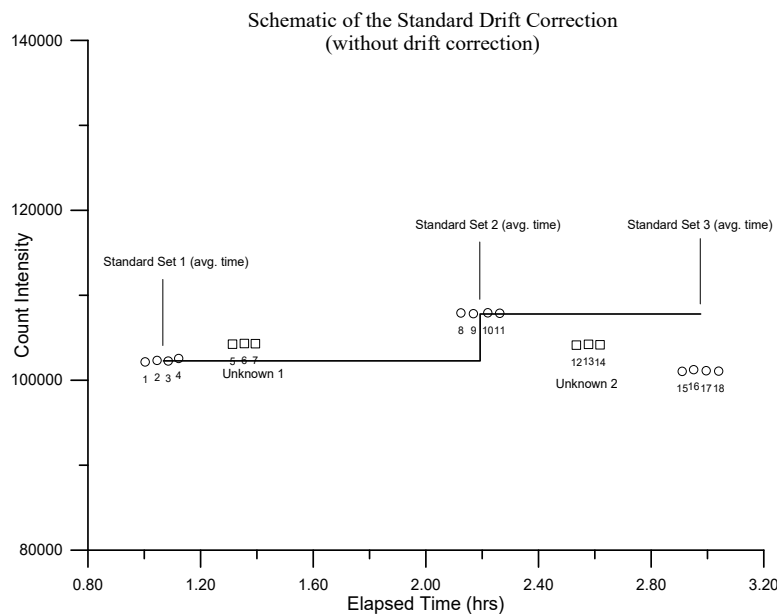
The second graph shows the standard intensities and how they are applied to unknown data *with* the use of a standard drift correction. The sloped horizontal lines drawn between the standard sets represents the standardization intensities. Note that each unknown data point uses the *interpolated* average intensity of the previous *and* the subsequent standardizations. In a situation where linear drift has occurred, the standard drift correction allows for the adjustment of standard intensities for intervening unknown analyses.

Schematic of the Standard Drift Correction
(with drift correction)
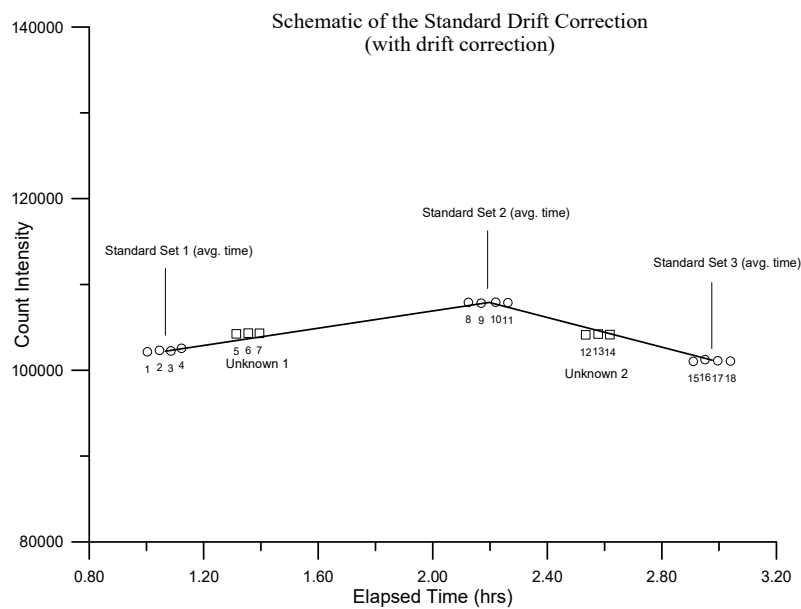
Note that because all quantitative samples (standard and unknowns) are treated as unknowns for the purposes of quantitative analysis, the standard drift correction is also applied to the analysis of standard samples. However, it is useful to note that for a given primary (assigned) standard sample, standard data points acquired *just before* the average time of acquisition of that standard are interpolated between the previous standard and the standard itself, while standard data points acquired *just after* the average time of acquisition of that standard are interpolated between the standard itself and the subsequent standard. Therefore, for primary standards, the data points within that standard are normally analyzed using two different standard intensity data sets. Furthermore, even in the case of no standard drift correction, the program will still utilize two different standard intensities when analyzing those data points just before or just after the average time of acquisition of the standard.

Use Assigned Interference Corrections on Standards and Unknowns

This option will either enable or disable the interference corrections for subsequent quantitative analysis. This option is automatically loaded if interference corrections are specified by the user. Use this option to easily determine the total effect of all of the interference corrections specified, on a quantitative analysis.

The "Do Not Use Full Quant On Interference Correction On Unknowns" option is for testing purposes only. It is should always be unchecked so that your interference corrections utilize the full matrix correction between the interference standard and the unknown sample.

The "Do Not Use Full Quant Interference Correction (use Gilfrich, et. al.)" is also for testing purposes to show what the interference correction would be using the traditional intensity ratio method.

Use Assigned or Self Time Dependent Intensity (TDI) Corrections on Unknowns

This option will either enable or disable the Time Dependent Intensity (TDI) element corrections for subsequent quantitative analysis. This option is automatically loaded if Time Dependent Intensity (TDI) element corrections are specified by the user. Use this option to easily toggle the Time Dependent Intensity (TDI) element corrections on or off, for all quantitative analyses. Note the VOL%: line in the log window also shows the relative percent change in the intensity due to the Time Dependent Intensity (TDI) correction.

Both the assigned Time Dependent Intensity (TDI) and Self Time Dependent Intensity (TDI) corrections are calculated based on the actual elapsed time of the calibration and the unknown intensity can be corrected for two different fit models:

- Use Linear Fit (slope coefficient only) for Time Dependent Intensity (TDI) Extrapolation
- Use Quadratic Fit (two coefficient) for Time Dependent Intensity (TDI) Extrapolation

The linear fit is a simple correction based on a straight line fit of the log intensities as a function of time. In other words the x data is elapsed time, the y data is the natural log of the count rate and the fit is a straight line fit in log space. The fit returned is of the $y = a + bx$ form where b is the slope and a is the intercept. In the case of the linear fit, only the slope of the fit is applied to the unknown intensities as shown here. This is the normal correction and works well for situations where the intensity change is linearly exponential.

$$ I_{corr} = e^{Ln(I_{raw})-bx} $$

where: I_{raw} is the uncorrected intensity (cps)

b is the slope of the fit to the natural log intensity versus time

x is one half the total elapsed time of the measurement in seconds

The quadratic fit uses both the slope and curvature coefficients to the log intensity 2nd order polynomial fit to handle situations where the intensity change is non-linear. This non-linear intensity change can occur when the beam current is too high or the beam is too focused. In these cases where the relative percent change in intensity can exceed 100%, it is sometimes helpful to apply the quadratic fit.

$$ I_{corr} = e^{Ln(I_{raw})-bx-cx^2} $$

where: I_{raw} is the uncorrected intensity (cps)

b is the slope of the fit to the natural log intensity versus time

c is the curvature of the fit to the natural log intensity versus time

x is one half the total elapsed time of the measurement in seconds

It is surmised that this quadratic non-linear or hyper exponential fit is the result of two separate exponential intensity change mechanisms with different time constants that are overlapping in time.

Note that these options are disabled for current versions of the software since these options are now specified on an element by element basis in the Standard Assignments dialog from the Analyze! window.

Use Time Weighted Data For TDI Fit

This option will apply a weighting factor to the TDI intensity data for the TDI fit based on the inverse square of the weighting factor starting with the shortest elapsed time intensity. For example, if the weighting factor is 2, then the program will load the first TDI intensity for the regression fit two times, the second TDI intensity will be loaded as usual once and so on. If the weighting factor is 4 then the first TDI intensity will be loaded four times, the second TDI intensity two times and the third TDI intensity once as usual.

The purpose of this weighting is to give more emphasis to the first few TDI intensities which should be more representative of the zero time intensity.

Use Absorption Corrected MAN Continuum Intensities

This option will either enable or disable the use of absorption corrected continuum intensities for calculation of the MAN background correction in subsequent quantitative analysis. For details on this procedure see Donovan and Tingle, 1996.

Use Particle and Thin Film Correction Parameters

This is a global option to turn on or off the particle and thin film parameters specified on a sample by sample basis in the Calculation Options dialog.

Check For Same Peak Positions in Unknown and Standard

Check this option to only use a standard intensity if the unknown and standard peak positions are within 0.005% of each other. For the JEOL this means the peak positions must be within 0.003 mm of each other at low Bragg angles and within 0.013 mm of each other at high Bragg angles. For Cameca instruments, the peak positions must be within 1 point at low Bragg angles and within 4 points at high Bragg angles.

This option is mainly used when multiple setups are being utilized in a single run and the setups have elements in common with the same keV, spectrometer, x-ray line and crystal, but not necessarily the same peak positions.

Check For Same PHA Settings in Unknown and Standard

Check this option to only use a standard intensity if the unknown and standard PHA settings are within 0.5% of each other. This option checks the baselines, windows, gains, biases and Integral/Differential modes.

This option is mainly used when multiple setups are being utilized in a single run and the setups have elements in common with the same keV, spectrometer, x-ray line and crystal, but not necessarily the same PHA settings.

Use Zero Point For Calibration Curve (Off-Peak Elements Only)

This analysis option is only applicable when using the Calibration Curve (multi-standard) option in the ZAF, Phi-Rho-Z, Alpha Factor and Calibration Curve Selections dialog. This option forces the program to utilize a synthetic zero intensity zero concentration data point for off-peak intensity data calibration curve calculations. It allows the use of a single standard for calibration curve calculations.

If this option is checked then the program will add an additional data point to the calibration curve fit of value 0,0. That is, zero counts and zero concentration. This option only applies to elements that have been acquired using off-peak backgrounds.

This option may be useful if some of the analyzed elements in the run have not been entered in the standard database with a concentration of zero and the user wishes to have the zero concentration data point included in the calibration curve fit.

Use Conductive Coating Correction for Beam Energy Loss

Calculates the incident beam energy loss due to the conductive coating. Only affects low over-voltage x-rays. The parameters may be set independently for the standards (Standard menu) and the unknowns (Elements/Cations dialog). Only necessary if the standards and unknowns have different thickness or different elemental coatings.

Use Conductive Coating Correction for X-ray Absorption

Calculates the x-ray absorption effect due to the conductive coating. Only affects low energy x-rays. The parameters may be set independently for the standards (Standard menu) and the unknowns (Elements/Cations dialog). Only necessary if the standards and unknowns have different thickness or different elemental coatings.

Do Not Use Fast Quantitative Analysis

This checkbox turns off the "fast" quantitative analysis feature. When this feature is enabled the program will only re-load the standard drift arrays and re-calculate the standard k-factors if the same has changed its configuration to require a re-load and re-calculate (or if a standard data point has been added or deleted within the run).

Use Empirical MAC Values

This option will either enable or disable the use of empirical MACs (mass absorption coefficients) for subsequent quantitative analysis. This option is automatically loaded if empirical MACs are specified by the user. Use this option to easily determine the total effect of all of the empirical MACs specified by the user, on a quantitative analysis. See the Analytical | Empirical MACs menu of the Probe For EPMA application to select empirical MAC values from the default EMPMAC.DAT database (a user editable text file).

Use Empirical APF Values

This option will either enable or disable the use of empirical APFs (Area Peak Factors) for subsequent quantitative analysis to correct for spectral peak shape and shift. This option is automatically loaded if empirical APFs are specified by the user. Use this option to easily determine the total effect of all of the empirical APFs specified by the user, on a quantitative analysis. See the Analytical | Empirical APFs menu of the Probe For EPMA application to select empirical APF factors from the default EMPAPF.DAT database (a user editable text file).

There are two options for Empirical APF factors:

- Use Empirical APF Factors (calculated from elemental composition)
- Use Specified APF Factors (based on a fixed composition)

Empirical (Compound) APFs

The first option calculates a compound APF correction based on binary APF factors for an element in a binary standard (for example O ka in Cr2O3) and sums all binary APF factors based on the weight fraction of the emitting element to create a "compound" APF that applies to the specific analyzed composition. This is ideal in cases where all the elements affecting the emitting element have measured binary (end-member) APF factors. The calculation for compound APFs is shown here:

$$APF_{Comp} = \sum APF_j * \frac{W_j}{Sum_{Partial}}$$

Where: APF_j is the binary (end-member) APF for elements other than the affected element

W_j is the weight fraction for elements other than the affected element

$Sum_{Partial}$ is the sum of all elements other than the affected element

A further normalization is performed on the compound APF to ensure that in situations where the partial sum is very low, the compound APF is not over applied to the affected (pure) element when only the trace elements are varying in precision. This calculation is show here:

$$APF_{Norm} = 1 + \frac{(APF_{Comp} - 1)}{1 \Big/ \left(\frac{Sum_{Partial}}{W_{Affected}} \right)}$$

Note that this APF normalization correction is only applied when the absolute value of the scaling factor :

$$\frac{1}{\left(\frac{Sum_{Partial}}{W_{Affected}} \right)}$$

is greater than or equal to 1.0 to avoid problems with over applying the correction on major elements.

Specified APFs

The second option is for more exotic absorbing systems when some elements have not been characterized for the binary APF (e.g., O ka in Na2O) and therefore it may be better to use a specified APF based on a measurement of the actual composition relative to the primary standard for the emitting element.

Use Aggregated Intensities for Duplicate Quantitative Elements

If this option is checked and the samples contain duplicate elements (same element and x-ray line) for standards or unknown quantitative samples, then the program will sum the on and off peak intensities for the duplicated elements to the first instance of the duplicated element and set the duplicated element intensities to zero.

Normally this is utilized when extreme trace element analyses are required for very low concentration elements and there is a need for improving the statistics by aggregating the intensities from several spectrometers acquiring at the same time.

CAUTION: It is important realize that measuring the same element more than once is a non-physical situation so far as regards the matrix correction. Obviously if one measures a major element on multiple spectrometers the resulting excessively high totals will make it clear that this analytical situation cannot be handled properly in the matrix correction.

In the case where a major or even minor element is measured as a duplicate element the onus is on the user to ensure that the matrix correction is properly calculated either by using the Aggregate Intensity option or by using the Disable Quant feature in the Elements/Cations dialog to have the element appear only once in the matrix correction.

However, even in the case for duplicate trace elements, one must consider this effect also. Note for the unknown sample matrix, even though the change in the sample matrix correction is small, for the standard k-factor calculation a significant error can be introduced. Consider the following examples of measuring Ti on two spectrometers in a blank Quartz standard, where the Ti concentration is essentially zero.

In this calculation the program calculates the matrix correction for the quartz standard run as an unknown and the matrix correction of the sample is properly calculated as SiO2. However, the standard k-factor for Ti in TiO2 should be 0.5547 at 15 keV, but is calculated as 0.5707 because the matrix is assumed to be Ti2O2.

Note that the program warns the user of the accuracy problem for duplicate elements in this first example of Ti as a duplicate element.

```
Un     2 std 14 SiO2
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 200.  Beam Size =    20
(Magnification (analytical) =   8000),     Beam Mode = Analog  Spot
(Magnification (default) =   600, Magnification (imaging) =    100)
Number of Data Lines:   5    Number of 'Good' Data Lines:   5
First/Last Date-Time: 02/26/2007 01:35:59 PM to 02/26/2007 03:03:33 PM
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Exponential Off-Peak correction for al ka
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Alternating On and Off Peak Acquisition

Average Total Oxygen:    53.256     Average Total Weight%:  100.000
Average Calculated Oxygen: 53.256     Average Atomic Number:   10.805
Average Excess Oxygen:     .000     Average Atomic Weight   20.029
Average ZAF Iteration     1.00     Average Quant Iterate:     2.00
```

```
Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction
Element Si is Calculated by Difference from 100%
WARNING- Duplicate analyzed elements are present in the sample matrix!!
Use Aggregate Intensity option or Disable Quant feature for accurate matrix
correction.

Results in Elemental Weight Percents

SPEC:    Si    O
TYPE:     DIFF    CALC

AVER:   46.740  53.256
SDEV:     .004    .002

ELEM:    Ti   Fe   Al    Ti     K
BGDS:    EXP      LIN     EXP      EXP      LIN
TIME:   600.00  600.00  600.00  600.00  599.92

ELEM:    Ti   Fe    Al    Ti     K    SUM
XRAY:     (ka)    (ka)     (ka)     (ka)     (ka)
   110   .000    .002     .000     .000     .000 100.000
   111   .000    .001     .000     .001     .000 100.000
   112   .000    .002     .005     .000     .006 100.000
   113   .000    .001     .000     .000     .000 100.000
   114   .000    .001     .000     .001     .001 100.000

AVER:     .000    .001     .001     .000     .002 100.000
SDEV:     .000    .000     .002     .000     .003
SERR:     .000    .000     .001     .000     .001
%RSD:    223.4    34.3    223.6     82.6    163.1
STDS:    22      395     374    22       374

STKF:    .5707   .6779    .0701    .5707    .1132   < k-factor for TiO2 is wrong
STCT:  28957.5 14598.6  3841.1 10912.1   2424.3

UNKF:    .0000   .0000    .0000    .0000    .0000
UNCT:    -.2    .2      .3     .1     .3
UNBG:     56.2    20.6     32.9     19.7     11.5

ZCOR:   1.2024  1.2061   1.2286   1.2024   1.1696   < matrix correction is correct
KRAW:    .0000   .0000    .0001    .0000    .0001
PKBG:    1.00    1.01     1.01     1.00     1.03
```

In the next example the aggregate intensity option (Analytical | Analysis Options menu) is turned on and the standard k-factor for the TiO2 standard is properly calculated because the x-ray counts from the two Ti channels are combined into a single channel.

Note that beam current and count time are ***averaged*** for the duplicate elements, since the calculation assumes that the aggregate intensity is simply increasing the geometric efficiency of the instrument. So two channels of Ti integrated at 600 seconds each is still displayed as at 600 seconds, but the total peak and off-peak counts are aggregated together to reflect the increased geometric efficiency.

```
Un    2 std 14 SiO2
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 200.  Beam Size =   20
(Magnification (analytical) =   8000),     Beam Mode = Analog  Spot
(Magnification (default) =   600, Magnification (imaging) =    100)
```

```
Number of Data Lines:   5   Number of 'Good' Data Lines:   5
First/Last Date-Time: 02/26/2007 01:35:59 PM to 02/26/2007 03:03:33 PM
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Exponential Off-Peak correction for al ka
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Alternating On and Off Peak Acquisition
WARNING- Using Aggregate Intensities for Duplicate Elements


Average Total Oxygen:     53.256     Average Total Weight%:  100.000
Average Calculated Oxygen: 53.256     Average Atomic Number:   10.805
Average Excess Oxygen:      .000     Average Atomic Weight:   20.029
Average ZAF Iteration:     1.00     Average Quant Iterate:    2.00


Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction
Element Si is Calculated by Difference from 100%


Results in Elemental Weight Percents


SPEC:    Si    O
TYPE:     DIFF    CALC


AVER:   46.740  53.256
SDEV:     .004    .002


ELEM:    Ti   Fe   Al   Ti     K
BGDS:    EXP      LIN     EXP      EXP      LIN
TIME:   600.00  600.00  600.00     .00  599.92


ELEM:    Ti   Fe    Al   Ti    K    SUM
XRAY:     (ka)    (ka)     (ka)     (ka)     (ka)
   110   .000    .002    .000    .000    .000 100.000
   111   .000    .001    .000    .000    .000 100.000
   112   .000    .002    .005    .000    .006 100.000
   113   .000    .001    .000    .000    .000 100.000
   114   .000    .001    .000    .000    .001 100.000


AVER:    .000    .001    .001    .000    .002 100.000
SDEV:    .000    .000    .002    .000    .003
SERR:    .000    .000    .001    .000    .001
%RSD:   213.9    34.3   223.6    .0    163.1
STDS:    22     395     374    22      374
```

STKF: .5547   .6779   .0701   .0000   .1132   < k-factor for TiO2 is correct
```
STCT:  39869.6 14598.6  3841.1    .0   2424.3


UNKF:    .0000   .0000   .0000   .0000   .0000
UNCT:    -.2    .2    .3    .0    .3
UNBG:     75.9    20.6    32.9    .0     11.5
```

ZCOR: 1.2024 1.2061 1.2286 1.0000 1.1696   < matrix correction is correct
```
KRAW:    .0000   .0000   .0001   .0000   .0001
PKBG:    1.00    1.01    1.01    .00    1.03
```

In this last example the standard k-factor is properly calculated because the second Ti channel is disabled for quantification using the Disable Quant feature in the Elements/Cations dialog. Note that the first Ti channel could be

disabled and the second Ti channel enabled to compare the two spectrometers. The duplicate element warning can be ignored in these cases.

```
Un    2 std 14 SiO2
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 200.  Beam Size =   20
(Magnification (analytical) =   8000),      Beam Mode = Analog  Spot
(Magnification (default) =   600, Magnification (imaging) =    100)
Number of Data Lines:   5    Number of 'Good' Data Lines:   5
First/Last Date-Time: 02/26/2007 01:35:59 PM to 02/26/2007 03:03:33 PM
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Exponential Off-Peak correction for al ka
WARNING- Using Exponential Off-Peak correction for ti ka
WARNING- Using Alternating On and Off Peak Acquisition
WARNING- Quantitation is Disabled For ti ka

Average Total Oxygen:     53.256     Average Total Weight%:  100.000
Average Calculated Oxygen: 53.256      Average Atomic Number:   10.805
Average Excess Oxygen:     .000     Average Atomic Weight:   20.029
Average ZAF Iteration:     1.00     Average Quant Iterate:     2.00


Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction
Element Si is Calculated by Difference from 100%
WARNING- Duplicate analyzed elements are present in the sample matrix!!
Use Aggregate Intensity option or Disable Quant feature for accurate matrix
correction.


Results in Elemental Weight Percents

SPEC:    Si    O
TYPE:     DIFF    CALC

AVER:   46.740  53.256
SDEV:     .004    .002

ELEM:   Ti   Fe   Al   Ti    K
BGDS:   EXP    LIN     EXP     EXP     LIN
TIME:   600.00  600.00  600.00  600.00  599.92

ELEM:    Ti-D   Fe   Al   Ti    K   SUM
XRAY:    (ka)    (ka)    (ka)    (ka)    (ka)
  110    .000    .002    .000    .000    .000 100.000
  111    .000    .001    .000    .001    .000 100.000
  112    .000    .002    .005    .000    .006 100.000
  113    .000    .001    .000    .000    .000 100.000
  114    .000    .001    .000    .001    .001 100.000

AVER:    .000    .001    .001    .000    .002 100.000
SDEV:    .000    .000    .002    .000    .003
SERR:    .000    .000    .001    .000    .001
%RSD:    .0    34.3    223.6    82.6    163.1
STDS:    22     395     374    22     374
```

STKF: .0000   .6779   .0701   .5547   .1132   < k-factor for TiO2 is correct
```
STCT:  28957.5 14598.6  3841.1 10912.1  2424.3


UNKF:    .0000    .0000    .0000    .0000    .0000
UNCT:    .0    .2    .3    .1    .3
```

```
UNBG:     .0    20.6    32.9    19.7    11.5
```

<span style="color:red">
```
ZCOR: 1.0000 1.2061 1.2286 1.2024 1.1696   < matrix correction is correct
KRAW: .0000   .0000   .0001   .0000   .0001
PKBG: .00   1.01   1.01   1.00   1.03
```
</span>

### *Use Blank Calibration Sample Trace Element Accuracy Corrections*

This option will globally turn on or off the assigned blank correction parameters (see Standard Assignments dialog under the Analyze! window) to quickly evaluate the effect of the quantitative iterated blank correction.

The blank correction is a powerful method to improve the accuracy of trace elements (and because it is fully matrix corrected can even be applied in the case of oxygen analyses for water by excess oxygen). The following example demonstrates the application of the blank correction to a Ti in quartz analysis.
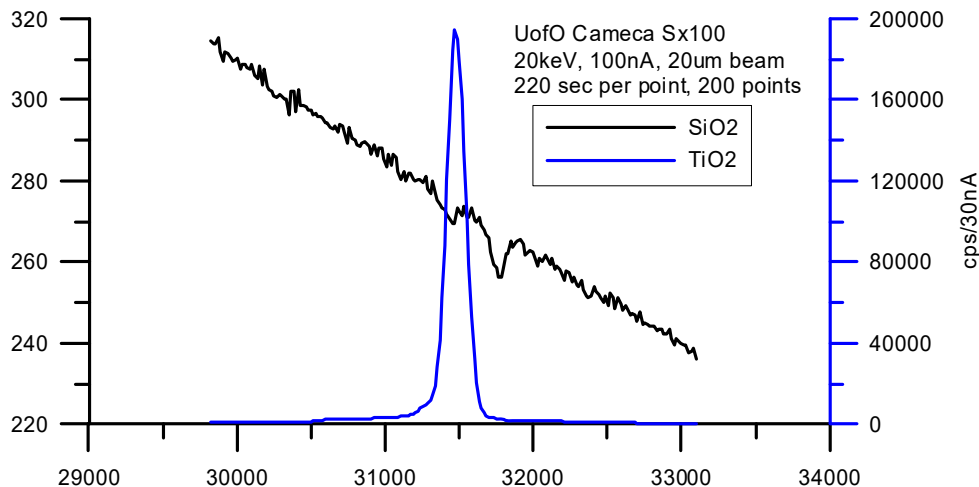


For example, spectrometer analyzing crystals have secondary lattice reflection planes which will produce small artifacts ("holes") in the spectrum  some directly underneath the analytical peak (depending on the mounting orientation). This produces a systematic accuracy error in trace element analyses that can easily exceed the precision of the measurement even with moderate beam current and count times.

```
ELEM:     Ti    Ti    Ti    Ti    Ti    Si     O     SUM
XRAY:     (ka)   (ka)   (ka)   (ka)   (ka)  ()    ()
   428 -.00023  .00029  .00005  .00076 -.00061 46.7430 53.2572 100.000
   429 -.00023 -.00003 -.00001 -.00009  .00022 46.7430 53.2569 99.9998
   430 -.00010  .00002 -.00011 -.00003  .00045 46.7430 53.2572 100.000
   431  .00016 -.00007 -.00009 -.00035  .00037 46.7430 53.2570 100.000
   432  .00019 -.00029  .00002 -.00016 -.00037 46.7430 53.2566 99.9990
```

AVER: ` -.00004 -.00002 -.00003  .00003  .00001 46.7430 53.2570 99.9999`
```
SDEV:    .00020  .00021  .00007  .00043  .00047  .00000   .00024
UNCT:    -.1    .0      -.1    .0     .0     .0     .0
```
KRAW: `   .00000  .00000  .00000  .00000  .00000  .00000   .00000`
PKBG: `   .99857  .99949  .99907 1.00219 1.00050  .00000   .00000`
```
BLNKL: .000000 .000000 .000000 .000000 .000000   ----     ----
```
BLNKV: ` -.00043 -.00009 -.00053 .000039 .000704   ----     ----`

By measuring the systematic offset (blank value line "BLNKV") on a "blank" standard which contains a zero, or known non-zero level ("BLNKL") for the element of interest in a similar matrix one can subtract the corresponding intensity from the sample during the matrix iteration for a rigorous treatment of all data including the k-ratio and P/B calculations.

Force Negative K-ratios to Zero In ZAF Calculations

This option will force any intensity k-ratios to zero during the matrix iteration since a negative intensity is not normally a physically real situation. However, in the case of trace element analysis near zero concentrations one should generally calculate the slightly negative intensities around zero so that the average intensity or compositional value is correctly calculated.

Calculate Electron and X-ray Ranges For Sample Compositions

This option will cause the program to calculate both the electron range Kanaya-Okayama incident electron scattering distance radii and effective x-ray transmission for a range of densities and thicknesses based on the actual sample composition at the current sample conditions (keV). This feature is disabled in CalcImage.

The expression:

$$electron\,radius = \frac{0.0276 \cdot A \cdot E^{1.67}}{\rho \cdot Z^{0.89}}$$

is used for the Kanaya-Okayama calculation and assumes, for compound specimens, that the average atomic number and average atomic weight are calculated based on the weight fractions of the elements in the specimen.

The expression:

$$transmission\,fraction = e^{-\mu \rho t}$$

is used to calculate the effective x-ray transmission, where μ is the mass absorption coefficient ρ is the density and t is the thickness and assumes, for compound specimens, that the average mass absorption coefficient is calculated based on the weight fractions of the elements in the specimen.

Use Oxygen From Halogens (F, Cl, Br and I) Correction

This option will allow the program to calculate the equivalent oxygen from the measured or specified halogen concentrations (F, Cl, Br and I) and subtract that amount from the amount of calculated stoichiometric oxygen.

During the calculation, since it requires two halogen atoms to replace one oxygen atom, one-half (by atom) of the halogens present are converted to equivalent oxygen and that amount is subtracted during the compositional iteration procedure. The adjustment is iterated along with the modified matrix correction factors, due to the change in overall composition. This option is applicable for ZAF/pr(z), Bence-Albee and calibration curve matrix correction calculations. This option applies only to samples where oxygen is calculated by stoichiometry and have measured or specified F, Cl, Br or I.

If this option is NOT used for samples where oxygen is calculated by stoichiometry and halogens are present, the software will simply report the oxygen equivalent of the halogens without subtracting the calculated amount. In this case, the user may then manually subtract the oxygen equivalent from the stoichiometric calculated oxygen, however, since the matrix correction is not adjusted for the change in oxygen concentration, the calculation of the other elements (especially F, due to its large correction factor in the presence of oxygen) will be slightly in error.

Finally it should be noted that to be internally consistent in the matrix calculations, all oxide standard compositions used in halogen analyses should reflect the same adjustment for equivalent oxygen in the standard database as is used for the unknown (or standard) analysis in CalcImage.

For example, the following standard composition is entered with the assumption that all cations have a full complement of stoichiometric oxygen:

```
St   112 biotite #3
```

```
TakeOff = 40  KiloVolts = 15
Oxide and Elemental Composition


Average Total Oxygen:     40.474    Average Total Weight%:  101.488
Average Calculated Oxygen:  40.474     Average Atomic Number:   13.413
Average Excess Oxygen:      .000     Average Atomic Weight:   21.358
Oxygen Equiv. from Halogen:  1.697


ELEM:    SiO2    Al2O3     FeO     MgO      CaO     Na2O      K2O     TiO2
XRAY:   ka   ka    ka    ka   ka    ka   ka    ka
OXWT:   38.622  10.721   18.131   14.011    .020     .690    9.210    2.290
ELWT:   18.053   5.674   14.093    8.449    .014     .512    7.646    1.373
KFAC:    .1368   .0382    .1205    .0528    .0001    .0024    .0689    .0119
ZCOR:   1.3201  1.4841   1.1692   1.6008   1.0860   2.1594   1.1093   1.1506
ATWT:   13.527   4.426    5.311    7.316    .007     .469    4.115     .603


ELEM:    MnO      BaO     Rb2O    Cl     F       H2O     O
XRAY:   ka   la    la    ka    ka     ka
OXWT:    .950     .111     .030    .020   4.020    2.663    .000
ELWT:    .736     .099     .027    .020   4.020     .298   40.474
KFAC:    .0062    .0008    .0002   .0002  .0112    .0030    .1826
ZCOR:   1.1891   1.3161   1.4008  1.2064 3.6053    .0000   2.2167
ATWT:    .282     .015     .007    .012   4.453    6.222   53.236
```

Note that the total for the above composition is actually greater than 100% due to the fact that in reality the fluorine and chlorine actually replace some of the cation oxygen in this mineral. Note also, the oxygen equivalent from all halogens (F, Cl, Br and I) is reported, but not subtracted from the stoichiometric oxygen (oxygen from cations).

Calculations using this standard composition and an adjustment for equivalent oxygen from halogens in the matrix correction procedure will be slightly in error due to the fact that the standard k-factor calculation will not reflect the proper reduction of stoichiometric oxygen due to the presence of halogens.

Since the default mode of this analysis option (unchecked) is to only display the equivalent oxygen and not actually utilize it in the matrix corrections, then results calculated using typical standard compositions will at least be internally consistent.

However, if it is desired to use this analysis option by reducing the calculated stoichiometric oxygen in the matrix correction then for internally consistent results, the user should make an adjustment (reduction) in the amount of stoichiometric oxygen in the standard composition. This is easily done by noting the actual amount of stoichiometric oxygen (adjusted) in the Standard Composition dialog of the Standard application (see menu Standard | Modify) and entering that value for the concentration of oxygen as seen here:

```
St  112 biotite #3
TakeOff = 40  KiloVolts = 15
Oxide and Elemental Composition


Average Total Oxygen:     38.777    Average Total Weight%:   99.791
Average Calculated Oxygen:  40.474     Average Atomic Number:   13.505
Average Excess Oxygen:    -1.697     Average Atomic Weight:   21.480
Oxygen Equiv. from Halogen:  1.697


ELEM:    SiO2    Al2O3     FeO     MgO      CaO     Na2O      K2O     TiO2
XRAY:   ka   ka    ka    ka   ka    ka   ka    ka
OXWT:   38.622  10.721   18.131   14.011    .020     .690    9.210    2.290
ELWT:   18.053   5.674   14.093    8.449    .014     .512    7.646    1.373
KFAC:    .1367   .0382    .1207    .0529    .0001    .0024    .0689    .0119
```

```
ZCOR:   1.3208  1.4841  1.1681  1.5982  1.0858  2.1546  1.1091  1.1499
ATWT:   13.836   4.527   5.432   7.483    .008    .479   4.209    .617


ELEM:   MnO     BaO     Rb2O    Cl    F      H2O     O
XRAY:   ka   la    la    ka   ka     ka
OXWT:    .950    .111    .030    .020   4.020   2.663  -1.697
ELWT:    .736    .099    .027    .020   4.020    .298  38.777
KFAC:   .0062   .0008   .0002   .0002   .0113   .0030   .1731
ZCOR:  1.1881  1.3153  1.4016  1.2073  3.5626   .0000  2.2398
ATWT:    .288    .016    .007    .012   4.555   6.364  52.168
```

Note that if excess oxygen from Fe is also present and reported, then that concentration needs to be added to the actual oxygen concentration after subtraction of the oxygen equivalent from the halogens.

Use Nth Point Calculation For Off-Peak Intensities (for testing only)

This menu is for demonstration purposes only and will force all points in a sample to use the off-peak intensity measurements from the first point in the sample for all points in the sample. It is intended only for demonstrating the possible errors arising from using the Nth Point Acquisition option in the Acquisition Options dialog under Acquire!

Use Count Overwrite Table Intensity Table for Data Calculations

This option will allow the program to utilize any non-zero "count overwrite" values to temporarily overwrite the actual measured x-ray intensities for the on-peak, high off-peak or low off-peak acquisition table values. This provides a convenient method to toggle between various "what-if" scenarios especially for use with various third party off-line background regression curves.

To learn the key stroke combination for adding overwrite intensity values to the CountOverwrite table please contact Probe Software directly. This information is not released generally to prevent users from accidently adding overwrite values to the table.

Force Negative Interference Intensities To Zero In Corrections

This option will force any negative interference intensities to zero during the matrix iteration since a negative intensity is not normally a physically real situation. However, in the case of trace element analysis near zero concentrations one should generally calculate the slightly negative intensities around zero so that the average intensity or compositional value is correctly calculated.

Use Automatic Format For Results

This option will allow the program to use maximum precision when formatting numbers for output rather than fixed format (F8.3). This option is useful when printing out trace element concentrations when more significant digits to the right of the decimal point are desired. This feature is disabled in CalcImage.

Use Detailed Printout for Data and Analytical Results

This option will disable the output of some of the printed output to the log window for a quantitative analysis. The output options not seen if this option is enabled include the standard and unknown k-factors and ZAF correction factors. This feature is disabled in CalcImage.

Print Analyzed and Specified On Same Line

This option will allow both analyzed (measured) and specified elements to be printed out on the same line in the log window. Normally the default is to print specified elements on a separate line from the analyzed elements. This causes the log window and Analyze! grid results to be more comparable in appearance. This feature is disabled in CalcImage.

Display Count Intensities Unnormalized To Time (in Analyze!)

This option displays the x-ray intensities in the Analyze! window unnormalized to count time. In other words it displays the raw intensities. The log window intensities will still be displayed normalized to count time.

Display Charge Balance Calculation

This option will output the calculated charge balance to the log window for the analyzed composition based on the Charge parameter as specified in the Elements/Cations dialog for each element.

Elemental Output Sort Order For JJD-2 and HW Custom Output

These options allow the user to specify the sort order for various outputs using either the Sort Stat and Data Grids In Geological or Atomic Number Order button in the Analyze! window and also several of the custom output formats.

The choices are traditional geological sort order based on cation oxidation ratio, low to high atomic number and high to low atomic number order.

Assign MAN Fits

This menu allows the user to display or modify the MAN (mean atomic number) background assignments and fits used for background correction. An interactive graphical display is provided to facilitate the assignment process.

The MAN method is an empirical calibration curve background correction which is based on the fact that most of the background (continuum) production in a sample is directly proportional to the average atomic number (Z-bar) of the sample. The method is available in CalcImage as an alternative to conventional off-peak background correction, It uses an iterated linear or polynomial fit of up to 10 background measurements on standards (which do not contain the element to be corrected) to provide quantitative correction over a wide mean atomic number range. As the background intensity is calculated rather than analyzed, off-peak images are not required and substantial acquisition time may be saved. In addition, the use of fixed monochromators such as in ARL microprobes requires MAN backgrounds for those channels, since they cannot be adjusted off-peak. Since the atomic number depends on the composition of the unknown which is not known at the outset, the MAN background correction must be applied during the ZAF iteration calculation.

The advantage of the MAN method is that it requires only a simple calibration of the analyzing channel over a range of atomic numbers that includes the standards and unknowns. If the average atomic number of the sample is low (for example, silicates) and the peak to background ratio is high (>10:1), then the MAN background correction method works quite well down to minor element concentrations, since the total background is often less than one standard deviation of the peak intensity of the characteristic x-ray signal. However, if measuring high average atomic number samples (greater than, for example, silicates) and/or trace concentrations, one will need to use the off-peak background correction method.

MAN Assignment and Fit

Intercept = 23.7133 Slope = .750027 Curvature = .032319 Rel % Deviation = .481

Click Channel Row to Plot MAN Fit

Chann	Eleme	X-Ray	Spect	Crysta	Order	AbsCc
1	na	ka	1	TAP	2nd	Yes
2	si	ka	2	LPET	2nd	Yes
3	al	ka	4	TAP	2nd	Yes
4	mg	ka	1	TAP	2nd	Yes
5	ca	ka	5	LIF	2nd	Yes
6	fe	ka	5	LIF	2nd	Yes

Standards (multi-select)

- 12 MgO synthetic
- 22 TiO2 synthetic
- 25 MnO synthetic
- 28 NiO synthetic
- 160 NBS K-412 mineral glass
- 162 NBS K-411 mineral glass
- 285 Ca10(PO4)6Cl2 (halogen c
- 336 Nepheline (partial anal.)

Update after changing assignments

Update Fit

Defaults

☑ Correct for Continuum Absorption
☐ Force Straight Line Fit
☑ Plot Last MAN Set Only

OK

Cancel

Re-Load >>   TakeOff 40   KeV 15

The MAN assignments are based on the element, x-ray, spectrometer number and crystal (and kilovolts and take-off angle) and are applied globally to all quantitative maps. If an element is analyzed on more than one set of x-ray, spectrometer number or crystal conditions, then the user is required to assign MAN fits for each additional set of conditions.

When opening the Assign MAN Fits window, the program loads all available standard count data from the .MDB file used in the project and graphically plots the standard intensities versus the respective Z-bars for the first element. If no MAN assignments have been made so far, the software will assign a default set of standards for each element. In this default selection, the program does not consider spectral interferences, but will only use standards for which the standards database lists a concentration of not more than 0.01 wt% of the element in question.

To view the MAN calibration curve for a certain element, click on the corresponding row in the table on the left hand side. The currently selected standards are highlighted in the Standards table on the right hand side. To modify the standard selection, hold down the shift key (to select a range) or the ctrl key (for multi-select) while clicking. Up to ten standards can be selected per element. To see the change in the calibration curve, click Update Fit to save the changes. The program will then calculate and display the updated fit. The intercept, slope and curvature coefficients and the average relative deviation in percent are displayed below the graph. Standards which contain the channel element or produce an interference must be avoided. These samples will show up as high points on the graph. MAN assignments can be changed at any time. If additional MAN backgrounds are necessary, further measurements can be acquired using Probe For EPMA.

Be sure to click the Update Fit button if any changes are made to the MAN assignments. This must be done after the changes to the MAN assignments to each element are made.

The Re-Load button can be used to re-load the global MAN assignments.
The Defaults button can be used to reset all assignments to the default selection.

Correct for Continuum Absorption

If specified, CalcImage will automatically perform an absorption correction for the continuum background counts. This correction is made using the ZAF or Phi-Rho-Z absorption correction selected by the user. Although it is not absolutely

correct to use the absorption correction for characteristic lines to correct absorption of the continuum, it is a good approximation and since the background correction itself is a second order effect the difference is negligible (Donovan, 1996).

The correction for absorption is made by simply multiplying the absorption correction for each analyzed element in each MAN background standard times the measured counts before fitting to the calibration curve. This results in a MAN background calibration curve corrected for absorption. Then, before subtracting the background correction for the standards or unknowns, the program uncorrects the calculated background counts obtained from the calibration curve based on the absorption correction for that specific standard or unknown. This effect is usually very small, on the order of 100 ppm, however if a large absorption edge is present it could improve the MAN background correction somewhat.

Note that when comparing the background fit with the actual calculated background counts, be aware that because the MAN background fit is based on counts corrected for absorption, the calculated background for a particular sample is automatically uncorrected for the absorption in the sample, by dividing the calculated background from the fit by the absorption correction term, before subtracting the background counts from the measured raw intensity. This of course only applies when using the correction for absorption on the MAN fits.

Force Straight Line Fit

This option can be used to force a straight line fit to the background counts and MAN for the selected standards when it seems that the program is over-fitting the data. By default the program will compute a second order polynomial.

Plot Last MAN Set Only

If this option is selected, only the last set of MAN standard intensities which was acquired is displayed, even if the .MDB file contains multiple sets of MAN intensities acquired over time.

Selecting Suitable Standards for the MAN Calibration

To start with you should have some idea of the range of Z-bar of your unknown samples. For silicates this will normally be in the 10.5 to 14 or 15 range, for oxides 10 or 12 to 20 or 22, for other samples use the Standard program to calculate the ranges or just look at a copy of the periodic table and estimate in your head (average atomic number is approximately calculated using the sum of the weight fractions of the atomic numbers in a compound). You then select standards (usually simple synthetic oxides or metals of high purity that will cover the range of Z-bar for both the standards and unknowns that you will be analyzing.

For example, in a silicate analysis of olivine the range of Z-bar will be from forsterite (10.6) to fayalite (18.7). Therefore you would select several standards in that range to use as MAN backgrounds including for instance MgO (Z-bar=10.4), Al_2O_3 (Z-bar=10.6), SiO_2 (Z-bar=10.8), TiO_2 (Z-bar=16.4) and NiO (Z-bar=21.2). These standards adequately cover the range of Z-bar for olivine analysis. Other pure oxides of similar Z-bar could, of course, be used also.

Some standards deviate from the calibration curve using "good" standards and must be excluded. If they plot above the curve they usually contain the element in question or interfering elements. Even if the element is not listed in the standards database it might be present. For many standards minor element concentrations are not known, unreliable, or inhomogeneous. Deviations can also be caused if the reference composition in the standards database is wrong or incomplete, e.g. when ignoring the water content of a hydrous silicate mineral.

Clear All MAN Assignments

This menu will clear the current probe database of all MAN (mean atomic number) background assignments so that the next time the Assign MAN Fits menu is selected the program will automatically load an appropriate set of MAN assignments based on the currently available standards. This is generally only necessary, when after loading in a setup from another run, the user significantly modifies the element/spectrometer setup resulting in "orphaned" MAN assignments. In this case it is sometimes easier to simply clear the MAN assignments loaded with the file setup and re-assign them using the Assign MAN Fits menu.

After clearing the existing MAN assignments, simply use the MAN Fits menu to load the default MAN assignments for the current element set in the run based on the loaded standards and then modify as necessary.

Use Off Peak Elements For MAN Fit

This menu will allow the program to utilize intensity data from standards that were acquired using off-peak backgrounds, for the MAN fit calibration. This means that elements in unknown or standard samples that were acquired using the MAN background acquisition option (no off-peaks), can utilize intensity data from standards that were acquired using the off-peak background acquisition option.

This is possible because an off peak element acquisition already contains the on-peak intensity acquired along with the off-peak intensities. When this option is utilized, the off-peak data for standards assigned for the MAN fit is NOT subtracted from the on-peak intensities so the "uncorrected" on-peak intensity can be utilized the purposes of the MAN background assignments. Normally, only standards that have been acquired using the MAN background acquisition option are utilized for the MAN assignments.
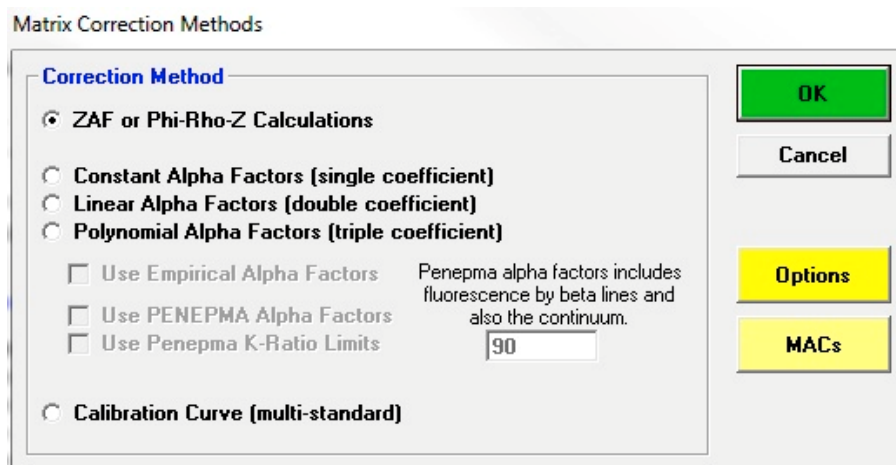
To enable this option, one must click the Use Off Peak Elements For MAN Fit menu, then one must clear the MAN fits using the Clear All MAN Assignments menu, and then re-assign the MAN fits using the Assign MAN Fits menu.

Use MAN Correction For Off Peak Elements

This menu will allow the user to perform MAN background corrections on element data that was originally acquired using off-peak background methods (assuming that the MAN calibration curves are properly assigned). This option may require the acquisition of MAN standards for the MAN calibration and for user to clear the MAN fits and re-assign the MAN assignments to make sure that the off-peak elements are assigned MAN calibration curves.

This option is very powerful in that the user can switch between MAN and off-peak background corrections on the same sample data set to see exactly what the difference between the two methods are. Once the off-peak elements have been properly assigned, there is no need to re-clear and re-assign the MAN assignments when subsequently using this menu option.

ZAF, Phi-Rho-Z, Alpha Factor and Calibration Curve Selections

This menu allows the user to modify or display the quantitative matrix correction options for all samples.

ZAF or Phi-Rho-Z Calculations

ZAF matrix corrections (included here are also the newer Phi-Rho-Z corrections) are a fundamental calculation of the x-ray intensities based on physical models of the atomic and electron interaction. It is the most accurate way available to correct for matrix effects without using an empirical calibration curve. It is also very calculation intensive and for that reason it helps to have a fast CPU when analyzing a large number of elements or samples. The following expression summarizes the ZAF correction:

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} [ZAF]_{\lambda_A}^u$$

where : $\dfrac{C_A^s}{[ZAF]_{\lambda_A}^s} \dfrac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}$ is the unknown k-ratio and

$[ZAF]_{\lambda_A}^u$ is the ZAF correction factor of the unknown

and : $I_A^u(\lambda_A)$ is the unknown intensity for element A at λ

$I_A^s(\lambda_A)$ is the standard intensity for element A at λ

C_A^s is the concentration of the element in the standard

$[ZAF]_{\lambda_A}^s$ is the ZAF correction for the element in the standard

The default selection is the Phi-Rho-Z correction optimized by John Armstrong for silicates. It is often the best choice for most compositions. The user will almost always find the default set of corrections satisfactory. Any changes to the default ZAF or Phi-Rho-Z selections will be saved along with any empirical MAC or APF data for the next time the run file is re-opened.

To change the ZAF or Phi-Rho-Z correction method, click options

Alpha-Factors

Alpha-Factor corrections based on ZAF or Phi-Rho-Z calculated k-ratio intensities and empirical a-factors from an ASCII disk file are also supported. There are two main reasons for this : first, alpha-factor corrections are very simple (once calculated for a run condition) and are therefore extremely fast. This is particularly useful when recalculating large (> 100-1000) data analyses.

By default the program calculates alpha factors based on the current ZAF or phi-rho-z and mass absorption coefficient table selections using the expression:

$$\alpha = (C/K - C)/(1 - C)$$

These binary alpha factors are combined into beta factors using the following expression (assuming a 2nd order polynomial fit):

$$\beta_B = \sum_1^{n_A} \left(\alpha_{1(B,A)} + C_A * \alpha_{2(B,A)} + C_A^2 * \alpha_{3(B,A)} \right) * C_A$$

Second, because it has been noted (Armstrong, 1988) that almost all reasonable ZAF or Phi-Rho-Z calculations will produce 2nd order polynomial fit alpha-factors with very similar slope and curvature terms (differing mainly in the intercept term), the use of a single binary standard empirically determined k-ratio allows the analyst to accurately

construct an exact calibration curve for especially difficult matrices. This is easily accomplished by editing a single ASCII file (EMPFAC.DAT) for the empirically determined alpha-factor terms measured and fit by the user. The alpha-factor correction is summarized by the following expression :

$$C_A^u = \frac{C_A^s}{Beta_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} Beta_{\lambda_A}^u$$

where : $Beta_{\lambda_A}^u$ is the unknown beta-factor

$Beta_{\lambda_A}^s$ is the standard beta-factor

Use Empirical Alpha-Factors

To utilize empirically determined Alpha-Factor terms, simply edit the EMPFAC.DAT file in the Probe for EPMA directory (usually C:\Probe Software\Probe for EPMA). If an Alpha-factor entry in the file matches the run conditions of the current run will can be used to overwrite the previously calculated alpha-factor terms. The format of the EMPFAC.DAT file is described below :

```
52.5   20.0   1   "au"   "la"   "ag"   1.142    0.000    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   1   "ag"   "la"   "au"   1.483    0.000    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   1   "au"   "la"   "cu"   1.347    0.000    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   1   "cu"   "ka"   "au"   0.758    0.000    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   2   "au"   "la"   "ag"   1.159   -0.056    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   2   "ag"   "la"   "au"   1.505   -0.071    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   2   "au"   "la"   "cu"   1.347   -0.014    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   2   "cu"   "ka"   "au"   0.759   -0.007    0.000 "NBS Spec. Pub. 260-28"
52.5   20.0   3   "au"   "la"   "ag"   1.121    0.127   -0.179 "NBS Spec. Pub. 260-28"
52.5   20.0   3   "ag"   "la"   "au"   1.458    0.170   -0.247 "NBS Spec. Pub. 260-28"
52.5   20.0   3   "au"   "la"   "cu"   1.332    0.061   -0.075 "NBS Spec. Pub. 260-28"
52.5   20.0   3   "cu"   "ka"   "au"   0.740    0.089   -0.096 "NBS Spec. Pub. 260-28"
```

Each line contains a single empirical alpha-factors fit for half of a binary pair (one emitter-absorber system per line) for various take-off angles, operating voltage, elements, x-ray lines, etc.

Columns 1 and 2 contain the takeoff angle (degrees) and operating voltage (KeV) that the alpha-factor was measured at. Column 3 is the fit flag (1 = constant expression, 2 = linear fit and 3 = polynomial fit). Columns 4 and 5 are the emitter element symbols and x-ray lines. Column 6 is the absorber element symbols. Note that CalcImage only supports the use of elemental alpha-factors. That is, referenced to elemental end-members as opposed to oxide end-members.

The three remaining columns are the alpha-factor terms. Note that constant alpha-factors have only one term, linear alpha-factors have two terms and non-linear or polynomial fit alpha-factors have three terms. For the non-linear alpha-factors, the first term is the intercept, the second term is the slope and the third term is the curvature term.

Empirical alpha-factors are calculated from experimentally measured k-ratios using a set of known binary (two element) standards covering a range of composition, by fitting the concentrations and intensity data to a plot of α vs. C, where C represents the standard concentrations and α is defined by the following expression :

$$\frac{\left(\frac{C}{K}\right) - C}{(1 - C)} = \alpha$$

Each binary data set can be fit to any or all of the alpha-factor fits, that is, constant (single term at 50/50 composition), linear (two terms) or polynomial (three terms).

Use Penepma Alpha Factors

This option allows the program to replace k-ratios calculated from the current ZAF or phi-rho-z method with k-ratios derived from Penepma (Penelope) monte-carlo calculations. These k-ratios are stored in the matrix.mdb file and is updated periodically as further intensities are re-calculated using the latest Penepma version.
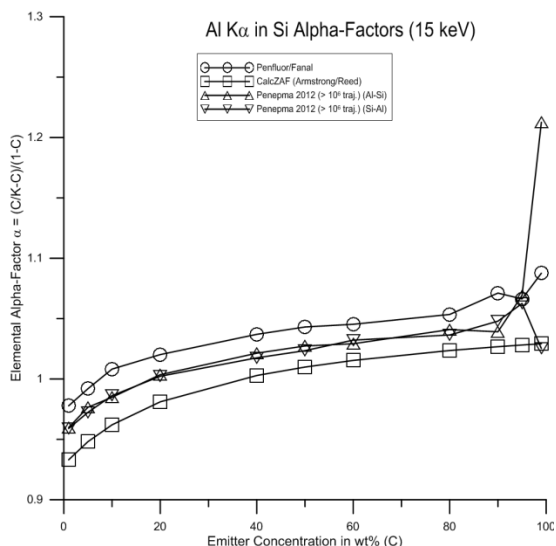
These monte-carlo derived k-ratios provide a full physics treatment of all matrix effects including secondary fluorescence by characteristic lines (including beta and other emission lines) and also by the continuum.

Use Penepma K-ratio Limits

This option can be utilized when the Use Penepma Alpha factors option is checked. It prevents the program from fitting to k-ratios greater than the specified weight percent of the emitting element. This is because as the concentration of the emitting element approaches the pure end-member of the binary, the calculation is especially sensitive to precision since one is subtracting two large numbers from each other in the alpha equation. On the other hand, the effect of the emitting element in itself approaches 1.0 in the beta equation

Calibration Curve (multi-standard)

In addition, CalcImage offers a sophisticated calibration curve based on a 2nd order polynomial fit to multiple standard intensities. This option is best employed in special situations such as the analysis of trace carbon or nitrogen in metal alloys and when a suitable set of standards are available. CalcImage will calculate a separate calibration curve for off-peak and MAN acquired data (MAN acquired data is not corrected for background with the Calibration Curve). If a standard is available that contains a zero concentration of the element, it will also be included in the Calibration Curve fit.

Generally, for best results, it is preferred to have a set of 4 or more standards with a similar matrix to the unknown and a range of the element of interest that brackets the unknown concentration. CalcImage will construct a separate set of calibration curves for both off-peak and MAN element data and fit a 2nd order polynomial expression that is used in the iteration procedure to determine the concentration of the element.

Elements calculated by difference or stoichiometry can be calculated also along with the calibration curve corrected elements. The program will print a warning if this correction method is selected.

Options

CalcImage includes the most commonly used corrections schemes for ZAF, Phi-Rho-Z and PAP matrix corrections. All these options are available with a single mouse click allowing the user to switch quickly between correction schemes in order to compare the results obtained. The main choices are:

    1 … Select Individual Corrections
    2 … Armstrong/Love Scott (default)
    3 … Conventional Philibert/Duncumb-Reed
    4 … Heinrich/Duncumb-Reed
    5 … Love-Scott I
    6 … Love-Scott II
    7 … Packwood Phi(pz) (EPQ-91)
    8 … Bastin (original) Phi(pz)
    9 … Bastin PROZA Phi(pz) (EPQ-91)
    10 … PAP- Pouchou and Pichoir - Full
    11 … PAP- Pouchou and Pichoir - Simplified

The default selection is the Armstrong/Love-Scott Phi-Rho-Z option. Note that depending on the actual mass absorption coefficients, atomic weights, x-ray emission and absorption edge energies and fluorescent yields used, the analytical results can vary slightly. The files used for these purposes are documented elsewhere (see CalcZAF.Exe) but are noted here as well:

    XLINE.DAT   Default x-ray line energies (copy XLINE1.DAT or XLINE2.DAT to this name)
    XEDGE.DAT   Default x-ray edge energies (copy XEDGE1.DAT or XEDGE2.DAT to this name)
    XFLUR.DAT   Default fluorescent yields (copy XFLUR1.DAT or XFLUR2.DAT to this name)

The following are the original files from two different sources that should be renamed to be utilized by the Probe for EPMA applications:

    XLINE1.DAT   Johnson and White x-ray line energies (no beta energies)
    XEDGE1.DAT   Johnson and White x-ray edge energies (no beta energies)
    XFLUR1.DAT   Armstrong ELEMINFO.DAT Fluorescent yields (no beta yields)

    XLINE2.DAT   Armstrong ELEMINFO.DAT x-ray line energies
    XEDGE2.DAT   Armstrong ELEMINFO.DAT x-ray edge energies
    XFLUR2.DAT   Armstrong ELEMINFO.DAT fluorescent yields (no beta yields)

The "Select Individual Corrections" option may be used to specifically select individual correction procedures from a large array of options. Note that many correction procedures will only work with other specific choices. The following is taken from John Armstrong's CITZAF documentation on how to select among the various matrix correction options :

Mean Ionization Potential Corrections

    1 … Mean Ionization of Berger-Seltzer
    2 … Mean Ionization of Duncumb-Da Casa
    3 … Mean Ionization of Ruste and Zeller
    4 … Mean Ionization of Springer
    5 … Mean Ionization of Wilson
    6 … Mean Ionization of Heinrich
    7 … Mean Ionization of Bloch (Love-Scott)
    8 … Mean Ionization of Armstrong (Springer-Berger)
    9 … Mean Ionization of Joy (Wilson-Berger)

Calculation #2 should only be used if the Philibert (#1) absorption correction and Duncumb-Reed atomic number (#1) correction are employed. Selection #1 is the default.

Backscatter Coefficients

1 … Backscatter Coefficient of Heinrich
2 … Backscatter Coefficient of Love-Scott
3 … Backscatter Coefficient of Pouchou and Pichoir
4 … Backscatter Coefficient of Hungler-Kuchler (A-W Mod.)

The default selection for backscatter is #2.

Backscatter Corrections

0 … No Backscatter (used for Packwood and Bastin original)
1 … Backscatter of Duncumb-Reed (FRAME-I)
2 … Backscatter of Duncumb-Reed (COR-II) and Heinrich
4 … Backscatter of Duncumb-Reed (COR-II) and Heinrich
5 … Backscatter of Love-Scott
6 … Backscatter of Myklebust-I
7 … Backscatter of Myklebust and Fiori (not implemented)
8 … Backscatter of Pouchou and Pichoir
9 … Backscatter of August, Razka and Wernisch
10 … Backscatter of Springer
11 … Backscatter of Donovan (Duncumb-Reed Mod.)

The conventional correction is #1. Corrections #1 and #4 give similar results. The default correction is #4. A new option is #11 which is the standard Duncumb/Reed correction with a modified backscatter loss calculation based on modified electron fractions as opposed to mass fractions. See Donovan and Westphal (2000). This modification is using a Z^0.85 power scaling to compensate for nuclear screening effects. This modified calculation works especially well when the standard and unknown are very different in average Z.

Absorption Corrections

1 … Absorption of Philibert (FRAME)
2 … Absorption of Heinrich (Quadratic Anal. Chem.)
3 … Absorption of Heinrich (Duplex 1989 MAS)
4 … Absorption of Love-Scott (1978 J. Phys. D.)
5 … Absorption of Sewell-Love-Scott (1985-I J. Phys. D.)
6 … Absorption of Sewell-Love-Scott (1985-II J. Phys. D.)
7 … Phi(pz) Absorption of Packwood-Brown 1982/XRS Alpha
8 … Phi(pz) Absorption of Bastin 1984/XRS Alpha
9 … Phi(pz) Absorption of Armstrong/Packwood-Brown 1981 MAS
10 … Phi(pz) Absorption of Bastin 1986/Scanning
11 … Phi(pz) Absorption of Riveros 1987/XRS
12 … Phi(pz) Absorption of Pouchou and Pichoir (Full)
13 … Phi(pz) Absorption of Pouchou and Pichoir (Simplified)
14 … Phi(pz) Absorption of Packwood (New)
15 … Phi(pz) Absorption of Bastin Proza (EPQ-91)

The conventional ZAF correction is #1 which is also used in the FRAME program developed by Kurt Heinrich at NIST (NBS). The best results for silicates and other oxide samples are obtained with the Phi(Rho-Z) correction (#9) and with the original Love/Scott correction (#4) or the Full or Simplified PAP correction. The default selection is #9.

Phi Equations

1 … Phi(pz) Equation of Reuter
2 … Phi(pz) Equation of Love-Scott
3 … Phi(pz) Equation of Riveros
4 … Phi(pz) Equation of Pouchou and Pichoir

5 … Phi(pz) Equation of Karduck and Rehbach
6 … Phi(pz) Equation of August and Wernisch
7 … Phi(pz) Equation of Packwood

Not applicable if one of the ZAF corrections (#1-6) or PAP was selected for the absorption correction. Both #1 and #2 give similar results. The default selection is #2.

Stopping Power Corrections

1 … Stopping Power of Duncumb-Reed (FRAME)
2 … Stopping Power of Philibert and Tixier
3 … Stopping Power (Numerical Integration)
4 … Stopping Power of Love-Scott
5 … Stopping Power of Pouchou and Pichoir
6 … Stopping Power of Phi(pz) Integration

The conventional correction is #1. Corrections #1 and #4 give similar results. When using #4, also use the Love/Scott expressions for backscatter coefficients and Phi(0). When using #1, use the Heinrich backscatter coefficients and Reuter Phi(0). Correction #6 may only be employed when one of the Phi(Rho-Z) absorption corrections are being used. Even then, it does not give as good results as #1 or #4 for silicates and oxides and it is seldom used. The default selection is #4.

Fluorescence Corrections

1 … Reed/JTA w/ M-Line Correction and JTA Intensity Mod.
2 … Reed/JTA (CITZAF.BAS- original with no M-Line Correction)
3 … Reed/JTA w/ M-Line Correction Only
4 … Reed/JTA w/ M-Line Correction and Reed Intensity Mod.

Probe for EPMA uses as a default a modified form of the REED/ARMSTRONG fluorescence from John Armstrong's CITZAF program. The two modifications are the addition of a fluorescence by M line correction, calibrated using data from Heinrich on Nb and U binary alloys and a modification of the fluorescence intensity (Armstrong, Microbeam Analysis, 1988). The analyst may also select the exact fluorescence correction from Armstrong's CITZAF code without the M line fluorescence or Armstrong ionization term. Also provided is a fluorescence correction with the fluorescence by M lines but without the Armstrong ionization term and a fluorescence correction with the Reed intensity expression.

MACs (Mass Absorption Coefficients)

CalcImage provides seven automatic lookup tables of mass absorption coefficients for use in the analytical calculations.

LINEMU.DAT is a compilation of Henke (unpublished, 1985) coefficients for energies less than 10 keV and Heinrich (1966) for energies greater than 10 keV.

CITZMU.DAT is the complete set of coefficients from Heinrich used by John Armstrong at CalTech/NIST which is from Heinrich (1966) and Henke and Ebisu for the light elements.

MCMASTER.DAT is a calculated set derived from equations (fits) from McMaster at Livermore National Laboratory (modified by Rivers).

MAC30.DAT is from Heinrich (1987), which is a fit to the Goldstein, et. al. MAC table.
MACJTA.DAT is from Armstrong's MACCALC program.

FFAST.DAT is a tabulation of the Chantler (et. Al.) 2005 MAC values provided by Nicholas Ritchie (NIST 2005). The original published NIST table is at: http://physics.nist.gov/PhysRefData/FFast/Text/cover.html

See: Chantler, C.T., Olsen, K., Dragoset, R.A., Kishore, A.R., Kotochigova, S.A., and Zucker, D.S. (2005), X-Ray Form Factor, Attenuation and Scattering Tables (version 2.1). [Online] Available: http://physics.nist.gov/ffast [Mar-2005].

National Institute of Standards and Technology, Gaithersburg, MD. Originally published as Chantler, C.T., J. Phys. Chem. Ref. Data 29(4), 597-1048 (2000); and Chantler, C.T., J. Phys. Chem. Ref. Data 24, 71-643 (1995).

USERMAC.DAT is a user defined table of mass absorption coefficients from any number of sources. It is not distributed by Probe Software but can be created by the user based on an existing selected MAC table and edited as desired.

The default mass absorption coefficient file is LINEMU.DAT. This default MAC file may be specified in the PROBEWIN.INI file. If one or more of the mass absorption coefficients in these tables are not acceptable, the user can select the use of other empirically derived values from the Analytical | Empirical MACs menu. Empirical mass absorption coefficients will override values specified from the MAC tables.

Processing

Change Current Image Palettes

Allows changing the color palette of currently open images to Gray, Thermal, Rainbow, Blue-Red, or Custom.

Change Subsequent Image Palettes

Allows changing the color palette for subsequent images to Gray, Thermal, Rainbow, Blue-Red, or Custom.

Classify Image (from CalcImage quantification)

This menu item allows phase classification of sets of quantified images based on the .DAT ASCII file generated by the Calculate Quantitative Images function during quantification. The software uses a Hartigan-Wong k-means clustering algorithm which only requires specifying the number of clusters (phases) and desired precision. Phase classification can be useful for a variety of purposes, for example to perform a modal analysis of a sample, to calculate average concentrations for the different phases present, or simply to visualize phases in distinct colors in a single image.
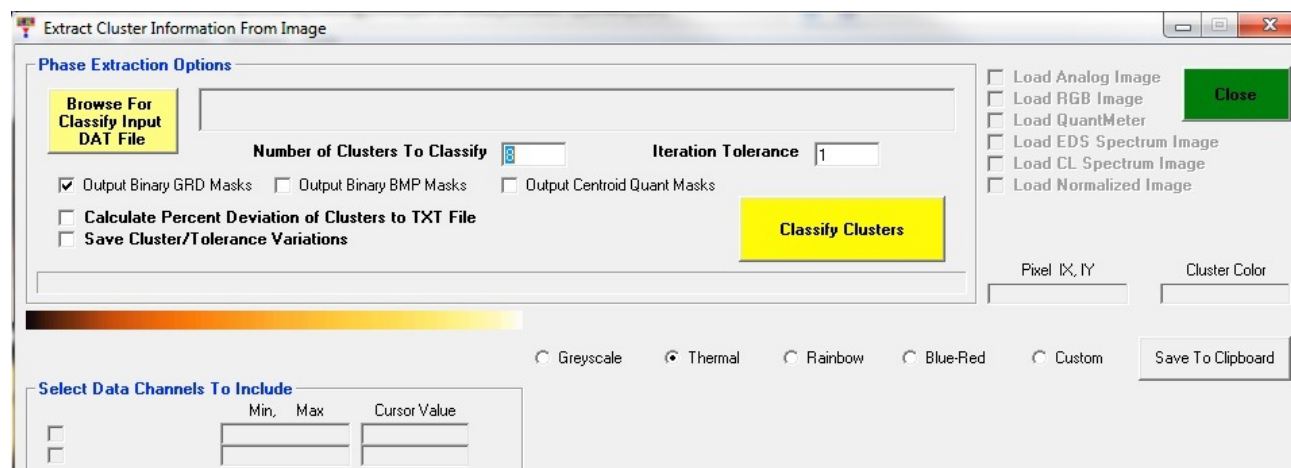
Browse For Classify Input DAT File

This button opens a file manager dialog to locate the .DAT ASCII input file generated during map quantification, usually <project name>_Quant_Image_Classify.DAT. Depending on the file size, loading this file can take some time.
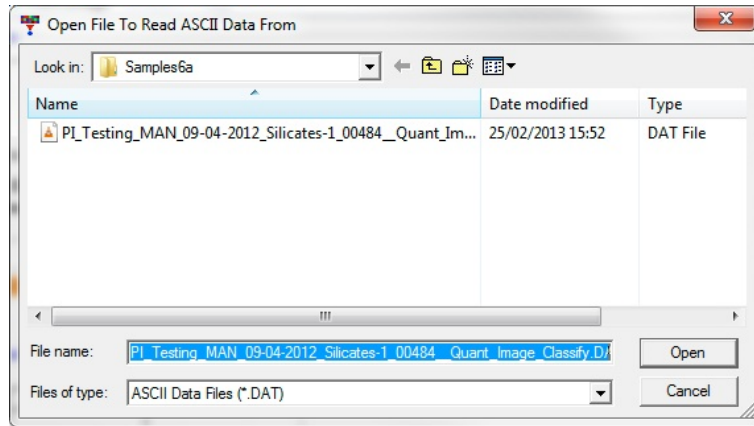
On loading, the program also creates an .INI file with the same name as the input file which contains global settings for parameters like number of clusters and iteration tolerance. The data channels are also populated with stage and pixel limits and concentration ranges for the different elements.
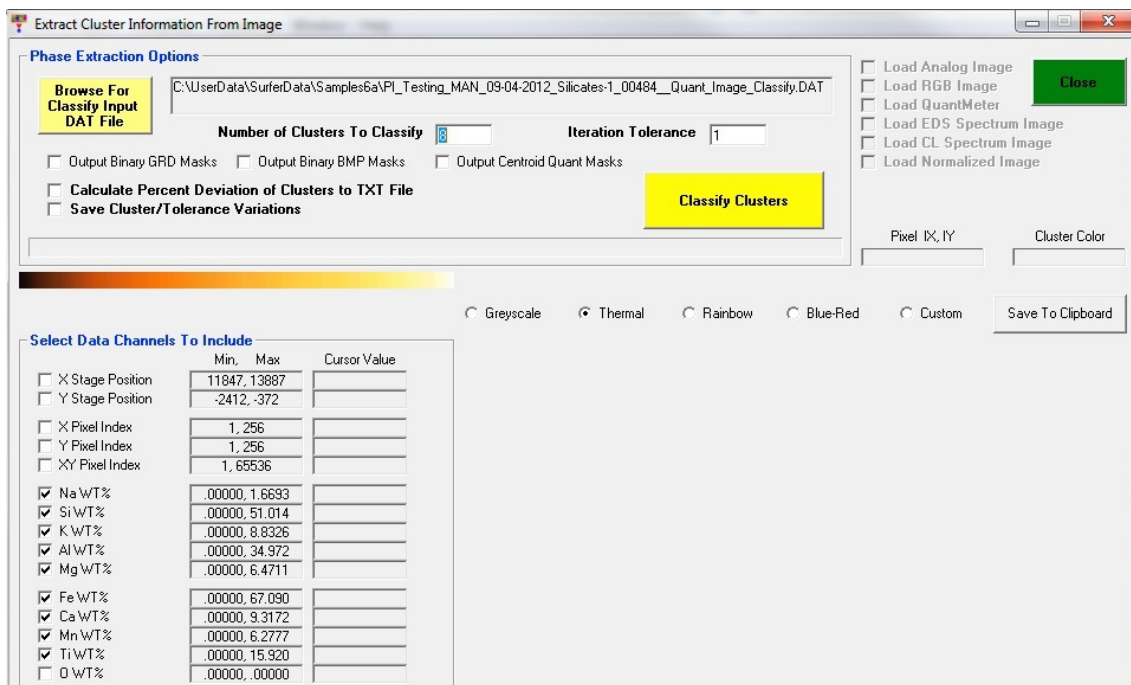
Classify Clusters

The Classify Clusters button starts the phase classification calculation based on the currently selected parameters. Depending on the map sizes and the settings the calculation can take a considerable amount of time.

After classification the classified image is displayed next to the data channels. Next to the data channels, 2 boxes with the channel colours for the minimum and maximum concentration for the respective element are shown. The color palette can be changed using the Greyscale, Thermal, Rainbow, Blue-Red, or Custom radio buttons. When moving the mouse over the image, the values for the data channels and the number of the cluster are displayed to the left and above of the image. The program writes the cluster numbers (NK) back into the first column of the <project file name>_Quant_Image_Classify.DAT input file.
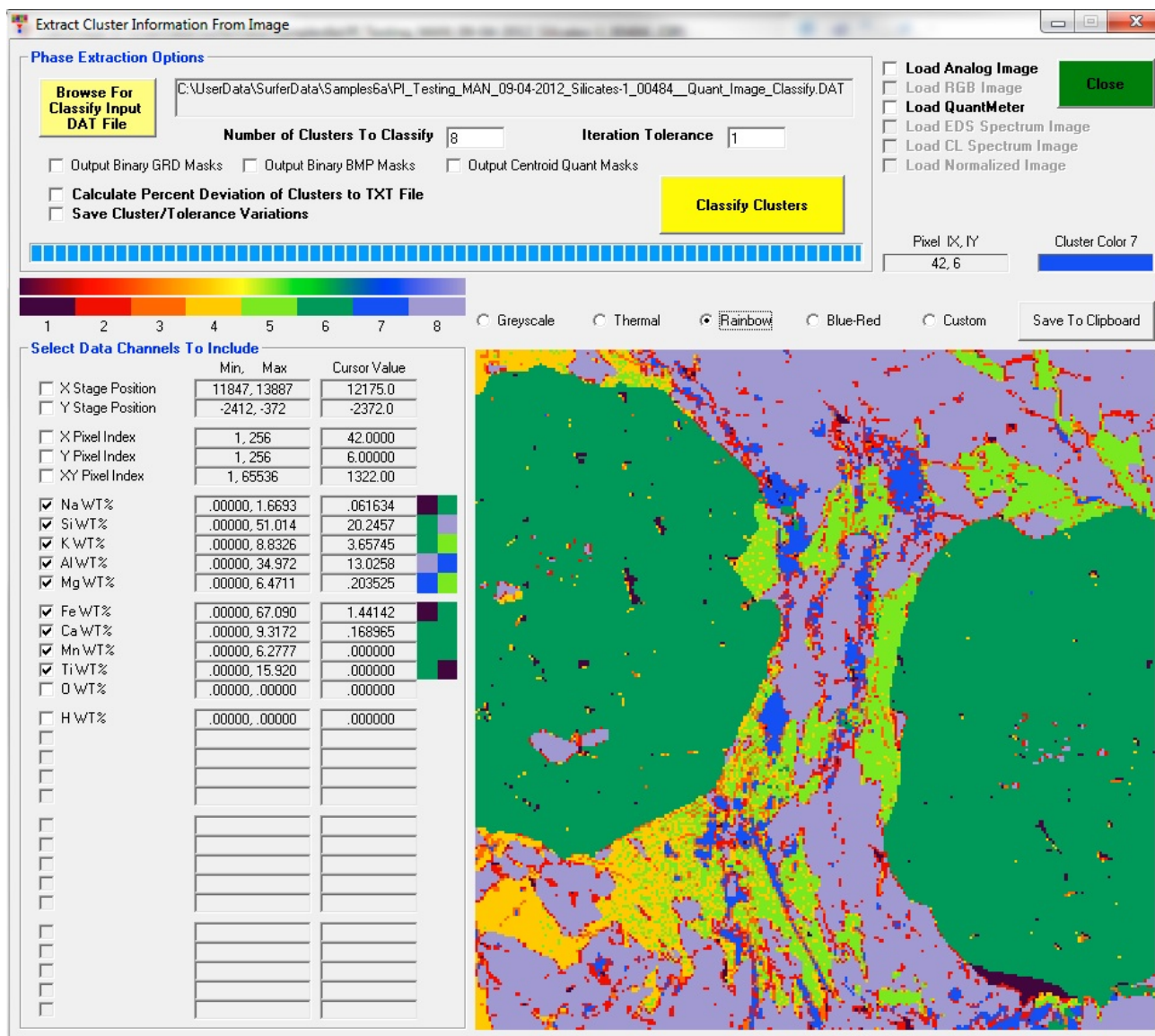
A .BMP and .GRD file of the classified image with the same name as the .DAT input file are created automatically and saved to the project folder, but the image can also be copied using The Save To Clipboard button.

The software also creates a .TXT file with the same name as the input file, which contains information about average composition of the phases, area % and so forth. The structure of the file is as follows:

Line 1: number of columns, number of clusters.
Line 2: column headers
Lines 3 and following: data for each cluster
Column 1: NK (cluster number)
Column 2 to n-4: calculated centroids (average weight % for elements in cluster), and optionally % standard deviation
Column n-3: area % of cluster (phase) in map
Column n-2: density, default value of 5, currently has to be edited manually in Calculate Modal Abundances window
Column n-1: mass %, requires correct densities, calculated in Calculate Modal Abundances window
Column n: best match in match database (e.g. DHZ), calculated in Calculate Modal Abundances window

Number of Clusters To Classify

Specify the number of clusters (phases) to classify in the set of maps. The number must be between 2 and 32.

Iteration Tolerance

Specify the iteration tolerance for classification. The number must be between 10 and 0.00001.This number is the iteration tolerance precision, i.e. a value of 0.01 corresponds to 1% precision. An example for the effect of the tolerance value is given below for a map of a complex Mg-Al-Gd-Sn-O material with 512 x 1024 pixels using 15 clusters. Typical calculation times are given in brackets.
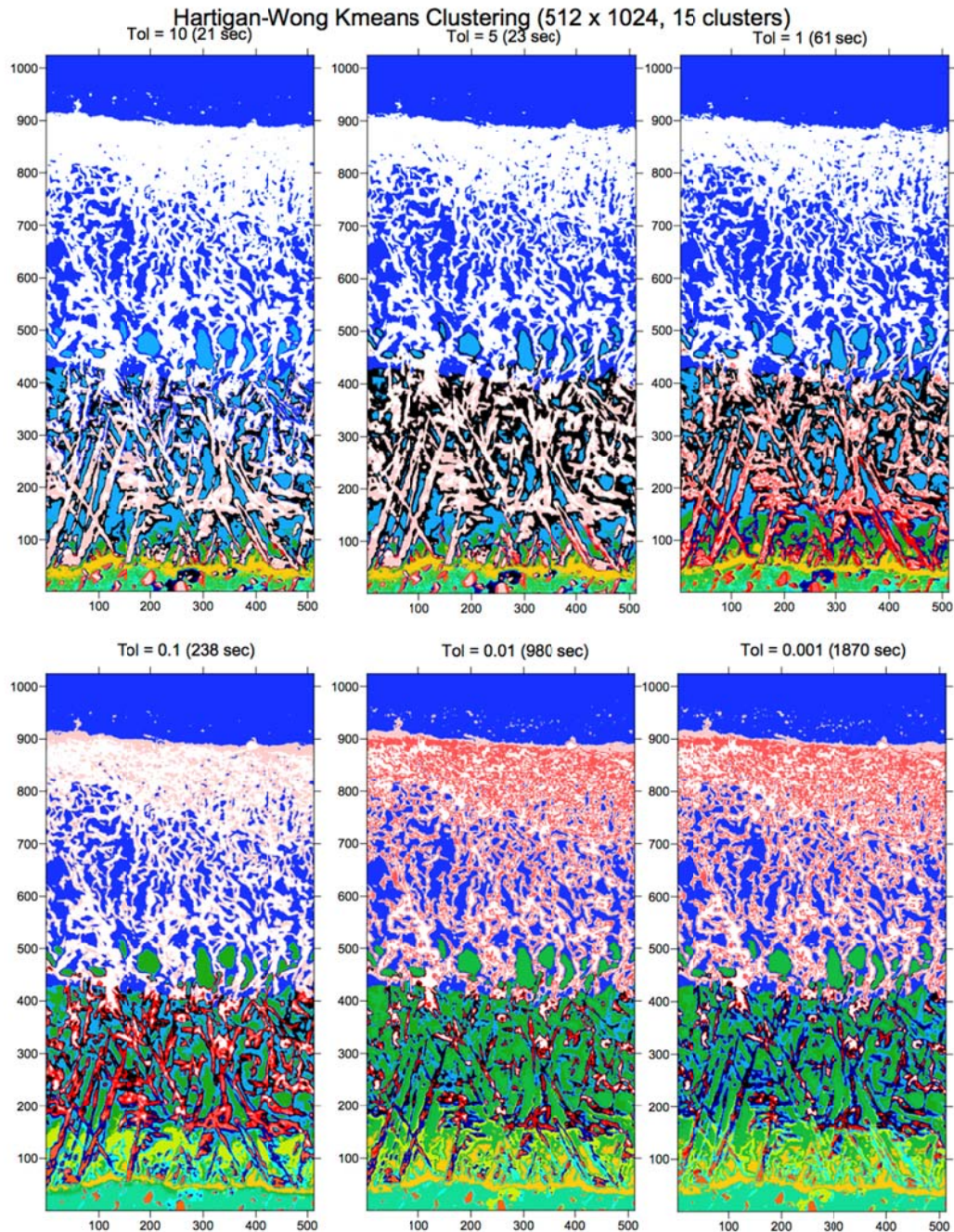
Output Binary GRD Masks

If this option is checked, Classify Clusters will also generate .GRD files with a binary image for each cluster. The files are named <input file name>_Cluster<cluster number>.GRD.

Output Binary BMP Masks

If this option is checked, Classify Clusters will also generate .BMP files with a binary image for each cluster. The files are named <input file name>_Cluster-<cluster number>.BMP.

Output Centroid Quant Masks

If this option is checked, Classify Clusters will also generate a .GRD file for each element with the centroid (average) composition for each cluster. The files are named <input file name>_Centroid-<element> WT%.GRD. Total and calculated oxygen images will also be generated if this option was checked before quantification in Specify Quantitative Parameters.

Calculate Percent Deviation of Clusters to TXT file

If this option is checked, Classify Clusters will calculate the standard deviations (1s, %) in the centroid clusters (average elemental compositions) and write them as additional columns in the .TXT output file.

Save Cluster/Tolerance Variations

If this option is checked, Classify Clusters will create an additional .BMP, .GRD, and .TXT file that includes the number of clusters and tolerance in the file name, e.g. <project file name>_8-Clusters_1-Tolerance.TXT for the text output file when using 8 clusters and a tolerance of 1. This is useful when experimenting with clusters and tolerance parameters, as files for different settings are not overwritten and can be compared.

Load Analog Image

This option opens a file manager dialog to load the analog image (SE, BSE…) corresponding to the classified image. It is displayed in a separate window. The mouse pointer position in the classified image in the main window is represented by the sight symbol.
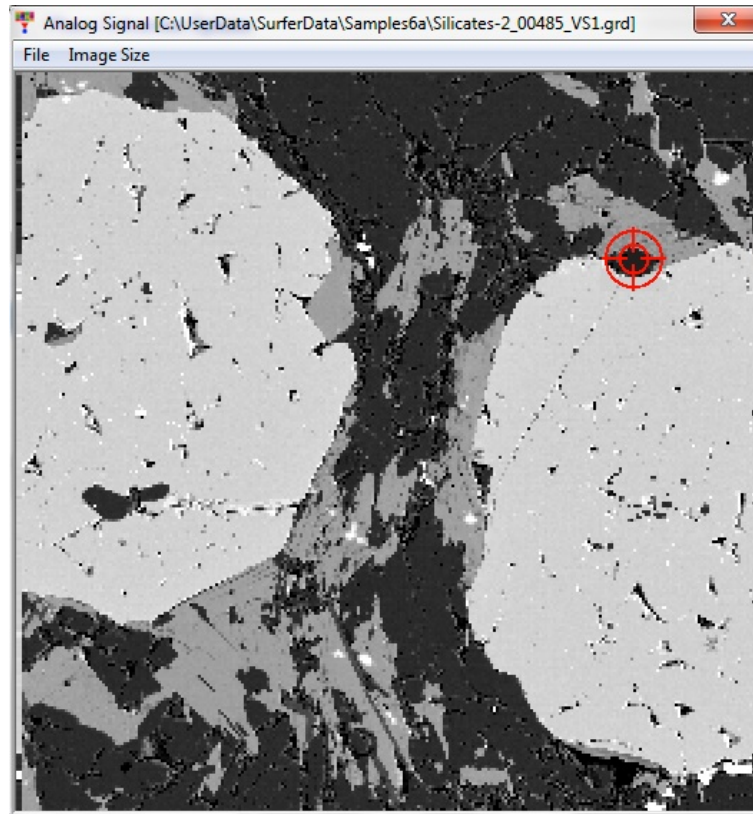
Load RGB Image

Currently not implemented.

Load QuantMeter

The QuantMeter displays the values for the different elements depending on the mouse pointer position in the classified image similar to a live ratemeter on an instrument. The color of the arrowheads corresponds to the color of the cluster (phase) currently under the mouse pointer. The scale is adjusted to the minimum and maximum values in the individual element channels.
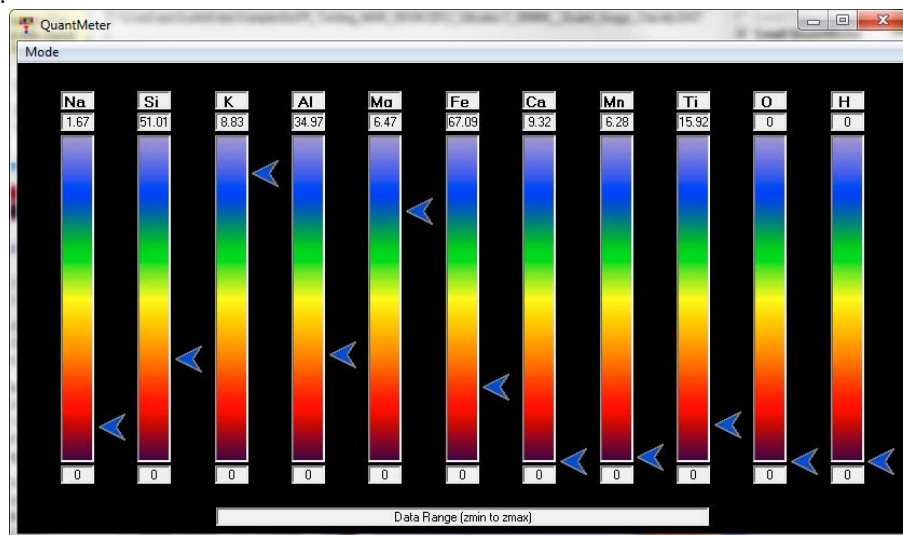
Load EDS Spectrum Image

Currently not implemented.

Load CL Spectrum Image

Currently not implemented.

Load Normalized Image

Currently not implemented.

Select Data Channels To Include

The tick boxes next to the channels allow selection and deselection of individual data channels. After classification, the Cursor Value fields also display the value for each channel at the mouse pointer position.

Classify Points (from Probe for EPMA quantification)

This menu performs similar operations as the previous menu but on Probe For EPMA point data (random points, traverses, rectangular or polygon grids), although if desired the CalcImage quantified .DAT file can also be loaded into this mode and treated as individual measurements.

Data can be exported from Probe For EPMA in the CalcImage cluster classification format using the Save Cluster Classification Format (for CalcImage) in the Output menu. The program will create a tab-delimited ASCII file with the same format as the Calculate Quantitative Images function of CalcImage. The default name for the file is <Probe database file name>_Quant_Point_Classify.DAT.

The Classify Points menu provides the same features for phase extraction as the Classify Image menu (see there for documentation), except for the .GRD image export options, which are not available as this mode is not dealing with maps. Instead of the display of the classified image, this window contains a table with the quantitative point data. The first column (NK) shows the cluster number, the third column (NS) the sample number from the Probe For EPMA database, the fourth column (NL) the line number from the Probe For EPMA database, and the fifth column (ND) a sequential number from export.

The following features are different from the Classify Image menu:

Calculate Random Fraction

This button can be used to test sampling statistics. It creates a new input .DAT file with the file name <previous input file name>_RandomFraction_<fraction value>_.DAT. This file can then be reloaded for further processing using the Browse For Classify Input DAT File button. The randomized fraction parameter can be set to a value between 0.01 and 1.0. A value of 0.5 would for example output a random fraction of 50% of the original data.

If the Do Not Output The First Line box is ticked, the first line of the previous .DAT input file containing the number of pixels and columns is not included in the new .DAT file for easier Surfer gridding input.

Send Classify Data to Excel

This button opens Microsoft Excel and copies the classified data table to a new Excel workbook. Disabled analysis lines (cluster number zero in first column) which were excluded using the Extract Range function will also be exported.

Extract Range

This feature can be used to exclude bad measurements from processing by specifying an allowed range of analysis totals (Min and Max fields, in wt%) and clicking the Extract Range button. The program will save the matching data to a new input DAT file with the name <previous input file name>_ExtractRange_<Min>-<Max>.DAT. This file can then be reloaded for further processing using the Browse For Classify Input DAT File button.

After reloading, the Classify Points window will show a message "Blanked data rows are not shown" next to the Close button to indicate that a reduced data set is loaded. The lines for the excluded analyses are actually still present in the new .DAT file but disabled, as indicated by the zero in the first column (cluster number NK). They are not visible in the table display of the Classify Points window.
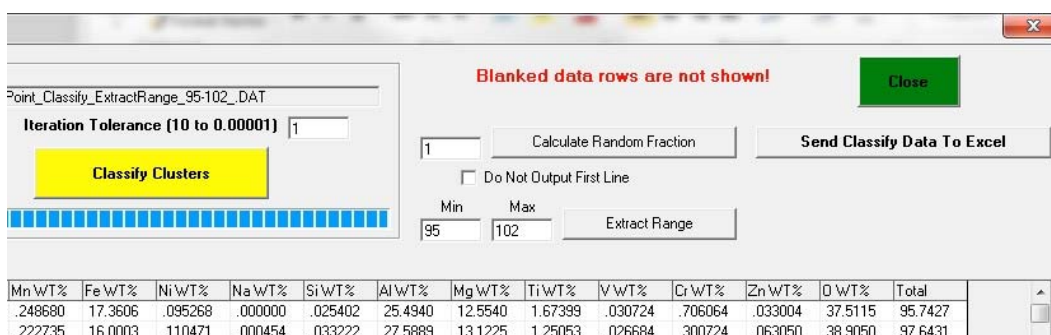
Calculate Modal Abundances (from CalcImage classification)

This menu allows further processing of the classification output to calculate modal abundances and mass fractions. It is also possible to match the cluster centroid (average phase) compositions to compositional databases. These include standards .MDB databases or the match databases supplied with Probe For EPMA like DHZ.MDB, which contains mineral compositions from the book on Rock-Forming Minerals by Deer, Howie & Zussman.

Initially the data table will be empty until the user has loaded a .TXT file containing classified data.
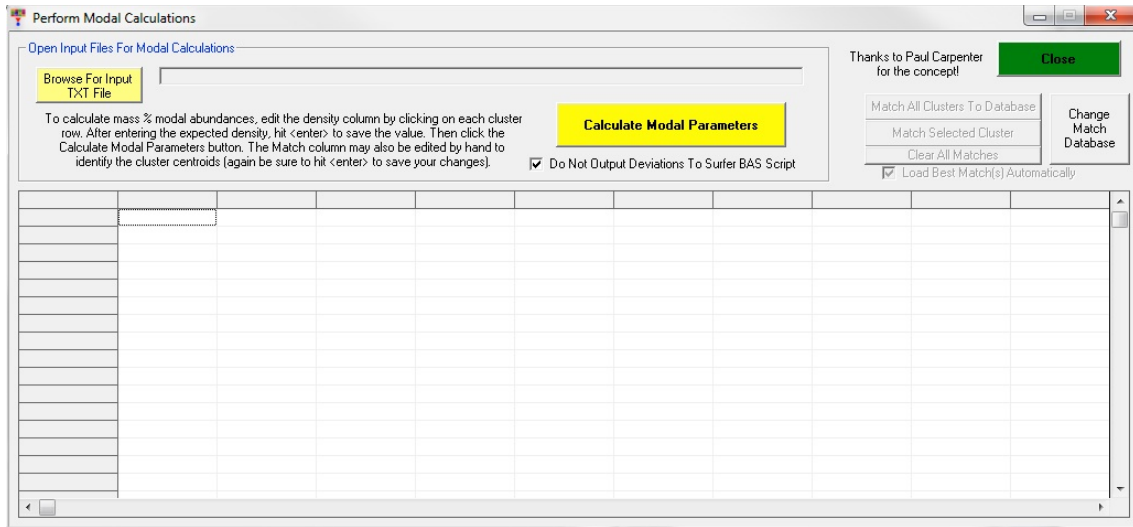
Browse For Input Text File

This button opens a file manager dialog to select the input file to load. This file must be a .TXT file generated with the Classify Image or Classify Points operations of CalcImage. It contains a separate line for each cluster centroid (average phase composition) and at least a value for the Area% of each cluster. The first column (NK) contains the cluster number corresponding to the CalcImage classification.

When loading a .TXT input file for the first time, the Density, Mass% and Match columns in the data table will not contain meaningful information, i.e. Density will be using a default value of 5, Mass% will be zero, and Match will be empty.
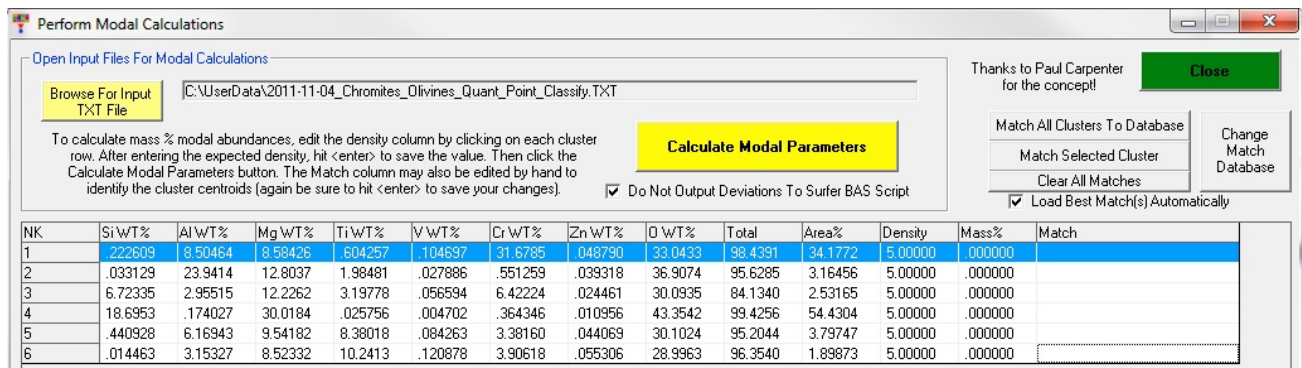
Calculate Modal Parameters

Calculate Modal Parameters will calculate the modal abundances in mass% (wt%) based on the area% and current density values and write the results back into the existing .TXT file.

The density values can be edited by clicking on the respective field in the table, typing the correct value and hitting <enter> to save the new value. If the density of a cluster centroid (phase) is unknown, the match operation can be performed first and densities for the matched minerals can be looked up externally, for example in internet databases like Mindat.org or Webmineral.com.

Match All Clusters To Database

This button starts an automatic matching run of all cluster centroids against the currently selected match database. If the Load Best Match(es) Automatically box is ticked, the best matches will automatically be written into the corresponding Match fields in the data table and the .TXT input file. A lesser match can also be selected from the drop down menu in each Match field, and the contents of this field can also be edited by hand if no suitable match is found in the databases. To edit, click on the respective field in the Match column, type in the correct description and hit <enter> to save the changes.

A range of match databases is provided with Probe For EPMA that can be used with CalcImage, such as DHZ.MDB (mineral compositions from the book on Rock-Forming Minerals by Deer, Howie, & Zussman), Dana.MDB (stoichiometric compositions of non-silicate minerals from Dana's Mineralogy), SRM.MDB (NIST standard reference materials database), and AMCSD.MDB (American Mineralogist "Standard Crystal Structure Database"). This latter database contains over 9500 mineral species based on formula stoichiometry and therefore takes some time to search.

The program opens the Match Unknown To Match Database window, which is the same as the Options | Match menu in the Standard application of Probe For EPMA.

The Input Composition section shows the composition of the current cluster centroid. The Enter Unknown button can be used to match arbitrary unknown compositions to the database by entering a string of elements with corresponding wt% values (e.g. Si46.7O53.3 for quartz), which can be useful for comparison purposes. The Match Standards button manually starts a matching operation for the currently selected composition. The value in the Minimum Vector field can be adjusted to change the minimum required "tightness" of the match, with a higher value corresponding to a "looser" match. The Change Match Database button allows selection of a different MDB database to match against.

The results of the match operation will be listed in the Standards Found field in order of decreasing match quality with the best match listed first. Each line begins with the v value (match "vector", goodness of fit), followed by the standard number in the database, and the standard description. The results can be copied to the clipboard using the Copy Standards Found to Clipboard button.

Match Selected Cluster

This button performs the same operation as Match All Clusters To Database, but only for the currently selected cluster centroid (average phase composition).

Clear All Matches

This button clears all current mineral matches from the data table.

Change Match Database

This button allows selection of a different MDB database to match against, see Match All Clusters To Database for more information.

Run

List Run Summary

This menu will output a summary of all major run and sample parameters (based on the current sample) to the log window. This summary may be worth printing out for record keeping purposes.

List Rows, Names, Conditions

This menu will output a summary of all standard, unknown and wavescan samples to the log window. Note that the first column of numbers listed here are the sample row numbers of the samples, which is also used as a pointer for saving and loading sample setups within the run.

This is followed by the sample names and sample acquisition conditions (beam mode, beam current, beam diameter).

Display PictureSnap

This menu opens the PictureSnap! Window which allows the user to open any scanned image, for example, from a flatbed or slide scanner, and calibrate the image to the stage coordinates of the microprobe stage.

After the image is calibrated using two diagonal positions on the image for which the stage coordinates can be located, the image will display the current stage coordinate as a live floating cursor. One can also double-click any image position and the stage will move to that position. Based on tests using a 4000 dpi slide scanner, one can calibrate the image so that individual grains can be located to within 5 um depending on the accuracy with which the image is calibrated.

In addition the software allows the user to display currently digitized points by clicking the Display menu items (RealTime mode only) or to display previously analyzed positions (on-line and off-line mode). Use the menus in the

PictureSnap window to display currently digitized position samples and use the Run menu items from the log window to display previously analyzed positions within the currently open probe database.

The displayed image plus the plotted stage positions (and floating scale bar) can be printed using the File | Print menu. To obtain a digital image use the File | Print Setup menu to select the Adobe Acrobat PDF printer. One can also use the Copy To Clipboard menus, though method 1 does not copy the plotted stage positions, while method 2 does, but not for the entire image area, just the portion visible in the scrollable image window.

Note that a live cursor is displayed in the window caption bar. It displays pixel (twip) coordinates in uncalibrated images and stage coordinates in calibrated images. Image calibrations are automatically saved to a .ACQ file which is automatically reloaded if the image is opened subsequently (on or off line).
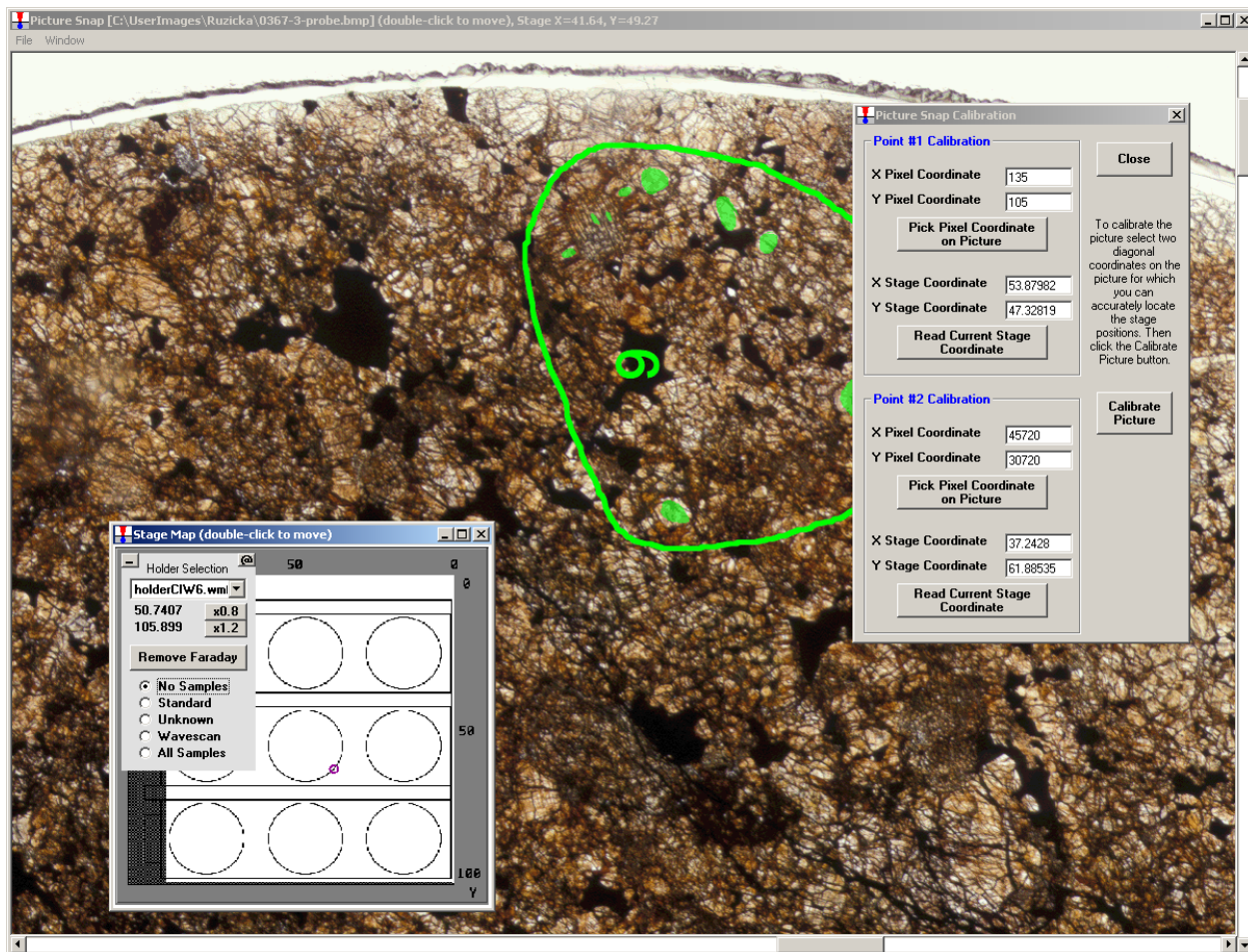
Note the Save As GRD File menu under the File menu which allows the user to export the image to a Surfer GRD file format along with any positions (and position sample or line numbers) that are currently displayed, to a .DAT file for using as a "post data" file in Surfer. Creation of publication quality images showing exact analysis positions is easy with this feature.

Display Acquired Standard Positions on PictureSnap

Click this menu item to display any previously analyzed standard positions on the calibrated image. Use the Display Line Labels on PictureSnap to show the line number labels.

Display Acquired Unknown Positions on PictureSnap

Click this menu item to display any previously analyzed unknown positions on the calibrated image. Use the Display Line Labels on PictureSnap to show the line number labels.

Display Acquired Wavescan Positions on PictureSnap

Click this menu item to display any previously analyzed wavescan positions on the calibrated image. Use the Display Line Labels on PictureSnap to show the line number labels.

Display Long Line Labels On PictureSnap

Display analysis line numbers with each analysis position using the format ,sample number>-<line number>.

Display Short Line Labels On PictureSnap

Display the analysis line numbers with each analysis position using only the analysis line number (no preceding sample number)

Skip Deleted Points On PictureSnap

Checkable menu to display or not display deleted analyses. The default is to display deleted points.

Skip Duplicate Points on PictureSnap

Checkable menu to display or not display analysis points that have identical stage positions. The default is to display points with duplicate stage positions.

Surfer Templates

This menu allows to select which script to use for the four different export options to Golden Software Surfer which are available in the Project menu: Normal quant image "presentation" output, slice, polygon, and multiple strip output. Either the default script or up to 4 different customizable scripts can be selected.

Beginning in v 10.4.4 of the ProbeForEPMA.msi file (not the quick .ZIP update), the installer will provide customizable "partial" Surfer script files in the Probe For EPMA application directory. Once they have been modified by the user they will not be overwritten by future Probe For EPMA updates. Why "partial"? Because these scripts do not contain specimen specific information, only the plot layout. This specimen specific information is appended to these "partial" scripts to create a fully functional script to run in the Surfer Scripter application (or automatically from CalcImage):

The following script files are available:

GRIDXY.BAS: Default quant presentation output script (will be overwritten on software updates, so do not edit normally)
gridxy_Custom1.bas, gridxy_Custom2.bas, gridxy_Custom3.bas, gridxy_Custom4.bas,: user customizable scripts for quantitative and raw data presentation output (will not be overwritten)

Similar for Slice output:
SLICEXY.BAS: default, do not edit
slicexy_Custom1.bas, slicexy_Custom2.bas: user customizable

Polygon output:
POLYXY.BAS: default, do not edit
polyxy_Custom1.bas, polyxy_Custom2.bas: user customizable
polyxy_Custom1.bas   User customizable script for polygon extraction data presentation output (will not be

Multi strip output:
STRIPXY1.BAS: default **equant** strip output, do not edit
stripxy1_Custom1.bas, stripxy1_Custom2.bas: **equant** strip output, user customizable
STRIPXY2.BAS: default **tall** strip, do not edit
stripxy2_Custom1.bas, stripxy2_Custom2.bas: **tall** strip output, user customizable
STRIPXY3.BAS: default **wide** strip, do not edit
stripxy3_Custom1.bas, stripxy3_Custom2.bas: **wide** strip output, user customizable
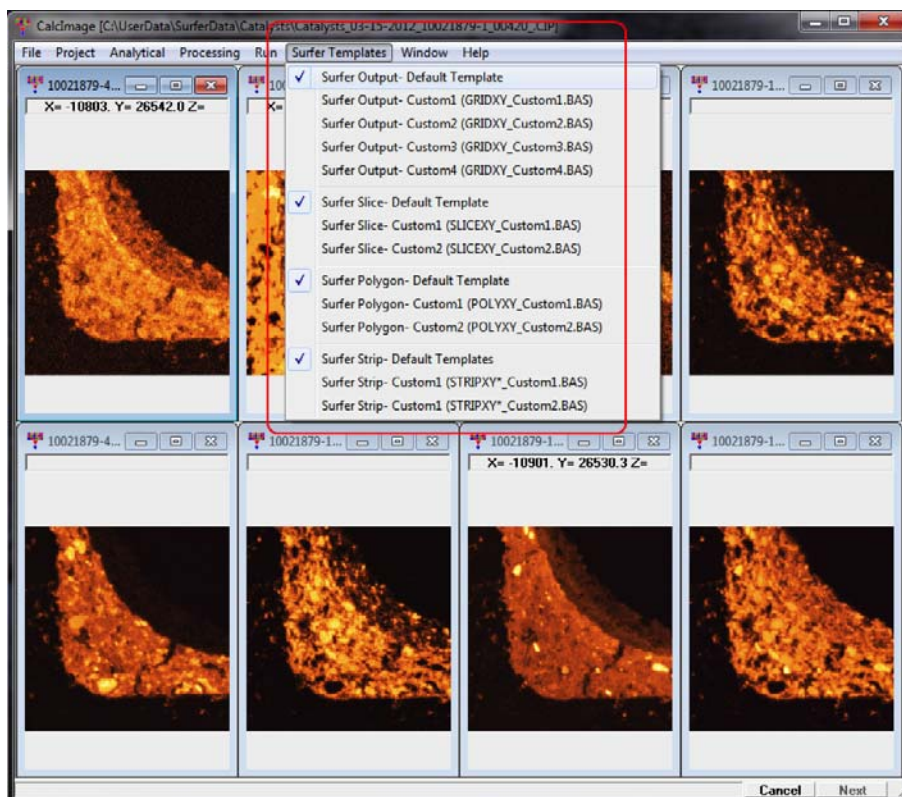
Window

Log Window

Opens the log window to view the progress of the quantitative calculations. If debug mode is selected (see below under Log Window menus) the details of the quantitative iterations are visible in the log window.

Tile Vertically

Tile the current x-ray maps (or quantitative images) vertically.

Tile Vertically

Tile the current x-ray maps (or quantitative images) horizontally.

Cascade

Cascade the current x-ray maps (or quantitative images).

Arrange Icons

Arrange the icons for the current x-ray maps (or quantitative images) that are minimized.

Use Hyper Cursor

This feature can be used to compare data values of pixels in corresponding images. When selected, a red circle is displayed under the mouse pointer when moved over an image, which is linked to similar red circles in all other open images of the same project. The X and Y values above the images correspond to the position, the Z value to the intensity or concentration.
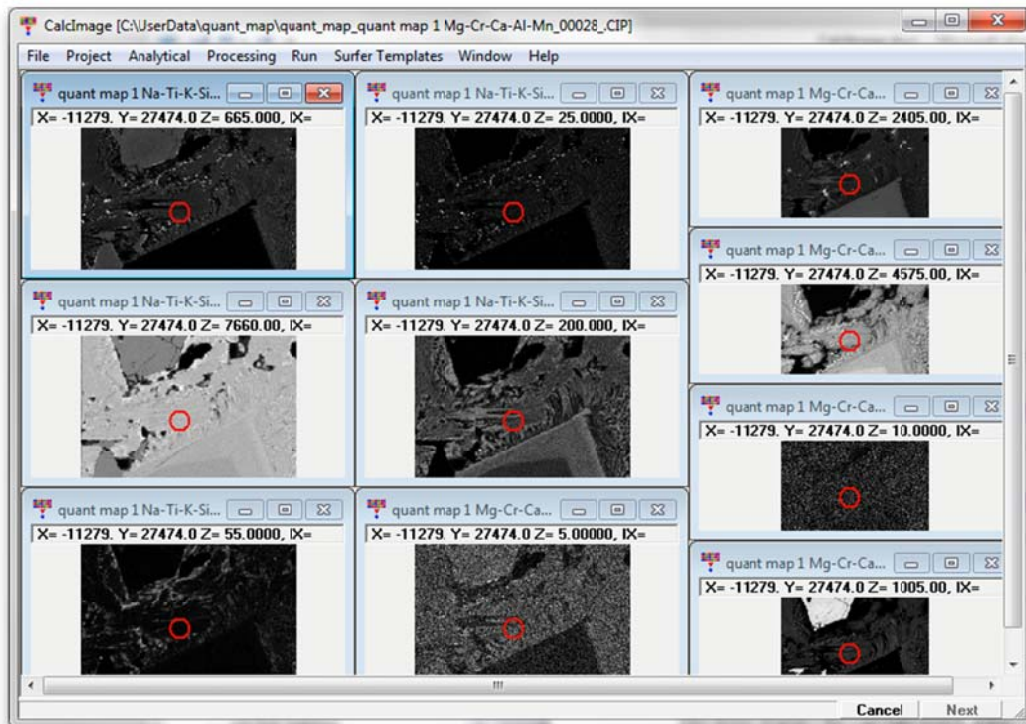
Help

About CalcImage

This menu displays the copyright notice, acknowledgments and contact information for users of CalcImage 95/98/NT.

Help On CalcImage

This menu opens this help file for hypertext help file viewing at the main table of contents. Note that both a searchable index and glossary are available for browsing by the user at any time during a run. Each help topic may be printed.

In addition, context sensitive help (that is, help that is applicable to the current program context) is available for each window in all applications by simply pressing the F1 key.

Log Window

The log window of CalcImage is a scrollable text window which will record all output and calculations. Open this windows from the Window | Log Window menu. This log window is a fully cut and paste enabled text window which can be used to transfer data or analysis results to any other Windows application such as a word processor or spreadsheet.

Simply click and drag the mouse to select text and use the <ctrl> c, <ctrl> x or <ctrl> v key combinations to copy, cut or paste text to or from the Windows Clipboard. Or use the Edit menu for these and other Clipboard functions.

The size of the log window buffer can be specified in the PROBEWIN.INI file and is limited only by the amount of memory available. If the Save Log to Disk File option is selected from the Output menu, then all log window output is mirrored to a text file, including any text manually entered by the user using the keyboard. The log window font and font size is specified in the PROBEWIN.INI file and may be changed during a run from the Output menu. To view a copy of the log file during a run, select the View Disk Log option from the Output menu.

Note that if this window is open, the calculation times required for converting x-ray maps to quantitative images will be increased significantly

Edit

Cut

This menu cuts the selected text from the log window to the Windows Clipboard.

Copy

This menu copies the selected text from the log window to the Windows Clipboard.

Paste

This menu pastes text from the Windows Clipboard to the log window.

Select All

This menu selects all text in the log window.

Clear All

This menu clears all text from the log window.

Output

Log Window Font

This menu allows the user to modify the current log window font type, size and appearance using the font Common dialog. It is strongly recommended to use a non-proportional font, such a New Courier, so that numeric column data is properly aligned in the log window.

Note that the default font and size of the log window may be permanently defined in the PROBEWIN.INI file.

Debug Mode

This menu toggles the program in and out of Debug mode. In Debug mode, the program generates an abundance of additional output to the log window for the purposes of debugging the program or viewing the analytical calculations in greater detail.

Debug mode is also useful to check the low level commands sent to the hardware interface. Note that in debug mode the Form level events are not protected against unanticipated errors. Program CalcImage normally runs in debug mode for more analytical detail.

Extended Format

This menu toggles the output option for printout to the log window of element data. If unchecked, the program automatically wraps element data output to 8 elements per line. Note that wavescan data is wrapped 4 elements per line. If this option is checked, the program does not wrap element data to the log window or disk file (if Save To Disk option is enabled), instead the data is written out as far as necessary to the right.

Save To Disk Log

This menu toggles the output option to mirror all log window output to a user specified text file. This may be useful for importing text or data from the log window to another non-Windows program. The default extension is .OUT but another extension may be entered by the user.

If a large amount of output is to be generated, this option will capture all output to the log window so that it can be printed out afterwards. If the output file selected by the user already exists, the program offers the option to overwrite or append subsequent output to the already existing file.

View Disk Log

This menu invokes the file viewer specified in the PROBEWIN.INI file (default file viewer is NotePad) to view the previously or currently opened disk log file.

If the file is currently open, the program will first close the disk log file before viewing it. Note that because the default file viewer (NotePad) is somewhat limited, it may be necessary to specify a more robust file viewer such as TextPad or Word for Windows. See the section on editing the PROBEWIN.INI file above to change the default file viewer.

Open Link To Excel

This menu will create an OLE (Object Linking and Embedding) link to an Excel application (if it is available). This link is available for sending both intensity and quantitative data to an Excel spreadsheet. This feature requires Excel 8 (Office 97) or higher.

Close Link To Excel

This menu will close an open OLE (Object Linking and Embedding) link to an Excel application (if it is available).

Glossary of Terms

ALPHA-FACTOR

Alpha-factors are based on the original Bence-Albee correction (Albee and Ray, 1972) and modified to utilize additional fit coefficients (linear and polynomial) for improved quantitative results after Rivers (pers. comm., 1990) and Armstrong (Armstrong, 1991). These factors are derived by fitting concentrations vs. alpha-factors, from calculated or measured k-ratios in a system of binary standards covering a range of composition. See also beta-factors. The expression for the calculation of a single alpha-factor is shown below:

$$\frac{\left(\frac{C}{K}\right) - C}{(1 - C)} = \alpha$$

where :   C   is the elemental weight fraction of the element

                K   is the calculated or measured k-ratio at that concentration

The calculation of the matrix correction for an unknown sample is shown below:

$$C_A^u = \frac{C_A^s}{Beta_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} Beta_{\lambda_A}^u$$

where : $Beta_{\lambda_A}^u$ is the unknown beta-factor

             $Beta_{\lambda_A}^s$ is the standard beta-factor

BETA-FACTOR

Beta-factors are the normalized sum of the weight fraction weighted alpha-factors for a given compound composition. These are utilized in the quantitative calculation of unknown compositions. See alpha-factor above.

CATION

The metal component of a chemical compound. For example, in the compound SiO_2 the Si or silicon is the metal or cation and the O_2 or oxygen is the anion. In this example, the subscript for Si is 1 and the subscript for oxygen is 2.

CPS

Counts per second. X-ray count rates are always given in cps units to normalize for different count times. To get the actual counts multiply the displayed x-ray counts by the count time used.

DEADTIME

The interval between the arrival of an x-ray pulse signal and the time that the system (including detector and amplifier electronics) is ready to receive the next one is defined as the deadtime. The deadtime correction is only significant at count rates above 10K to 20K counts per second (cps). For example, if the deadtime is 1 us and the count rate is 10K cps, the count rate will be reduced by 1%.

The best way to determine the deadtime constant is to measure it by the function of count rate vs. beam current. The normal deadtime correction is given by the expression below:

$$I = \frac{i}{1.0 - i\tau}$$

Where : i is the raw measured counts in cps
            τ is the deadtime constant in seconds
            I is the deadtime corrected counts in cps

An optional high precision expression is also available for very high count rates (> 50K cps) and is shown here :

$$I = \frac{i}{1.0 - \left(i\,\tau + i^2\,\frac{\tau^2}{2}\right)}$$

Note that CalcImage supports the use of a hardware "enforced" deadtime for rigorous correction of the deadtime effect if available on the microprobe (e.g. Cameca SX-50/51). In this situation, an arbitrary deadtime constant, that is larger than the largest deadtime measured on the spectrometer, is utilized by the amplifier electronics to gate off any pulses that are received by the amplifier after the initial pulse, within the value specified. This has the net result of masking the "intrinsic" deadtime of the system, which has been noted by several observers to be quite dependent upon the energy of the pulses received from the detector. Hence, the "enforced" deadtime value is used in software to correct the intensities without regard to any dependence upon pulse energy.

To facilitate the measurement of the intrinsic deadtime of your PHA amplifiers, an easy to use but rigorous Excel spreadsheet from Paul Carpenter of Cal Tech is available from Advanced MicroBeam.

GRID

(Grid File) A file format used by SURFER (Golden Software) to store single precision floating point data with 3 coordinates of information (X, Y and Z). The file is a binary file and may be read from VB, FORTRAN, C or Pascal. A grid file always has the extension ".GRD". The format is as follows :

cdum	a 4 byte string containing the characters 'DSBB' (not null terminated)
ixgrid, iygrid	two integer*2 values containing the grid density
xmin, xmax	two real*8 values containing the X data minimum and maximum
ymin, ymax	two real*8 values containing the Y data minimum and maximum
zmin, zmax	two real*8 values containing the Z data minimum and maximum
data	ixgrid * iygrid real*4 values containing the Z data values

The grid file format is also compatible with Micro-Image for Windows, a full featured image acquisition and analysis application available from Advanced MicroBeam.

INTERFERENCE

An analytical situation when a peak from another element overlaps a primary analytical line used in the analysis. Ignoring this interference will often result in an incorrect analysis. This is sometimes seen as a high total when the interference is large. However when the interfered element is only a minor or trace quantity, even a small interference can result in a large error on the interfered element without affecting the overall total significantly. These primary line interferences can be completely and quantitatively corrected for using Probe. Be aware however, that interferences on your off-peak positions need to be checked for, before acquiring any off-peak sample data, especially for trace and minor element analyses.

INTERFERENCE STANDARD

A standard used for the quantitative interference correction in CalcImage. A standard used for the interference correction can also be used for the analytical calibration and need only be analyzed once, although additional interference standardizations can be used in the automatic drift corrections if they are available. To use the quantitative interference corrections in CalcImage you must analyze for both the interfered element (obviously) *and* the interfering element. To use a standard as an interference standard, it must contain a known concentration of the interfering element, *and* it must not contain the interfered element, nor can it contain any other elements that interfere with the interfered element. You can add additional standards to a CalcImage run using the Standard | Add Standards To Run menu.

ITERATION

A technique which is used to calculate a result when you have more unknowns than coefficients. CalcImage used an iterative loop for the ZAF and Phi-Rho-Z matrix calculation and an additional iteration loop around that to calculate other compositionally dependent parameters such as the spectral interference, MAN background correction and the APF correction.

K-FACTOR

The standard k-factor is the concentration of the element in a standard divided by the ZAF correction of the element in the standard. See also raw k-ratio, unknown k-ratio and ZAF. The expression is :

$$K_{std} = \frac{C_A^s}{[ZAF]_{\lambda_A}^s}$$

where : C_A^s is the concentration of element A in the standard

$[ZAF]_{\lambda_A}^s$ is the ZAF correction for element A in the

standard

K-RATIO

See raw k-ratio, unknown k-ratio, k-factor and ZAF.

MAC

Mass Absorption Coefficient. A physical constant in units of cm^2/gm, which describes the amount of absorption of an x-ray of specific energy in a pure element matrix. Used by the ZAF and Phi-Rho-Z matrix corrections.

MAN

Mean Atomic Number. The average atomic number of a sample used in the on-peak background correction. A calibration curve type of background correction in which the background count rate is measured while the spectrometer is tuned to the element of interest on samples of varying atomic number each not containing the element of interest. A function is then fitted to a plot of counts vs. average atomic number and used in the compositional iteration to calculate a background correction. This method works quite well for major and even minor elements in low to moderate average atomic number matrices, since the background of a sample is almost entirely dependent upon atomic number. See the above section on MAN backgrounds.

MATRIX CORRECTION

An algorithmic calculation to correct for the effects of other elements present in the analyzed sample. These can include absorption, fluorescence and atomic number effects. CalcImage supports several types of both ZAF and Phi-Rho-Z matrix corrections. See also ZAF.

NOMINAL

Nominal is defined in the Oxford American Dictionary as "in name only" or "a token fee". However, in the CalcImage software it is meant to indicate that the value referred to is not necessarily the actual value. This use of the word is also seen in the lumber trade, where a 2 by 4 is the nominal dimension, but the actual dimension is often less.

For example, in this sense, the *nominal beam current* is not the actual measured beam current but only a close approximation that is used to calibrate the beam drift correction. The beam drift correction only uses the nominal beam current to set the magnitude of the correction. If the nominal beam current is close to the actual measured beam current then the correction is close to 1.0 and the beam drift corrected counts displayed will be close in magnitude to the counts displayed on the screen scalers.

PHI-RHO-Z

A method used to correct x-ray intensities for the effects of matrix by combining the absorption and atomic number corrections into an expression describing the true x-ray distribution with depth. The expression is often written as $\phi(\rho z)$. This is an alternative method to the ZAF matrix correction which can be more easily verified using so called tracer and wedge experiments.

POLYNOMIAL

A mathematical expression of the form : $Y = A + BX + CX^2 + ...$ The MAN background correction used in CalcImage NT uses an iteration of this expression to calculate for major element backgrounds without the need for off-peak measurements. The user may select a 1st order (straight line) or 2nd order (parabolic) fit to the MAN data. The parabolic fit is the default.

RAW K-RATIO

A k-ratio is the ratio of unknown intensity relative to a reference intensity. Several varieties of these are defined. The raw k-ratio is defined as the ratio of the unknown counts to the standard counts for an element. The intensities are usually corrected for beam drift, dead time, background and standard drift. See also unknown k-ratio, k-factor and ZAF. The expression is :

$$ K_{raw} = \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} $$

where : $I_A^u(\lambda_A)$ is the unknown intensity for element A at λ

$I_A^s(\lambda_A)$ is the standard intensity for element A at λ

RELATIONAL DATABASE

A data file storage and retrieval model based on a set of defined relationships between two dimensional tables consisting of fields (table items) and rows (data items). From both the programmer and end user point of view, these tables behave like spreadsheets where each row is a record and various operations such as browsing and searching can be performed without knowledge of the actual physical file structure.

SPECIFIED CONCENTRATION

A concentration which is used in the matrix correction calculation to provide a more accurate matrix correction. These concentrations are used in two ways in CalcImage. Standards which contain elements which are not being analyzed for, will have their concentrations automatically loaded by the program for possible use in analyzing a standard.

Second, if you are analyzing an unknown which contains elements that you are not analyzing for, but whose concentrations you know or can estimate, you can add these

elements as specified elements and specify their concentrations. This will result in an improved matrix correction for those elements that you are analyzing for.

SPECIFIED ELEMENT

An element included in sample matrix corrections that is constant in concentration, and therefore, not being analyzed. It is included to account for its effect on x-ray absorption and fluorescence in the sample matrix.

UNKNOWN K-RATIO

The unknown k-ratio can then be defined as the product of the raw k-ratio and the standard k-factor. See also raw k-ratio, k-factor and ZAF. The expression is :

$$K_{unk} = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}$$

where :

$I_A^u(\lambda_A)$ is the unknown intensity for element A at λ

$I_A^s(\lambda_A)$ is the standard intensity for element A at λ

C_A^s is the concentration of the element in the standard

$[ZAF]_{\lambda_A}^s$ is the ZAF correction for the element in the standard

ZAF

A method for the matrix correction of fluorescent x-rays. The method calculates the effects of atomic number (Z), absorption (A) and characteristic fluorescence (F) separately, hence the name ZAF. To put all of this in perspective, here is the complete ZAF correction expression for x-ray intensities solved for the concentration of an unknown concentration :

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}[ZAF]_{\lambda_A}^u$$

where : $\dfrac{C_A^s}{[ZAF]_{\lambda_A}^s} \dfrac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}$ is the unknown k-ratio and

$[ZAF]_{\lambda_A}^u$ is the ZAF correction factor of the unknown

$I_A^u(\lambda_A)$ is the unknown intensity for element A at λ

$I_A^s(\lambda_A)$ is the standard intensity for element A at λ

C_A^s is the concentration of the element in the standard

$[ZAF]_{\lambda_A}^s$ is the ZAF correction for the element in the standard

Because the ZAF correction factor for the unknown is exactly that : unknown, the calculation requires a iterative solution. See also Phi-Rho-Z.