Probe for Windows 95/98/NT/2000 v. 6.18

User's Guide and Reference

Enterprise Edition

Probe for Windows

Analysis and Automation for EPMA

ENTERPRISE EDITION

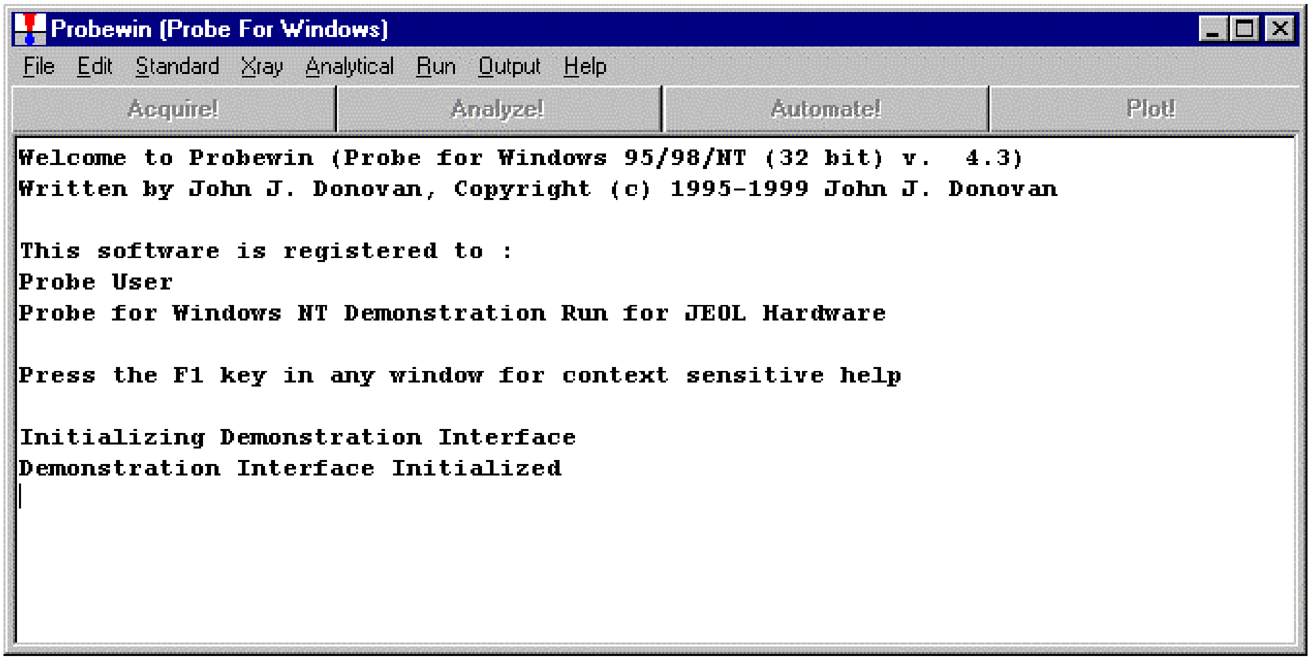
(c) 1995-2003 By John J. Donovan

Distributed by Advanced Microbeam, Vienna , OH

Probe for Windows

Overview

The main program for data acquisition and analysis is PROBEWIN.EXE. The menu for this program is found in the Probe for Windows menu group under the Start button. Click the menu to start Probe for Windows Enterprise.



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Welcome to Probewin (Probe for Windows 95/98/NT (32 bit) v.  4.3)
Written by John J. Donovan, Copyright (c) 1995-1999 John J. Donovan

This software is registered to :
Probe User
Probe for Windows NT Demonstration Run for JEOL Hardware

Press the F1 key in any window for context sensitive help

Initializing Demonstration Interface
Demonstration Interface Initialized
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When Probe for Windows Enterprise is started it will ask first whether to attempt to interface to the microprobe hardware. If data acquisition or automation is desired, then click Yes for confirmation of the spectrometer, stage and crystal positions. If only re-processing previously acquired x-ray intensities, click No.

If the users clicks Yes, the program will attempt to communicate with the microprobe hardware based on the interface type defined in the PROBEWIN.INI file. Note that if the specified hardware is not actually present, this could cause the program to "hang". Be sure to click No if only processing microprobe data off-line.

One may also run Probe for Windows in "demonstration" mode, e.g. for training new users offline. In that case, which normally will occur on a standalone computer not connected to a probe, you only need to have previously edited the probewin.ini file line under "Hardware" such that InterfaceType=0. Several other keywords or paths may need to be edited to match those in the computer (e.g., FileViewer under [Hardware], and UserDataDirectory under [Software]).

To open an existing Probe for Windows database file, click File | Open. To open a new Probe for Windows database file, click File | New. To browse available Probe for Windows data files, click the Find File menu item.

Creation of a new PFW file (Microsoft Access database file, actually) raises an important issue: how does one best name it? By user name? By mineral type? By date? Related to this is the issue of how the files are organized. There are many valid schemes; one that works is to organize a tree of folders (may be a couple levels deep, by Department, then Professor, then student), but where each user will have her/his own folder with all their data stored there. In this scenario there is no need for the user name in the new file title. From there, there are many options. One possibility would be something like YL-zirc-031102 that would allow the user to instantaneously recall that this file contains data from Yellowstone zircons that was initially begun on that date (the file date on the computer gets modified whenever the file is opened, so you cannot count on trusting that date). Or Eire-basalt-022201 could contain plagioclase, olivine, oxide and pyroxene data on a suite of basalts. All data -- from standards and unknowns, including wavelength scans on both -- are stored in one file, and easily retrieved and post processed later.

Log Window

The main window of Probe for Windows is a scrollable text window which will record all acquisition and analysis results. 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 simply 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.

Menus

The Probe for Windows log window contains a main menu for easy access to many program functions. Most of these functions are file dependent and are only enabled if a Probe for Windows database file is opened.

Menu items always available are the Standard | Standard Database and X-Ray menus. The Standard Database menu item launches the Standard for Windows application as a separate process, while the X-Ray Database menu item opens the NIST x-ray database as a modal window in Probe for Windows. The other X-Ray menus list various x-ray data to the log window.

Buttons

The Probe for Windows log window also contains four buttons for easy access to modeless windows that may be open at the same time. A modeless window is defined as a window that may remain open while allowing the focus to shift to another window. Probe for Windows has four main modeless windows plus a number of smaller windows such as Move, Locate and Position Database modeless windows.

To activate an already open window, simply click the window. If you can't see one of the four main modeless windows because it is hidden by another window, simply click the corresponding button on the Probe for Windows log window form, and it will be brought forward. The four buttons will in turn activate the Acquire!, Analyze!, Automate! or Plot!

windows. To close a modeless window, simply double click the upper left corner of the window, however these windows will retain there size and position if left open or at least minimized for the duration of the run.

To conserve screen space, it might be wise to minimize windows that are not actively being used at a particular time. To do this, simply click the minimize button in the upper right corner of the window.

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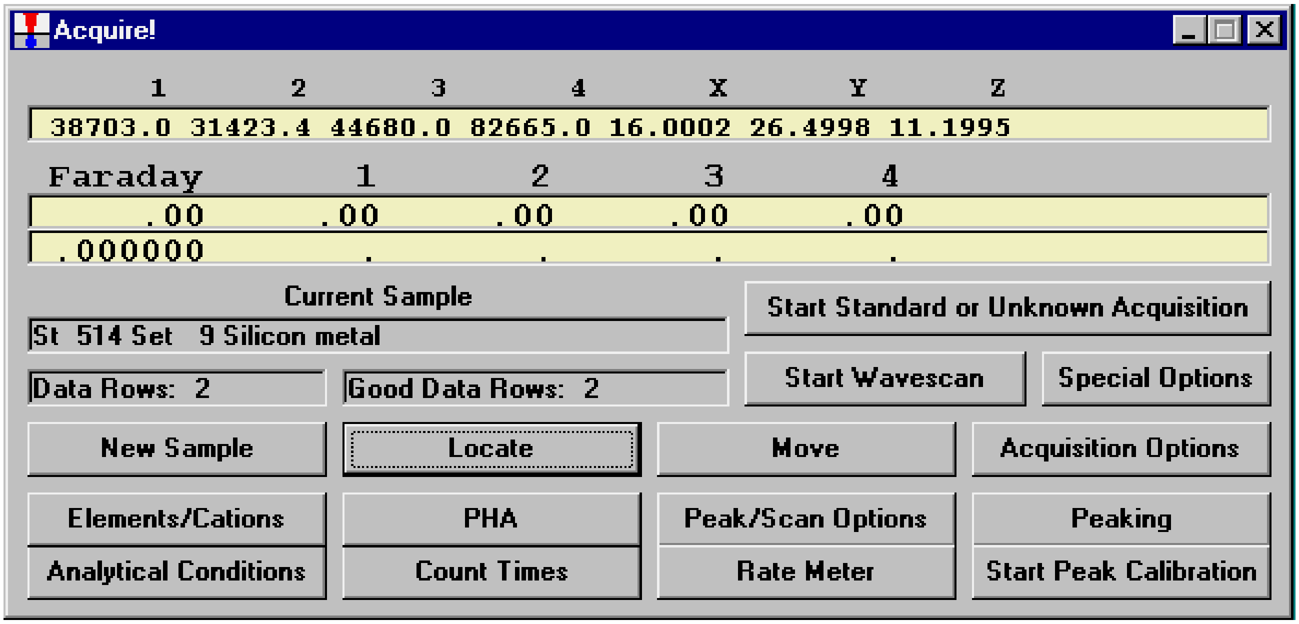
Probe Window Details

Acquire!

The Acquire! window is used to manually create new standard, unknown or wavescan samples, and to manually acquire x-ray intensity data for them. Other buttons from this window allow the operator to set up all acquisition parameters for the current or subsequent sample (the program will not allow acquisition parameters to be modified on samples that already contain data).



When the Acquire! window is first opened in a new run, the program will prompt the user that the nominal beam current may be acquired. The nominal beam current is used to provide a scaling factor for the beam drift correction (see below under beam drift correction). When the instrument conditions are properly configured (kilovolts and beam current), click Yes to start the nominal beam current acquisition. To skip the acquisition of the nominal beam current until the next time the Acquire window is activated, click No, or to not acquire the nominal beam current simply click Cancel. In this last instance, the program will use load the nominal beam current as zero for the demo and AM interfaces or load the default beam current from the PROBEWIN.INI file for all other interfaces. To disable the beam drift correction or to manually change the nominal beam current, click the Count Times button and enter the new value in cps for the demo or AM interfaces or in nA for all other interfaces.

Other than zero (no beam drift correction) two possible nominal beam current values are 1 (Cameca microprobes use this normalization constant, thus counts are always listed are counts/sec/1 nA) or the value you are actually using (i.e. 20, if you set your current in Analytical Conditions as 20), thus your counts listed are counts/sec/20 nA. There is no "incorrect" nominal value. However, the counts that are listed in the log or Analyze! window are already normalized to this value. Thus if you were running 100 nA beam current, but you never adjusted the nominal value from a value of "1" that was set during initial installation, your count values would seem very low.

Manual standard and unknown sample data can be acquired on a line by line basis, while manual wavescan samples will automatically acquire a complete set of wavescan data for each element in the wavescan sample. If more than one element is assigned to a given spectrometer, then the program will automatically acquire the additional elements as soon as the previous element wavescan is completed.

At the top of the Acquire! window the current x, y, z stage coordinates, stage rotation (W-motor) index (for JEOL 733 only), and the spectrometer/scanner positions are displayed as label fields. During data acquisition, real time counts, respective count times, the elements being acquired and the faraday beam counts can be observed as well.

In addition, the current sample name and the number of data points appended to it are displayed just above the New Sample button.

The current sample is, by definition, the last sample created by either the user or the automated procedures. This current sample is the only sample to which data can be acquired and appended to. However, the name and description may be altered easily in the Analyze! window. This is useful when the operator has made an incorrect guess as to the exact phase in a multiphase sample prior to data acquisition and analysis.

Note that wavescan samples can only have data acquired and appended to them once. Be sure that the current sample is the sample to which data should be appended to. Otherwise be sure to create a new sample using the New Sample button.

New Sample

Click the New Sample button to start a new sample for the currently open run. This will open the New Sample dialog box. New users should create their first sample as an unknown sample which can then be utilized as a 'template" for creating other samples.

All subsequent new samples (standard, unknown or wavescan) are created based on the **last unknown sample** and the current real-time acquisition parameters specified by the user. Exceptions: if a wavescan sample already exists, the new wavescan is based on the last wavescan, or if no unknown samples exist, the new sample is based on the last standard sample, or if no unknown or standard samples exist, then the new sample is based on the last wavescan sample. The main reason for this is because if the last sample is a standard that was acquired using the "Quick" standard automation option, then all the unknown analyzed elements may not be present.

It is important to keep in mind that because all assigned sample parameters such as standard assignments, interference assignments, calculation options, specified elements, etc. are loaded from the last unknown sample, if any changes to the sample assignments are *not* made to the last unknown sample, then these sample assignments will *not* be carried forward to the next new sample that is created.

To change the analytical setup, it is required to either change the analytical setup of the last unknown sample (if it contains no data) or create a new unknown sample and modify it. Note that count time can be changed at any time, even for samples that already contain data.

The New Sample dialog allows the user to create a new standard, unknown or wavescan sample. A new sample name and a sample description can be entered. The lower-most portion of the new sample dialog box lists which standards are currently in the run. In order for a standard sample to be created, it must first be added to the run. This is done by first clicking the Standard | Add Standards To Run menu item from the Probe for Windows log window menus.

Once the sample type is selected and the name is entered, the user can simply click OK and the new sample will be created. If this is the first sample for a new run, the program will create a sample with no analyzed elements. The user may add analyzed elements using the Elements/Cation button described below.

Load Element Setup

To add or remove elements from the sample, or to save or load element setups to or from the element setup database (SETUP.MDB), click the Load Element Setup button.

This dialog provides a method to save and load element setups that have been calibrated for peak positions and PHA parameters for use in creating new analytical setups. If the element setup is saved from a standard sample that has had data acquired for it, the intensity data is automatically saved to the element setup database for evaluation purposes. Note that element setups can be saved anytime, even when not interfaced to the microprobe hardware, from the Analyze! window using the Elements/Cations and Load Element Setup buttons.

Probe for Windows Enterprise also includes the complete wavescan and peaking parameter data for each element to be saved and recalled from the setup database. However, note that element setup data imported from the 16 bit version of Probe for Windows will not contain any wavescan or peaking parameter data and therefore those fields will be blank, although when loaded into a new sample, those blank fields will be replaced with appropriate defaults.

The element setup database can be browsed using the data cursor in the upper right of the window, or all occurrences of a specific element can be browsed by entering the element symbol in the Search Element field. To return the browser to display all elements, simply delete the element symbol from the Search Element field.

The browser displays element setups in the order that they were saved to the setup database. To go to the most recent setup, click the extreme right end of the data cursor. The number of element setups currently in the database is shown also.

Although element setups can be deleted, it may be desirable to keep all element setups for possible evaluation of position or intensity trends for microprobe performance records.

Load Sample Setup

To save or load sample setups to or from the current run, click the Load Sample Setup button. This button allows the user to load sample setups previously saved **within the current run** for later use in acquisition of new samples.

Loading a previously saved sample setup (see Elements/Cations | Save Sample Setup buttons in the Analyze! Window) to a new sample means that all sample parameters for the new sample will be based on that sample setup. Any modifications to the real-time parameters from the Acquire! Window, such as kilovolts, beam current, beam size, count times, PHA, peak positions, etc. are applied only to the current sample and will not affect the original sample setup.

For example, it might be useful to create several sample setups within a run, if it is known that several different phases will be analyzed, each of which are significantly different in their elemental compositions. In other words, it is possible to create one sample setup containing the elements Fe, Ni and Cr as the analyzed elements and another sample setup containing the elements Al, Mg, and Cu as the analyzed elements, all within the same run.

These setups can be referenced for use with the automation actions for tremendous flexibility during the automated acquisition of different phases within a single run by using the Setups button in the Automate! window during the digitization of position samples.

However, if the sample pointed to by the sample setup contains any data, the element setup cannot be changed later on. For this reason it might be best to only reference samples that do not contain any data lines but only if one wishes to have the ability to modify the original sample setup.

Note that the sample setup is actually a pointer to the row number of the selected sample. Any changes in the selected sample parameters will be automatically included when the sample setup is selected later on. This row number may be viewed for all samples in the current run from the Run | List Sample Names menu.

Sample setups may be loaded (or saved for the current sample), if it does not contain any data, by clicking the Elements/Cations button from the Acquire! window and then clicking the Load Sample Setup button. A previously created sample can be saved as a sample setup by using the Elements/Cations button from the Analyze! window.

When saving a sample setups (from the Analyze! Window using the Elements/cations button) always enter a generic name to indicate the purpose of the sample setup. It may be best to name the sample setup something descriptive, such as, "olivine setup" or "volatile calibration setup" so that the correct sample setup may be easily remembered.

To utilize the full flexibility of PFW for setting up separate setups for different phases, you will also want to make sure one has set the proper standard assignments (Analyze!-Standard Assignments), and Calculation Options (e.g. Oxygen by stoichiometry, maybe mineral formula type), as well as any various operating conditions in Acquire! (e.g., current, beam size). Once these are set, and the sample setup is saved, ALL these acquisition and data analysis parameters will be used for the appropriate phase.

Alternatively one can save all selected samples as sample setups using the existing sample names by clicking the Add To Setup button in the upper right of the Analyze! Window.

Note that the Save Setups button (in the Analyze! Window) saves all element setups (not sample setups) for standards in the run that are referenced in the selected sample based on the standard assignments.

Load File Setup

To load the entire sample setup from another run file, including the standard list and MAN assignments, click the Load File Setup button. With this dialog, it is possible to load an entire sample setup from another run for immediate use or modification.

Because this dialog provides a listing of the sample setup from each filename clicked, it is an easy matter to browse through all available runs to find a suitable sample setup to load.

Note that loading a file setup will overwrite all current run parameters for the Run, Sample and Element database tables. Only the Nominal Beam and Volatile Element correction sample assignments are ignored from the file setup.

After, the file setup (based on the last unknown from the specified file) has been loaded, the program will ask whether to also load the standard intensities. Select Yes, to load the standard intensity data beginning with the last standard and going backwards to the beginning. The standard intensity data will be time stamped with the current date and time. Note that if a standard intensity has already been loaded, the program will not load that particular standard intensity.

Load Multiple Setups

This button is used to load multiple sample setups based on sample setups that have been previously saved sample setups within the current run. All considerations for Samples Setups apply for Multiple Setups (see Sample Setups above). To create sample setups for digitizing position samples, use the "Elements/Cations" button in the Analyze! Window or by clicking the Add To Setup button in the Analyze! window.

When more than one sample setup is specified by the user in the New Sample dialog, the program will automatically combine the specified sample setups into a single sample. This is useful in several situations, for example, when performing major and trace element acquisition it may be desired to acquire the major elements at one set of column conditions (kilovolts, beam current and/or beam size) and the trace elements using a different column condition (kilovolts, beam current, etc.).

In this case, each element will be evaluated and if different column conditions are required, all elements with similar column condition will be acquired before the program attempts acquiring elements with a different column condition. This is analogous to using the "Combine Multiple Setups" check box in the Automate! window. There are, however, important differences. When you "Load Multiple Setups" you create a NEW setup which now has, say, two conditions. Those two conditions are applied immediately to each and every point, meaning that the column is constantly changing from the first condition to the second for each spot before proceeding to the next spot. The alternate procedure, Combine Multiple Setups in the Automate! window, applies both (if 2) setups to the digitized set of points, but here proceeds through the complete list of points only with the first setup; after the last point is acquired, it will return to the first point and now acquire with the second setup.

The way the program actually combines multiple setup with multiple column condition samples (in either the Acquire! Or Automate! is as follows: first the program looks at the first spectrometer used and finds the first element on that spectrometer. What the first element is, of course depends on the acquisition order option used. It might be channel order, ascending or descending angstroms or user defined order. Whatever conditions that "first" element uses, that is the first condition that is run. You must to add a "dummy" element to the first spectrometer of the first setup if one is not present,
to be sure that that setup actually is run first, if that is desired.

After all elements with that condition have been run, then the program looks for the next element (not already acquired) on the first used spectrometer and runs that condition and so on. So keep this is mind when creating "combined" column condition setups.

Elements/Cations

Clicking the Elements/Cations button opens the analyzed and specified elements dialog box. The analyzed and specified dialog box lists the currently selected elements for analysis. If this is the first sample of a new run then no analyzed elements are present. To edit or add elements, one of the following procedures may be performed :

1. Click the Load Element Setup button to load previously saved element setups from the element setup database. Element setups in samples created before the current sample may be saved as element setups from the Elements/Cations button in the Analyze! window.

2. Click the Load Sample Setup button to load a previously saved sample setups in the currently open run. Samples created before the current sample may be saved as a sample setup from the Elements/Cations button in the Analyze! window. If you are loading a multiple sample setup, only one column condition will be preserved. You need to check and set it for the appropriate setting for your next step, e.g. peaking.

3. Click the grid row of the element of interest or an empty row to add new elements. This action activates the element properties dialog box. One then selects an element by either typing the element symbol or by clicking the drop down list of all elements and scrolling to and highlighting the desired element.

Default settings for the analyzed x-ray line, cations, and oxygen proportions are loaded automatically. These can be edited via the drop down menu associated with each based on the user's preferences. The cation/oxygen ratios (subscripts) for Fe:O are calculated hre for those doing charge balance calculations:

Fe	O	Fe2+	Fe3+
1	1	100	0
8	9	85	15
7	8	83	17
6	7	80	20
5	6	75	25
7	9	60	40

3	4	50	50
5	7	33	67
2	3	0	100

Leave the x-ray line field blank to indicate an unanalyzed element (specified, by difference or stoichiometry). The defaults for these fields can be modified in the ELEMENTS.DAT file in the Probe for Windows directory. Note that Probe for Windows will retain any modifications of these defaults for the duration of the run.

Disable Acq

To disable an element for acquisition, check the Disable Acq checkbox. The element parameters will still be saved, but the acquisition routines will skip the element for standards, unknowns or wavescan samples. To enable the element for acquisition, first create a new sample and then uncheck the option before acquiring any more data.

Disable Quant

To disable the element for quantitative calculations, check the Disable Quant checkbox. The program will set the intensity to zero for the matrix correction calculations. To restore the element for quantitative calculations, simply uncheck the box. Normally this is only used for special reprocessing situations.

Multiple Peak Calibration

Special note: if the "UseMultiplePeakCalibrationOffset" parameter is set in the PROBEWIN.INI file and the fit coefficients have been properly calibrated using the Peak/Scan Calibrate Parameters dialog in program StartWin, the program will load "corrected" spectrometer peak positions in the Elements/Cations dialog when the user selects an element and x-ray line. See the Calibrate Peak Center help in the StartWin section for more details.

Background Types

The choice of background measurement either off-peak or MAN can be specified here. Off-peak correction types include linear, average, high only, low only, exponential and polynomial. MAN backgrounds are based on a calibration curve fitted to appropriate standards that do not contain the element of interest (Donovan and Tingle, 1996). The MAN calibration is assigned from the Analytical | MAN Fits menu after the standards to be used in the MAN fit have been acquired.

Note that one can utilize on-peak intensities for MAN background calculations even if the standards were acquired using off-peak background types but selecting the "Use Off-Peak Elements for MAN Fit" menu (under the Analytical menu).

Note that because the background type flags may be specified differently for standards and unknowns, the Off/MAN flags specified here will be saved for only the current sample type. This means that if the current sample type is an unknown, then the MAN flags defined in the Element/Cation Properties dialog will only be applied to unknown samples. To define the MAN flags for both the standards and unknowns, select them from the Acquisition Options window by clicking the Acquisition Options button in the Acquire! window.

Off-Peak Backgrounds

The off-peak background correction measures the background on the sample of interest (i.e., your standard or unknown) with the spectrometer adjusted to a position on each side of the analytical peak.

Probe for Windows can individually off-peak correct each point analysis for standard and unknown samples. If the element concentration is very small, it may be necessary to use the off-peak corrected sample method. The program is very flexible in that it allows you to use all MAN or all off-peak background corrections or any combination of the two methods on each element of an acquisition.

Note that since the off-peak positions are saved on a sample by sample basis, one must always start a new standard or unknown sample after changing the off-peak positions or adjusting them graphically using the mouse from a wavelength scan from the Plot! window. Probe for Windows uses a linear slope calculation as the default off-peak background correction. Because of this, unsymmetrically offset background position measurements can be easily handled. One can even position both of the off-peak measurements on the same side of a peak and extrapolate the background correction.

In addition, the user can also specify that the program calculate the off-peak counts using the average of the off-peak counts, or only the high or only the low off-peak counts. Finally, the user can specify an exponential slope calculation for curved backgrounds. If one changes the off-peak background type for an element, it may be necessary to change it for both the unknown samples, as well the standards, depending on the analytical situation. This is easily done in the Model Background dialog which can be reached from the Graph dialog from the Plot! Window Output button, by selecting all samples that you wish to assign the new background type to and clicking Ok.

Off Peak Background Correction Types

Probe for Windows allows the user to select the off-peak type for the background correction. The default slope calculation is the most accurate, except in cases where the user has moved both off-peak positions to the same side of the analytical peak and adjusted the off-peaks excessively close together resulting in a large extrapolation. The off-peak correction types are as follows :

1. = linear slope interpolation or extrapolation
2. = average of both high and low off-peak counts
3. = use only the high off-peak counts
4. = use only the low off-peak counts
5. = use exponential off-peak calculation (based on exponent)
6. = slope-high (based on high off-peak and slope coefficient)
7. = slope-low (based on low off-peak and slope coefficient)
8. = polynomial (based on high and low off-peak and three coefficients)

These off-peak background correction types may be assigned on a sample by sample basis either on or off-line. Note that the actual values of the polynomial fit coefficients are dependent on the absolute magnitude of the count intensities. For this reason it is important to avoid changing the value of the nominal beam current once any polynomial fit coefficients have been assigned to samples in the run. The calculations for linear slope and exponential calculation are shown below :

Linear Slope Calculation

$$I_{off} = I_{low} + (I_{high} - I_{low}) \bullet \frac{(P_{on} - P_{low})}{(P_{high} - P_{low})}$$

where :

I_{off} = the off-peak count correction
I_{high} = the x-ray counts for the high off-peak position
I_{low} = the x-ray counts for the low off-peak position
P_{high} = the high off-peak position
P_{low} = the low off-peak position
P_{on} = the on peak position

Exponential Slope Calculation

$$I_{off} = \frac{ce^{-aP}}{P^{N}}$$

where : I_{off} = the off-peak background intensity
P = the spectrometer position
c = a fit parameter
a = a fit parameter
e = the exponential
N = a user specified exponent

See the Model Background button the Graph dialog. This button is accessible when a wavescan sample is displayed from the Plot! Window.

Same Side Off-Peaks
Beware of placing same-side off-peaks too close together. A large extrapolation can cause a very large error in the off-peak background correction if the background standard deviation is large and you are not using the average, high only or low only background type. The program will print a warning if it feels that the same-side off-peak extrapolation is excessive. In cases where the same side off-peak extrapolation is excessive, the user may want to use the average of the off-peak counts. Of course, averaging the off-peak counts is really only applicable in situations where the background slope is zero.

MAN Backgrounds
MAN (mean atomic number) background corrections can be utilized when the P/B is sufficiently high or when the use of fixed spectrometers are required. The user can specify the standards used to calibrate the background fit for the polynomial MAN iteration of an analyzed sample. The MAN background correction method works because the primary cause of background (aside from trace contamination and peak over-lap interferences) is the average atomic number of the sample. Therefore a function can be fit to appropriate standard data and applied to the analysis of unknown samples. Since the atomic number depends on the composition and that is unknown to begin with, the MAN background is not applied until the analytical calculation iteration. Remember :

- MAN backgrounds can be used whenever the ratio of x-ray peak to background is high (>10:1), and this is usually the case with WDS microanalysis

- MAN backgrounds must be used for any fixed spectrometers

- Trace element concentrations require the use of off-peak measurements

Spectrometer Number and Analyzing Crystal
The spectrometer used to analyze the element should be specified based on the crystal arrangement of the microprobe. Enter a number or use the drop down menu option. This automatically loads a default crystal type, on-peak and off-peak positions that may be modified.

Interferences
The High and Low Off-Peak Interference buttons can be used when both the potential interfering and interfered elements are already present in the sample setup to determine the approximate magnitude of the off-peak interferences. This calculation is based on a gaussian peak shape and various crystal defaults and is intended as a guideline only for off-peak position entry.

The program assumes 100% of the interfering element and 0.1% of the interfered element in each binary pair calculation. For example, if the percent interference is calculated as 10%, then that indicates that instead of measuring 0.1 wt. % of the element, it is likely that a concentration of 10% greater than 0.1 wt. % or 0.11 wt. % will be measured. Note that since this is only a nominal calculation, it should only be used as an indicator of possible problematic analytical situations.

PHA

The PHA parameter settings (baseline, window, inte/diff (integral or differential) mode, gain, bias, and deadtime) can be specified here. Defaults are loaded from the configuration files and can be modified at any time.

Note that if the UseEmpiricalPHADefaults flag is set in the [Software] section of the PROBEWIN.INI file, then the PHA defaults loaded, are actually calculated from coefficients stored in the EMPPHA.DAT file instead being loaded from the SCALERS.DAT file.

The PHA parameters entered here will be used to configure the microprobe hardware, if supported by the interface type during the acquisition. The PHA settings for the current sample (if it contains no data) can also be modified from the PHA button in the Acquire! window.

The current PHA settings from the microprobe can also be read (if supported by the hardware and specified in the PROBEWIN.INI file) by clicking the Get PHA button.

Detector Parameters

If the proper microprobe interface support is present for detector control, the detector slit size, slit position and mode (usually FPC or SPC) may also be specified for automatic control during the analysis. If the microprobe interface does not support automated detector parameter control, these fields can be used simply to document the parameters. See the documentation on the DETECTORS.DAT file in the Configuration Files section above.

Integrated Intensity Options

For standard and unknown samples, if the element is acquired on a tunable spectrometer, the program offers an option acquire the integrated intensity over the peak instead of simply the peak intensity. If this option is checked, the program will start scanning at the low or high off-peak limit using the Initial Step Size specified and scan to the other off-peak limit.

The actual step size is modified based on the acquired intensity so that as the intensity increases, the step size decreases to the Minimum Step Size specified. This improves statistics where it is needed the most. The default step size is 1/10th of the off-peak range and the default minimum step size is 1/100th of the off-peak range.

The program accumulates the intensities over the off-peak range and this is stored as the on-peak data. The off-peak intensities are also measured normally and the integrated background is calculated based on the background type selected and the off-peak intensities. All off-peak options may be used with the integrated intensity option. The reported integrated intensities are in units of counts per second times spectrometer units.

If an element is acquired using the integrated intensity option, the standard intensities for that element must also be acquired using the integrated option.

Variable Step Wavescan Options

For wavescan samples, the user may specify the use of variable wavescan steps. In this mode the program will acquire wavescan samples using a step size that is inversely proportional to the intensity using the following expression:

$$S_{size} = \sqrt{\frac{I_B}{I}} \cdot S_{initial}$$

where: I_B is the background count rate

I is the current count rate

$S_{initial}$ is the initial step size

From this we can see that the wavescan will begin with the initial step size and as the intensity increases (the peak), the step size will decrease according to the equation until the minimum step size specified is reached. This option may be useful in cases where improved accuracy is necessary on the peak maximum.

Specified Area Peak Factors (fixed composition APF)
As an alternative to the "calculated" Area Peak Factors, Probe for Windows offers the use of "fixed" composition Area Peak Factors. These are single values that are applied to the element intensity on an emitter basis (as opposed to calculated based on the actual absorber concentrations in the matrix).

These factors may be useful in certain situations where the compositional range is limited and binary Area Peak Factors are not available for some or all elements in the matrix (e.g., Na, K or Ca in an oxygen matrix). This option may be turned off or on in the Analysis Option dialog under the Analytical menu.

Load Element Setup

This button opens the element setup database dialog. Here the user can add element setups to the new sample or save element setups to the setup database. Generally, one usually saves standard sample element setups for elements that are assigned to that standard to the setup database. Later, one can retrieve these calibrated setups for use in creating new sample setups for acquisition in another run.

The element setup database can be browsed using the data cursor in the upper right of the window, or all occurrences of a specific element can be browsed by entering the element symbol in the Search Element field. To return the browser to display all elements, simply delete the element symbol from the Search Element field.

The browser displays element setups in the order that they were saved to the setup database. To go to the most recent setup, click the extreme right end of the data cursor. The number of element setups currently in the database is shown also.

Load Sample Setup

To save or load sample setups to or from the current run, click the Load Sample Setup button. This button allows the user to load sample setups previously saved **within the current run** for later use in acquisition of new samples.

For example, it might be useful to create several sample setups within a run, if it is known that several different phases will be analyzed, each of which are significantly different in their elemental compositions. In other words, it is possible to create one sample setup containing the elements Fe, Ni and Cr as the analyzed elements and another sample setup containing the elements Al, Mg, and Cu as the analyzed elements, all within the same run.

These setups can be referenced for use with the automation actions for tremendous flexibility during the automated acquisition of different phases within a single run by using the Setups button in the Automate! window during the digitization of position samples.

However, if the sample pointed to by the sample setup contains any data, the element setup cannot be changed later on. For this reason it might be best to only reference samples that do not contain any data lines.

Note that the sample setup is actually a pointer to the row number of the selected sample. Any changes in the selected sample parameters will be automatically included when the sample setup is selected later on. This row number may be viewed for all samples in the current run from the Run | List Sample Names menu.

Sample setups may be loaded (or saved for the current sample), if it does not contain any data, by clicking the Elements/Cations button from the Acquire! window and then clicking the Load Sample Setup button. A previously created sample can be saved as a sample setup by using the Elements/Cations button from the Analyze! window.

When saving a sample setups always enter a generic name to indicate the purpose of the sample setup. It may be best to name the sample setup something descriptive, such as, "olivine setup" or "volatile calibration setup" so that the correct sample setup may be easily remembered.

Analytical Conditions

Clicking the Analytical Conditions button opens the analytical conditions dialog box. The operator can then edit the kilovolts, beam current, and beam size settings for the selected sample. In addition, if the hardware interface is supported, the user may specify a column condition string to indicate the desired analytical conditions of the instrument.

If the hardware support for these parameters is not present, then all parameters (other than kilovolts) are simply available for documentation purposes only. Note also that if the instrument has the ability to check the current analytical conditions, then the program will make sure that the analytical condition have not changed since they were last set. If the analytical conditions have changed by an amount greater than that specified by the "OperatingVoltageTolerance" and "BeamCurrentTolerance" in the PROBEWIN.INI file [hardware] section, then the program will force the analytical or column condition to be reloaded.

Analytical Conditions versus Column Conditions

In the first method, (using specified values for kilovolts, beam current and beam size) the user directly specified the analytical conditions. In the second method, a specified string is used to indicate a column condition that is stored internally in the instrument. In this latter case, because the actual value of the operating voltage (kilovolts) in the column condition string is ambiguous, the user should be sure that the single value fields are also correctly specified based on the column condition string specified.

For example, the SX50 supports the use of internally stored column conditions that are indicated by a four character string. Therefore, if the column condition option is selected, and the column condition string is specified as "hv15" (indicating a column condition at 15 keV), then the user should also be sure that the kilovolts field is correctly specified as 15 keV. Failure to properly specify the kilovolts field when using column condition strings will cause the ZAF or Phi-Rho-Z matrix corrections to be inaccurate. The beam current field is also used in some cases to check for beam drift.

For accurate documentation purposes it is also preferred that the beam current and beam size fields are also properly specified when using column condition strings. If, as in the above example, the "hv15" column condition string also includes a beam current of 10 nA and a beam size of 10 um, then those values should also be specified in the single values fields even though are not actually used in the acquisition procedure. This maintains the accuracy of the documented sample conditions.

Note that because samples at different operating voltages can be acquired in a single run, standards at the corresponding voltages must also be acquired for quantitative calculations.

Force Size or Force Column Conditions

The Force Size option (when checked) specifies that the program should send the size command to the instrument for each acquisition. This is useful because with most instruments it is not possible to determine the current beam size. Therefore, if the user has manually changed the beam size then if the box is checked, the program will ensure a consistent beam size for acquisition. This option only applies to condition be set using the "Use Analytical Conditions" option (keV, beam current, beam size).

The Force Column Condition box (when checked) specifies that the program should send the column condition command for each acquisition. This is useful since the program is usually unable to determine the current column condition with most instruments. Therefore if the user has changed any column conditions, then the program can ensure that a consistent set of column conditions are loaded for each acquisition. This option only applies to the "Use Column Conditions" option.

Faraday Stage

A new feature is support for a specimen based faraday cup that is specified by stage coordinates. See the [Faraday] section of the PROBEWIN.INI file documentation for information on how to specify the default location of the stage faraday cup. The Faraday Stage button will bring up a dialog box that allows the user to update the faraday cup stage location in the program and make a manual measurement. During standard or unknown acquisitions, the software will move to the faraday stage location, make the measurement and then return the original stage location for the next analysis.

Locate

Clicking the Locate button opens the locate sample positions dialog box.

All acquired sample positions can be accessed from this dialog. Double-clicking on a sample entry displays the stage coordinates for each line acquired. To move to a sample position, highlight a position sample and click Go. This will move the stage to the first undeleted stage coordinate of the sample selected. If a specific line coordinate is selected from the position grid, then clicking Go will move to that specific coordinate (deleted or not).

By clicking the Copy Position Coordinates to Clipboard, the sample position coordinates shown will be copied to the Windows clipboard for pasting into another application if desired.

PHA

Clicking the PHA (pulse height analysis) button opens the PHA parameters dialog box.

Here all currently analyzed elements are listed detailing their respective baseline, window, inte/diff (integral or differential) mode, gain, bias, deadtime factors. To edit any of these values, simply click the element row to be edited and the element PHA parameters window will appear.

If the proper microprobe interface support is present for detector control, the detector slit size, slit position and mode (usually FPC or SPC) may also be specified for automatic control during the analysis. See the documentation on the DETECTORS.DAT file in the Configuration Files section above.

The PHA parameters dialog provides buttons to both set (write) PHA parameters to the microprobe and get (read) the PHA parameters from the microprobe (if the necessary hardware interface is available).

Note that if a gain and bias hardware interface is available, and the bias (detector high voltage) values on a given spectrometer are different for multiple elements, the acquisition will pause for two seconds before proceeding with the acquisition. For this reason the program will warn the user if the bias values are different between elements on a single spectrometer.

In addition a graphical PHA distribution may be acquired, based on the PHA count time and intervals specified.

The PHA distribution should be adjusted by first adjusting the bias until the region of flat response is found. This "plateau" will provide the most stable count intensities since any small changes in the bias will not cause a change in the detector count rate. Next the gain of the PHA amplifier is adjusted to place the PHA distribution is the approximate center of the amplifier range. If the argon escape peak is close to the signal peak, the gain should be adjusted so that the escape peak is either completely included or completely excluded from the PHA distribution.

Count Times

Clicking the Count Times button opens the count times dialog box. This dialog also allows the user to modify the beam current integration time and the nominal beam current.

This dialog displays the current analyzed elements and the counting time for on-peak, off-peak, wavescan, peaking and quick scans. Each element may utilize a different count time for each on and off-peak measurement. The wavescan count time is applied to wavescan samples, the peak scan count time is applied to the peaking pre-scan acquired before a spectrometer peak center is run (if that option was selected) and the quickscan count time is applied to wavelength quick scans.

The count times for a range of elements may be specified by first clicking the Update Selected Element check box and then clicking and dragging a range of elements in the element list. Any changes to the count times dialog will be applied to all selected element in this case.

The Max Counts is used to specify a statistics based count time. By default, Max Counts is set to 100,000,000 (100 million total counts), so that it will normally not effect the acquisition. However, it may be desirable to specify a specific maximum count that is to be acquired for each element. The default max Counts may be set in the PROBEWIN.INI file in the [counting] section.

For example, the count time and max counts could be configured so that each element will count for 30 seconds or 10000 total counts (that is 1% precision), whichever comes first. The advantage of this method is that on samples with high count rate elements, the actual time required to acquire data is shortened, while low count rate elements are counted for a full 30 seconds. In this way also, the statistical significance of all element count rates with the same Max Counts is more comparable.

The Unknown Count Time Factor is also displayed, which is actually used for trace element analysis in two different ways. The first method is as a factor applied to the default count time for acquiring unknown sample elements relative to the count time used for the standards. This is especially useful in trace element analysis when the standard only requires a 10 second count time but the unknown requires say, 100 seconds for the desired detection limit. By simply specifying an Unknown Count Time factor of 10, this can be achieved.

The other way in which the Unknown Count Time Factor can be used is when the Use Alternating On and Off Peak Acquisition flag is checked in the Acquisition Options window. In this case the total acquisition time is calculated as above but in addition, the program will automatically divide up the acquisition of on and off-peak count times into alternating intervals based on the Unknown Count Time Factor for each element.

For example, if the Use Alternating On and Off Peak Acquisition option is checked and the on peak count time for an element is 10 seconds and the off-peak count time is 5 seconds and the Unknown Count Time Factor is set to 3 then the program will first acquire 10 seconds on peak followed by 5 seconds on each off-peak, in three separate repetitions. The counts are automatically totaled at the completion of all repetitions. This option is especially useful in situations where the sample measurement could be affected by extended acquisition times due to beam damage, carbon contamination or surface charging.

Note that in both instances, the Unknown Count Time Factor entered, can be a an integer or real number. Also be aware that the option exists to combine intensities for duplicate elements from multiple spectrometers. See Aggregate Intensity option.

Beam Current Measurement and Beam Drift

The integration time for beam current measurements and the nominal beam (in cps for AM hardware or nA for other hardware) can also be specified here.

The nominal beam current is used as a scaling factor for the beam drift correction. Any non-zero value will suffice, however to have the count rates reported close to the actual count rates, a nominal beam current should be used that is similar to the actual beam current used during the acquisition. That is, the counts displayed in the log and Analyze! Window is the beam drift corrected intensities (normalized to the nominal beam current in the Count Times dialog). The beam count time is in seconds for AM hardware and number of averaged beam current integrations for other hardware.

For aperture beam current measurement probes (ARL SEMQ) the beam is always measured (counted) simultaneously with the x-ray counting and therefore is normalized based on the nominal beam counting time. Because the measured beam current is therefore the portion of the beam that is intercepted by the beam current aperture support housing, one must take special precautions to avoid changing the geometry of the electron optics during the quantitative run. This usually means making no changes to the condenser lens, gun bias, or filament alignment. However, since the objective lens is usually below the beam current aperture, the electron beam focus can normally be adjusted with no detrimental effects to the quantitative calibration. The advantage of the aperture beam current method is that since the beam current and x-ray counts are simultaneously acquired, any non-linear change in the beam current is automatically corrected for by the beam drift correction.

On the other hand, microprobes which use a faraday cup (JEOL and Cameca) for the beam current measurement, require an extremely stable and regulated beam current since the beam current measurement occurs after the x-ray count acquisition. The benefit of the faraday cup beam current measurement method is that the electron optics geometry (i.e., sample current) can be changed during the quantitative run without affecting the beam drift calibration.

The beam drift correction calculation is shown here :

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

Where :

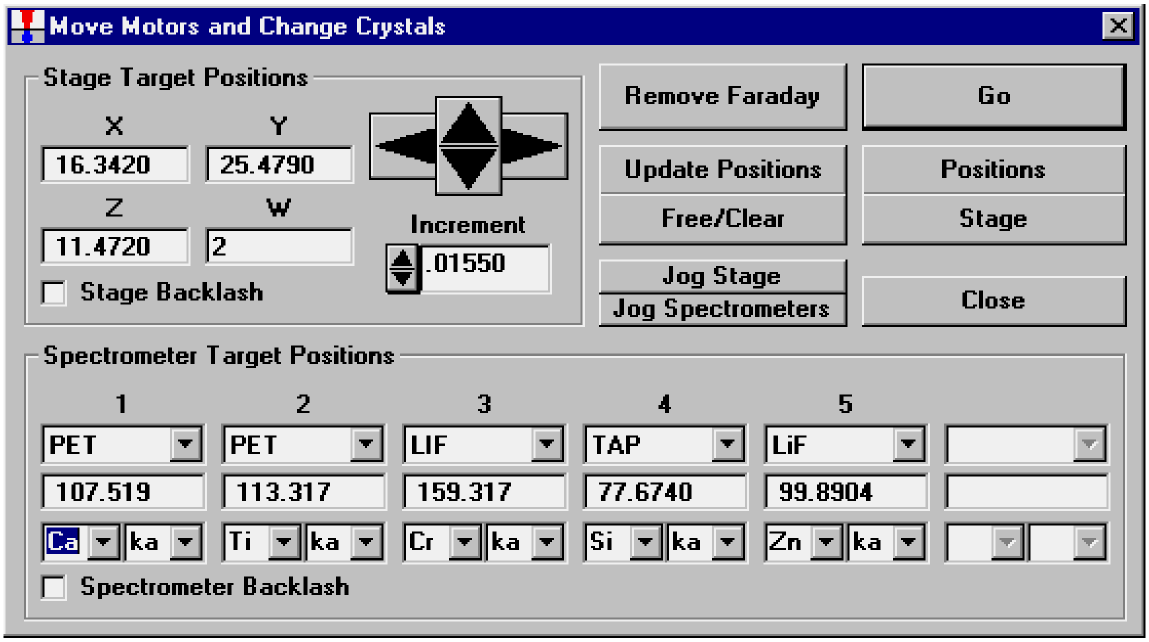
I_C	is the beam drift corrected unknown intensity
I_U	is the uncorrected unknown intensity
B_N	is the nominal beam current
T_U	is the count time for the unknown intensity
T_N	is the count time for the nominal beam current measurement
B_U	is the beam current for the unknown intensity

If you do not want a beam drift correction (it is recommended to always use a beam drift correction for the most quantitative work), one can either enter a nominal beam current of zero or disable the beam drift correction from the Analytical | Analysis Options menu.

Move

Clicking the Move button opens the move motors and change crystals dialog box. If crystal flipping is not supported by the interface hardware, then the crystal lists are disabled.

To manually flip a crystal when automated crystal flipping is not available, first drive to the crystal flip position (using the JOYWIN application if necessary) and manually flip the crystal. Then, after moving to a valid spectrometer position, exit the program and restart the application and confirm the new crystal positions in the Confirm dialog.



Stage Target Positions

X	Y
16.3420	25.4790

Z	W
11.4720	2

Increment .01550

☐ Stage Backlash

Spectrometer Target Positions

1	2	3	4	5	
PET	PET	LIF	TAP	LiF	
107.519	113.317	159.317	77.6740	99.8904	
Ca ka	Ti ka	Cr ka	Si ka	Zn ka	

☐ Spectrometer Backlash

The operator can adjust the stage coordinates as well as the spectrometer motors positions and crystal types.

The large four-way directional arrows can be used to increment the stage by the micron increment number listed in the cell below. The value of the micron increment can also be adjusted up or down using the spin controls or edited by hand.

One can set stage, spectrometer and crystal targets by entering the positions manually or by selecting an element and x-ray symbol from the spectrometer target position lists. *Special note: if the "UseMultiplePeakCalibrationOffset" parameter is set in the PROBEWIN.INI file and the fit coefficients have been properly calibrated using the Peak/Scan Calibrate Parameters dialog in program StartWin, the program will load "corrected" spectrometer peak positions in the Move dialog when the user selects an element and x-ray line. See the Calibrate Peak Center help in the StartWin section for more details.*

This modeless window can be accessed using the Move button on either the Acquire! or Automate! windows. Note that during automated acquisitions this window will be automatically unloaded to prevent hardware access conflicts.

The Stage and Spectrometer backlash check boxes in the Move window are applied only to stage or spectrometer motion from the Move window. Exception: if the stage backlash option is unchecked in the Move window, no stage backlash will be applied during the automation actions. See the Acquisition Options dialog (accessed from the Acquire! window) to enable or disable stage and/or spectrometer backlash for sample acquisitions.

Faraday In/Out or Beam Blanked/Unblanked

The faraday cup on faraday equipped microprobes can be inserted or removed and the beam blank state can be toggled by the user using the Faraday In/Out or Beam Blanked/Unblanked button.

The insert and remove faraday delay times can be specified in the PROBEWIN.INI file. This may be useful to give the hardware sufficient time to complete the operation before proceeding.

An additional Faraday/Beam Blank button is provided in the Stage BitMap window used for graphical stage moving (Stage button).

Update Positions

This button when clicked, updates the Move dialog for the current stage and spectrometer positions for those interfaces that do not constantly poll the microprobe hardware. Normally, the Advanced MicroBeam hardware accesses the hardware constantly to update the Move dialog, while other slower interfaces do not.

Jog Stage

Clicking this button causes the stage motors to jog by an amount specified in the PROBEWIN.INI file backlash factors. Use this button to remove any stage backlash that may be present when manually digitizing stage positions. The jog is based on the current stage positions for all stage motors.

Note that the stage backlash flag must be set (checked), in order to use the sample specific stage backlash flags as specified in the Acquisition Options windows for automated samples.

Jog Spectrometers

Clicking this button causes all spectrometers to jog by an amount specified in the PROBEWIN.INI file backlash factors. Use this button to remove any spectrometer backlash that may be present when manually adjusting the spectrometer positions. The jog is based on the current spectrometer positions for all spectrometer motors.

This flag is duplicated in the Acquisition Options window, which can be accessed by clicking the Acquisition Options button in the Acquire! window.

Free/Clear

This button stops and deactivates all current stage and spectrometer motor motion. It is equivalent to clicking the Cancel button on the Automation Status window except that a motor de-energize is also performed on the Advanced MicroBeam hardware.

If a serial interface (SESAME or TRACOR) is specified, the program will instead clear the serial buffers to re-set any line errors.

Positions

Clicking this button opens the Position Database dialog box. This list of position samples is similar to that seen in the Automate! position list.

All currently digitized position sample stage coordinates, (standards, unknowns, and/or wavescans) for the position database can be displayed. Double-clicking on any entry will display the stage coordinates for that position sample.

One can move to any selected position sample by clicking the Go button on this window. The program will move to the first undeleted stage position for the selected sample. If a specific position coordinate is selected in the lower coordinate display grid, the program will move to that specific position.

The Re-Load will refresh the position sample list in case it was modified by another dialog.

The currently selected position sample coordinates can be updated using the Update button based on the current stage position.

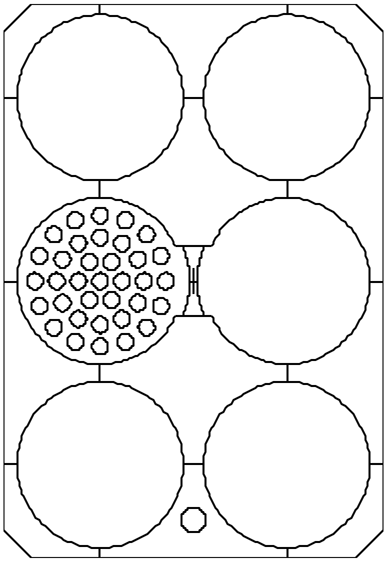
The Edit button will allow the user to manually edit certain fields for the position samples including the position sample name fiducial set and setup number.

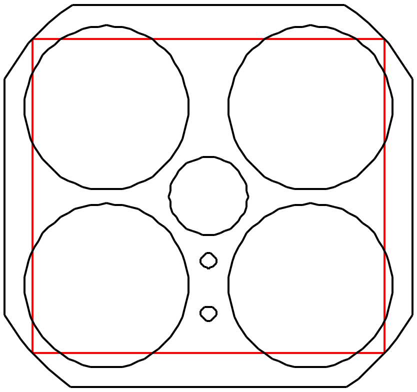
Stage

The Stage button will open a Stage Bit Map window to allow the user to move to a stage position by simply clicking on a specific area on an image of the stage. More than one image file (up to MAXBITMAP%) can be specified in the PROBEWIN.INI file under the "Standards" section. To select another stage bit map simply select the file from the list box. The current stage position is indicated as a red circle.

The frame containing the stage bit map list box, cursor position and Faraday/Beam Blank button can be dragged to a different area of the window if the present position covers an area of interest.

To re-size the Stage Bit Map window simply drag any corner of the window to the desired size and shape. To enable the Stage button or add additional Stage Bit Maps files to the program, see the [Standard] section in the PROBEWIN.INI file. Some sample Stage Bit Map files are shown here for the Cameca SX50 and ARL SEMQ respectively:





Close

Clicking this button will close the Move dialog box and return to the Acquire! window.

Go

Clicking the Go button activates the motors to send all stage and/or spectrometers to their listed target positions. If the crystal positions were changed, the crystals will also be flipped before the spectrometers are driven to their final positions (if supported by the hardware interface).

Since the Go button is the default button in this window, typing <enter> from the keyboard will also cause the motors (and crystals) to move.

Peak/Scan Options

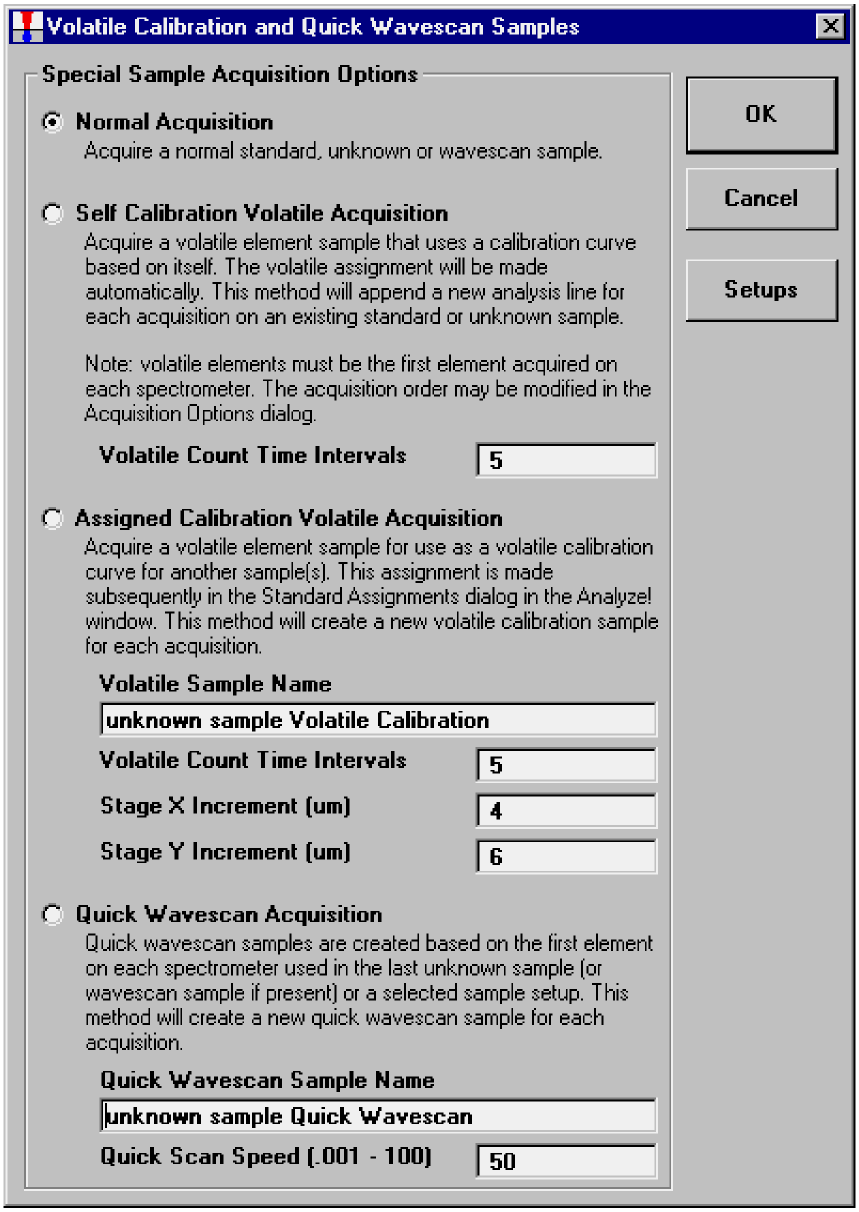
Clicking the Peak/Scan Options button displays the spectrometer peak center and wavescan parameters for each element.

All currently analyzed (tunable spectrometer) elements are displayed, along with their values for the current sample, for on and off-peaks, wavescan limits, peakscan limits, peaking parameters.

Click an element row to edit any peak and scan parameter. Clicking any element row opens the peak and scan properties dialog box. Spectrometer positions may be entered in either spectrometer units or angstrom units and either in absolute position units or relative offsets.

The Move To On Peak button will actually move the current spectrometer to the on-peak position of the current element. The Update On Peak button will update the on-peak (and all other offset positions) to the current position of the spectrometer. This is useful when manually tuning a spectrometer position. The Move To On Peak button will also automatically set the PHA parameters if supported by the hardware.

Note that there is an option to have the stage position "bumped" during the wavescan acquisition. Because the spectrometers are usually operated in an asynchronous mode, the stage is incremented for the specified microns at each specified interval (0-60 seconds). For example, if the user has set the stage increment value to 5 microns and the stage increment interval to 10 seconds, then the program will increment the stage by 5 microns every 10 seconds, during the wavescan acquisition



Volatile Calibration and Quick Wavescan Samples

Special Sample Acquisition Options

● Normal Acquisition
Acquire a normal standard, unknown or wavescan sample.

○ Self Calibration Volatile Acquisition
Acquire a volatile element sample that uses a calibration curve based on itself. The volatile assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing standard or unknown sample.

Note: volatile elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Volatile Count Time Intervals: 5

○ Assigned Calibration Volatile Acquisition
Acquire a volatile element sample for use as a volatile calibration curve for another sample(s). This assignment is made subsequently in the Standard Assignments dialog in the Analyze! window. This method will create a new volatile calibration sample for each acquisition.

Volatile Sample Name: unknown sample Volatile Calibration
Volatile Count Time Intervals: 5
Stage X Increment (um): 4
Stage Y Increment (um): 6

○ Quick Wavescan Acquisition
Quick wavescan samples are created based on the first element on each spectrometer used in the last unknown sample (or wavescan sample if present) or a selected sample setup. This method will create a new quick wavescan sample for each acquisition.

Quick Wavescan Sample Name: unknown sample Quick Wavescan
Quick Scan Speed (.001 - 100): 50

Rate Meter

Clicking the rate meter button opens the Rate Meter Display window. The faraday cup will be removed to show a real time graphical display of each spectrometer and its associated counts per second numeric value for the currently selected spectrometer motor position.

The rate meter dialog is disabled automatically during a sample acquisition to prevent hardware conflicts.

Special Options

Clicking the Special Options button opens the Volatile Calibration and Quick Wavescan Samples dialog. There are two different methods that may be used in Probe for Windows for the correction of volatile elements in unknown samples and another method for the acquisition of "quick" wavescan samples.

Volatile element calibration corrections can only be applied to elements that are the first element acquired on a given spectrometer. The acquisition order of the elements may be modified in the Acquisition Options dialog. This option should be used for both elements "lost" during the acquisition (e.g. Na, K in glass) as well as elements "grown in" (e.g. Si and Al).

"Quick" wavescan samples are spectrometer wavescans that automatically cover the entire range of each spectrometer available in the run.

Self Calibration Volatile Acquisition

In the self calibration method, the software acquires the on-peak data for the volatile element during the normal sample acquisition process for unknown samples.

Click the Self Calibration Volatile Acquisition option so that the next sample acquisition will be acquired using the self calibration method. The number of count time intervals used is specified in the Volatile Count Time Intervals text field. Up to 50 intervals may be used in a volatile acquisition.

For example, if the user enters 5 in the Volatile Count Time Intervals text field, and the default on-peak count time is 10 seconds, then the software will automatically count five 2 seconds intervals for the on-peak elements that are first in spectrometer order. Off-peak acquisitions are not affected.

To view the volatile calibration data, click the Standard Assignments button in the Analyze! window and select the element to view. Click the Display Volatile Fit to view the data for all lines in the sample. Note that the volatile calibration caption will indicate a self calibration correction. That is, the unknown number used for the calibration is itself.

Assigned Calibration Volatile Acquisition

Another method for volatile element calibration corrections is the assigned calibration method. In this method an unknown sample is automatically acquired one element at a time by clicking the Assigned Calibration Volatile Acquisition option to allow the volatile element effect to be calibrated precisely on a single sample. This sample will be started automatically using the sample name in the Volatile Sample Name field the next time a sample acquisition is started.

The count time is adjusted based on the Volatile Count Time Interval parameter. For example, if the user enters 5 in the Volatile Count Time Intervals text field, and the default on-peak count time is 10 seconds, then the software will automatically count five 2 seconds intervals for the on-peak elements that are first in spectrometer order. Off-peak acquisitions are not affected.

The stage is automatically moved in X and Y for each element to ensure that a fresh sample spot is utilized for the volatile calibration.

The volatile element calibration can be assigned to any element in a sample or range of samples provided that it was acquired as the first element on that spectrometer. See the Analyze! window Standard Assignments button for the volatile element calibration display and assignment.

Setups

Pressing the Setups button opens the sample setup window. Here an available sample setup can be selected and used as the basis for the assigned volatile calibration sample. This feature is intended for assigned calibration volatile corrections when it is desired to acquire a subset of the actual elements to which the volatile correction will be assigned.

Quick Wavescan Acquisition

Clicking the Quick Wavescan Acquisition option will start a quick wavescan sample the next time a wavescan is started.

A sample name and scan speed percentage can be specified. The program will move each spectrometer currently being used to it's extreme limit and continuously scan the spectrometer while acquiring count data at the same time. This is a very useful feature if an EDS detector is not available or WDS resolution is required.

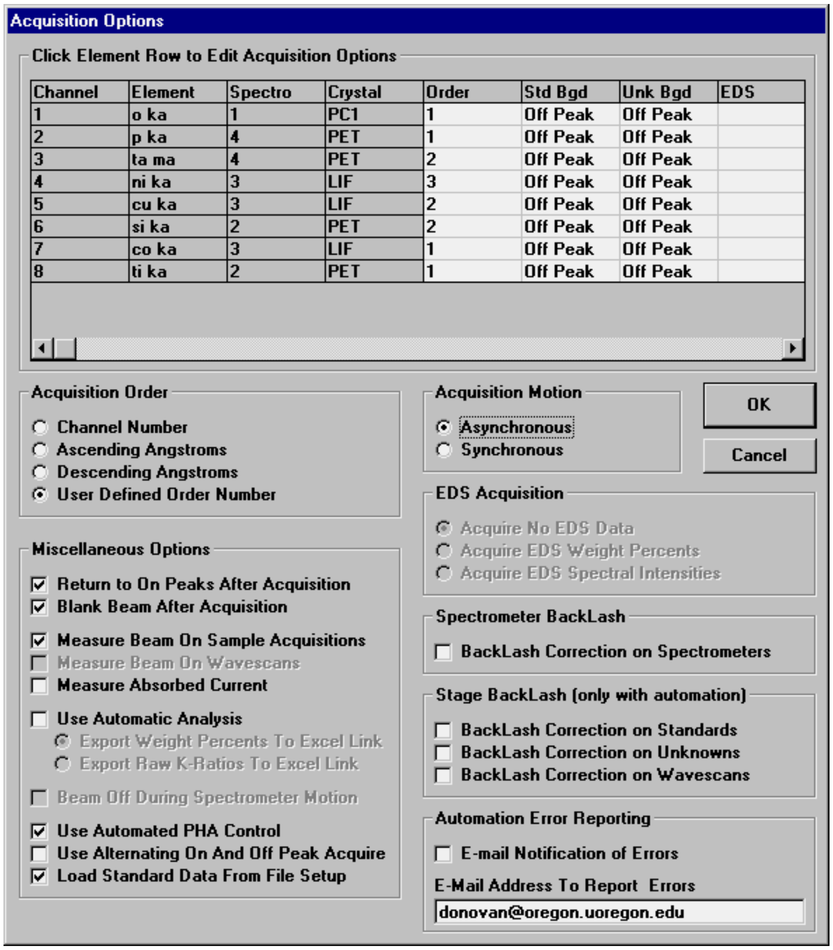
The count time used for the quickscan is specified in the Count Times dialog. Note that the program uses the element configuration for the first acquired element (order=1) on each spectrometer in the sample to create the quickscan sample.

Setups

Pressing the Setups button opens the sample setup window. Here an available sample setup can be selected and used as the basis for the quickscan.

Acquisition Options

Clicking the Acquisition Options opens the Acquisition Options dialog box.



Acquisition Options

Click Element Row to Edit Acquisition Options

Channel	Element	Spectro	Crystal	Order	Std Bgd	Unk Bgd	EDS
1	o ka	1	PC1	1	Off Peak	Off Peak	
2	p ka	4	PET	1	Off Peak	Off Peak	
3	ta ma	4	PET	2	Off Peak	Off Peak	
4	ni ka	3	LIF	3	Off Peak	Off Peak	
5	cu ka	3	LIF	2	Off Peak	Off Peak	
6	si ka	2	PET	2	Off Peak	Off Peak	
7	co ka	3	LIF	1	Off Peak	Off Peak	
8	ti ka	2	PET	1	Off Peak	Off Peak	

Acquisition Order
- ○ Channel Number
- ○ Ascending Angstroms
- ○ Descending Angstroms
- ● User Defined Order Number

Miscellaneous Options
- ☑ Return to On Peaks After Acquisition
- ☑ Blank Beam After Acquisition
- ☑ Measure Beam On Sample Acquisitions
- ☐ Measure Beam On Wavescans
- ☐ Measure Absorbed Current
- ☐ Use Automatic Analysis
  - ● Export Weight Percents To Excel Link
  - ○ Export Raw K-Ratios To Excel Link
- ☐ Beam Off During Spectrometer Motion
- ☑ Use Automated PHA Control
- ☐ Use Alternating On And Off Peak Acquire
- ☑ Load Standard Data From File Setup

Acquisition Motion
- ● Asynchronous
- ○ Synchronous

OK

Cancel

EDS Acquisition
- ● Acquire No EDS Data
- ○ Acquire EDS Weight Percents
- ○ Acquire EDS Spectral Intensities

Spectrometer BackLash
- ☐ BackLash Correction on Spectrometers

Stage BackLash (only with automation)
- ☐ BackLash Correction on Standards
- ☐ BackLash Correction on Unknowns
- ☐ BackLash Correction on Wavescans

Automation Error Reporting
- ☐ E-mail Notification of Errors

E-Mail Address To Report Errors: donovan@oregon.uoregon.edu

All elements analyzed in the current run are listed along with their order of analysis and background type (for both standard and unknown samples). The acquisition order for the elements on each spectrometer may be specified by channel number, ascending or descending angstroms or user-defined order number.

Stage and spectrometer backlash flags for sample acquisitions can be set. Asynchronous or synchronous spectrometer motion can be specified. Note that the sample specific stage backlash flag seen here are only used when performing automated sample confirmation or acquisition. These sample specific backlash flags will be ignored if the Stage Backlash option is not checked in the Move window before the automation is started.

Note that the program will attempt to determine if a backlash is required based on the last direction of motion for each motor. If the backlash factor is positive and the last motion was from a higher to a lower position and the size of the motion was larger than the backlash size, then a backlash will not be performed on the next occurrence of the backlash adjustment.

Other options include beam blanking after each acquisition, returning to on-peaks after acquisition, and beam current measurement modes. If an absorbed current interface is available, the measurement can be turned on or off here also.

The acquisition options for each element can be edited by clicking the desired element row. The spectrometer order number (if user defined was selected) and background type for both standards and unknowns can be specified. If entering the spectrometer order number as user defined, be sure to set the acquisition order for all elements on that spectrometer before exiting the Acquisition Options dialog.

The Use Automatic PHA Control option only applies to those interfaces that support computer control of the baseline, window, gain, bias, integral/differential and/or deadtime parameters. If any of these parameters are under computer control and this option is checked (the default) then the computer will control them for acquisition and automation purposes. If this option is not checked then these parameters will not be set by the program and must be set manually outside the program.

The Use Alternating On And Off Peak Acquisition flag will cause the program to acquire the on and off peak intensities alternately based on the number of repetitions determined by the Unknown Count Time factor parameters in the Count Times dialog. This option applies only to unknown samples. This flag is ignored for Volatile Assigned Calibration acquisition and also for elements (acquisition order = 1) that are acquired using the Volatile Self Calibration acquisition.

The Load Standard Data From File Setup is used to specify whether standard intensity data from a file setup should automatically be imported during automated acquisition using the File Setup option. When a file setup is imported from the new Sample dialog, the user is offered a choice whether or not to load the standard intensity data.

EDS Acquisition

Probe for Windows supports two different methods for EDS acquisition and a variety of EDS interfaces for both for combined WDS and EDS acquisition. The EDS Weight Percents acquisition acquires only the EDS weight percent results from the EDS system. The EDS Spectral Intensity acquisition acquires the complete spectra for each analysis and saves it to the probe data file to allow the user to add or change elements calculated from EDS at any time after the data is acquired.

EDS Weight Percent Acquisition

To utilize this feature either the Acquire EDS Weight Percents or the Acquire EDS Spectral Intensities check box must be checked. If using the EDS Weight Percents interface, the elements to be acquired using EDS must be already suitably configured using the specific EDS package and selected from the Acquisition Properties window (click the element row in the Acquisition Options window).

To add an element for EDS acquisition, first add the element to the current sample as a specified (blank x-ray line) from the Elements/Cations window. Then, from the Acquisition Options | Properties window click the EDS Acquisition Option check box. If the EDS element is properly configured, the program will list the Acquisition Option under EDS as Yes.

During the acquisition, the program will initiate an EDS acquisition, using the EDS software interface defined in the PROBEWIN.INI file, and when the EDS weight percent value is returned by the EDS interface, it will be stored in the probe database for use in the analytical calculations.

To include these EDS acquired elements in the analytical calculations, simply go to the Calculation Options window from the Analyze! window and make sure that the EDS Data Options has the Use EDS Weight Percents option selected.

EDS Spectral Intensity Acquisition
To utilize this feature the Acquire EDS Spectral Intensities check box must checked. Note that EDS spectra data needs to be acquired on suitable standards for this EDS interface acquisition method. This is very important to remember since an element can only be added later to the analysis, if the standard intensity has been acquired.

To include these EDS acquired elements in the analytical calculations, simply go to the Calculation Options window from the Analyze! window and make sure that the EDS Data Options has the Use EDS Spectral Intensities option selected.

Peaking

Clicking the peaking button opens the peak center window. All currently analyzed elements are listed. The Peak Center method can be specified. A choice of Interval Halving, Parabolic, ROM based (if supported by the hardware) and Manual peaking is available. The default peak center method can be specified from the PROBEWIN.INI file. With all methods the program will perform a peak to background measurement to determine if the peak is statistically significant enough to attempt a peak center.

Four options are offered, the first an option move the spectrometers to their on-peak positions if selected in the element list. This option is useful for moving the spectrometers to calibrated peak positions for x-ray mapping purposes.

The second option forces the program acquire a "pre-scan" wavescan just prior to the peak center procedure to allow the user to select an initial peak center start position. This last option is particularly useful in cases where the nominal spectrometer position is badly out of mechanical calibration and the actual peak position is some distance from the theoretical peak position. One can also specify as a third option a "post scan" to be executed after a peak center to confirm that the peak center method was properly performed. This option gives the operator maximum control over the automated determination of the peak "center". Here the peak center found by one of the 3 methods can be verified, by a slow step across the top of the centroid.

The Plot Selected Peak Center button will display graphically, the last peak center attempted for the selected element. The points displayed are numbered in the order acquired. Therefore, for example, if the parabolic peak center was performed, and an optimum peak center was obtained, there will be four points displayed: the three (on, hi, lo) for the parabolic fit and a fourth new on-peak based on the calculated peak center.

> The **Interval Halving** method is the most accurate, but the slowest. It is based on a peak crawl that changes direction and halves the step size whenever the count intensity drops by more than a standard deviation.
>
> The **Parabolic** method peak center uses a moving three point fit on the peak top that is fit to a 2nd order polynomial. The centroid of the parabola is returned as the new peak center. This method is the fastest, if the spectrometer position is already close to the actual on-peak position.
>
> The **ROM Based** method peak center is available if the hardware interface supports a ROM peak center. The actual method used for the ROM Based peak center depends on the microprobe hardware.
>
> The **Manual** method peak center is very simple, utilizing only a pre-scan, P/B check and post-scan.

The program will automatically select elements in the element list that were not peaked in the previous peak center when the window is re-opened again. Note that the element list is multi-select so that any combination of elements can be peaked. If more than one element on the same spectrometer was selected, then the program will automatically peak center them one at a time. The Plot Selected Peak Center button may be used to display the last peak center count-position data for the selected element.

The move to on-peak option is useful for moving a spectrometer (and setting the PHA conditions) to it's on-peak position for imaging purposes. Remember : the elements to peak center (or move to on-peaks) must be highlighted before closing the dialog.

Spectrometer Peak Center Scans

All spectrometer peak center procedures may be prefaced with a spectrometer peak scan to allow the user to manually specify the nominal peak center position. This spectrometer peak scan is performed using the number of peak scan steps as defined in the Peak/Scan Options dialog. The count time for each peak scan point is based on the peak count time (divided by 4) as defined in the Count Times dialog.

Initial Peak-To-Background Measurements

The program always performs a peak-to-background and peak intensity check before the actual peak center procedure. The peak-to-background is calculated by measuring the count rate at the nominal peak position and the current off-peak positions using the peak count time for each position. The measured count data must meet the required minimum peak-to-background and minimum peak count intensity as defined in the Peak/Scan Options dialog, before performing the actual peak center procedure.

If performing the peak center from the Automate! dialog, the program will not proceed with acquisition of sample data if one or more spectrometer fails to complete a peak center procedure for any reason.

Spectrometer Peak Center Procedure

Three peak center procedures are used by Probe for Windows. They are the Interval Halving, the Parabolic Fit and the ROM based peak center procedures.

Interval Halving

Interval halving is a peak center procedure based on a peak crawl starting at the nominal peak position. The step size of the peak crawl is halved and the direction reversed whenever the count rate drops by more than a single standard deviation (square root of the intensity). The interval halving procedure is slow but extremely precise.

The initial peak step interval is always in a positive direction and the peak interval size is based on the Peaking Start Size as defined in the Peak/Scan Options dialog. Note that the default peaking start and stop sizes from the SCALERS.DAT file are modified by the following expression :

$$S_{actualstart} = S_{start} \bullet \sqrt[3]{\frac{2d_{OnPeak}}{2d_{LiF200}}}\,(*2.0)\,\sqrt{\frac{P_{LoLim} + ABS\,(P_{HiLim} - P_{LoLim})}{P_{OnPeak}}}$$

Where :

$S_{actualstar}$	is the actual calculated step size
S_{start}	is the spectrometer default start or stop size
P_{HiLim}	is the spectrometer high limit
P_{LoLim}	is the spectrometer low limit
P_{OnPeak}	is the spectrometer on-peak position
$2\,d_{OnPeak}$	is the 2d spacing of the analyzing crystal
$2\,d_{LiF\,200}$	is the 2d spacing for LiF (4.0267)

From this expression one can see that the actual start and stop sizes are unchanged at the spectrometer high limit when an LiF crystal is used, and are increased for lower spectrometer positions and larger crystal 2d spacings. The calculated start and stop sizes are also doubled when the crystal 2d spacing is larger than 30 angstroms (LDE crystals).

When the interval step size has been halved to a value less than the peaking stop size, the spectrometer is considered to be peak centered and the current position is saved as the new peak position.

If the number of intervals measured exceeds the "Maximum Peaking Cycles" as defined in the Peak/Scan Option dialog, the program terminates the peak center procedure with an error.

Parabolic Fit

The parabolic peak center procedure is based on a moving three point triplet that attempts to fit an inverted parabola. The three positions measured are the middle, high and low positions. The middle position is initially the nominal peak position and the high and low positions are offset from the middle position based on the value of the Peaking Start Size, which is calculated using the process described in the interval peaking procedure above. Ideally the Peaking Start Size calculation should be adjusted to yield an offset which places the high and low positions at a position which produces approximately 1/2 the maximum intensity of the peak, for a more precise parabolic fit.

The peak center procedure then determines if the high and low position intensities are at least one standard deviation less than the middle position intensity. If the three intensities meet this criteria, the program calculates the centroid of a parabola based on the count-position data triplet. The results of the centroid peak fit can be viewed by placing the program into "Debug Mode" under the Output menu.

If the data cannot be fit to a parabola, the middle position is shifted by an amount equal to 1/2 of the Peaking Start Size and the middle, high and low position intensities are measured again.

If the number of count-position data triplets measured exceeds the "Maximum Peaking Cycles" as defined in the Peak/Scan Option dialog, the program terminates the peak center procedure with an error.

ROM Peaking

The ROM peaking procedure is available for those interfaces that support an integrated ROM based peaking procedure. These are the JEOL, Sesame, Tracor, SX100 and SX50 interface types.

The actual peaking procedure utilized by each interface is somewhat different but usually based on a parabolic fit of some variety. The program passes the "Peaking Start Size" to each interface specific ROM Peaking routine where is it modified if necessary.

> **JEOL 8900 Direct (InterfaceType=2)-** The "Peaking Start Size" is not used. Instead a peak parameter of 1 (fine scan) is always used.
>
> **Sesame (InterfaceType=3)-** The "Peaking Start Size" is not used by the Sesame interface. The function simply sends the "PEAK" command for the specified motor, at the current position.
>
> **Tracor (InterfaceType=4)-** The Tracor peak center procedure uses a two step peak center (an initial peak center based on the "Peaking Start Size" and a final peak center based on the "Peaking Stop Size"). The total number of steps is hard-coded since the PAC cannot update this system parameter while another spectrometer is being peaked. The number of TRACOR motor steps per peak scan point is calculated from the number of motor steps per l-unit conversion factor (from the MOTORS.DAT file), the "Peaking Start Size", (or) the "Peaking Stop Size" and the number of peak scan steps (hard-coded to 40). The following expression is used to calculate this value, and assumes a TRACOR peak scan width equal to ten times the Peaking Start Size :

$$sp = M * P * 10 / N$$

where	sp	is the Tracor ROM peak center scan motor steps per point
	M	is the motor steps to units conversion factor (from MOTORS.DAT)
	P	is the Peaking Start Size (initial) or Peaking Stop Size (final)
	N	is the number of peak scan steps (hard-coded to 40)

The Tracor step count time is calculated from the Peaking Count Time (divided by four). Note that the PAC Crystal Factor variable must be set to 1 on all spectrometer-crystals for this procedure to perform correctly.

After the initial Tracor peak center has completed, the procedure moves the motor position to the calculated centroid returned from the PAC, then a final Tracor peak center is performed, before the new peak intensity is measured.

SX100 (InterfaceType=5)- The "Peaking Start Size" is modified to produce a number between 0 and 4 by utilizing the following expression :

$$pw = (M_{high} - M_{Low}) * P / 3000000$$

where	pw	is the SX100 peak center width
	M_{high}	is the motor high limit
	M_{low}	is the motor low limit
	P	is the Peaking Start Size

SX50 (InterfaceType=6)- The "Peaking Start Size" is modified to produce a number between 0 and 4 by utilizing the following expression.

$$pw = (M_{high} - M_{Low}) * P / 3000000$$

where	pw	is the SX50 peak center width
	M_{high}	is the motor high limit
	M_{low}	is the motor low limit
	P	is the Peaking Start Size

If the SX50 peak center width is less than or equal to 2, the SX50 driver sends the "PE" command for the specified motor. Otherwise, if the SX50 peak center width is greater or equal to 3, the SX50 driver sends the "PE WIDE" command instead.

JEOL 8900 Rlogin (InterfaceType=7)- The "Peaking Start Size" is not used. Instead a peak parameter of 1 (fine scan) is always used.

Manual Peaking

The Manual method peak center is very simple. First a wavelength pre-scan is performed, after which the user is allowed to select the actual peak position. This is followed by a peak to background check, after which a wavelength post-scan is performed at a finer scale to allow the user to confirm the selected peak position. The user is then once again given the chance to adjust, confirm or cancel the peak center process.

Note that the final wavelength post-scan data will be saved to the Plot Peak Center array (see the Peaking dialog) for subsequent plotting or output by the user. Note that the post-scan range is 5% (+/- 2.5%) of the pre-scan range.

Final Peak-To-Background Measurements

After a successful peak center procedure the peak-to-background is re-calculated by simply measuring the on-peak count rate at the new peak position. This result can be compared with the initial peak-to-background to evaluate the peak center procedure performance.

Post Scan Peak Confirmation

This option gives the operator maximum control over the automated determination of the peak "center". Here the peak center found by one of the 3 methods can be verified, by a slow step across the top of the centroid. Optimal centering is left to the discretion of the user, but one strategy is to look for the small flat plateau that normally is present at the peak centroid, or looking at the centroid at 99% of maximum intensity. The values used are, respectively, the time value of the "peaking" in Count Times and the step width using 1/20 (5% or +/- 2.5%) of the width for peakscan limits, in Peak/Scan options.

Start Peak Center

Clicking Start Peak Center starts a manual peak center (and peak pre-scan and/or post scan if selected) on the elements selected from within the Peaking button window. If more than one element on the same spectrometer was selected, then the program will automatically peak center them one at a time.

Select the elements to be peak centered and the peak center method from the Peaking dialog accessed from the Acquire! window.

Start Sample Count

Clicking the Start Sample Count button starts a standard or unknown sample acquisition based on the current sample. Data is automatically appended to the current sample which is displayed in the Acquire! window. Be sure that current sample is the correct sample to avoid appending data to the wrong sample.

The program will check the sample parameters before starting an acquisition to make sure that the sample is a valid sample for the configured hardware. For example, if the sample uses Fe ka LiF on spectrometer 2, but the current crystal on spectrometer 2 is PET and the crystal flip interface is not enabled, the program will warn the user that the crystal must be flipped manually before starting the acquisition.

Start Wavescan

If the current sample is designated as a wavescan sample, then clicking this button opens the Wavescan Acquisition window and automatically starts a wavescan sample acquisition.

All elements in the wavescan sample will be scanned, even if more than one element is on a spectrometer. This provides an easy method to scan all elements in a quantitative sample for off-peak interferences and optimal background offset positions.

During the acquisition the wavescan graph may be viewed in greater detail, simply click the wavescan graph to toggle the display size. The wavescan window contains fields to display the mouse cursor position in spectrometer, angstrom and count units. In addition, options for loading the NIST x-ray database window based on the x-ray range of the wavescan graph clicked and a button to save the graph data to an ASCII file are available.

Once the wavescan has been acquired, the user can view the off-peak interferences, by using the Plot! window to display the wavescan sample graphically.

Note that the current sample must be a wavescan sample without any data already acquired. To start a new manual wavescan sample use the New Sample button from the Acquire! window.

Analyze!

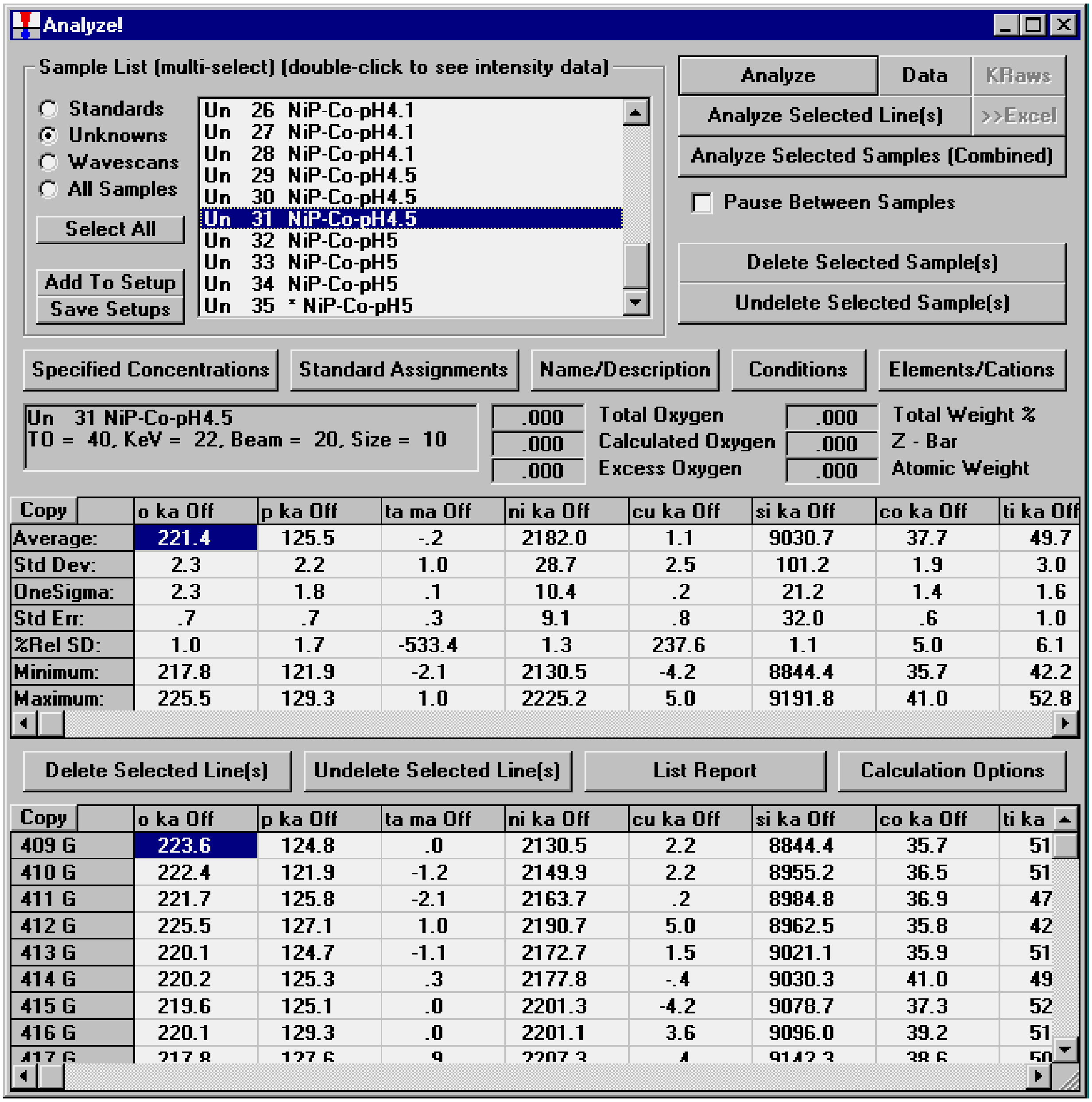
The Analyze window is a modeless dialog that lists both data and processed data for standard, unknown and wavescan samples. The average, standard deviation and other statistical calculations are shown in the upper data grid and the individual data points in the lower data grid. In addition buttons are provided to allow the user to specify elements by fixed composition, standard and interference assignments, volatile element assignments and plots, edit sample name and description, and specify sample calculation options and many other parameters. See the detailed descriptions below for more information.

When making changes to the standard and/or unknown samples for any of these parameters, be sure that the last unknown sample in the list is also selected so that the changes made will be included in the next new sample that is created (unless loading a previously saved sample setup). Probe for Windows, by default, always uses the last unknown sample as the basis for the next standard or unknown that is created.

The Save Setup button is used to quickly save a pointer to an unknown sample so the sample can later be used as the basis for creating a new sample. It will save all selected samples as sample setups using the sample name already given. If it is desired to use a different name for the sample setup, use the Save Sample Setup button from the Elements/Cations dialog. The sample setup can be loaded for new samples by using the Load Sample Setup button in the New Sample dialog.

Analyze

This button is used to convert previously acquired x-ray count data to elemental, oxide, atomic or formula results. The samples currently selected in the sample list will be analyzed and the analysis output is directed to both the Analyze! window and the log window.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

☐ Pause Between Samples

Un 26 NiP-Co-pH4.1
Un 27 NiP-Co-pH4.1
Un 28 NiP-Co-pH4.1
Un 29 NiP-Co-pH4.5
Un 30 NiP-Co-pH4.5
Un 31 NiP-Co-pH4.5
Un 32 NiP-Co-pH5
Un 33 NiP-Co-pH5
Un 34 NiP-Co-pH5
Un 35 * NiP-Co-pH5

Un 31 NiP-Co-pH4.5
TO = 40, KeV = 22, Beam = 20, Size = 10

.000 Total Oxygen
.000 Calculated Oxygen
.000 Excess Oxygen
.000 Total Weight %
.000 Z - Bar
.000 Atomic Weight

Copy	o ka Off	p ka Off	ta ma Off	ni ka Off	cu ka Off	si ka Off	co ka Off	ti ka Off
Average:	221.4	125.5	-.2	2182.0	1.1	9030.7	37.7	49.7
Std Dev:	2.3	2.2	1.0	28.7	2.5	101.2	1.9	3.0
OneSigma:	2.3	1.8	.1	10.4	.2	21.2	1.4	1.6
Std Err:	.7	.7	.3	9.1	.8	32.0	.6	1.0
%Rel SD:	1.0	1.7	-533.4	1.3	237.6	1.1	5.0	6.1
Minimum:	217.8	121.9	-2.1	2130.5	-4.2	8844.4	35.7	42.2
Maximum:	225.5	129.3	1.0	2225.2	5.0	9191.8	41.0	52.8

Copy	o ka Off	p ka Off	ta ma Off	ni ka Off	cu ka Off	si ka Off	co ka Off	ti ka
409 G	223.6	124.8	.0	2130.5	2.2	8844.4	35.7	51
410 G	222.4	121.9	-1.2	2149.9	2.2	8955.2	36.5	51
411 G	221.7	125.8	-2.1	2163.7	.2	8984.8	36.9	47
412 G	225.5	127.1	1.0	2190.7	5.0	8962.5	35.8	42
413 G	220.1	124.7	-1.1	2172.7	1.5	9021.1	35.9	51
414 G	220.2	125.3	.3	2177.8	-.4	9030.3	41.0	49
415 G	219.6	125.1	.0	2201.3	-4.2	9078.7	37.3	52
416 G	220.1	129.3	.0	2201.1	3.6	9096.0	39.2	51
417 G	217.8	127.6	.9	2207.3	.4	9142.3	38.6	50

The Analyze! window will display the totals, calculated oxygen (if any) and z-bar and atomic weight along with the last specified results in the following order :

- Elemental Weight Percents
- Oxide Weight Percents
- Atomic Weight Percents
- Formula Atoms

All calculations (including homogeneity statistics and mineral end-members) are also output in the above order to the log window as text. To reduce the detail level of the output, see the options in the Analytical | Analysis Options menu. To see a complete output of all intermediate steps of the analysis calculations use the Output | Debug Mode menu to turn on debug printout and re-run the analysis.

If more than one sample is selected for analysis, it may be desirable to check the Pause Between Samples check box. If this is selected, then the program will automatically pause after each analysis until the user clicks the Cancel or Next buttons on the Analysis Status window. This allows the user to view the results of each analysis and delete data points if necessary before proceeding to the next analysis. This is especially useful when analyzing the standards as unknowns after a standardization has been acquired to check for problems in the standard calibration data.

The Copy buttons in the two grids can be used to copy the displayed results into the Windows Clipboard buffer, from which it can be pasted into other applications as tab delimited text.

Error Messages

Several problems can occur when performing analyses of quantitative samples. If data for a standard is missing, the program will print "No count data for standard __ for __". This means that either that the standard was not acquired at all or that the standard assignments were changed to a channel that was not acquired due to a "quick" standardization. Simply acquire data for the specified element on the specified standard or re-assign the standard to correct the problem.

If the message "No count data for interference standard __ for __" is seen, a similar problem exists. Note that standards used in the interference corrections should not be run as "quick" standards to avoid this problem. If the warning message persists, you may be assigning an interference correction where none exists. Check your wavelength tables to be sure. If you find no interference, then remove the interference correction for the element. Remember, interferences are quite dependent on spectrometer resolution (slit width) and PHA settings (for higher order lines) and so the magnitude or presence of the interference may change from run to run.

Problems With the Analysis

Performing quantitative analysis is always beset with many difficulties and it is often difficult to pinpoint the cause of "bad" analyses. More often than not, the effect is the sum of more than one problem. However, there are several things that can be checked. First of all start by examining the standards. It is in situations like this that the use of secondary standards can really be helpful in determining what is going on. If the primary and secondary standards do not agree with each other, there is a problem.

First of all, are the standards really "good" standards? That is, have their compositions been determined by a reliable analytical method? In general, major element standard concentrations need to be determined using classical wet chemistry methods. Second, are the concentrations entered into the STANDARD.MDB database correct and without typographical errors? Third, was the right standard actually acquired? It is easy to get lost at 300-400 magnifications when using a standard mount which contains many standards.

Some other things to consider :

1. Is the operating voltage correct specified? Is the correct x-ray line tuned for each element? Check the on-peak position offsets from the Peak/Scan Option dialog and see if they are reasonable. The program will usually type a warning if the actual and calculated peak positions are very different. Be sure that the spectrometer is not tuned on a nearby line of another element if using multi-element standards.

2. Be sure that no bad data points are in the standards samples used for the quantitative calibration. The best way to check for this is to analyze each standard and examine the results to look for points with obviously bad or low totals (epoxy, inclusions, bad surface polish, bad carbon coat, etc.). If a bad point is found, one can delete it. Remember, one can always undelete data later on. A deleted point is simply not used in calculating the analytical calculations but is still present. A good rule of thumb is to only delete points that have low totals since generally most of the problems mentioned above will result in fewer x-ray counts. Avoid deleting points just to get better agreement between the primary and secondary standards. Points that have high totals should not be arbitrarily deleted. It may be necessary to look for other problems such as points with low totals in the primary standards.

3. Look for interferences on the analyzed elements. One easy way to do this is to use the Interferences button in the Element Parameters window (see the Elements/Cations button in the Acquire! or Analyze! window). The best method is to perform a wavelength scan and display possible interfering peak markers. Then not only can the interferences be seen but one an also select background positions free from interferences. If the element causing the interference is present in significant concentrations in your unknowns, and is not being analyzed for, it may be necessary to add the interfering element to the run by creating a new sample with the interfering element as an analyzed element. Be sure that the proper standards are available to use for the interference correction.

4. If none of the above suggestions seem to help, try acquiring the standards again. Probe for Windows uses an automatic standard drift corrections which can make a significant difference in situations where one or more of the standard intensities are drifting. Note that since the program will perform an automatic drift correction not only on the standards, but also the interference standards and the MAN background standards, it might be also be necessary to run additional sets of those standards or MAN standards.

5. In the case of trace or minor elements, also check to see that none of the off-peak positions are interfered with by another peak. This can cause a reduction in the on-peak counts, sometimes enough to result in a negative k-ratio. Always run at least one wavelength scan on a sample, using the same count time as your quantitative analyses, and if a peak is seen interfering with the off-peak marker, use the Low and/or High buttons in the Graph Data window to select a new off-peak position that is not interfered with.

6. Finally are the standards really "good" standards? That is, homogeneous and whose compositions are accurately and precisely known. Some may have been analyzed by classical "wet" chemical methods (e.g. Smithsonian mineral and glass standards) of small quantities of separates. Second, are the concentrations entered into the STANDARD.MDB database correctly? (no typos)

7. Low totals may result from charging due to a poor conductive (e.g. carbon) coating on insulated materials. Many year-old carbon coats have been known to fail. Also, a carbon-sputtered coating is not necessarily equivalent to a carbon-evaporated coating; both standards and unknowns may need to be recoated by the same process

8. Peaks shifts both may need to be considered. The later are generally well recognized for the K lines of "light" elements (including Al), but less so for some L lines. If you recall that this results from the outer shell electron bonding or configuration being involved in X-ray production, those elements with M shell electrons (e.g. Co) also can have significant peak shifts.

9. Peak positioning: you may want to verify that the peak centering method you have selected is giving you optimal peak centers. It would not hurt to run the post-scan verification option where you step across the peak that the automation has chosen.

Description of the Analysis Printout

When the analysis is printed out you will see the sample type (st or un), sample number and name printed on the first line. If the sample is a standard, then the sample set number is also shown. The microprobe takeoff angle and the operating voltage is shown.

The next line indicates the total number of lines (or data points) that are contained in the sample. One may have 1 to 50 points in each sample. In the same line are the number of points that have status of "G" for good, meaning that this many points are undeleted. A sample with all points deleted will have the number of "G" points equal to 0 and will not be used in any calibrations or recalculations and therefore cannot be quantitatively analyzed, unless using the Analyze Selected Lines button.

Next, the average elemental totals and the total, calculated and excess oxygen is displayed. The calculated oxygen is the amount of oxygen calculated by cation stoichiometry (if selected) and the excess oxygen is the difference between the measured and oxygen calculated if the Display As Oxide option was selected. This excess oxygen is often very useful in determining if the selected cation ratios are correct, especially for iron bearing oxides.

Next is the atomic weight and average Z-bar for the sample. This is followed by the average number of ZAF iterations needed to converge each data point for the sample and the MAN iterations, which are the iterations required to converge the MAN background, interference, APF (Area Peak factor) and volatile element corrections. The Z-bar is defined as the sum of the weight fraction of the atomic numbers of all elements in the sample including specified elements.

Following this are the weight percentages and standard deviation of any elements specified for the sample by fixed concentration, difference or stoichiometry.

The specified element type is listed for each specified element. The type "SPEC" means that the element concentration is truly specified. That is, either specified by the user or (for standard samples) loaded from the standard composition database. The other types are "DIFF" for element by difference, "CALC" for element by stoichiometry to stoichiometric oxygen and "RELA" for an element by stoichiometry to another element.

The next two lines indicate the type of background correction used for each element ("MAN" for mean atomic number corrected and "OFF" for off-peak corrected elements) and the average count times for each element in the sample. Remember that the count times for each element can be different for each line in the sample. To see the actual counting time details use the Data button in the Analyze! window with the Debug Mode menu checked.

Note that if fixed spectrometers are used in the run, or a MAN background corrected sample was analyzed, the program will also indicate the magnitude of the absorption correction to the continuum background counts in the line labeled "%ABS" if the element is MAN corrected.

The analyzed element symbols are printed next and listed below are the weight percentages calculated for each data point for each element. The elemental weight results are then followed by the average, "AVER" of each element column, the standard deviation, "SDEV" and the standard error, "SERR". The standard deviation is basically the range of the results and the standard error is essentially the precision of the average. Finally the percentage relative standard deviation, "%RSD" of the results are printed which is simply the standard deviation divided by the average times 100.

Note that one can perform analyses of samples which are not unknowns, e.g. it is possible to have the program analyze a standard as though it were an unknown. Therefore, if the sample is a standard sample, the program next lists the published, "PUBL" weight percentage value for the element as entered in the default standard database. If the element is not found in the standard database it is shown as "n.a." or "not analyzed". The next line lists the per cent variance, "%VAR" from the published value for each element compared to the actual measured average for the standard. This can provide a valuable check on the quality of your analyses for secondary standard elements. That is, element channels which are not assigned as the primary calibration for that element. After this, is the line labeled "DIFF" which is a simple difference between the "AVER" and "PUBL" values.

The actual primary standard used for each element is displayed on the next line "STDS" since the standard assignments can be made on a sample by sample basis.

Note that sometimes the average analyzed value of a standard that is assigned, appears to be not exactly the value shown in the "PUBL" line. It seems reasonable that they should always be exactly the same, but remember that because PROBE treats all samples (standards and unknowns) as unknowns when performing an analysis, you may see a small discrepancy if the standard contains other analyzed elements that are also not assigned. This is because Probe for Windows calculates the correction factors for an analysis of a sample, based on the actual analyzed composition of the sample, not the theoretical composition in the STANDARD database. Of course, for the analytical calibration, PROBE for Windows uses the database composition for the calculation of standard k-factors.

Below this are shown the average standard k-factors "STKF" or the standard beta-factors "STBE" if using alpha-factors, the average standard counts "STCT" followed by the normalized unknown k-ratio, "UNKF", the unknown count rate "UNCT", the unknown background counts "UNBG" (either MAN or off-peak measured), the ZAF correction factor, "ZCOR" if using ZAF or Phi-Rho-Z or the "UNBE", unknown beta-factor if using alpha-factors, and the average raw k-ratio, "KRAW", which is the normalized and background corrected unknown counts divided by the standard counts.

The "KRAW" value shown is corrected for all corrections except the matrix correction. These include the deadtime, count time, beam drift, MAN or off-peak background, and the quantitative interference and APF (area peak factor) corrections. The peak to background ratio for each element is shown in the "PKBG" line. A peak to background of close to 1.0 means that no peak was present.

Below this are listed the per cent correction to the counts for any interference corrections that were performed on the sample in the line labeled "%INT".

Finally, if the volatile element extrapolation was selected, the program will show the per cent change in the x-ray counts due to the volatile element extrapolation in the line labeled "VOL%" and the average deviation in the volatile fit data "DEV%". Also if any area peak factors (APF) were selected, the program will print the sum of the APFs (1.00 indicates no APF correction) for each element affected in the line labeled "APF:".

If the user elected to calculate the detection limits and/or sample statistics, the program will then print those calculations.

Following this are formula and atomic per cent calculations if they were selected. All sample calculation options can be assigned to a single sample or a range of samples.

Example of Analysis Printout

```
St  358 Set   1 diopside (Chesterman)
TakeOff = 40  KiloVolts = 15  Beam Current = 30  Beam Size = 2
Number of Lines:  5 Number of 'Good' Lines:  5
Current Date and Time: 12/14/98 2:27:03 PM

Elemental Wt. % Total:   99.916     Average Total Oxygen:      .000
Average Calcu. Oxygen:     .000    Average Excess Oxygen:      .000
Average Atomic Weight:   21.657    Average Atomic Number:    12.230
Average ZAF Iteration:     4.00    Average MAN Iteration:      2.00

Results in Elemental Weight Percents

SPEC:        O
TYPE:     SPEC

AVER:   44.316
SDEV:     .000

ELEM:       Si      Fe      Mg      Ca      Al
BGDS:      LIN     LIN     LIN     LIN     LIN7
TIME:    10.00   10.00   10.00   10.00   10.00

ELEM:       Si      Fe      Mg      Ca      Al   SUM
    41  25.850    .060  11.323  18.372    .000  99.921
    42  25.984    .032  11.086  18.551    .004  99.974
    43  25.853    .039  11.223  18.609    .017 100.057
    44  25.862    .046  11.239  18.369    .061  99.893
    45  25.847    .034  10.974  18.542    .022  99.735

AVER:   25.879    .042  11.169  18.489    .021  99.916
SDEV:     .059    .011    .139    .111    .024
SERR:     .026    .005    .062    .050    .011
%RSD:       .2    26.3     1.2      .6   115.0
```

```
PUBL:   25.925    .047  11.192  18.489    .016  99.985
%VAR:     -.18  -10.09    -.21     .00   30.46
DIFF:    -.046   -.005   -.023    .000    .005
STDS:       14     263      12     358      13

STKF:    .4101   .5004   .4738   .1693   .4353
STCT:   4105.3  5026.8  4758.6  1692.8  4354.5

UNKF:    .2089   .0004   .0770   .1693   .0001
UNCT:   2091.2     3.5   773.7  1692.8     1.1
UNBG:     17.3    30.0    26.3    23.7    18.0

ZCOR:   1.2388  1.1999  1.4499  1.0919  1.4223
KRAW:    .5094   .0007   .1626  1.0000   .0003
PKBG:   122.39    1.12   30.47   72.64    1.07

Results in Oxide Weight Percents

SPEC:        O
TYPE:     SPEC

AVER:     .066
SDEV:     .085

ELEM:     SiO2     FeO     MgO     CaO   Al2O3   SUM
    41  55.303    .077  18.777  25.706    .000  99.921
    42  55.590    .042  18.383  25.957    .008  99.974
    43  55.309    .050  18.611  26.038    .032 100.057
    44  55.329    .059  18.637  25.702    .115  99.893
    45  55.296    .044  18.197  25.944    .042  99.735

AVER:   55.365    .054  18.521  25.869    .039  99.916
SDEV:     .126    .014    .230    .155    .045
SERR:     .056    .006    .103    .069    .020
%RSD:       .2    26.3     1.2      .6   115.0

Results in Atomic Percents

SPEC:        O
TYPE:     SPEC

AVER:   60.035
SDEV:     .060

ELEM:       Si      Fe      Mg      Ca      Al   SUM
    41  19.942    .023  10.094   9.931    .000 100.000
    42  20.049    .013   9.884  10.030    .004 100.000
    43  19.935    .015  10.000  10.055    .013 100.000
    44  19.956    .018  10.021   9.932    .049 100.000
    45  19.982    .013   9.803  10.045    .018 100.000

AVER:   19.972    .016   9.960   9.999    .017 100.000
SDEV:     .046    .004    .116    .062    .019
SERR:     .021    .002    .052    .028    .009
%RSD:       .2    26.2     1.2      .6   115.0

Results Based on 6 Atoms of o

SPEC:        O
TYPE:     SPEC
```

```
AVER:    6.000
SDEV:     .000

ELEM:       Si      Fe      Mg      Ca      Al   SUM
    41   1.994    .002   1.009    .993    .000   9.998
    42   2.004    .001    .988   1.003    .000   9.996
    43   1.994    .002   1.000   1.006    .001  10.003
    44   1.995    .002   1.002    .993    .005   9.996
    45   1.994    .001    .978   1.002    .002   9.977

AVER:    1.996    .002    .995    .999    .002   9.994
SDEV:     .005    .000    .012    .006    .002
SERR:     .002    .000    .006    .003    .001
%RSD:       .2    26.3     1.2      .6   115.0
```

Data

Click this button to see the raw count rate data for the sample. The count data will also be printed to the log window. This information includes the average "AVER", standard deviation "SDEV" and the one sigma (ideal) standard deviation, "1SIG", the sigma ratio (standard deviation divided by one sigma), "SIGR" and the standard error "SERR" and percent relative standard deviation "%RSD" which is the standard deviation divided by the average.

The upper data grid will display the count statistics for the sample averaged data including the standard deviation, one sigma, percent relative standard deviation, minimum and maximum values.

The one sigma values represent a predicted standard deviation based on the count rate and the counting time used for the acquisition. It is calculated by dividing the square root of the count rate by the square root of the average counting time. Therefore when counting at one second count times, the one sigma value will be exactly equal to the square root of the count rate. For sample sets using a 10 second counting time, the one sigma value will be smaller than the simple square root by the square root of 10 or approximately 3.162.

Use the one sigma value to evaluate whether a given average count rate represents a homogeneous set of sample data. Standard deviations larger than the one sigma value indicate the possibility of actual compositional variation within the data set. The percent relative standard deviation is simply the standard deviation divided by the average count rate.

Use the Copy buttons to copy this data as tab delimited data to the Windows Clipboard for pasting into another application. The data will automatically formatted as tab delimited text.

The log window will contain additional information including the stage positions for each point in the sample, the on and off-peak positions (absolute and relative offset), the average on-peak and high and low off-peak count times, and for unknown samples only, the Unknown Count Factor multiplier "UNFAC:" and Maximum Counts "MAXCT:", and finally the Volatile Calibration Assignment "VOL#:" which is equal to the unknown sample number for the volatile self calibration or equal to another unknown sample number in the case of the assigned volatile calibration.

This is followed by the background acquisition type of Mean Atomic Number (MAN), or off-peak (OFF), spectrometer motor number, crystal type, and acquisition order and the MAN or off-peak corrected counts for the sample.

After this, the calculated off-peak counts are also printed out along with the background calculation type (if applicable) of Linear interpolation (LINEAR), high off-peak only (HIGH), low off-peak only (LOW), average of high and low (AVER), slope high (S-HIGH), slope low (S-LOW), exponential interpolation (EXPON) and polynomial (POLY).

Example of Data Printout

```
St  358 Set   1 diopside (Chesterman)
TakeOff =  40   KiloVolts =  15    Beam Current =  20   Beam Size =  5
Number of Lines:  5 Number of 'Good' Lines:  5
```

```
Stage (or Beam Deflection) Coordinate Positions:
        X        Y        Z        W              X        Y        Z        W
  146G  -6791.0  -6774.0  91.0000  .000000   147G  -6785.0  -6774.0  91.0000  .000000
  148G  -6779.0  -6774.0  91.0000  .000000   149G  -6773.0  -6774.0  91.0000  .000000
  150G  -6767.0  -6774.0  91.0000  .000000

Last (Current) On and Off Peak Count Times ("----" indicates default max count):
ELEM:    si ka   al ka   fe ka   mg ka   cr ka   ti ka   mn ka   ca ka  BEAM
BGD:       OFF     OFF     OFF     OFF     OFF     OFF     OFF     OFF
MOTOR:       1       1       2       4       3       3       2       5
CRYST:     TAP     TAP     LIF     TAP     LIF     LIF     LIF     PET
ONTIM:   20.00   20.00   20.00   20.00   20.00   20.00   20.00   20.00
HITIM:   10.00   10.00   10.00   10.00   10.00   10.00   10.00   10.00
LOTIM:   10.00   10.00   10.00   10.00   10.00   10.00   10.00   10.00

On-Peak (off-peak corrected) or MAN On-Peak X-ray Counts (and Faraday Current):
ELEM:    si ka   al ka   fe ka   mg ka   cr ka   ti ka   mn ka   ca ka  BEAM
BGD:       OFF     OFF     OFF     OFF     OFF     OFF     OFF     OFF
MOTOR:       1       1       2       4       3       3       2       5
CRYST:     TAP     TAP     LIF     TAP     LIF     LIF     LIF     PET
ORDER:       1       2       1       1       1       2       2       1
  146G  8340.8     5.4     1.7  3305.2     -.4     -.3      .4  2335.1  20.063
  147G  8331.9     6.9     1.9  3287.4     -.3     -.3      .3  2350.0  20.059
  148G  8347.0     4.4      .9  3289.6      .8     -.7     2.4  2347.0  20.067
  149G  8355.2     7.9     2.3  3303.1      .5      .1      .9  2346.5  20.081
  150G  8340.0     4.3     1.9  3274.8      .1      .0     1.5  2369.2  20.072

AVER:   8343.0     5.8     1.8  3292.0      .1     -.2     1.1  2349.6  20.068
SDEV:      8.7     1.6      .5    12.4      .5      .3      .9    12.4    .009
1SIG:     20.4      .5      .3    12.8      .1      .1      .2    10.8
SERR:      3.9      .7      .2     5.6      .2      .1      .4     5.5
%RSD:       .1    27.4    29.4      .4   401.5  -137.7    79.6      .5

Off-Peak (calculated) X-ray Counts (and Absorbed Current):
ELEM:    si ka   al ka   fe ka   mg ka   cr ka   ti ka   mn ka   ca ka  BEAM
TYPE:   LINEAR  LINEAR  LINEAR  LINEAR  LINEAR  LINEAR  LINEAR  LINEAR
  146G    35.2    22.8     4.2    16.5     2.6     1.6     3.4    11.9    .000
  147G    34.3    22.3     5.0    15.9     3.0     1.6     3.7    13.4    .000
  148G    32.9    22.1     4.6    16.4     2.0     1.7     2.5    13.3    .000
  149G    33.7    20.7     4.4    17.2     2.2     1.3     3.3    14.1    .000
  150G    34.2    23.1     4.6    15.1     2.5     1.3     2.7    13.8    .000

AVER:     34.0    22.2     4.6    16.2     2.5     1.5     3.1    13.3    .000
SDEV:       .9      .9      .3      .8      .4      .2      .5      .8    .000

Raw Hi-Peak X-ray Counts (and Absorbed):
ELEM:    si ka   al ka   fe ka   mg ka   cr ka   ti ka   mn ka   ca ka  BEAM
  146G    32.1    19.3     4.0    15.5     2.9     1.6     3.6    11.5    .000
  147G    31.3    19.4     5.3    15.8     3.2     1.1     3.4    13.0    .000
  148G    28.2    18.6     4.7    14.9     2.1     1.5     2.0    14.9    .000
  149G    29.4    18.1     4.1    17.5     2.2     1.3     3.4    15.0    .000
  150G    31.5    19.5     4.7    14.8     2.6     1.6     2.6    12.8    .000

AVER:     30.5    19.0     4.6    15.7     2.6     1.4     3.0    13.4
SDEV:      1.6      .6      .5     1.1      .5      .2      .7     1.5

Raw Lo-Peak X-ray Counts (and Absorbed):
ELEM:    si ka   al ka   fe ka   mg ka   cr ka   ti ka   mn ka   ca ka  BEAM
  146G    40.1    26.5     4.6    17.8     2.2     1.6     3.1    12.3    .000
  147G    39.0    25.5     4.2    16.0     2.7     2.1     4.3    13.8    .000
```

```
  148G    40.0    26.0     4.5    18.3     2.0     2.0     3.3    11.7    .000
  149G    40.2    23.5     5.1    16.9     2.2     1.4     3.1    13.1    .000
  150G    38.4    26.9     4.5    15.4     2.4     1.1     2.9    14.8    .000

AVER:     39.5    25.7     4.6    16.9     2.3     1.6     3.4    13.1
SDEV:       .8     1.3      .3     1.2      .3      .4      .5     1.2
```

KRaws

Click this button after performing a quantitative analysis and the raw k-ratios will be displayed in the Analyze! grid. This button is disabled until an analysis is performed.

The raw k-ratio is defined as the unknown count rate divided by the standard count rate. The calculation uses background corrected count rates.

Note that Probe for Windows also corrects the raw k-ratios for MAN backgrounds, on-peak interferences, APF (Area Peak factors) and volatile element corrections. This provides very useful information for importing into other recalculation programs (film thin analysis software for example).

Use the Copy buttons to copy this data as tab delimited data to the Windows Clipboard for pasting into another application.

Example of K-Raw Output

```
Line   si ka Off     fe ka Off     mg ka Off     ca ka Off     al ka Off
 41 G    .50845        .00100        .16490        .99360       -.00042
 42 G    .51184        .00054        .16137       1.00339        .00007
 43 G    .50878        .00065        .16337       1.00663        .00027
 44 G    .50874        .00076        .16369        .99344        .00098
 45 G    .50920        .00057        .15963       1.00294        .00036
```

Analyze Selected Line(s)

To analyze a subset of the data lines in the selected sample, first select the lines in the data grid and then click this button. The results, average and statistics of only the selected lines will be calculated and displayed even if they were previously deleted.

The sample lines not selected and analyzed are temporarily flagged as deleted and are therefore eliminated from the analytical calculations and averages.

Analyze Selected Samples (Combined)

This button will combine the currently selected samples into a single sample and calculate the matrix corrections as though they were a homogenous composition. This is useful if the multiple sample setups option was used in the Automate! window and the major and trace elements were acquired separately. It can also be used to demonstrate the effect of non-homogenous samples.

Delete Selected Sample(s)

Click this button to delete the currently selected samples. The program will flag each data line in the sample as "B" for bad. This will prevent the data in this sample from being used in any analytical calculation or calibrations (if the sample is a standard).

However, if the Analyze Selected Lines option is used, even the deleted lines will be analyzed if they were selected using this option.

Any deleted line or sample can be undeleted by using the Undelete buttons described below. An undeleted line is displayed with a "G" flag for good.

Undelete Selected Sample(s)

Click this button to undelete the currently selected samples. The program will flag each data line in the sample as "G" for good. This will allow the data in this sample to be used in any analytical calculation or calibrations (if the sample is a standard).

Specified Concentrations

Probe for Windows 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.

To specify the concentration of an element not analyzed for in an unknown sample (standard samples will have elements not analyzed for (declared but not acquired), loaded automatically from the standard database), first select the samples to assign the specified concentrations to from the Analyze! sample list box.

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. 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 go back to the Specified Concentrations button and click the specified element. Enter the composition and click OK or type <enter>.

Remember that the specified concentrations for unknown samples will be automatically loaded into each new unknown sample that is created based on the last unknown sample.

Standard Assignments

The standard assignments dialog is used to select the primary standard for the calibration of the quantitative analysis. Each analyzed element must have a standard assigned to it. This dialog is also used to specify the quantitative correction of on-peak interferences and the volatile element correction. Remember that although the program will automatically load the standard assignments based on the last unknown sample, the standard assignments may be assigned at any time on a sample by sample basis, e.g. for post-processing of data.

The program will load a default set of standard assignments the first time this dialog is opened. These default standard assignments are simply based on the standard containing the highest concentration of each element. It will sometimes be necessary to modify these defaults standard assignments depending on the analytical situation.

Generally when assigning standards for use in the analytical calibration, it is best to use primary standards which contain a major concentration of the element. Standards not assigned but also containing the element are secondary standards and are valuable for checking the quality of the calibration. This can be seen by examining the "%VAR" line in the analysis printout, if they have been acquired as standards, not as unknowns.

Although standards can be reassigned at any later time, the user should be aware that the use of "quick" standards may restrict one's ability to reassign standards off line since the required data may not have been acquired. When running connected to the microprobe (on line) however, you can rerun the affected "quick" standards after changing the standard assignments to obtain the necessary calibration data.

Users may also create subsets of the same elements to acquire on several standards, permitting maximum flexibility. Say you have a sample with feldspars and pyroxenes, and your complete element list holds Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, and Fe, and you have several silicate standards: albite, microcline, anorthite, wollastonite, enstatite, forsterite, fayalite (as well as others for Ti, Cr and Mn). It would take too long to acquire all elements on all standards, but you don't want to run quick standards either, as you'd like to acquire several elements on multiple standards for maximum flexibility. After peaking all elements and checking pulse height settings, you would save an "all elements" sample setup. Then create a new unknown, feldspar, and delete the Mg, Ti, Cr, and Mn. Save this sample setup as "feldspar". Then create a new unknown, this time recalling the "all elements" sample setup, this time deleting the K and Cr, and saving this as "pyroxene". You could then later "tag" the appropriate standard with the appropriate list of elements, under Automate!.

Virtual Standard Intensities

A new option is the use of "virtual" standard intensities. These are calculated intensities based on interpolation and matrix corrected similar (atomic numbers) elements measured on the same crystal, spectrometer and voltage as the unknowns. This may be useful in cases where a physical standard is not available (e.g., Ar).

See the Calculate Virtual Standard Intensity menu under the Analytical menu for the interactive dialog for use in calculating and storing these parameters.

Spectral Interferences

Probe for Windows allows the user to select a fully quantitative correction for spectral interferences. To help inform the user of possible on-peak interferences, the program will give the user the option of displaying all possible interferences based on the current set of analyzed and interfered elements. However, remember that the program can only correct for interferences if both the interfered and interfering element intensities are acquired. In addition, an interference calibration standard must be acquired that contains a major concentration of the interfering element and none of the interfered element or any other elements that interfere with the interfered element.

The interference correction used by Probe for Windows is similar to that used by some investigators (Snetsinger, Bunch and Keil, 1968), but is quantitative and more general, and can be applied easily to the analysis even if the spectral line type of the interfering element is not known.

To specify an interference simply select the element that is interfered with from the Standard and Interference Assignments window and select the interfering element from the element list of analyzed elements. If the interfering element is not already an analyzed element, it must be added to the sample setup using the Elements/Cations button in the Acquire! window. Next select a standard to be used for the interference calibration from the list of standards in the run. If the standard is not currently in the run, it must be added to the run using the Standards | Add Standards To Run menu item and have data acquired for it.

Standards which may be used in the interference corrections should not be run as "quick" standards unless they have already been assigned for the unknown sample. Data for the interfered channel is necessary to calibrate the correction which may not be present with a "quick" standard. If you find that you need to apply an interference correction which has already been run as a "quick" standard, you can simply re-run the standard again, this time though ***not*** as a "quick" standard. It is not necessary to delete the previous "quick" standard as the program will automatically find the necessary intensities.

Note that once a sample setup has had interferences assigned, the program will automatically acquire the necessary intensity data even if the quick standard option has been selected.

As an example of the interference assignment, consider the following : when analyzing for iron and manganese, you may notice that when high concentrations of manganese are present, that small amounts of iron will also appear to be present due to an interference of Mn Kβ with the Fe Kα analytical line. To correct for this interference you need a standard that contains manganese but does not contain any iron. Often, you can assign the same standard that is used for the primary standard calibration, also for the interference calibration, in this case, a MnO synthetic crystal. You could also use any other manganese standard not containing appreciable iron such as a synthetic manganese silicate.

Note that if you needed to analyze for Fe, but Mn was not present in any significant quantity, you could justifiably ignore the interference, since you would never see it. What can be considered an insignificant interference is something that needs special consideration.

One useful suggestion is to use either the Standard for Windows program's Interference menu item or, even better, use the Interferences button in the standard assignment dialog to provide an approximate calculation of the interference. The program will calculate the interference based on a gaussian peak shape by assuming a worst case of 0.1% of the analyzed element and 100% of each of the other analyzed (and possibly interfering elements).

Note that in the above case, Mn interferes with Fe, but the reverse is not true : Fe does not interfere with Mn. However in some cases both elements interfere with each other. Probe for Windows can also handle this situation because the interference correction is an iterated solution. For example : consider the case of Ti Kα and Ba Lα. Both lines interfere with each other and both lines are used for quantitative analysis. To correct for this double Ti and Ba interference, the analyst will be required to analyze for both Ti and Ba. In addition, two interference standards will be required. To correct for the interference on Ti, a standard will be needed that contains Ba, but no Ti. To correct for the interference on Ba, a standard will be needed that contains Ti, but no Ba. In practice, if you used TiO_2 for the Ti and barite ($BaSO_4$) for Ba, as the analytical standards, you can also use Barite as the Ti interference standard and TiO_2 as the Ba interference standard.

The actual form of the quantitative interference within the ZAF iteration loop is given below :

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I^u(\lambda_A) - \frac{[ZAF]_{\lambda_A}^{\bar{s}}}{C_B^{\bar{s}}} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^{\bar{s}}(\lambda_A)}{I_A^s(\lambda_A)}$$

Where the following notation has been adopted :

C_i^j	is the concentration of element i in matrix j
$[ZAF]_{\lambda_i}^j$	is the ZAF (atomic #, absorption and fluorescence) correction term for matrix j (Z and A are for wavelength λ_i and F is for the characteristic line at λ_i for element i)
$I_i^j(\lambda_i)$	is the measured x-ray intensity excited by element i in matrix j at wavelength λ_i.
$\bar{s}$	refers to an interference standard which contains a known quantity of the interfering element B, but none of the interfered with element A.

The quantitative interference corrections in Probe for Windows allow the user to correct for up to 5 interfering elements per channel. Since the solution is iterated the program can correct for interferences when two (or more) analytical lines interfere with each other. See Donovan, et al., (1993) for more details on the derivation of the quantitative interference correction used here.

Note also that you can use a standard for the analytical calibration, even if the element channel used for the calibration is interfered with, as long as you correct for the interference as described above. In the case of a standard that contains interfered elements, the correction of the standard counts is simple, since the composition, is by definition, already known from the standard database. Therefore, in the case of standards at least, an iterated procedure is not required.

Area Peak Factors and Standard Assignments

Another consideration in assigning standards concerns the use of Area Peak Factors (APFs) for corrections to effects of peak shift and shape changes. These occur for light element K lines as well as L lines of certain elements, e.g. Co (recall that this is due to involvement of electrons from the valence shell, L shell for K lines, M shell for L lines). These changes are most noticeable on TAP and Pb-stearate, barely if at all with the layered synthetic diffractors. When analysis of the affected elements/lines is to be performed (typically oxygen, nitrogen, carbon and boron but possibly silicon, aluminum and sulfur), you need to plan the use of APF corrections for the most accurate results. The actual APF values selected will depend upon the standard assigned, and also the specific crystal used on the spectrometer.

For example, when analyzing for C Kα and using Fe_3C as your carbon standard, your APF value for C Kα in a Cr_7C_3 matrix might be 0.80. However, if instead, you re-assigned your carbon standard to TiC, you must use APF values relative to TiC rather than Fe_3C. If they are available in the Empirical APF database (EMPAPF.DAT), just change the APF values for C Kα. Otherwise you would need to calculate the Fe_3C APF values relative to TiC. Some typical Fe_3C APF values for C Kα, recalculated relative to TiC and Cr_7C_3, are shown in the table below :

APF Relative To :	**Fe_3C (APF/1.000)**	**TiC (APF/0.868)**	**Cr_7C_3 (APF/0.80)**
Fe_3C	1.000	1.152	1.25
TiC	0.868	1.000	1.085
Cr_7C_3	0.80	0.92	1.00

Checking (Secondary) Standards

Once the primary standards are assigned it is recommended to analyze the standards to check for internal consistency. For this, the acquisition of secondary standards is preferred. Secondary standards are standards in which no elements (or only some) are not assigned as the primary standard for the analyzed elements.

There are two ways to check your standards, either using the Evaluate utility to graphically view together all standards that have an element acquired, or by viewing the result (in Analyze!) of using the primary standard to analyze a secondary standard.

Evaluate! runs as a standalone utility, with the mdb file being read in and the user then selecting an element-spectrometer pair. All standards with counts on that pair (e.g. Si Ka-Sp4) will be plotted with the declared element wt% on the X axis. The user selects the specific type of count data to be plotted on the Y axis, e.g. ZAF-corrected average counts. A set of good standards would then all fall on a straight line through all the points as well as (0,0). This is discussed in more detail elsewhere.

The other method is to review the secondary standards one by one, in the Analyze! Window. First select all the standards. Then check the Pause Between Sample check box. Then click the Analyze button. The program will pause between each sample analysis to allow the user to view the results. Look over the results carefully. Standards whose x-ray intensities have been assigned as the standard for that element will normally look close to perfect since they are by definition the primary standard. The other unassigned elements are treated as unknowns and by observing the "%VAR" (percent variance) line, one can get an idea of the quality of the standardization by examining these secondary standards.

For example, assume that you are analyzing for Si, Al, Na and K and your assigned standards are SiO_2 for Si, $NaAlSi_3O_8$ (albite) for Al and Na, and $KAlSi_3O_8$ (orthoclase) for K. In this case SiO_2 is your primary standard for Si, and both albite and orthoclase can serve as secondary standards to check the quality of the Si calibration since they are measured for but not assigned as calibration standards for Si. In addition, the orthoclase standard can be used as a secondary standard in the example above, to check the Al calibration. Therefore, orthoclase is the primary standard for K, but is a secondary standard for both Si and Al, and albite is the primary standard for Al and Na, but is a secondary standard for Si only, while SiO_2 is the primary standard for Si only. Note that a pure standard such as synthetic SiO_2 can be used to check the quality of the background correction on the Al, Na and K channels in this example, since pure SiO_2 should not contain those elements in significant quantities.

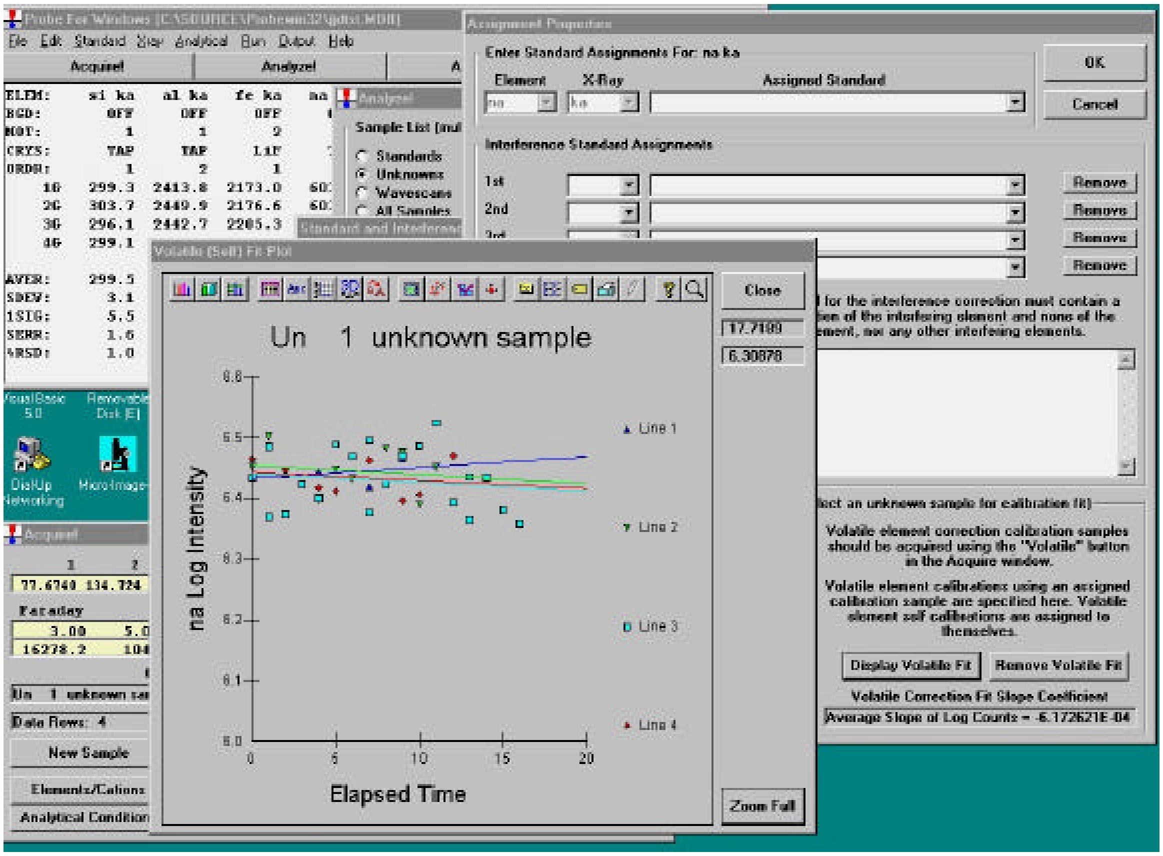
While looking over the standard results, look carefully for "bad" points. By this, it is meant points whose total compositions are anomalously low. These could be points where the beam was on epoxy or perhaps the surface was poorly polished. In any case you will see this as a low total. These points may be deleted.

Note that points whose totals are high, on the other hand, should not be deleted arbitrarily. High totals indicate that something else is wrong. Check for low total points on another standard or for the presence of spectral interferences or inclusions.

Volatile Element Corrections

It is well known that measurements of x-ray intensity in glass matrices of certain elements, such as Na and K, show a sharp drop off in count rate under normal beam currents (10 or 20 nA). This is informally known as volatile element behavior, although technical explanations suggest electron implantation in insulators and/or heating cause migration of atoms either deeper into the material, or out of the sample into the vacuum (Linebarger ref). Coincident with the effective loss of one element, there may be an increase in x-ray counts of other elements in the material (such as Si and Al), referred to as "grow in" (Morgan and London, 1996). There are several ways to minimize this effect (lower beam current, defocus beam), but they may not be useful in certain circumstances.

Probe for Windows offers a volatile element extrapolation, whereby a short time series of measurements are made for the element(s) in question. This can be done for both the volatile element and any grow-in elements, as well as for other situations where X-ray intensity changes during beam irradiation, e.g. carbon contamination, beam damage, etc. This correction is useful for samples that are too small to utilize a defocused beam, and allows the user to apply higher beam currents to improve the analytical sensitivity.



```
ELEM:    si ka   al ka   fe ka   na
BGD:      OFF     OFF     OFF
ROT:        1       1       2
CRYS:     TAP     TAP     LiF
ORDR:       1       2       1
  1G    299.3  2413.8  2173.0   60
  2G    303.7  2449.9  2176.6   60
  3G    296.1  2442.7  2205.3
  4G    299.1

AVER:   299.5
SDEV:     3.1
1SIG:     5.5
SERR:     1.6
%RSD:     1.0
```

17.7189

6.30878

Enter Standard Assignments For: na ka

Element: na

X-Ray: ka

Assigned Standard

Interference Standard Assignments

1st

2nd

3rd

...for the interference correction must contain a ...tion of the interfering element and none of the ...ement, nor any other interfering elements.

...lect an unknown sample for calibration (R)

Volatile element correction calibration samples should be acquired using the "Volatile" button in the Acquire window.

Volatile element calibrations using an assigned calibration sample are specified here. Volatile element self calibrations are assigned to themselves.

Volatile Correction Fit Slope Coefficient

Average Slope of Log Counts = -6.172621E-04

Acquire!: 1 77.6740, 2 134.724

Faraday: 3.00, 5.0; 16278.2, 104

Un 1 unknown sa...

Data Rows: 4

Two different methods are utilized by Probe for Windows to correct for volatile element behavior: the first is an assigned method where an unknown sample is acquired and then later assigned for use as a calibration curve for one or more samples. The other is a "self" calibration where intermediate intensities are saved as the data is acquired and later used as the basis for calculating the volatile correction.

Mathematical Method

In both cases, the slope coefficient is calculated using a linear fit of intensity versus elapsed time. Intensities that are less than or equal to zero are ignored. The count data is normalized to counts per second and the natural log taken. The elapsed time is converted to seconds and the linear (straight line) fit is calculated. Only the slope parameter is saved for the actual volatile correction to allow the correction to be applied to a variety of samples that may contain different absolute intensities at different times (due to beam or standard drift).

Once the slope is calculated it is used in the following expression to adjust the unknown intensity for volatile element loss (or gain):

$$I_C = e^{Log(I_R) - m \cdot t}$$

where: I_R = Raw (uncorrected) intensity in counts per second

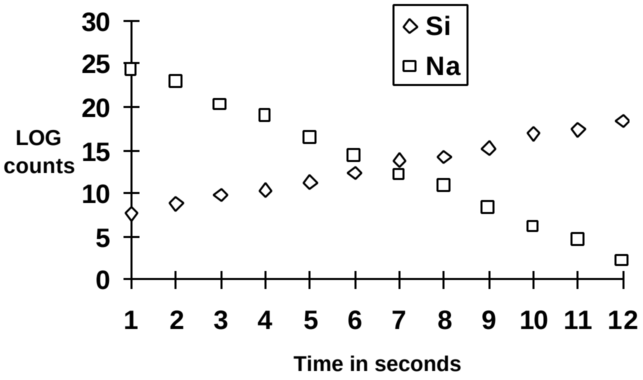
m = Volatile slope coefficient from linear fit of Log intensity versus time

t = Count time for the raw (uncorrected) intensity

Typical Situation for Volatile Correction

For instance, when sodium loss in observed in an alkali glass sample, a corresponding gain in silicon and aluminum x-rays may be noted. The extrapolation correction used in Probe for Windows can be applied to some or all elements in an sample, regardless of whether the x-ray intensities are decreased or increased during the acquisition **(as long as the elements to be corrected are acquired as the first element on each spectrometer, i.e., order number = 1)**.

The correction assumes that the change in counts is linear versus time when the natural LOG of the x-ray counts are plotted (Nielsen and Sigurdsson, 1981) as shown here :



Depending on the sample, this may or may not be a valid assumption. Under certain conditions, with very volatile hydrous alkali glasses, the change in count rate may actually decrease more quickly than a simple log decay. In this case, it may be necessary to defocus the beam slightly or reduce the beam current before acquisition.

How to Use the Volatile Correction

To utilize the volatile correction first decide if you require an assigned calibration curve type correction or a self calibration curve type correction. In the self calibration correction the user simply selects the "Self-Calibration" option (see Special Options button in the Acquire! Window) and acquires the data point(s) as one would normally. In the assigned volatile correction the user first selects a sample that is similar in volatile characteristics to the sample to which the assigned calibration curve will be assigned to (it could be the actual sample itself) and then selects the "Assigned Calibration" option (see Special Options button in the Acquire! Window). The next acquisition that is started will create a calibration curve sample that can be assigned to one or more samples for the purpose of correcting volatile loss or grow-in.

The difference between the two methods is that the assigned calibration curve will apply the same slope correction to all points within the assigned sample. Therefore the variation seen in the (assigned calibration) corrected sample concentrations reflects only the actual variation in the sample. On the other hand, the self calibration method acquires a calibration curve separately for each data point and therefore the variation from point to point may be partially due to statistical variation between the self-calibration curves.

Both of the calibration corrections are quantitative in that the correction is based on a calibration curve acquired during the run, on the sample itself or another sample of similar characteristics, and is applied during the ZAF or Phi-Rho-Z iteration phase of the analysis to correct for changes in the matrix correction due to the extrapolation correction. Any number of calibration samples may be acquired and any sample or range of samples can be assigned to use any of the calibration samples for the extrapolation correction. Note that the a previously assigned volatile element correction is automatically loaded for new unknown samples.

Note that the correction uses the actual elapsed time for all calculations to produce the best quantitative results. Nevertheless, the user should be aware that the technique must be applied carefully to obtain the best results.

One possible source of error, with this calculation, is that the correction is not applied to the standard calibration itself. For this reason, it is essential to use standards for all the analyzed elements that are stable under the beam. If it is not possible, for instance, to run your albite standard without affecting the count intensities in the acquisition time used, it would be better to avoid the volatile element extrapolation and use a standard that is similar to the unknown sample itself.

Another concern is with samples that contain more than one affected element on a given spectrometer. Exactly how the volatile element correction should be applied in such situations is not clear, and therefore Probe for Windows will only apply the volatile element correction for elements that are acquired first on a given spectrometer.

Name/Description

Probe for Windows allows the user to change the sample name and description fields at any time. Use the Insert <cr> button to add a carriage return to the description field for multi-line comments.

The name field is limited to 64 characters and the description field is limited to 255 characters. Any printable characters may be used along with spaces for the name or description of the sample(s).

Conditions

The conditions dialog can be used to display the sample conditions. These include the operating voltage in kilovolts, the takeoff angle in degrees, the beam current in nA and the beam size in microns. These fields are used for documentation purposes only, unless the hardware interface is supports controlling these instrument parameters.

For the SX50 interface (InterfaceType=6) and if the BeamSizePresent flag is true in the PROBEWIN.INI file, the beam size parameter will force the instrument into FIX mode and set the beam size using the SIZE command. In this mode the instrument beam scanning is disabled. Therefore if beam scanning is desired, the beam size should be set to zero so that a SIZE OFF command is sent to the instrument which will enable the beam scanning.

Elements/Cations

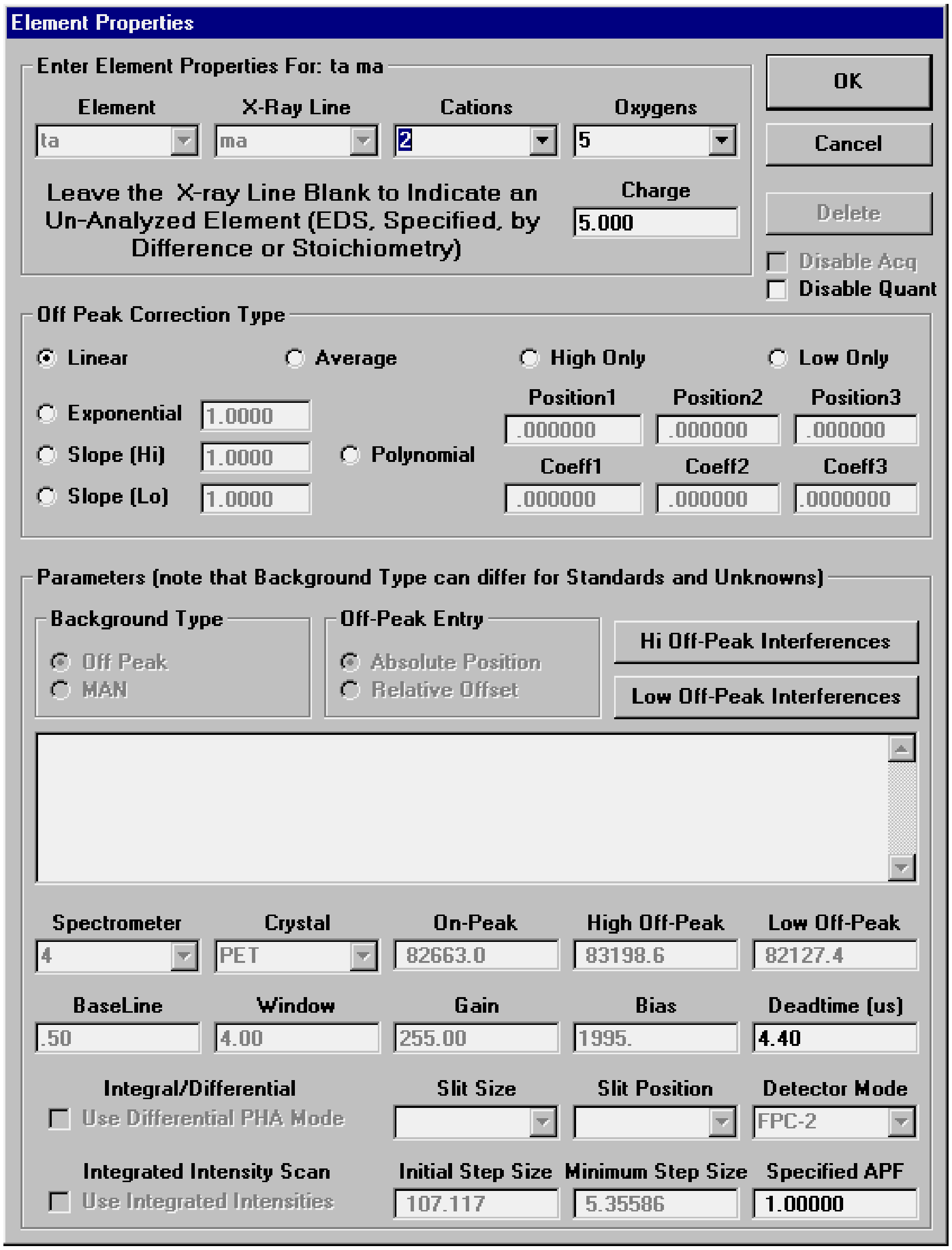
Clicking the Elements/Cations button opens the analyzed and specified elements dialog box. The analyzed and specified dialog box lists the currently selected elements for analysis and calculations.

Use this button to add specified elements (elements calculated as fixed concentrations or by difference or stoichiometry) to the selected samples. Also the element cations and oxygens can be changed on a sample by sample basis for the calculation of oxide weight percents.

> **Use the Save Element Setup button to save element setups to the element setup database for use in future runs. Normally one should save the element setup of an element that is assigned as the standard for that element. In this case the standard intensity data is saved to the element setup database for reference purposes.**
>
> **Use the Save Sample Setup button to save the currently selected sample as a sample setup for use in creating subsequent samples within the current run. Note that selecting a previous sample setup will update the current element setup with the selected sample setup.**

If the element was disabled for acquisition the Disable Acq checkbox will be checked. To uncheck this option for a sample containing data, first create a new sample and then uncheck the Disable Acq option.

To disable the element for quantitative calculations, check the Disable Quant checkbox. The program will set the intensity to zero for the matrix correction calculations. To restore the element for quantitative calculations, simply uncheck the box. Normally this is only used for special reprocessing situations.



Enter Element Properties For: ta ma

Element: ta
X-Ray Line: ma
Cations: 2
Oxygens: 5
Charge: 5.000

Leave the X-ray Line Blank to Indicate an Un-Analyzed Element (EDS, Specified, by Difference or Stoichiometry)

☐ Disable Acq
☐ Disable Quant

Off Peak Correction Type

● Linear
○ Average
○ High Only
○ Low Only
○ Exponential 1.0000
○ Slope (Hi) 1.0000
○ Slope (Lo) 1.0000
○ Polynomial

Position1	Position2	Position3
.000000	.000000	.000000

Coeff1	Coeff2	Coeff3
.000000	.000000	.0000000

Parameters (note that Background Type can differ for Standards and Unknowns)

Background Type
● Off Peak
○ MAN

Off-Peak Entry
● Absolute Position
○ Relative Offset

Spectrometer	Crystal	On-Peak	High Off-Peak	Low Off-Peak
4	PET	82663.0	83198.6	82127.4

BaseLine	Window	Gain	Bias	Deadtime (us)
.50	4.00	255.00	1995.	4.40

Integral/Differential
☐ Use Differential PHA Mode

Slit Size:
Slit Position:
Detector Mode: FPC-2

Integrated Intensity Scan
☐ Use Integrated Intensities

Initial Step Size: 107.117
Minimum Step Size: 5.35586
Specified APF: 1.00000

From the Analyze! window, only samples with no data can have their acquisition parameters modified. Parameters for samples that contain data can only be viewed. However, the off-peak type and deadtime parameter can be modified in either case. Off-peak correction types include linear, average, high only, low only, and exponential in addition to slope and polynomial fit backgrounds. Plot a wavescan sample(s) in the Plot! Dialog and click the Model Backgrounds button to see the various background options graphically.

Probe for Windows uses a linear slope calculation as the default off-peak background correction. Because of this, unsymmetrically offset background position measurements can be easily handled. One can even position both of the off-peak measurements on the same side of the peak or even ignore one background measurement if an error is discovered after-the-fact, that one off-peak position was interfered with.

Off Peak Background Correction Types

Probe for Windows allows the user to select the off-peak type for the background correction. The default slope calculation is the most accurate, except in cases where the user has moved both off-peak positions to the same side of the analytical peak and adjusted the off-peaks excessively close together resulting in a large extrapolation. The off-peak correction types are as follows :

0 = linear slope interpolation or extrapolation
1 = average of both high and low off-peak counts
2 = use only the high off-peak counts
3 = use only the low off-peak counts
4 = exponential off-peak calculation (based on exponent)
5 = slope-high (based on high off-peak and slope coefficient)
6 = slope-low (based on low off-peak and slope coefficient)
7 = polynomial (based on high and low off-peak and three coefficients)

These off-peak background correction types may be assigned on a sample by sample basis either on or off-line. Note that the actual values of the polynomial fit coefficients are dependent on the absolute magnitude of the count intensities. For this reason it is important to avoid changing the value of the nominal beam current once any polynomial fit coefficients have been assigned to samples in the run. The calculations for linear slope and exponential calculation are shown below :

Linear Slope Calculation

$$I_{off} = I_{low} + (I_{high} - I_{low}) \bullet \frac{(P_{on} - P_{low})}{(P_{high} - P_{low})}$$

where :
I_{off} = the off-peak count correction
I_{high} = the x-ray counts for the high off-peak position
I_{low} = the x-ray counts for the low off-peak position
P_{high} = the high off-peak position
P_{low} = the low off-peak position
P_{on} = the on peak position

Exponential Slope Calculation

$$I_{off} = \frac{ce^{-aP}}{P^{N}}$$

where :
I_{off} = the off-peak background intensity
P = the spectrometer position
c = a fit parameter
a = a fit parameter
e = the exponential

N = a user specified exponent

Note that the slope and polynomial off-peak corrections are calculated for each sample line based on the actual measured off-peak intensities for the sample. The coefficients can be modeled from the Plot! Window by displaying a wavescan sample in the Graph dialog and clicking the Model Background button.

Same Side Off-Peaks

Beware of placing same-side off-peaks too close together if you are using a background type other than average, high only or low only (for example, the default: linear extrapolation). A large extrapolation can cause a very large error in the off-peak background correction if the background standard deviation is large and using a linear fit. The program will print a warning if it feels that the same-side off-peak extrapolation is excessive. In cases where the same side off-peak extrapolation is excessive, the user may want to select using the average of the off-peak counts. Of course, averaging the off-peak counts is really only applicable in situations where the background slope is zero.

For example, there may be some situations where interferences either above or below the peak require placing both off-peak background measurements on one side. There is nothing wrong with this, as long as "average" is used. A linear extrapolation in many situations, especially when the 2 positions are very close together, will produce an obviously incorrect background model if the background standard deviation is large. The program will print a warning alerting the user to the possibility of possible incorrect background selection. Averaging the off-peak counts is applicable where the background (arithmetic) slope is zero (or equivalent to a "slope-factor" of 1.0).

Interferences

The High and Low Off-Peak Interference buttons can be used when both the potential interfering and interfered with elements are already present in the sample setup to determine the approximate magnitude of the off-peak interferences. This calculation is based on a gaussian peak shape and various crystal defaults and is intended as a guideline only for off-peak position entry.

The program assumes a nominal concentration of 100% of the interfering element and 0.1% of the interfered with element in each binary pair calculation. For example, if the percent interference is calculated as 10%, then that indicates that instead of measuring 0.1 wt. % of the element, it is likely that a concentration of 10% greater than 0.1 wt. % or 0.11 wt. % will be measured. Note that since this is only a nominal calculation, it should only be used as an indicator of possible problematic analytical situations.

Specified Area Peak Factors (fixed composition APF)

As an alternative to the "calculated" Area Peak Factors, Probe for Windows offers the use of "fixed" composition Area Peak Factors. These are single values that are applied to the element intensity on an emitter basis (as opposed to calculated based on the actual absorber concentrations in the matrix).

These factors may be useful in certain situations where the compositional range is limited and binary Area Peak Factors are not available for some or all elements in the matrix (e.g., Na, K or Ca in an oxygen matrix). This option may be turned off or on in the Analysis Option dialog under the Analytical menu.

Save Element Setup

This button opens the element setup database dialog. Here the user can save element setups to the setup database for re-use in another run or sample setup.

Generally, one usually saves standard sample element setups for elements that are assigned to that standard to the setup database. Later, one can retrieve these calibrated setups for use in creating new sample setups for acquisition in another run.

It is recommended that the user save element setups after selecting the primary standard for that element. In this way the element setup database will preserve a record over time of the peak intensities and peak to background ratios for evaluation purposes.

Save Sample Setup

This button activates the Sample Setup dialog box. Here the operator can save sample setups for starting a new sample based on the previous sample setup within the current run.

Subsequently the user can use the Load Sample Setup button in the New Sample dialog (accessed from the Acquire! window) to create new analytical samples or the Setup dialog from the Automate! window when digitizing position samples for automated acquisition.

Note that the saving of a sample setup actually saves only a pointer to the sample selected. This means that any changes to the sample setup calculation options, elements/cations, standard assignments, etc. will be utilized when a new sample is created based on the modified sample setup.

Delete Selected Line(s)

Use this button to *delete* a single data point or a contiguous range of data points (using the mouse to click and drag a range). Any data points thus deleted will be flagged "B" for "bad" and will not be used in any analysis or calculations until it is undeleted. Points already deleted are not affected.

Select the lines to be deleted in the Data grid by clicking and dragging the mouse. Only contiguous ranges of lines of data may be deleted using this feature. Non-contiguous points will have to be deleted individually.

When analyzing your standards, look carefully for "bad" points. By this, it is meant points whose total compositions are anomalously low. These could be points where the beam was on epoxy or perhaps the surface was poorly polished. In any case you will see this as a low total. These points should usually be deleted. Note that points whose totals are high, on the other hand, should not be deleted arbitrarily. High totals indicate that something else is wrong. Check for low total points on another standard, check for inclusion s using BSE, or run a wavescan to look for the presence of spectral interferences both on and off-peak. Off peak interferences usually produce negative k-ratios while on-peak interferences can produce high values (high totals in extreme cases).

Undelete Selected Line(s)

Use this button to *undelete* a single data point or a range of data points. Any data points thus undeleted will be flagged "G" for "good" and will be used in any analysis or calculations until it is deleted. Points already undeleted are not affected.

Select the lines to be undeleted in the Data grid by clicking and dragging the mouse. Only contiguous ranges of lines of data may be undeleted using this feature. Non-contiguous lines must be undeleted individually.

List Report

This button will list all standard, background and interference calibration intensities that are associated with the currently selected sample(s) to the log window for inspection. This is useful to determine, for example, the drift in count rates from one standardization to another or the magnitude of the interference overlaps.

Because each sample can be assigned different standard and interference assignments, be sure that the desired sample is selected before clicking this button to see the specific standard and interference standard intensities. This output also includes the measured or calculated background count rates on each standard set.

It is possible to use this button on multiple selected samples, even if they contain different element setups and assignments. In this case, the program will print a complete report for each different element setup selected.

Calculation Options

The following calculation options are available from the Analyze! window. Note that these options do not need to be explicitly set for use from the Plot! window with the exception of the Formula element and basis.

Do Not Use/Use EDS Weight Percent Data/Use EDS Spectral Intensities

If integrated EDS/WDS acquisition data is available for this sample then this option will allow the user to choose whether to use or not use the EDS data stored in the user data file when the matrix correction is calculated. See the Acquisition Options dialog for this acquisition option.

Do Not Use/Use Integrated Intensities

If integrated WDS intensity data is available for this sample, then this option will allow the user to choose whether to use or not use the stored integrated intensities in the quantitative calculations. See the Elements/cations dialog for this acquisition option.

If this user chooses to use the integrated intensities then the program will calculate the deadtime and beam drift correction for the raw integration data and then calculate the integrated area. Finally the program will then calculate the integrated background based on the currently selected background model and subtract that from the integrated intensities. Note that standards acquired using the integrated intensity option must also be acquired for this option.

If the user chooses not to use the integrated intensities then the program will use the peak intensity from the integrated data. Again, for this mode, the standards must still be acquired using the integrated acquisition intensity option and also have the integrated intensities analysis option turned off.

Display Results As Oxides and Calculate With Stoichiometric Oxygen

Probe for Windows allows the user to display the results of an analysis in oxide weight percents 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.

Formula and Mineral Calculations

The program can compute formulas based on any number of oxygens for oxide runs or any analyzed or specified element in elemental runs. In addition you may select either an olivine, feldspar, garnet (2 varieties) or pyroxene end-member calculation if you choose a formula based on oxygen.

It should be noted that the formula calculations are based only on atomic weight and do not consider charge balance and site occupancy for the calculations. For more complicated mineral calculations it is recommended to utilize a 3rd party mineral recalculation software. Please contact Advanced Microbeam for more information.

Calculate Atomic Percents

The program can compute the analyses in atomic percent also. The program will calculate the results based on atomic weight and normalized to 100%. This calculation is sometimes known also as elemental mole percents.

Note that this calculation should not be used if the elemental weight per cent total indicates a serious problem with the analysis, i.e. less than 98 or more than 102 wt %.

Element by Difference

An element by difference can be included in this way also to account for its affect 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 acquire just the cations (Fe, Mg, Ca, etc.) intensities 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.

The following is an analysis example of carbon calculated by stoichiometry to oxygen in a carbonate sample for an oxide run :

```
Analysis of sample  st 135   set  2   calcite (analyzed)
Total Number of Data Points =   5            Number of "G" Data Points =   5
Average Beam Counts =   45527.                  Average Base Time =    10.00
Average Sample Z-bar =   12.572            Average BNA Iterations =   11.000
Element : C   is Calculated Relative to Stoich. Oxygen at   .333 to 1.0 Atom

Results in Weight Percent :

        CO2     Cl      MgO     FeO     MnO     O       SUB

SPEC   43.82     .00     .00     .00     .00     .00   43.82
SDEV     .19     .00     .00     .00     .00     .00

BGD:   MAN     MAN     MAN

        CaO     SO3     P2O5    SUM
  29   55.60     .01    -.01   99.12
  30   56.18     .04    -.01  100.22
  31   56.16     .01     .00  100.10
  32   56.02    -.01    -.02   99.77
  33   56.10    -.01     .01  100.00

AVER   56.01     .01    -.01   99.84
SDEV     .24     .02     .01
SERR     .11     .01     .00
PUBL   56.01    n.a.    n.a.   99.90
%VAR     .00     .00     .00
          *

BFAC  1.0314   .9925  1.0285
KRAW  1.0001   .0001  -.0001
P/B:  277.12    1.02     .87
```

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 stoichiometry (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! The following is an example of how this calculation looks :

```
Analysis of lines:
   23   24   25   26   27   28   29   30
Total Number of Data Points =   8            Number of "G" Data Points =   8
Average Beam Counts =   98504.                  Average Base Time =    10.00
Average Sample Z-bar =   10.816           Average ZAF Iterations =    5.000
Element : Al  is Calculated Relative to Stoich. Oxygen at   .666 to 1.0 Atom
Element : O       is Calculated by Stoichiometry

Results in Weight Percent :

        Se      O       Al      Si      SUB

SPEC     .00   46.68   52.41     .05   99.14
SDEV     .00     .02     .02     .00

BGD:   OFF     OFF     OFF

        Zn      Cu      Pd      SUM
  23     .59     .30     .01  100.02
  24     .56     .30     .01  100.02
  25     .57     .32     .00  100.02
  26     .58     .33     .00  100.02
  27     .53     .33     .02  100.02
  28     .55     .39     .01  100.02
  29     .54     .26     .00  100.02
  30     .56     .31     .01  100.02

AVER     .56     .32     .01  100.02
SDEV     .02     .04     .01
SERR     .01     .01     .00

KRAT   .0047   .0027   .0000
ZCOR  1.2009  1.1976  1.2321
```

```
KRAW   .0093   .0027   .0000
P/B:    2.70    2.29    1.02
%INT    -.05     .00     .00


Results in Oxide Weight Percents using Custom Cation Oxide Ratios :

       Se      O       Al2O3   SiO2

AVER    .000    .000  99.029    .107
SDEV    .000    .000    .040    .000

       Zn      Cu      Pd      SUM
  23    .592    .302    .006 100.022
  24    .556    .300    .015 100.022
  25    .574    .323    .000 100.022
  26    .581    .330    .000 100.022
  27    .528    .332    .018 100.022
  28    .550    .386    .008 100.022
  29    .543    .262    .001 100.022
  30    .561    .308    .013 100.022

AVER    .561    .318    .008 100.022
SDEV    .021    .035    .007
```

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 (acquired) or specified element as the stoichiometric basis element.

This calculation can be used in combination with the other calculations to handle unusual analytical situations. For example, in the following analysis of an silica sample, the results revealed significant contamination of the material with Fe and Ca. Investigation using other techniques, implied that the Fe was in the form of Fe_2O_3 (hematite), and the Ca was present as $CaCO_3$ (calcium carbonate). Aside from the effect of inhomogeneity on the matrix correction, it was desirable to improve the calculation by calculating Si by difference and C by stoichiometry to Ca as follows :

```
Analysis of sample  un   2   seoj #3 random
Total Number of Data Points =   6            Number of "G" Data Points =   3
Average Beam Counts =   79092.                  Average Base Time =    10.00
Average Sample Z-bar =   11.480            Average ZAF Iterations =    2.333
Oxygen Calculated by Cation Stoichiometry and Included in  Matrix Correction
Element : Si  is Calculated by Difference from a Sum of 100.0 Weight Percent
Element : C   is Calculated Relative to Element Ca   at    1.000 to 1.0 Atom

Results in Weight Percent :

       O       Si      C       La      F       SUB

SPEC  51.526  39.743   1.134    .000    .000  92.403
SDEV   2.932  11.897   1.939    .000    .000

BGD:   MAN     MAN     MAN     MAN     MAN     MAN
```

```
       Fe      Al      Ca      Mg      Mn      S       SUM
 133    .054    .018    .012    .009    .000    .000 100.000
 134  10.696    .467  11.253    .010    .054    .000 100.000
 135    .119    .013    .083    .004    .000    .000 100.000

AVER   3.623    .166   3.782    .008    .018    .000 100.000
SDEV   6.126    .261   6.470    .003    .031    .000
SERR   3.537    .151   3.735    .002    .018    .000

KRAT   .0306   .0013   .0353   .0001   .0001   .0000
ZCOR  1.1992  1.2245  1.0981  1.3804   .9338   .8713
KRAW   .0451   .0029   .2072   .0001   .0002   .0000
P/B:   14.07    4.78   43.69    1.45    1.07     .92


Results in Elemental Mole Percents :

       O       Si      C       La      F

AVER  65.743  28.728   2.004    .000    .000
SDEV   1.571   7.841   3.430    .000    .000

       Fe      Al      Ca      Mg      Mn      S       SUM
 133    .019    .014    .006    .007    .000    .000 100.000
 134   4.069    .368   5.965    .009    .021    .000 100.000
 135    .043    .010    .041    .003    .000    .000 100.000

AVER   1.377    .130   2.004    .006    .007    .000 100.000
SDEV   2.332    .206   3.430    .003    .012    .000


Results in Oxide Weight Percents using Custom Cation Oxide Ratios :

       O       SiO2    CO2     La2O3   F

AVER    .000  85.024   4.153    .000    .000
SDEV    .000  25.452   7.104    .000    .000

       Fe2O3   Al2O3   CaO     MgO     MnO     SO3     SUM
 133    .077    .035    .017    .014    .000    .000 100.000
 134  15.293    .883  15.745    .017    .070    .000 100.000
 135    .170    .024    .116    .006    .000    .000 100.000

AVER   5.180    .314   5.292    .013    .023    .000 100.000
```

Note that Fe was recalculated as Fe_2O_3 and C was added relative to Ca by stoichiometry. This calculation can be applied in numerous other ways to a variety of analytical situations. Consider the example below. Here, the user decides to calculate CO_2 on the basis of moles of CaO, rather than by stoichiometry to oxygen.

```
Analysis of sample  st 141   set  1   dolomite (Harvard #105064)
Total Number of Data Points =   3            Number of "G" Data Points =   3
Average Beam Counts =    9102.                  Average Base Time =    10.00
Average Sample Z-bar =   10.875            Average BNA Iterations =    5.000
CO2   is Calculated Relative to Oxide CaO    at    2.000 to 1.0 Mole

Results in Weight Percent :
```

```
       CO2     SUB

SPEC  47.791  47.791
SDEV    .071

BGD:   MAN     MAN

       CaO     MgO     SUM
   9  30.501  21.735 100.109
  10  30.424  21.769  99.947
  11  30.420  22.135 100.301

AVER  30.448  21.880 100.119
SDEV    .046    .222
SERR    .026    .128

PUBL  30.560  21.880 100.186
%VAR   -.365   -.001
                  *

UNBE  1.0496  1.2242
KRAW   .5338  1.0000
P/B:     .00     .00


Results in Oxide Mole Percents :

       CO2

AVER  50.002
SDEV    .139

       CaO     MgO     SUM
   9  25.053  24.841 100.000
  10  25.028  24.917 100.000
  11  24.922  25.233 100.000

AVER  25.001  24.997 100.000
SDEV    .069    .208
```

Calculate Detection Limits and Homogeneity

The user may also select a calculation of the sample detection limits based on the standard counts and the unknown background counts and including the magnitude of the ZAF correction factor. The calculation is adapted from Love and Scott (1983). This detection limit calculation is useful in that it can be used even on inhomogeneous samples and can be quoted as the detection limit in weight percent for a single analysis line with a confidence of 99% (assumes 3 standard deviations above the background).

$$CDL = (ZAF)\frac{3}{I_S}\sqrt{I_B}\cdot 100$$

Where :	ZAF	is the ZAF correction factor for the sample matrix
	I_S	is the raw counts on the analytical (**pure element**) standard

I_B is the raw background counts on the unknown sample

After this, a rigorous calculation of analytical error also for single analysis lines is performed based on the peak and background count rates also from Love and Scott. The results of the calculation are displayed after multiplication by a factor of 100 to give a percent analytical error of the net count rate. This analytical error result can be compared to the percent relative standard deviation (%RSD) displayed in the analytical calculation (both are one standard deviation confidence levels). The analytical error calculation is as follows:

$$e_{P-B} = \frac{\sqrt{\dfrac{N_P}{t_P^2} + \dfrac{N_B}{t_B^2}}}{\left(\dfrac{N_P}{t_P} - \dfrac{N_B}{t_B}\right)}$$

Where : N_P is the total peak counts

N_B is the total background counts

t_P is the peak count time

t_B is the background count time

A more comprehensive set of calculations for analytical statistics is also performed. These statistics are based on equations adapted from "Scanning Electron Microscopy and X-Ray Microanalysis" by Goldstein, et. al. (Plenum Press, 1992 ed., 1981) p. 432 - 436. All calculations are expressed for various confidence intervals from 60 to 99 % confidence.

The calculations are based on the number of data points acquired in the sample and the measured average and standard deviation for each element. This is important because although x-ray counts theoretically have a standard deviation equal to square root of the mean, the actual standard deviation is usually larger due to variability of instrument drift, x-ray focusing errors, and x-ray production. The statistical calculations include :

1. The range of homogeneity in plus or minus weight percent.

$$W_{1-\alpha} = \pm C \frac{t_{n-1}^{1-\alpha}}{n^{1/2}} \frac{S_C}{\overline{N}}$$

2. The level of homogeneity in plus or minus percent of the concentration.

$$\pm \frac{W_{1-\alpha}}{C} = \pm \frac{(t_{n-1}^{1-\alpha}) S_C (100)}{n^{1/2} \overline{N}}$$

3. The trace element detection limit in weight percent.

$$C_{DL} = \frac{C_S}{\overline{N}_S - \overline{N}_{SB}} \frac{2^{1/2} (t_{n-1}^{1-\alpha}) S_C}{n^{1/2}}$$

4. The analytical sensitivity in weight percent.

$$\Delta C = C - C' \geq \frac{2^{1/2}\, C\, (t_{n-1}^{1-\alpha})\, S_C}{n^{1/2}\, (\overline{N} - \overline{N}_B)}$$

Where :	C'	is the concentration to be compared with
	C	is the actual concentration in weight percent of the sample
	C_S	is the actual concentration in weight percent of the standard
	$t_{n-1}^{1-\alpha}$	is the Student t for a 1-α confidence and n-1 degrees of freedom
	n	is the number of data points acquired
	S_C	is the standard deviation of the measured values
	$\overline{N}$	is the average number of counts on the unknown
	$\overline{N}_B$	is the continuum background counts on the unknown
	$\overline{N}_S$	is the average number of counts on the standard
	$\overline{N}_{SB}$	is the continuum background counts on the standard

The homogeneity test merely compares the 99 % confidence range of homogeneity value with 1 % of the sample concentration for each element. If the range of homogeneity is less than 1 % of the sample concentration then the sample may be considered to be homogenous within 1 %.

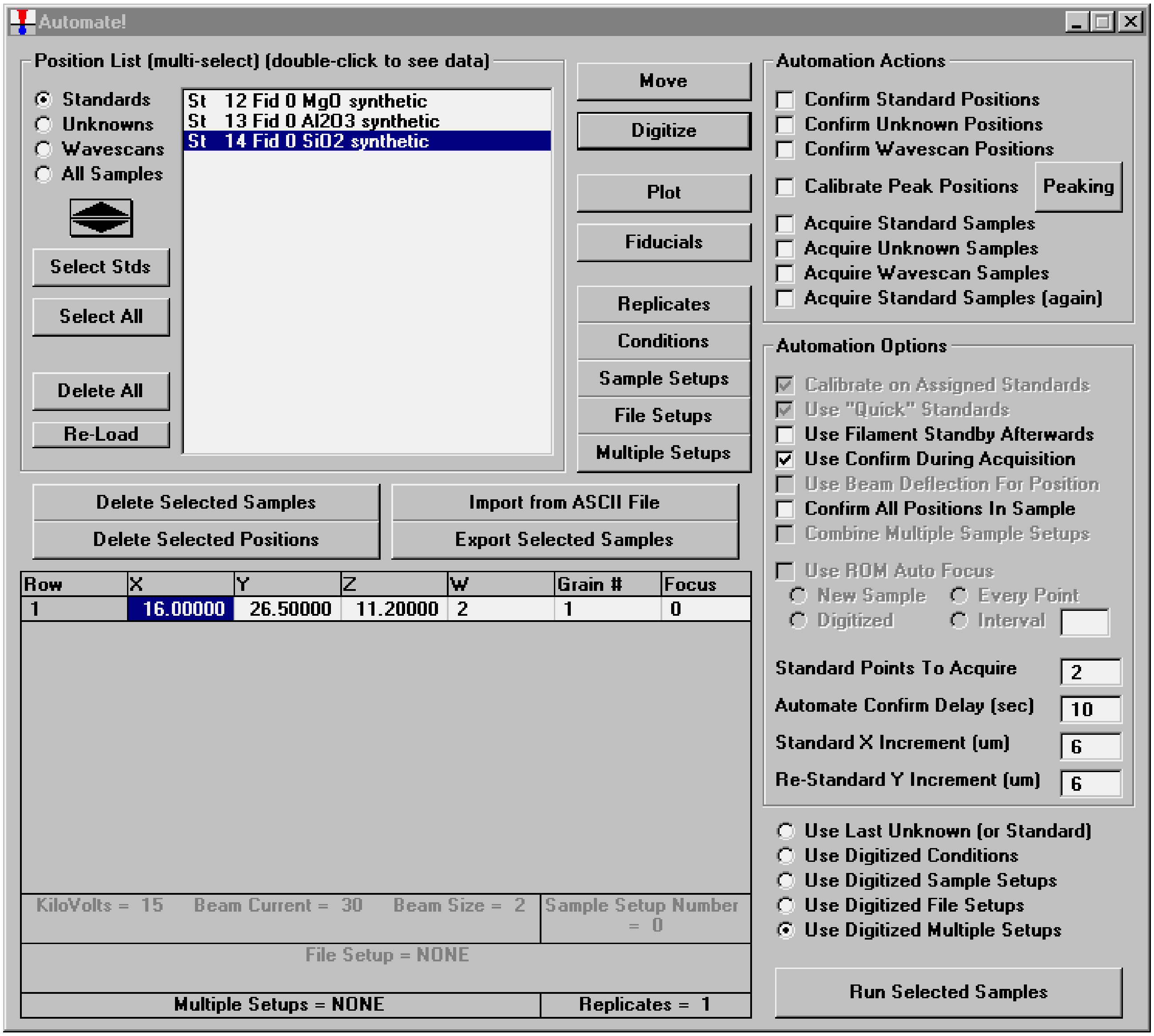
The detection limit calculation here is intended only for use with homogenous samples since the calculation includes the actual standard deviation of the measured counts. This detection limit can, however, be quoted for the sample average and of course will improve as the number of data points acquired increases. Note that the homogenous sample detection limit calculation are ignored for those elements which occur as minor or major concentrations (> 1 %).

Conversely, the analytical sensitivity calculation is ignored for elements whose concentrations are present at less than 1%.

Finally there is an alternative calculation for modeling the detection limit and/or required counting time in the program CalcZAF that is extremely useful for predicting sensitivity or analysis conditions.

Automate!

The Automate modeless window provides for automation of standard, unknown and wavescan samples, position confirmation and peak centering. Also import, export and digitization of standard, unknown and wavescan coordinates.



Position List (multi-select) (double-click to see data)

- ● Standards
- ○ Unknowns
- ○ Wavescans
- ○ All Samples

St 12 Fid 0 MgO synthetic
St 13 Fid 0 Al2O3 synthetic
St 14 Fid 0 SiO2 synthetic

Row	X	Y	Z	W	Grain #	Focus
1	16.00000	26.50000	11.20000	2	1	0

KiloVolts = 15 Beam Current = 30 Beam Size = 2 Sample Setup Number = 0

File Setup = NONE

Multiple Setups = NONE Replicates = 1

Automation Actions

- ☐ Confirm Standard Positions
- ☐ Confirm Unknown Positions
- ☐ Confirm Wavescan Positions
- ☐ Calibrate Peak Positions
- ☐ Acquire Standard Samples
- ☐ Acquire Unknown Samples
- ☐ Acquire Wavescan Samples
- ☐ Acquire Standard Samples (again)

Automation Options

- ☑ Calibrate on Assigned Standards
- ☑ Use "Quick" Standards
- ☐ Use Filament Standby Afterwards
- ☑ Use Confirm During Acquisition
- ☐ Use Beam Deflection For Position
- ☐ Confirm All Positions In Sample
- ☐ Combine Multiple Sample Setups
- ☐ Use ROM Auto Focus
  - ○ New Sample ○ Every Point
  - ○ Digitized ○ Interval

Standard Points To Acquire 2

Automate Confirm Delay (sec) 10

Standard X Increment (um) 6

Re-Standard Y Increment (um) 6

- ○ Use Last Unknown (or Standard)
- ○ Use Digitized Conditions
- ○ Use Digitized Sample Setups
- ○ Use Digitized File Setups
- ● Use Digitized Multiple Setups

Up/Down Arrow

This "spin button" allows the user to change the acquisition order of unknown and wavescan samples. Select a single sample and then using the mouse click the arrow in the desired direction of placement.

Select Stds

This button will select all standard position samples in the list that have been added to the run using the Standard | Add Standards To Run menu from the main menu.

This is useful for quickly selecting only those standard position samples of interest to the current run. Note that if a standard position sample is selected in the Position List and run as an automated acquisition, the program will automatically add the standard to the run.

Select All

This button will select all position samples shown in the position sample list. Normally this button is used for exporting all listed position samples to an ASCII .POS file.

Delete All

This button will delete all position samples shown in the position sample list. This is especially useful when starting a new run which will require a completely different position sample set from the previous user. New position samples are imported using the Import From ASCII File button described below.

Note that samples not shown in the list (unknowns or wavescans if the Standard option is selected) will **not** be deleted from the position database. To delete all samples in the database, first click the All Samples option and then the Delete All button.

Note that if all position samples that reference a fiducial calibration set are deleted, then the program will ask the user whether to delete the fiducial set that is no longer referenced by any position samples. Normally, the user should allow the program to delete unreferenced fiducial sets unless they plan to digitize additional position samples to the already confirmed fiducial set.

Re-Load

This button will force the position database to be reloaded. This is useful when the position data in the position database has been modified by another application (for example STAGE.EXE while PROBEWIN.EXE is running).

Move

The large listbox at the top of the Automate! window holds all currently digitized positions resident in the POSITION.MDB file. This file is a separate file from the user's database and is intended as a temporary repository of the digitized positions that the current user is working with.

It can grow unnecessary large if it is not continually cleaned out; that is, each user should only have to contend with his or her standard, unknown and wavescan positions. Once the unknown and wavescan positions have been run and data acquired, those positions are saved in the user's run database, and there is no reason to keep them in the position.mdb file. As far as standards go, a user who will consistently be using the same set of standards should save the those standard positions, and then recall them at the next run. This is done with the Export Selected Samples, and Import from ASCII File buttons, described below.

Move

This button will recall the Move dialog for manual stage (and spectrometer and crystal) motion. The Move window is a modeless window which may remain open and accessible during the digitization of position samples.

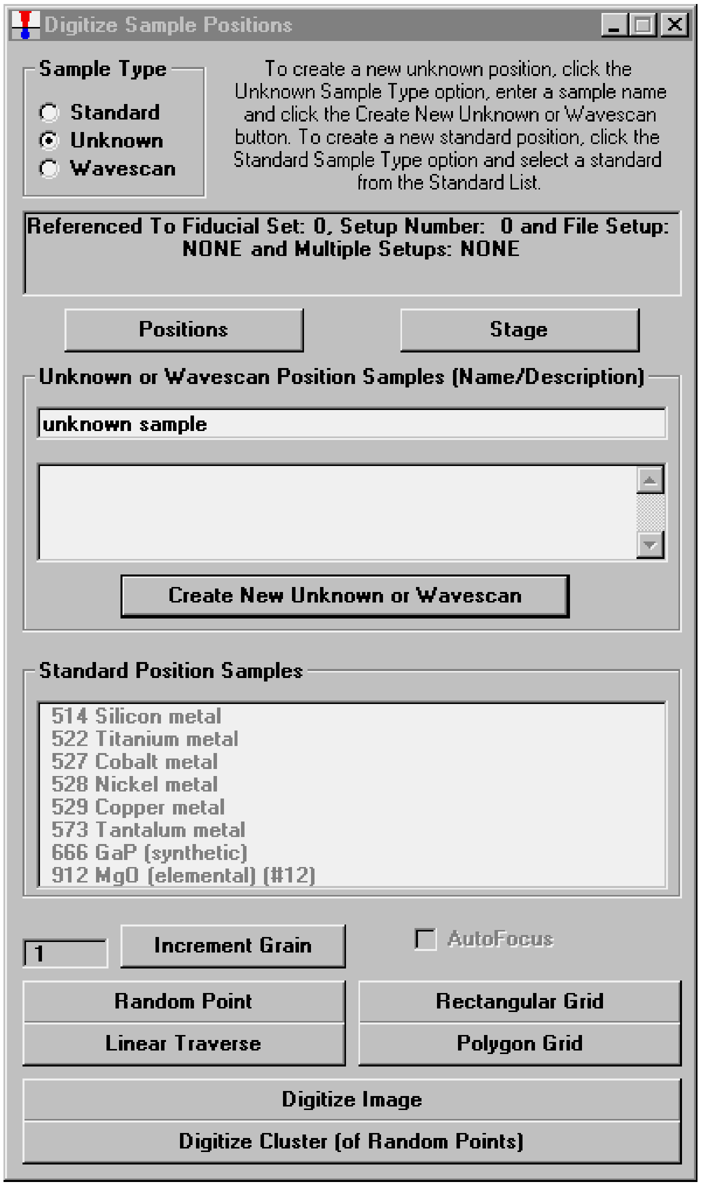
To move quickly and easily to a position already digitized in the Automate! (or Position) window lists, simply double-click the sample, to list the position coordinates for that sample, and then double-click on the specific coordinate (row) that one desires to move to. The program will automatically move to that stage position.

From the Move dialog one may select to open the Stage Map or the Position Database dialogs, both of which are very useful for digitization of standards and unknown position samples.

Digitize

This button will load the Digitize dialog, where the user can digitize standard, unknown or wavescan positions based on random (individual) points, linear traverses or rectangular or polygon gridded areas.

In addition, the user may use the Digitize Image button to open a dialog that can be used to acquire an analog image for the purposes of digitizing sample coordinates by simply clicking on various locations on the image.



Sample Type
○ Standard
● Unknown
○ Wavescan

To create a new unknown position, click the Unknown Sample Type option, enter a sample name and click the Create New Unknown or Wavescan button. To create a new standard position, click the Standard Sample Type option and select a standard from the Standard List.

Referenced To Fiducial Set: 0, Setup Number: 0 and File Setup: NONE and Multiple Setups: NONE

unknown sample

514 Silicon metal
522 Titanium metal
527 Cobalt metal
528 Nickel metal
529 Copper metal
573 Tantalum metal
666 GaP (synthetic)
912 MgO (elemental) (#12)

1

To digitize standard positions, the standard to be digitized must first be added to the run using the Standard | Add Standards To Run menu (see menus in main log window of Probe for Windows).

To create a new standard position sample, first select the sample type as Standard and then simply click the desired standard from the list box. The standard position sample will automatically be created (in the Automate! position sample list) if it did not already exist. Normally a single random (individual) digitized position is sufficient for the digitization of a standard position if the standard is large and homogeneous to permit automatic incrementing based on the X and Y increments in the Automate! window. The program will automatically increment the X and Y positions for subsequent point acquisitions based on the increment fields in the Automate! window. However, if specific positions are digitized for a standard position sample, the program will use those positions for automated acquisitions.

To create unknown or wavescan position samples, first select the sample type as before and then enter the sample name in the sample name field. Finally, click the Create New Unknown Or Wavescan Position Sample button and the position sample will appear in the Automate! position sample list. Next proceed to digitize points using the random, traverse or grid buttons.

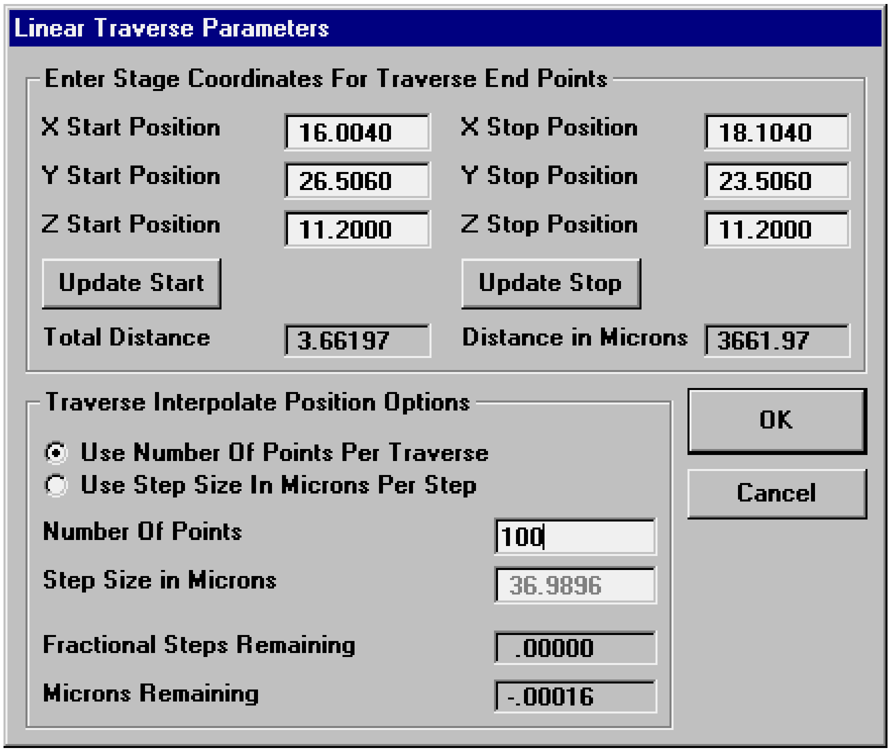
Random (Individual) Point

To digitize a sample of random (individual) points, simply click the Random Points button. each time the button is clicked, it will add a digitized position based on the current position to the currently selected position sample.

Note that any number of random (individual) points can be digitized in a single position sample. At the time of acquisition the program will sub-divide them into appropriate sized samples using the keyword sample name "continued" for points in any subsequent samples.

Linear Traverse

The linear traverse dialog allows for digitizing a straight line series of sample positions based on two given end-points. The default start and stop positions are loaded with the current position, therefore it is best to move to the desired start or stop position before clicking the Linear Traverse button.



Linear Traverse Parameters

Enter Stage Coordinates For Traverse End Points

X Start Position	16.0040	X Stop Position	18.1040
Y Start Position	26.5060	Y Stop Position	23.5060
Z Start Position	11.2000	Z Stop Position	11.2000
Total Distance	3.66197	Distance in Microns	3661.97

Traverse Interpolate Position Options

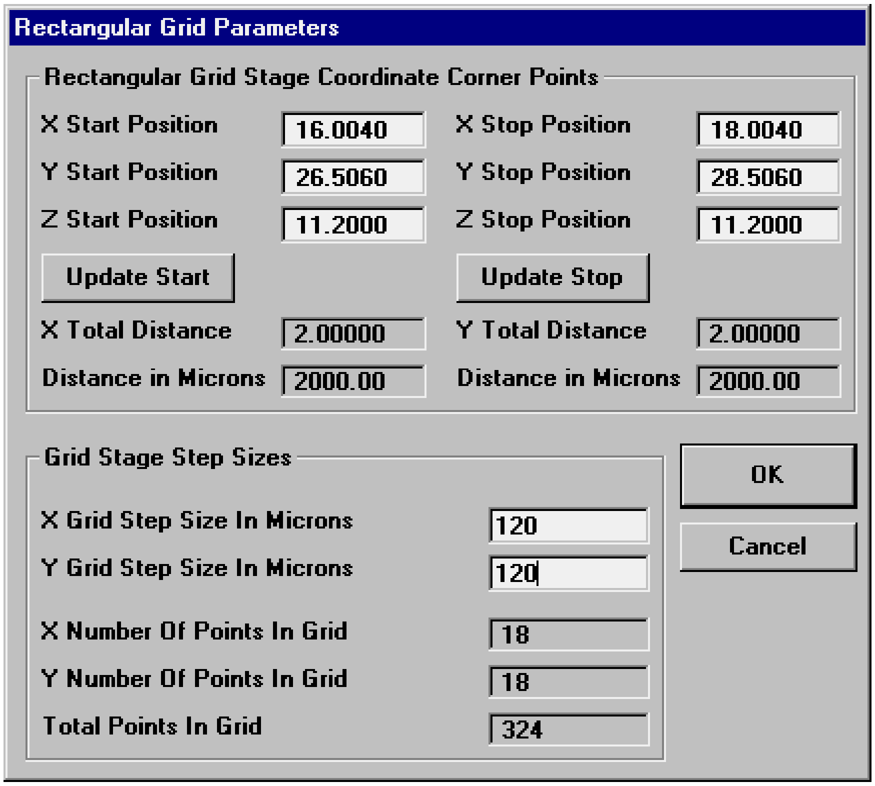
● Use Number Of Points Per Traverse
○ Use Step Size In Microns Per Step

Number Of Points	100
Step Size in Microns	36.9896
Fractional Steps Remaining	.00000
Microns Remaining	-.00016

Select either a specified number of points per traverse (including the end-points) or a specified distance between points.

Rectangular Grid

The Rectangular Grid dialog allows an offset grid of points to be digitized based on any two opposite corners. The grid spacing is calculated by the X and Y distance in microns specified by the user.



Rectangular Grid Parameters

Rectangular Grid Stage Coordinate Corner Points

X Start Position 16.0040
Y Start Position 26.5060
Z Start Position 11.2000
X Stop Position 18.0040
Y Stop Position 28.5060
Z Stop Position 11.2000
X Total Distance 2.00000
Distance in Microns 2000.00
Y Total Distance 2.00000
Distance in Microns 2000.00

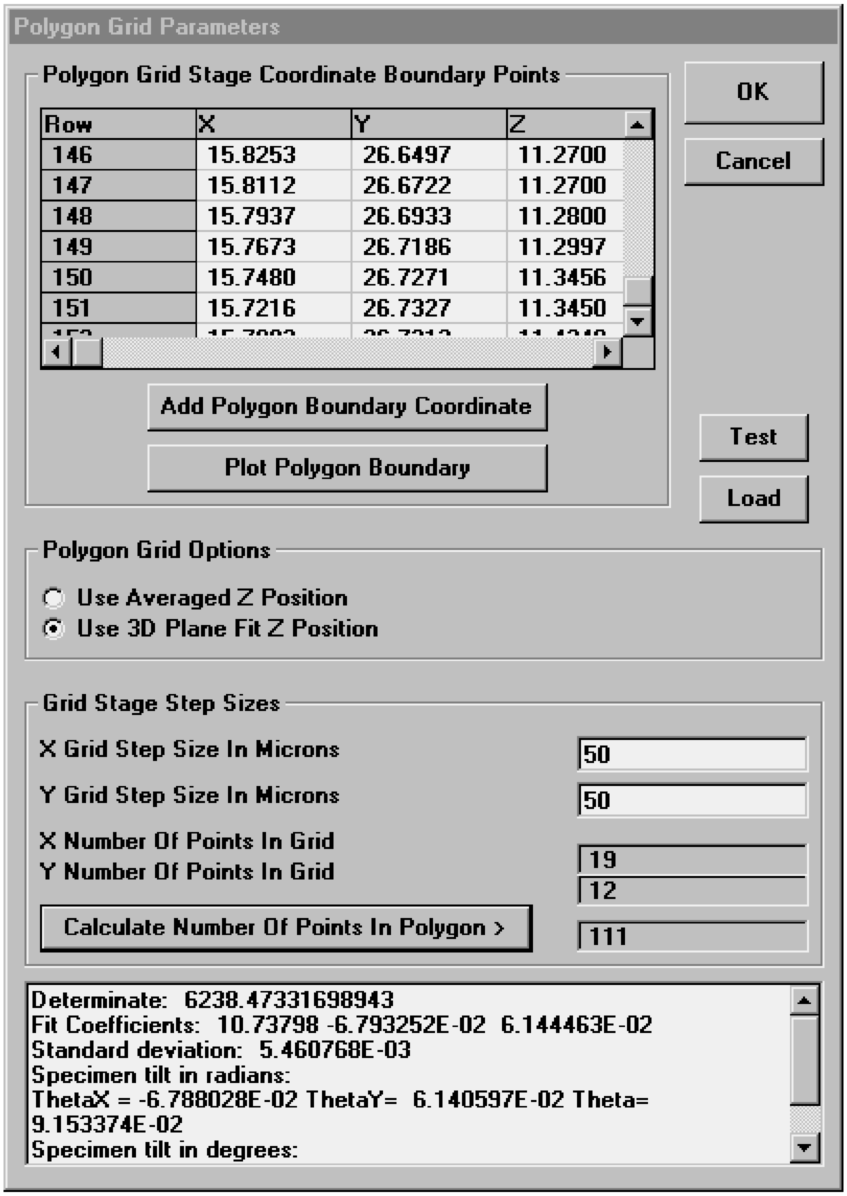
Grid Stage Step Sizes

X Grid Step Size In Microns 120
Y Grid Step Size In Microns 120
X Number Of Points In Grid 18
Y Number Of Points In Grid 18
Total Points In Grid 324

As the grid points are digitized, the positions are calculated in a "serpentine" manner to reduce stage motion to a minimum during acquisition.

Polygon Grid

The Polygon Grid dialog allows the user to digitize an offset grid of points which is delimited by an arbitrary boundary digitized by the user. This boundary may contain any number of points and is saved along with the grid points for use in exporting to a .BLN boundary file used to create SURFER 3-D surface and/or contour output.



Row	X	Y	Z
146	15.8253	26.6497	11.2700
147	15.8112	26.6722	11.2700
148	15.7937	26.6933	11.2800
149	15.7673	26.7186	11.2997
150	15.7480	26.7271	11.3456
151	15.7216	26.7327	11.3450

○ Use Averaged Z Position
● Use 3D Plane Fit Z Position

X Grid Step Size In Microns: 50
Y Grid Step Size In Microns: 50
X Number Of Points In Grid: 19
Y Number Of Points In Grid: 12
Calculate Number Of Points In Polygon >: 111

```
Determinate:  6238.47331698943
Fit Coefficients:  10.73798 -6.793252E-02  6.144463E-02
Standard deviation:  5.460768E-03
Specimen tilt in radians:
ThetaX = -6.788028E-02 ThetaY=  6.140597E-02 Theta=
9.153374E-02
Specimen tilt in degrees:
```

To create a boundary for the polygon grid, use the focused reflected light and/or BSE image to simply move the stage and then click the Add Polygon Boundary Coordinate button for each position to be included in the boundary. Depending on the desired level of detail, any number of coordinates may be used to digitize the boundary feature.

The boundary can be plotted during the digitization process by clicking the Plot Polygon Boundary button and the first and last points are automatically assumed to be closed to complete the polygon boundary. Because the grid algorithm is quite robust, boundaries of any arbitrary shape may be digitized.

The Test button is only visible in demonstration mode and is used to load a default polygon to demonstrate the polygon gridding process.

The Load button is used to load a previously digitized set of polygon grid boundary coordinates. This is useful when the user decides that a different grid spacing is preferred but with the same digitized boundary. By using this feature, the user is not required to re-digitize the boundary coordinates. Typically, one should create a new position sample (with no positions) when loading a previously digitized polygon boundary for the purpose of changing the grid step sizes.

Two methods for determining the Z axis interpolated position are available. The first is based on the average Z position of all boundary positions, the second is a 3-D plane fit to the Z position of all boundary positions.

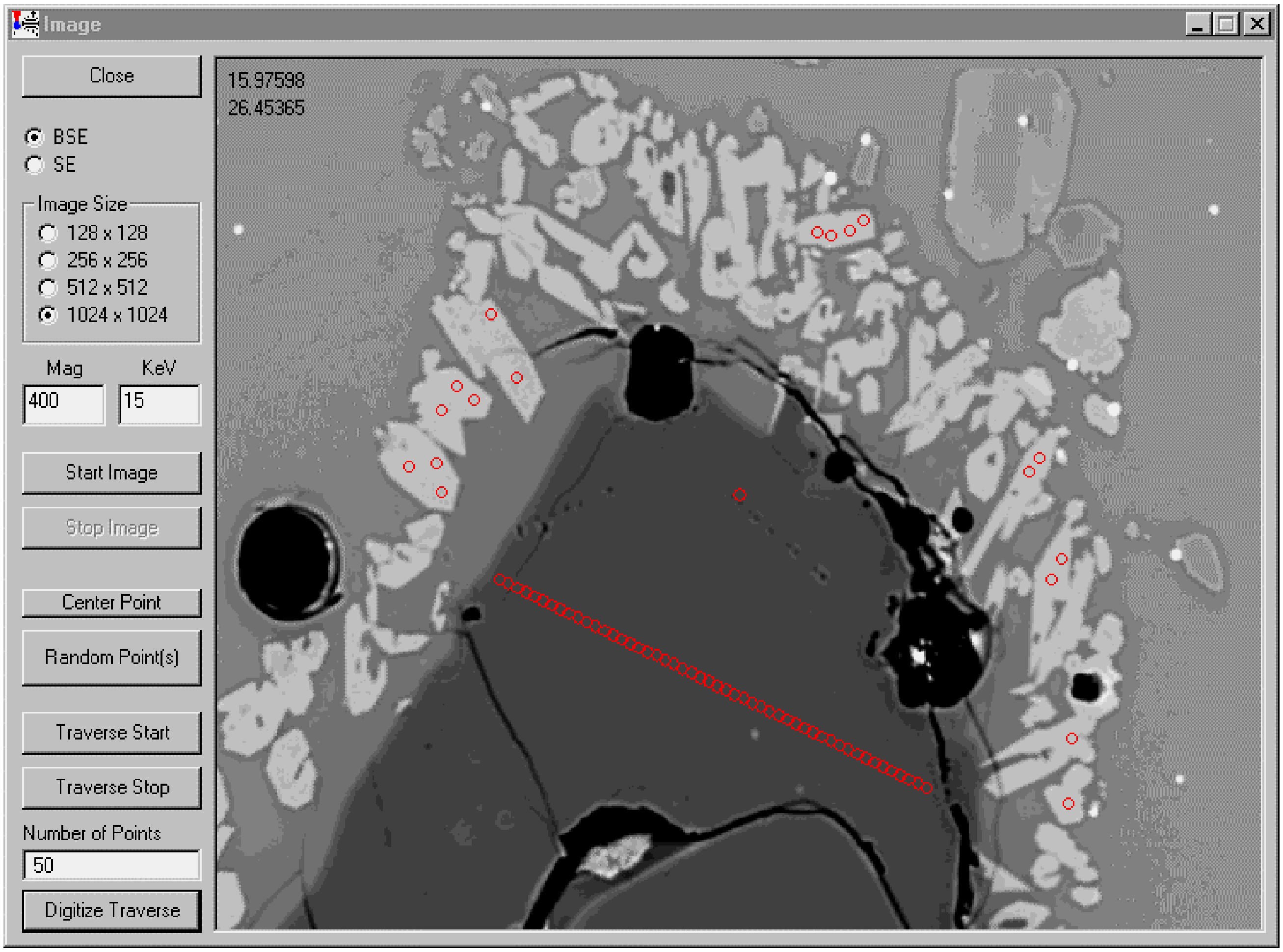
Adjust the number of points to be gridded during the digitization by entering X and Y grid step sizes in microns. For example, a 100 x 100 micron rectangle (4 boundary points) will produce 121 analysis positions if a 10 micron spacing is used for both X and Y (11 by 11).

The program will prompt the user if the number of grid positions are excessively large by assuming a "rectangular" boundary. To see the actual number of grid points that will fit inside the digitized boundary, click the Calculate Number of Points in Polygon button to determine the actual number points that will be digitized.

Click OK when ready to digitize the grid based on the polygon boundary coordinates and the X and Y grid step sizes. Click Cancel to not digitize any polygon grid positions and not save the boundary coordinates.

Digitize Image

This button is used to open a dialog that can be used to digitize stage positions based on an SE or BSE analog image supplied by the system. This feature can acquire images from either the MicroImage-32 software, or the Win30 A/D-D/A board directly. The imaging system requires calibration in order to associate stage coordinates to beam deflection positions before it can be utilized for digitizing. See the parameters defined in the PROBEWIN.INI file [Image] section.



15.97598
26.45365

● BSE
○ SE

Image Size
○ 128 x 128
○ 256 x 256
○ 512 x 512
● 1024 x 1024

Mag: 400
KeV: 15

Number of Points: 50

Both random points and traverse coordinates may be saved to the position database by simply clicking the mouse on the displayed image. If the image is supplied by MicroImage, any type of X/Y registered analog image that MicroImage is capable of acquiring may be used for the purpose (beam, stage or mosaic beam/stage scan images included) at any magnification supported by the instrument; in the case of the WIN30 direct interface only beam scan images may be acquired.

Use the Image Size options to select the image resolution, then click the analog source and click the Start Image button. The image acquisition will start. To halt the current image acquisition, click the Stop Image button. An image must be acquired before the user can begin to digitize position coordinates.

The Mag (magnification) and KeV (kilovolts) fields are used by some interfaces (SX50/51/100) to set the actual beam scan conditions for the image acquisition. For other interfaces the actual setting made to the instrument manually must be entered here so that the stage positions are correctly calculated.

The Center Point button can be used to digitize the first point of the position sample in the exact center of the beam scan area if desired.

Once an image is acquired, use the Random (individual) Point(s) button to digitize one or more random (individual) position coordinates by simply clicking the image at the desired location(s). The stage coordinates of each mouse click is stored in the position database for sample automation purposes.

Use the Traverse Start to indicate the start position of a linear traverse, the Traverse Stop button to indicate the stop position of the linear traverse and the Number of Points field to specify the number of points in the traverse. Click the Digitize Traverse button to actually digitize the traverse and store it in the position database.

Digitize Cluster (of Random Points)

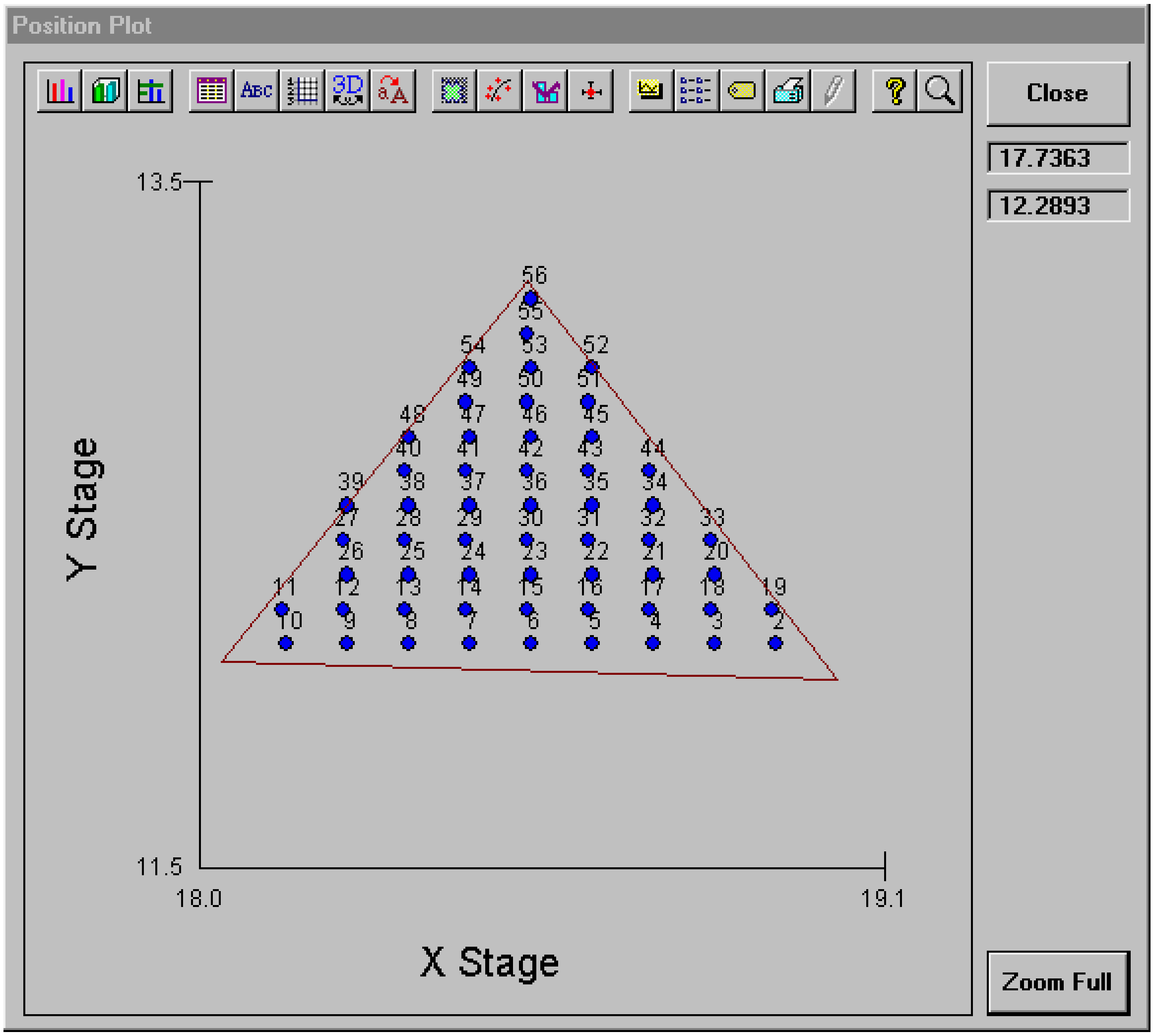
This dialog allows the user to define a circular or square areas of a given diameter or width and specify the number of randomly distributed positions within the area. There is also an option (by default) to save a polygon boundary of the area and the number of points to define the area (round area only).

In addition the user can specify the minimum distance between random points to prevent the beam from analyzing the same spot more than once. Note that if the minimum distance is too large or the cluster diameter or width is too small or the number of points is too large, the program may be unable to find enough evenly spaced coordinates.

This feature is useful when performing careful homogeneity tests when it is important to eliminate instrument drift and grid pattern artifacts. Note that the circular boundary creating when digitizing round areas can be re-used in the polygon gridding dialog using the Load button.

Plot

The Plot button will display the digitized X and Y stage coordinates for the selected position sample. Only one position sample can be plotted at at time.



The example above shows a plot of a Polygon grid consisting of 55 points digitized using three boundary points.

If the position sample is a polygon gridded position sample then the digitized polygon boundary will also be displayed. The coordinates of the cursor are displayed as the cursor is moved across the plot area.

Fiducials

The Fiducials button will display the current digitized fiducial sets in the position database. To select a different fiducial set to reference subsequent digitized position to, simply select it from the list. In addition, this dialog will allow the user to modify, confirm, create new or delete fiducial sets in the position database.

Although standard positions are normally referenced to fiducial coordinates, it may also be desirable to reference unknown or wavescan coordinates to physical fiducial marks for the purposes of precisely relocating the acquired positions even after they have been removed and later re-loaded into the microprobe.

For this purpose, it is required that the sample mount have been previously scribed or otherwise marked to allow the user to locate 3 points that will be used for the fiducial coordinates. These fiducial coordinates must be permanent and easily re-located in the same order that they were defined to allow the program to calculate a transformation matrix when the sample is re-loaded later on. Once the positions have been referenced and digitized to a selected calibrated fiducial coordinate set, they can be exported to an ASCII file for subsequent use at another time.

See the section Import from ASCII File below for details on using the fiducial coordinates to transform digitized coordinates.

Peaking

Clicking the peaking button opens the peak center window. All currently analyzed elements are listed. The Peak Center method can be specified. A choice of Interval Halving, Parabolic and ROM based (if supported by the hardware) is available. The default peak center method can be specified from the PROBEWIN.INI file. With all methods the program will perform a peak to background measurement to determine if the peak is statistically significant enough to attempt a peak center.

Three options are offered, the first an option move the spectrometers to their on-peak positions if selected in the element list. This option is useful for moving the spectrometers to calibrated peak positions for x-ray mapping purposes.

The second option forces the program acquire a "pre-scan" wavescan just prior to the peak center procedure to allow the user to select an initial peak center start position. This last option is particularly useful in cases where the nominal spectrometer position is badly out of mechanical calibration and the actual peak position is some distance from the theoretical peak position. One can also specify as a third option a "post scan" to be executed after a peak center to confirm that the peak center method was properly performed. This option gives the operator maximum control over the automated determination of the peak "center". Here the peak center found by one of the 3 methods can be verified, by a slow step across the top of the centroid.

The Plot Selected Peak Center button will display graphically, the last peak center attempted for the selected element. The points displayed are numbered in the order acquired. Therefore, for example, if the parabolic peak center was performed, and an optimum peak center was obtained, there will be four points displayed: the three (on, hi, lo) for the parabolic fit and a fourth new on-peak based on the calculated peak center.

> The **Interval Halving** method is the most accurate, but the slowest. It is based on a peak crawl that changes direction and halves the step size whenever the count intensity drops by more than a standard deviation.
>
> The **Parabolic** method peak center uses a moving three point fit on the peak top that is fit to a 2nd order polynomial. The centroid of the parabola is returned as the new peak center. This method is the fastest, if the spectrometer position is already close to the actual on-peak position.
>
> The **ROM Based** method peak center is available if the hardware interface supports a ROM peak center. The actual method used for the ROM Based peak center depends on the microprobe hardware.
>
> The **Manual** method peak center is very simple utilizing only a pre-scan, P/B check and post-scan.

The program will automatically select elements in the element list that were not peaked in the previous peak center when the window is re-opened again. Note that the element list is multi-select so that any combination of elements can be peaked. If more than one element on the same spectrometer was selected, then the program will automatically peak center them one at a time. The Plot Selected Peak Center button may be used to display the last peak center count-position data for the selected element.

The move to on-peak option is useful for moving a spectrometer (and setting the PHA conditions) to it's on-peak position for imaging purposes. Remember : the elements to peak center (or move to on-peaks) must be highlighted before closing the dialog.

Spectrometer Peak Center Scans

All spectrometer peak center procedures may be prefaced with a spectrometer peak scan to allow the user to manually specify the nominal peak center position. This spectrometer peak scan is performed using the number of peak scan steps as defined in the Peak/Scan Options dialog. The count time for each peak scan point is based on the peak count time (divided by 4) as defined in the Count Times dialog.

Initial Peak-To-Background Measurements

The program always performs a peak-to-background and peak intensity check before the actual peak center procedure. The peak-to-background is calculated by measuring the count rate at the nominal peak position and the current off-peak positions using the peak count time for each position. The measured count data must meet the required minimum peak-to-background and minimum peak count intensity as defined in the Peak/Scan Options dialog, before performing the actual peak center procedure.

If performing the peak center from the Automate! dialog, the program will not proceed with acquisition of sample data if one or more spectrometer fails to complete a peak center procedure for any reason.

Spectrometer Peak Center Procedure

Three peak center procedures are used by Probe for Windows. They are the Interval Halving, the Parabolic Fit and the ROM based peak center procedures.

Interval Halving

Interval halving is a peak center procedure based on a peak crawl starting at the nominal peak position. The step size of the peak crawl is halved and the direction reversed whenever the count rate drops by more than a single standard deviation (square root of the intensity). The interval halving procedure is slow but extremely precise.

The initial peak step interval is always in a positive direction and the peak interval size is based on the Peaking Start Size as defined in the Peak/Scan Options dialog. Note that the default peaking start and stop sizes from the SCALERS.DAT file are modified by the following expression :

$$S_{actualstart} = S_{start} \bullet \sqrt[3]{\frac{2d_{OnPeak}}{2d_{LiF200}}} (*2.0) \sqrt{\frac{P_{LoLim} + ABS\ (P_{HiLim} - P_{LoLim})}{P_{OnPeak}}}$$

Where :

$S_{actualstar}$	is the actual calculated step size
S_{start}	is the spectrometer default start or stop size
P_{HiLim}	is the spectrometer high limit
P_{LoLim}	is the spectrometer low limit
P_{OnPeak}	is the spectrometer on-peak position
$2\ d_{OnPeak}$	is the 2d spacing of the analyzing crystal
$2\ d_{LiF\ 200}$	is the 2d spacing for LiF (4.0267)

From this expression one can see that the actual start and stop sizes are unchanged at the spectrometer high limit when an LiF crystal is used, and are increased for lower spectrometer positions and larger crystal 2d spacings. The calculated start and stop sizes are also doubled when the crystal 2d spacing is larger than 30 angstroms (LDE crystals).

When the interval step size has been halved to a value less than the peaking stop size, the spectrometer is considered to be peak centered and the current position is saved as the new peak position.

If the number of intervals measured exceeds the "Maximum Peaking Cycles" as defined in the Peak/Scan Option dialog, the program terminates the peak center procedure with an error.

Parabolic Fit

The parabolic peak center procedure is based on a moving three point triplet that attempts to fit an inverted parabola. The three positions measured are the middle, high and low positions. The middle position is initially the nominal peak position and the high and low positions are offset from the middle position based on the value of the Peaking Start Size, which is calculated using the process described in the interval peaking procedure above. Ideally the Peaking Start Size calculation should be adjusted to yield an offset which places the high and low positions at a position which produces approximately 1/2 the maximum intensity of the peak, for a more precise parabolic fit.

The peak center procedure then determines if the high and low position intensities are at least one standard deviation less than the middle position intensity. If the three intensities meet this criteria, the program calculates the centroid of a parabola based on the count-position data triplet. The results of the centroid peak fit can be viewed by placing the program into "Debug Mode" under the Output menu.

If the data cannot be fit to a parabola, the middle position is shifted by an amount equal to 1/2 of the Peaking Start Size and the middle, high and low position intensities are measured again.

If the number of count-position data triplets measured exceeds the "Maximum Peaking Cycles" as defined in the Peak/Scan Option dialog, the program terminates the peak center procedure with an error.

ROM Peaking

The ROM peaking procedure is available for those interfaces that support an integrated ROM based peaking procedure. These are the JEOL, Sesame, Tracor, SX100 and SX50 interface types.

The actual peaking procedure utilized by each interface is somewhat different but usually based on a parabolic fit of some variety. The program passes the "Peaking Start Size" to each interface specific ROM Peaking routine where is it modified if necessary.

JEOL 8900 Direct (InterfaceType=2)- The "Peaking Start Size" is not used. Instead a peak parameter of 1 (fine scan) is always used.

Sesame (InterfaceType=3)- The "Peaking Start Size" is not used by the Sesame interface. The function simply sends the "PEAK" command for the specified motor, at the current position.

Tracor (InterfaceType=4)- The Tracor peak center procedure uses a two step peak center (an initial peak center based on the "Peaking Start Size" and a final peak center based on the "Peaking Stop Size"). The total number of steps is hard-coded since the PAC cannot update this system parameter while another spectrometer is being peaked. The number of TRACOR motor steps per peak scan point is calculated from the number of motor steps per l-unit conversion factor (from the MOTORS.DAT file), the "Peaking Start Size", (or) the "Peaking Stop Size" and the number of peak scan steps (hard-coded to 40). The following expression is used to calculate this value, and assumes a TRACOR peak scan width equal to ten times the Peaking Start Size :

$$sp = M * P * 10 / N$$

where	sp	is the Tracor ROM peak center scan motor steps per point
	M	is the motor steps to units conversion factor (from MOTORS.DAT)
	P	is the Peaking Start Size (initial) or Peaking Stop Size (final)
	N	is the number of peak scan steps (hard-coded to 40)

The Tracor step count time is calculated from the Peaking Count Time (divided by four). Note that the PAC Crystal Factor variable must be set to 1 on all spectrometer-crystals for this procedure to perform correctly.

After the initial Tracor peak center has completed, the procedure moves the motor position to the calculated centroid returned from the PAC, then a final Tracor peak center is performed, before the new peak intensity is measured.

SX100 (InterfaceType=5)- The "Peaking Start Size" is modified to produce a number between 0 and 4 by utilizing the following expression :

$$pw = (M_{high} - M_{Low}) * P / 3000000$$

where	pw	is the SX100 peak center width
	M_{high}	is the motor high limit
	M_{low}	is the motor low limit
	P	is the Peaking Start Size

SX50 (InterfaceType=6)- The "Peaking Start Size" is modified to produce a number between 0 and 4 by utilizing the following expression.

$$pw = (M_{high} - M_{Low}) * P / 3000000$$

where	pw	is the SX50 peak center width
	M_{high}	is the motor high limit
	M_{low}	is the motor low limit
	P	is the Peaking Start Size

If the SX50 peak center width is less than or equal to 2, the SX50 driver sends the "PE" command for the specified motor. Otherwise, if the SX50 peak center width is greater or equal to 3, the SX50 driver sends the "PE WIDE" command instead.

JEOL 8900 Rlogin (InterfaceType=7)- The "Peaking Start Size" is not used. Instead a peak parameter of 1 (fine scan) is always used.

Manual Peaking

The Manual method peak center is very simple. First a wavelength pre-scan is performed, after which the user is allowed to select the actual peak position. This is followed by a peak to background check, after which a wavelength post-scan is performed at a finer scale to allow the user to confirm the selected peak position. The user is then once again given the chance to adjust, confirm or cancel the peak center process.

Note that the final wavelength post-scan data will be saved to the Plot Peak Center array (see the Peaking dialog) for subsequent plotting or output by the user. Note that the post-scan range is 5% (+/- 2.5%) of the pre-scan range.

Final Peak-To-Background Measurements

After a successful peak center procedure the peak-to-background is re-calculated by simply measuring the on-peak count rate at the new peak position. This result can be compared with the initial peak-to-background to evaluate the peak center procedure performance.

Post Scan Peak Confirmation

This option gives the operator maximum control over the automated determination of the peak "center". Here the peak center found by one of the 3 methods can be verified, by a slow step across the top of the centroid. Optimal centering is left to the discretion of the user, but one strategy is to look for the small flat plateau that normally is present at the peak centroid, or looking at the centroid at 99% of maximum intensity. The values used are, respectively, the time value of the "peaking" in Count Times and the step width using 1/20 (5% or +/- 2.5%) of the width for peakscan limits, in Peak/Scan options.

Replicates

This dialog allows the user to specify "replicate" acquisitions for the selected or subsequently digitized position samples. For example, if the number of "replicates" is set to one (the default) the program will acquire one data acquisition for each digitized stage coordinate. However, if the number of "replicates" is set higher, for example 3, then the program will acquire 3 acquisitions per digitized stage coordinate.

The "replicate" field only applies to unknown sample acquisitions run from the Automate! window..

Conditions

Although Probe for Windows normally acquires automated samples based on the last unknown sample conditions, the program will support the automatic acquisition of samples under various analytical conditions (if the interface hardware supports it).

There are two different options for analytical conditions, the first is using specified values for kilovolts, beam current and beam size, the second is using a specified string to indicate a column condition that is stored internally in the instrument. In this latter case, because the actual value of the operating voltage (kilovolts) in the column condition string is ambiguous, the user should be sure that the single value fields are also correctly specified based on the column condition string specified.

For example, the SX50 supports the use of internally stored column conditions that are indicated by a four character string. Therefore, if the column condition option is selected, and the column condition string is specified as "hv15" (indicating a column condition at 15 keV), then the user should also be sure that the kilovolts field is correctly specified as 15 keV. Failure to properly specify the kilovolts field when using column condition strings will cause the ZAF or Phi-Rho-Z matrix corrections to be inaccurate.

For accurate documentation purposes it is also preferred that the beam current and beam size fields are also properly specified when using column condition strings. If, as in the above example, the "hv15" column condition string also includes a beam current of 10 nA and a beam size of 10 um, then those values should also be specified in the single values fields even though are not actually used in the acquisition procedure. This maintains the accuracy of the documented sample conditions.

By using either the analytical conditions and column condition methods, it is possible to automatically acquire a number of digitized positions using a different kilovolts/beam current/beam size values. This is useful for many purposes, for example, automated thin film analysis, where the acquisition of k-ratios at various operating voltages can improve the analysis considerably.

To utilize this acquisition type, be sure to select the Use Digitized Sample Conditions option before clicking the Run Selected Samples button.

Sample Setups

Although Probe for Windows normally acquires automated samples based on the last unknown sample conditions, the program will support the acquisition of samples based on previously saved sample setups with a variety of elements or multiple keV or nA conditions.

This is especially useful when the need to acquire data on samples with a variety of elements are present. For example, there may be a number of quite different phases present that each require a more or less different set of analyzed elements. By previously creating a number of sample setups and saving them, it is possible to have the program automatically acquire a different set of analyzed elements by referencing the various available sample setups during the digitization process.

Sample setups may be created from the Acquire! window by first starting a new sample and then modifying the sample setup to the desired configuration. Then use the Save Sample Setup button from either the Analyze! Window or within the Elements/Cations window (accessed from the Analyze! window) to create a pointer to the sample setup for use later on during the creation of new analyzed samples or the digitizing of position samples.

To utilize this automated acquisition method, you will need to "tag" each set of samples: with a sample (or set of them) highlighted, click the Sample Setups button and then highlight the particular sample setup to be used, and click OK. If there are other samples to be digitized using different sample setups, then tag those. Before clicking the Run Selected Samples button, make sure the Use Digitized Sample Setups option is checked (it will be done automatically by the program when you select the setups).

File Setups

Although Probe for Windows normally acquires automated samples based on the last unknown sample conditions, the program will support the acquisition of samples based on previously created file setups from other Probe for Windows runs. These may be Probe database files that contain one or more specific sample setups and may or may not also contain standardization count intensity data.

This is especially useful when the need to acquire data on samples with a variety of elements are present. For example, there may be a number of quite different phases present that each require a more or less different set of analyzed elements. By previously creating a number of file setups, it is possible to have the program automatically acquire a different set of analyzed elements by referencing the various available file setups during the digitization process. Note that the specified file setup must be available to the program when the automation is run or an error will occur.

To utilize this automated acquisition method, be sure to select the Use Digitized File Setups option before clicking the Run Selected Samples button.

Multiple Setups

This button is used to assign multiple sample setups to current or newly created digitized position samples. All considerations for Samples Setups apply for Multiple Setups (see Sample Setups above). To create sample setups for digitizing position samples, use the "Elements/Cations" button in the Analyze! Window.

This procedure is affected by the state of the "Combine Multiple Sample Setups" checkbox in the Automation Options frame. If this checkbox is not checked, then a separate sample, based on each multiple setup, will be acquired for each position sample. This is particularly useful for situations where the same elements need to be measured several times with different operating voltages, for example, in thin film analysis, when it is necessary to acquire different voltages on the sample position. Here one would specify two or more sample setups that have the same elements but different kilovolt operating conditions.

If the checkbox is checked, then all specified multiple setups will be combined into a single combined condition sample for the position sample, and the software will adjust the column condition as necessary to acquire the elements. When more than one sample setup is specified by the user, the automation routine will acquire the position sample for each sample setup that is specified. This is useful in several situations, for example, when performing major and trace element acquisition it may be desired to acquire the major elements at one set of sample conditions and the trace elements using a sample setup with different sample conditions (kilovolts, beam current, etc.).

In the former case of major and trace element analysis, each sample setup acquired will create a different analytical sample. To combine the elements into a single sample for quantitative analysis, simply select all the samples that are to be combined and click the "Analyze Selected Samples (Combined)" button in the Analyze! Window.

Delete Selected Samples

This button will delete the currently selected position samples from the position database in the window above the button. If all position samples that reference a fiducial set are deleted, the program will ask whether to delete the fiducial set from the position database also. Normally one should allow the program to delete unreferenced fiducial sets to avoid confusion.

Delete Selected Positions

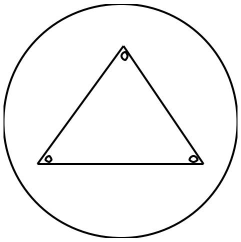
This button will delete the position coordinates that are currently selected in the position grid display below the button. This option will only delete contiguous position coordinates listed in the position grid. Delete non-contiguous digitized positions individually.

Import From ASCII File

The Import button allows the user to import an ASCII file of sample positions for automated acquisition. Standard, unknown and wavescan coordinates can be imported separately or in a single file.

Fiducial Marks

The program will ask the user whether the imported coordinates should be transformed using a fiducial based matrix transformation. The fiducial positions on the standard or unknown sample mount should generally be laid out in an easy to re-locate pattern. Generally it is preferred to place the fiducials marks in the corners of a scribed (or partially scribed-corners only) triangle on the mount surface as shown here :



The fiducial marks should be deep enough to withstand repeated re-polishing but small enough to be precise for re-location of the digitized coordinates.

A sample import file of two unknown samples and corresponding positions is shown here. Note that a new standard, unknown or wavescan sample is created automatically by the program during the acquisition process, whenever the sample number changes (for standards), or if the sample name changes (for unknowns or wavescans).

Special note: there are two varieties of formats (type = 1 or type = 2) used in position import and export files. The format of the position import and export file is specified by the PositionImportExportFileType parameter in the PROBEWIN.INI file. If the parameter is not specified in the INI file then the default of type = 1 is used.

The first format is the original import/export format (type = 1) and contains the fields shown in the example below without the autofocus flag and analytical setup number fields shown in parentheses at the end of the position lines.

The second format is a newer import/export format (type = 2) which contains two additional integer fields and an additional string field for each position lines. These additional integer fields are used for an auto focus flag and an analytical setup number. The analytical setup number can be used by Probe for Windows to specify which previously saved sample setup is to be used when acquiring data for the position sample. Note that all positions in a single position sample must use the same setup number. If more than one setup number is specified within a position sample, the program will use the last analytical setup specified. If the setup number specified is not available in the current Probe for Windows run, then the program will base the automated acquisition on the last unknown sample. The autofocus flag is used to define a "digitized" autofocus (if supported by the hardware interface) for each position. If this autofocus flag is zero, then no autofocus is attempted, if the flag is -1 or 1 then an autofocus will be attempted at that position. The adjustment from the auto-focus will be applied to all positions in that position sample.

The additional string field is used to specify a file setup name that can be used for automated designation of a file setup from an existing Probe for Windows data file. The specified Probe for Windows data file must reside in the Probe for Windows application directory (usually **C:\Program Files\Probe for Windows-E**).

The importing positions with a pre-defined file setups, analytical setup numbers (and autofocus flag) are useful when digitizing position samples off-line on an optical microscope using program STAGE. However, it is important when digitizing off-line to ensure that the setup number specified during the digitizing process will eventually correspond to the correct setup number created in the Probe for Windows run in which the digitized position samples will be automatically acquired. Also that the specified file setup data file exists and is updated with valid standardization data.

```
0.0, 0.0, 0.0, 0.0
0.0, 0.0, 0.0, 0.0
0.0, 0.0, 0.0, 0.0
2,     1,     "metallic phase #1", 15.234, 18.12, 10.873, 1.0, 1, (1, 4, "")
2,     1,     "metallic phase #1", 15.547, 18.43, 10.873, 1.0, 1, (0, 4, "")
2,     1,     "metallic phase #1", 15.698, 18.56, 10.873, 1.0, 1, (0, 4, "")
2,     2,     "Si3N4 ceramic matrix",15.747, 18.34, 10.873, 1.0, 1, (1, 7, "")
2,     2,     "Si3N4 ceramic matrix",15.747, 18.34, 10.873, 1.0, 1, (0, 7, "")
2,     2,     "Si3N4 ceramic matrix",15.747, 18.34, 10.873, 1.0, 1, (0, 7, "")
```

The format of these standard, unknown or wavescan position import files (the above example contains two unknown position samples with three positions each) is described below. Note that the first three lines are always used to define the coordinates of the 3 physical fiducial marks used for transformation of pre-digitized standard mounts. All parameters are comma, space or tab delimited.

Following the first 3 lines which define the x, y, z, and w coordinates for the three fiducial marks (used for transformation of pre-digitized standard mounts), each position line has the following format :

- the first column contains the sample type (1 = standard, 2 = unknown, 3 = wavescan)

- the second column contains the sample number, which for standards is the standard number for a standard as defined in the STANDARD.MDB database. For unknowns and wavescans it is an arbitrary number that is ignored.

- the third column is the sample name, which is optional for standard position samples and must be enclosed in double quotes

- the fourth, fifth, sixth and seventh columns contains the x, y, z and w coordinate positions. The w motor position is only used for JEOL 733 microprobes

- the eighth column value is the grain number, which is used for automatically blanking the beam between successive points if different from the preceding point

- the ninth column value (only if PositionImportExportFileType = 2 or greater) is the autofocus flag, which is used for automatically performing an auto focus for each position. Specifically the third autofocus flag option (1= every sample, 2=every point, 3=digitized, 4=interval).

- the tenth column value (only if PositionImportExportFileType = 2 or greater) is the analytical setup number, which is used for automatically loading a previously created sample setup in a Probe for Windows data file. If the specified analytical setup number is not found, the program will load a sample setup based on the last unknown sample in the run.

- the eleventh column value (only if PositionImportExportFileType = 3) is the analytical file setup name. If the specified file setup name is not found, an error is generated.

Note that standard coordinates can be imported in any order and all positions of a single standard will be appended to a single standard sample automatically. However, if a standard position sample already exists, the program will ask if the user wants to overwrite the existing standard coordinate data, so generally it is a good idea to group all coordinates for a single standard contiguously.

If no fiducial transformation of the imported positions is required, simply click "No" when asked whether to perform the fiducial transformation.

For unknown and wavescan positions these fiducial positions may used for transformation of sample positions digitized on an optical microscope equipped with a digitizing stage using a different coordinate system than the microprobe stage. All linear transformations in scale, rotation and translation are handled. Although the use of three fiducial coordinates means that the procedure is capable of a three dimensional transformation (using x, y and z), the z coordinate transformation may be ignored, if desired by the user, for unknown or wavescan position transforms. The w coordinate is for reference purposes only.

Export Selected Samples

This button can be used to export selected position samples to an ASCII file. This operation is intended primarily for saving digitized standard positions to the STDPOS*.POS file names defined in the PROBEWIN.INI file; individual users can save specific subsets of their standard positions. Unknown and wavescan positions can also be exported to ASCII files.

If the selected position samples were referenced to fiducials, then the program will also export the fiducial positions for subsequent fiducial coordinates transformation at another time.

Automation Actions

The automation "actions" desired to be run are to be selected here. The program will execute each automation action for all selected samples in the order listed. Any combination of automation actions may be selected by the user.

Use the Confirm actions to simply confirm the position coordinates of the selected samples and the Acquire actions to actually acquire the data for the selected samples. To confirm positions and/or acquire data for both standards and unknown position samples, select the All samples option and select the standards and unknowns desired. If a confirm action was selected, the program will ignore the setting of the Use Confirm During Acquisition for the confirmation of positions.

Use the "Acquire Standard Samples (again)" if it is desired to run the standards AFTER the unknown or wavescan samples have been run; of course this assumes that the specified standard mounts will still be present in the sample holder inside the instrument.

If the Peak Center action was selected, the program will cease the automation process if one or more of the elements selected for peaking did not peak properly rather than continue any selected acquisition actions.

Automation Options

The following automation options are supported by Probe for Windows. Some options may not be available depending on the interface type and microprobe hardware.

Calibrate On Assigned Standards

This option forces the program to only attempt a peak center on a standard position sample if the standard is assigned as the primary standard for that element. If the element has no assigned standard, then the program will attempt to assign one automatically based on the highest concentration of the element present among the standards in the run. To add additional standards to the run use the Standard | Add Standards To Run menu.

It is a good idea to check the standard assignments in the Analyze! window before running a peak center with this option selected to insure that the correct standard position samples are selected for peak centering.

Use "Quick" Standards

Although it is generally recommended to acquire a complete analysis (acquire all elements based on the last unknown sample setup) for all selected standards, Probe for Windows includes a feature which allows the acquisition of "quick" standardizations to save time. In this mode the program will, for each standard acquisition, acquire only those elements that are actually assigned to that standard. This includes both the primary standard assignments and the interference standard assignments (see the Standard Assignments button in the Analyze! Window), and also any MAN (mean atomic number) standard assignments for background fitting (See the MAN Fits menu under the Analytical menu).

Considerations in the Use of "Quick" Standards

Although the use of "quick" standardizations can save considerable time, it is important to remember, that a complete acquisition (and hence analysis) of a standard enables the analyst to note the accuracy (Ziebold, 1967) of secondary standard elements and to observe on-peak and off-peak interferences. In addition, the complete acquisition (Use Quick Standards not checked) of data on standards used for the quantitative interference corrections is essential for this feature to work correctly if they have not been previously assigned.

However, sometimes for well characterized samples, it is feasible to acquire standard data only for those channels that are used as the assigned standard element for that channel. In these "quick" standardizations, Probe for Windows will skip elements that do not contain any assigned elements for that standard.

In a typical run, one would normally acquire standard samples without the use of the "Quick" standards option. The resulting data can then be checked for interferences and background anomalies. Once these concerns have been addressed, then subsequent standardizations can be acquired using the "quick" standards option to save time.

Use of "Quick" Standards

"Quick" Standards can only be acquired from the Automate! window and are based on the standard assignments of the last unknown (or last standard, if there are no unknowns in the run) as long as the Use Last Unknown (or Standard) option is selected. If another option is selected, for example, the Use Digitized Sample Setups option, then the program will based the "quick" standard on the standard assignments of the digitized sample setup.

For each selected standard in the position list, (in order from top to bottom), the program will check the primary standard, interference, and MAN standard assignments to determine whether an element should be acquired for a quick standard. If the an element in the sample is actually utilized by the "quick" standard being acquired, then the program will retain it for the acquisition of intensities, otherwise the element will be skipped during the acquisition. Note that if no elements in the sample for a standard are assigned for any of these purposes (a true secondary standard), the program will acquire all the elements in the current sample setup for that standard.

Note that the program may warn the user that the element acquisition order has been changed to user defined to internally facilitate the acquisition of "quick" standards. However, the program will not change the actual order that the elements are being acquired.

Use Filament Standby After

This option (if supported by the hardware interface) is used to perform a filament shutdown after the automation actions have been completed. This is most useful for extended acquisitions overnight or over the weekend when it is desirable that the filament life be conserved as much as possible.

Use Confirm During Acquisition

This option will allow the user to perform a stage X, Y and Z adjustment just before the sample data is acquired on the first point of each position sample. The default confirm delay time is specified in the PROBEWIN.INI file. This option is ignored for Confirm automation actions.

Use Beam Deflection For Position

This option is available if an imaging interface is supported by the hardware interface (see the ImageInterfacePresent and ImageInterfaceType parameters in PROBEWIN.INI file). If this option is unchecked then normal stage motion is used to position the sample for acquisition. If this option is checked, then the program will utilize beam deflection for positioning the sample (beam position) for acquisition. This option affects only unknown and wavescan position samples (not standards).

This option is primarily intended for situations where very small beam diameters (low overvoltage) are used for precise positioning and acquisition at scales finer than the stage mechanism is capable of. Note that care must be taken to digitize positions that are all within the range of the current beam scan parameters and that a high enough magnification is utilized so that no spectrometer defocusing occurs.

Confirm All Positions In Sample

This option forces the program to move to EACH position in the selected position sample and allow the user to confirm the coordinates of that single point. This applies both to the explicit confirm action and to acquisition actions when the Use Confirm During Acquisition option is checked.

Note that even if this option is selected, only the first point in a position sample will be used for a peak calibration procedure. In addition, any coordinates for a standard position sample that are "automatically generated" during the acquisition process will be ignored for the explicit confirm action even if the Confirm All Positions In Sample option is checked.

Combine Multiple Sample Setups

This option allows the user to either run, for each position sample, each specified multiple sample setup as a separate sample (unchecked) or as a single combined sample (checked). This option only affects position samples that have been assigned multiple sample setups.

Specifically, if this checkbox is not checked, a separate sample based on each setup will be acquired for each position sample based on each setup specified in the multiple setup dialog. If it is checked then all specified multiple setups will be combined into a "combined condition" sample (each element can have different column condition parameters) and the software will adjust the column conditions as necessary to acquire the elements as defined. Note that these defined multiple setups are just sample setups that could contain single column conditions or could even be multiple column conditions sample setups themselves.

Use ROM Auto Focus

This option (if supported by the hardware interface) is used to perform an automatic ROM based automatic focus on the sample surface. This option supports the following types of auto focus during an automated acquisition:

1 = auto focus on a new position sample only
2 = auto focus on every point in each sample
3 = auto focus using the digitized auto focus flags (or imported from a .POS file)
4 = auto focus using the specified auto focus interval

Standard Points To Acquire

This parameter specifies the number of standard point acquisitions to acquire on each standard. If fewer than this many points are actually digitized in the position database, the program will automatically increment the X stage axis by the amount specified in the Standard X Increment field.

Since Probe for Windows automatically uses the average of the sample count data for the calibration of quantitative intensities, it is recommended to acquire at least 5 to 15 points on each standard for accurate quantitative analysis.

Automate Confirm Delay

This is the time in seconds that the program will utilize for the Confirm action. To change the default confirm delay, edit the parameter in the PROBEWIN.INI file.

Standard X Increment

The is the distance in microns that the program will automatically increment the X stage axis for each standard coordinate acquisition, if the number of points specified in Standard Points To Acquire is less than the number of standard coordinate positions actually contained in the position database. This value can be set to any distance from zero to 100 microns.

Re-Standard Y Increment

This is the distance in microns that the program will automatically increment the Y stage axis for each re-standardization. This parameter is used to avoid analyzing the same sample spot on the standard and should be set to a value somewhat larger than the typical beam size of the microprobe. This value can be set to any distance from zero to 100 microns.

Run Selected Samples

This button starts the selected automation actions based on the selected samples. The program will confirm the number of standard, unknown and wavescan samples to be acquired during the automation.

The automation can acquire sample positions based on five different methods :

Use Last Unknown (Or Standard)

The default method the program uses to acquire automated samples is to base the acquisition on the last unknown sample setup. If no unknown samples exist, the program will base the acquisition on the last standard sample setup.

If no unknown or standard samples exist, the program will not be able to run automated samples. Always create a default sample from the Acquire! window using the New sample button before attempting to run automated samples.

Use Digitized Sample Conditions

If the microprobe interface supports computer control of the kilovolts, beam current and beam size then the user can specify that the program base the acquisition on the last unknown sample setup with these parameters based on the sample conditions specified when the sample positions were digitized. See the Conditions button above for more details on using this feature.

Use Digitized Sample Setups

Another method that can be used to acquire automated samples is to base the acquisition on sample setups that were specified when the sample positions were digitized. In this way, one can automatically data for different sample positions using different sample setups for tremendous flexibility. See the Sample Setups button above for more details on using this feature.

Use Digitized File Setups

Yet another method that can be used to acquire automated samples is to base the acquisition on file name setups that were specified when the sample positions were digitized. In this way, one can automatically data for different sample positions using different previously created file setups for tremendous flexibility. See the File Setups button above for more details on using this feature. Note that standard intensity data from the file setup will be automatically loaded (if it has not been already) unless the option has been turned off from the Acquisition Options window.

Use Digitized Multiple Setups

Finally as a last option one can acquire automated samples based on multiple sample setups, specified when the samples were digitized. This is of course similar to the sample Setups option above except that one can acquire more than one sample setup for each position sample. See the Multiple Setups button above for more details on using the feature.

Plot!

The Plot! modeless windows provides graphical plotting of numerous data types in Probe for Windows. Standard, unknown and wavescan sample data may be displayed. Digitized data associated with a polygon digitization may also be displayed or output.

Wavescan samples can display KLM markers from the NIST database based on the analyzed elements in the range, all elements in the range or a specific element in the range.

Background types (linear, high only, low only, average, etc) can be modeled based on existing wavescan samples, evaluated and updated for both standard and unknown samples using the Model Background dialog.

Select All

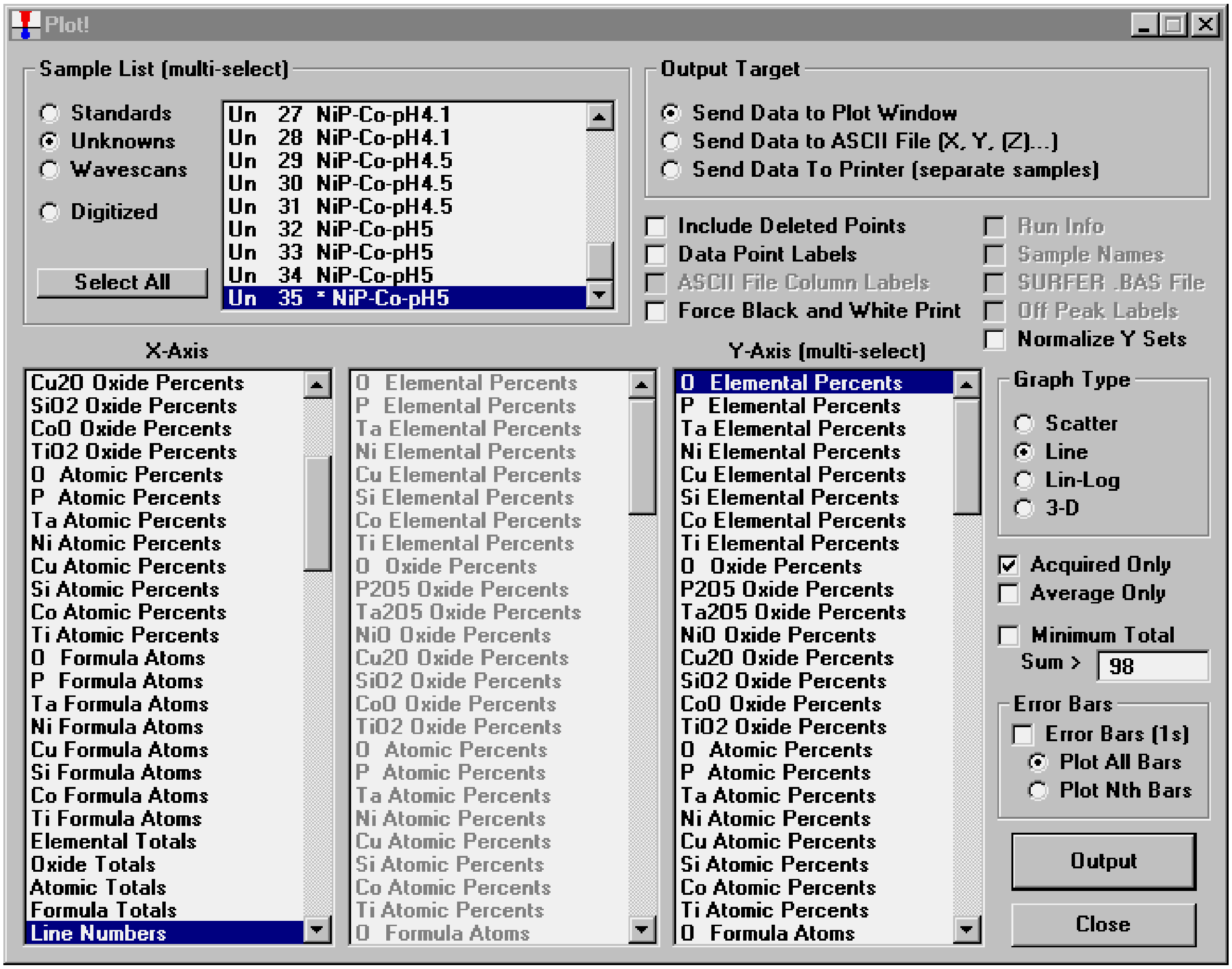
This button will select all samples displayed in the Plot! sample list. Note that because each sample may contain a different set of acquired elements, the axis list boxes are updated each time a different sample is selected.

Output Target

The user may select either output to the Graph window or to a tab delimited ASCII file or to have each sample plot data automatically output to the default printer. If ASCII file output is selected, the program will ask for the output filename (*.DAT extension) after calculation of all data has been performed. The default is to send data to the graph window for viewing.

Include Deleted Points

This option, if selected, will output data from samples even if the data has been previously flagged as deleted. This option has no effect on quantitative sample output, which means that the deleted points will be output to the graph or output file, but the calculated values will be replaced with a small number (NotAnalyzedValue! = 0.00000001) equal to 10^{-7}.



Data Point labels

This option will display a line number for each value plotted in the graphical display mode. This option has no effect if ASCII file output is selected.

ASCII File Column Labels

This option will output a line of data column labels for each column of data in the ASCII file. The labels will be enclosed in double quotes. If the elements being output change during the output process, the program will automatically write a new column label line. This option has no effect if Graph output is selected.

Run Info

This option will output a header to the ASCII file including the user, title and description of the current run. In addition the current time and date will be displayed also. This option has no effect if Graph output is selected.

Sample Names

This option will output a line containing the sample name in double quotes before the data for that sample is output to the ASCII file. This option has no effect on data sent to the graph window.

Force Black and White Print

This option will force a color printer to print graphs in black and white instead of in color. This option applies to both the Print button in the Graph window as well as the Send To Printer option in the Plot! Window. In color mode monochrome printers (laser printers) will print grayscale and color printers will print color. In the Force Black and White mode, both types of printers will print black and white only. This option saves toner for monochrome printers, because the lightly colored background is not printed at all.

Off Peak Labels

This option will add off-peak labels to the off-peak markers. Note that both actual and current off-peak markers and labels are shown. Actual off-peak markers are the positions of the off peaks when the sample was acquired while the current off-peak markers are the off-peak positions that are currently specified.

SURFER .BAS File

If the SURFER .BAS File option is selected, Probe for Windows, will, in addition to the actual data file, create a script file for use with SURFER for Windows (from Golden Software) for automatically generating contour and surface plots of your data. This assumes that the sample data is applicable to this type of processing.

Be sure that the SurferOutputVersionNumber parameter is correctly specified in the PROBWIN.INI file when using this option. Probe for Windows assumes Surfer v. 6.0, unless the parameter is specifically indicated. Due to changes in the file formats expected by Surfer v. 6 and Surfer v. 7, the correct script format must be output or the script will not run properly.

If the sample was a digitized polygon area grid, then the program will also automatically output a .BLN file for use with the SURFER for Windows surface and contour plot boundary feature. Notice that the digitized polygon grid coordinates are saved automatically and can be viewed, once the data is acquired, using the "plot" window to display digitized samples.

> *Be aware that SURFER for Windows expects X and Y coordinate data in the first two columns of the .DAT file, followed by multiple columns of Z data for plotting contours or surfaces. To accomplish this, be sure to select the 3-D graph type and select the X coordinate data in the x-axis list box, the Y coordinate data in the y-axis list box and the Z data (weight percents, etc.) in the z-axis list box using multiple selection.*

The creation of the SURFER .BAS file requires that the GRIDBB.BAS to be present in the default directory (usually **C:\Program Files\Probe for Windows-E**).

SURFER for Windows Instructions

Probe for Windows can create a .BAS basic script file containing OLE code for creating contour and surface plots, or just screen display for testing purposes. This .BAS basic file is only to be used with the GS Scripter utility that comes with SURFER for Windows 95/NT v. 6.0 or higher.

To run the .BAS script, double click the GS Scripter icon, select File, Open and double click the correct .BAS file. Then click Run, Start to begin the automated plotting.

IMPORTANT! Note that the default output mode of the script file is "TEST", which will only output the plots to the screen and will produce a log of the plotting operations. To produce output to the default printer, comment out the line : OutputType$ = "TEST" by inserting a single quote in front of the line like this : 'OutputType$ = "TEST", and UNcomment the line : OutputType$ = "SURF" by removing the single quote in front of it.

Remember, the last uncommented "OutputType$" line will select the output. If necessary, the "GridMethodType%" can also be changed in the same fashion to change the gridding method used by the grid module. Note also, that any element column plot can be skipped by simply commenting out the appropriate "ZLabel$" lines, by inserting a single quote in front of the line.

Normalize Y Sets

This option will normalize data from different Y (axis) datasets for both Graphing and ASCII output. Only dta from the Y-axis list will be normalized. This might be useful to compare trends between different elements.

Normalize Samples (Y Sets)

This option will treat each Y-axis data separately, but will normalize Y data sets between different selected samples. This can be useful when comparing wavescan data from two separate wavescans. Note that the Normalize Y Sets and the Normalize Samples (Y Sets) options can be combined.

Graph Type

The various graph types are selected here. The default graph type may be set from the PROBEWIN.INI file. Currently the following graph types are supported :

- Scatter (x and y data as points)

- Line (x and y data as points connected by lines, suitable for wavescan samples)

- Lin-Log (x data on a linear axis and y data on a log axis

- 3-D (x, y and z data as points)

Analyzed Elements Only

This option will re-load the axis lists to display either the analyzed elements only, or both the analyzed and specified elements. This option is used to allow the user to graph or output those elements calculated by difference or stoichiometry.

This option can also be utilized in order to output all elements in a run, even if the last sample does not contains elements analyzed and/or specified in other samples. Consider that because the elements listed in the axis lists are based on the last sample selected, if a selected sample prior to the last selected sample contains additional elements not in the last selected sample, they will not be output simply because they cannot be selected. Therefore, if it is desirable that these additional elements be output, follow these directions:

- From the Analyze! window sample list, select the last sample that will be output from the Plot! window.
- Click the Elements/Cations button.
- Add, as specified elements (no x-ray symbol), all additional elements (found in previous samples) that are desired to be output, that are not already in the last sample.
- Click OK and return to the Plot! window and uncheck the Analyzed Only button. This will allow the program to display all elements in the last selected sample, including the specified elements just added.
- Select all elements to be output. The program will output the selected elements whether they are analyzed or specified.

Average Only

This option will output only the data average of each sample to the plot window or the output ASCII data file. Note, if data point labels are selected for the plot window, instead of line numbers the program will use sample numbers.

Minimum Total

This option (if selected) will output only those data lines whose totals are at least the value specified. This option must be used with at least one column of quantitative data selected for graph or file output.

Error Bars

This option will allow the program to calculate one sigma error bars for certain data types, specifically the Elemental, Oxide Percents and On Peak Counts data types only.

Plot All Bars

This option will allow the program to plot one sigma error bars for each data point in each data set. The bars will be centered on the data point.

Plot Nth Bars

This option will allow the program to plot one sigma error bars for each data point in each data set as above, however the frequency of the plotted errors bars will depend on the number of data points displayed according to the following table:

Less than or equal to 50 points	Plot error bars for all points
Less than or equal to 100 points	Plot error bars for every other data point
Less than or equal to 150 points	Plot error bars for every 3rd data point
And so on…	

Error Bar Calculations

The formula for these error calculations are as specified:

On Peak Counts Errors:

$$\Delta I = \sqrt{I_P}$$

Where: I_P = On-peak counts (including background, de-normalized for deadtime, beam current and time)

Note that the result is normalized to deadtime, beam current and count time after the square root is calculated and before it is displayed.

K-Ratio Errors:

$$\Delta K = \frac{\sqrt{I_U}}{\left(I_S * ZAF_S\right)}$$

Where: I_U = Unknown on peak counts (background corrected, de-normalized for deadtime, beam and time)
I_S = Standard on peak counts (background corrected, de-normalized for deadtime, beam and time)
ZAF_S = ZAF correction for standard counts (to obtain pure element counts)

Note that the result is normalized to deadtime, beam current and count time after the square root is calculated and before it is displayed.

Elemental (or Oxide) Weight Percent Errors:

$$\Delta C = \Delta K * ZAF$$

Where: ΔK = K-ratio error (from above)
ZAF = unknown ZAF correction factors

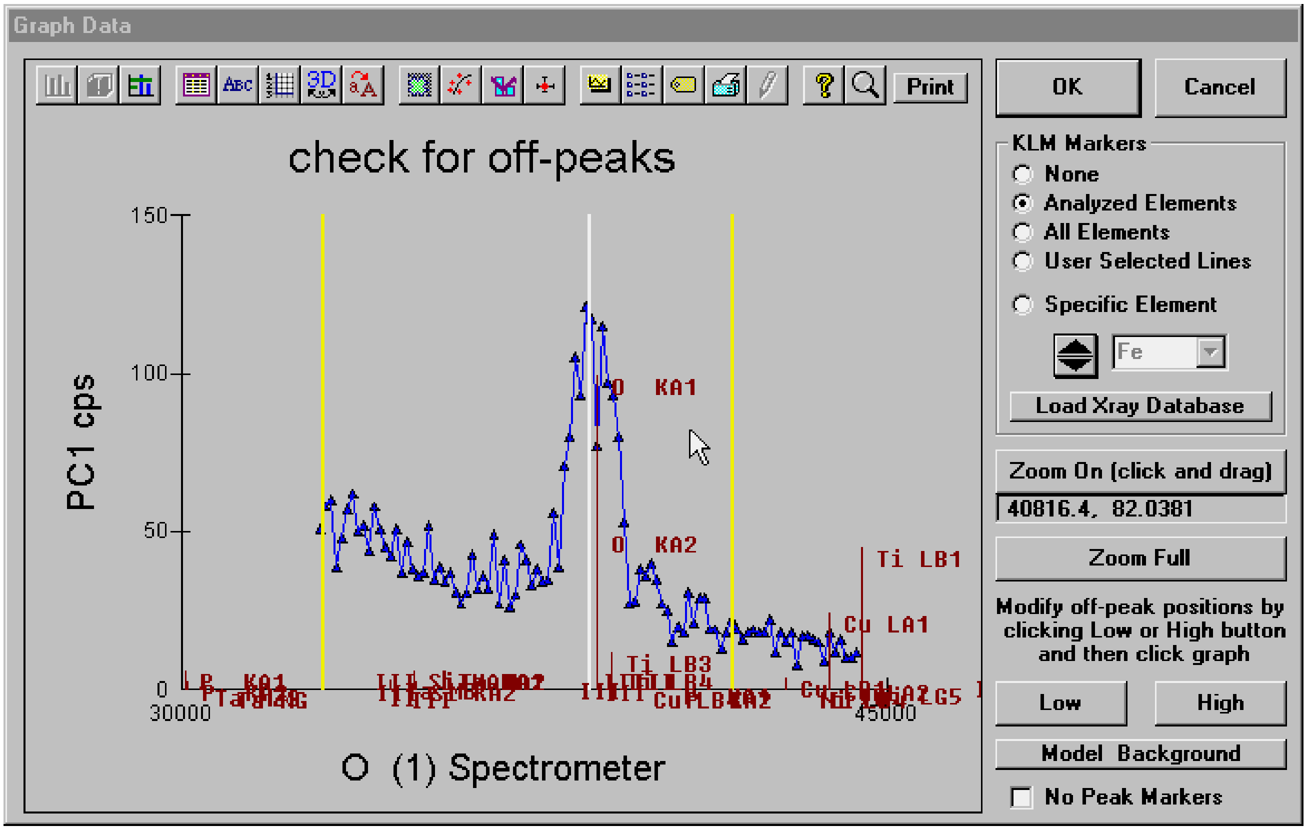
Output

This button will start the output process selected based on the Output Target type (graph window or ASCII file) selected by the user.

Graph Data

The Graph Data window is used in two modes. The first to plot x-ray intensity or compositional data from standard and unknown samples, and the second to plot x-ray intensity and spectrometer position data for wavescan samples. Multiple Y data is automatically plotted and listed in a color coded legend if specified in the Plot! window.

Digitized x and y position data from polygon boundary acquisitions may also be plotted in this window if this data exists in the current probe database file.



KLM Markers
○ None
● Analyzed Elements
○ All Elements
○ User Selected Lines
○ Specific Element
Fe

40816.4, 82.0381

Modify off-peak positions by clicking Low or High button and then click graph

☐ No Peak Markers

Numerous plot properties may be modified using the tool bar buttons at the top of the graph. A print button has also been added to facilitate printing but other print and output options can be accessed using the System tool bar button (printer icon).

ASCII File Output

If ASCII file output was selected, the program will calculate data for the specified samples and then prompt the user for a path and filename to save the data to. All data files will be <tab> delimited and will normally have a .DAT extension.

Plotting Standard and Unknown Data

Both x-ray and compositional data may be plotted in the Graph Data window. Click and drag any portion of the graph for zooming into a region of the graph.

Click the Zoom On button to use "Hot Hit" mode which allows the user to click near a specific symbol to get the exact x and y data values. In this mode the click and drag zoom feature is disabled. Click the "Hot Hit" button to restore click and drag zooming.

Plotting Wavescan Data

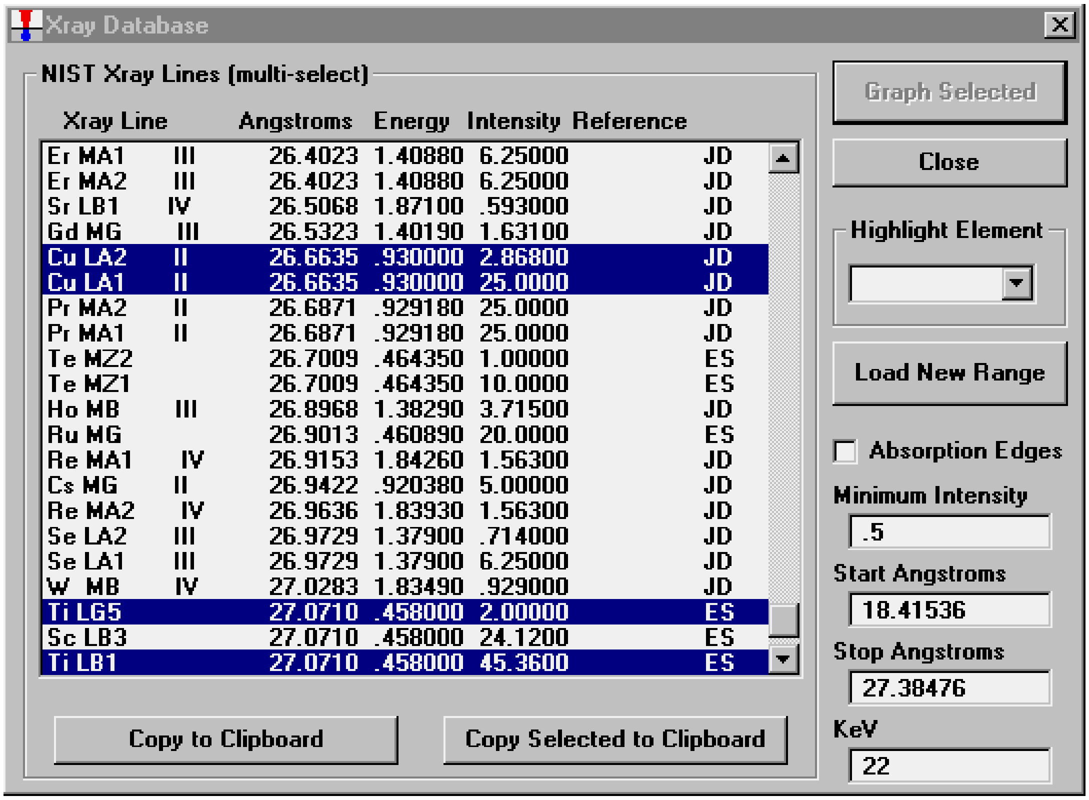
When wavescan data is plotted in the Graph Data window additional options for wavelength dispersive data are enabled.

KLM Markers

- None:	No KLM markers (default).
- Acquired only:	All KLM markers for all elements in the wavescan sample (acquired and specified).
- All Elements:	All KLM markers for all elements in range.
- User Selected Lines:	Only lines selected by the user in the Load Xray Database window.
- Specific Element	Only lines for the element selected in the list.

Load X-ray Database

Allow the user to see a list of all files in the graph range. If the User Selected Lines option is clicked, the users can select specific lines for graphing.



Xray Line		Angstroms	Energy	Intensity	Reference
Er MA1	III	26.4023	1.40880	6.25000	JD
Er MA2	III	26.4023	1.40880	6.25000	JD
Sr LB1	IV	26.5068	1.87100	.593000	JD
Gd MG	III	26.5323	1.40190	1.63100	JD
Cu LA2	II	26.6635	.930000	2.86800	JD
Cu LA1	II	26.6635	.930000	25.0000	JD
Pr MA2	II	26.6871	.929180	25.0000	JD
Pr MA1	II	26.6871	.929180	25.0000	JD
Te MZ2		26.7009	.464350	1.00000	ES
Te MZ1		26.7009	.464350	10.0000	ES
Ho MB	III	26.8968	1.38290	3.71500	JD
Ru MG		26.9013	.460890	20.0000	ES
Re MA1	IV	26.9153	1.84260	1.56300	JD
Cs MG	II	26.9422	.920380	5.00000	JD
Re MA2	IV	26.9636	1.83930	1.56300	JD
Se LA2	III	26.9729	1.37900	.714000	JD
Se LA1	III	26.9729	1.37900	6.25000	JD
W MB	IV	27.0283	1.83490	.929000	JD
Ti LG5		27.0710	.458000	2.00000	ES
Sc LB3		27.0710	.458000	24.1200	ES
Ti LB1		27.0710	.458000	45.3600	ES

☐ Absorption Edges

Minimum Intensity: .5

Start Angstroms: 18.41536

Stop Angstroms: 27.38476

KeV: 22

To change the range enter the start and stop (ending) angstroms limits and click the Load New Range button. The KeV parameter will limit the appearance of higher order lines that cannot be excited below the specified voltage. The Graph Selected button is only active if the User Selected Lines option is selected in the Graph dialog. The reference indicates the source. Specifically, ES is Eric Steele tabulated the first order lines, the higher order lines were calculated by JD (John Donovan).

Low and High Off Peak Positions

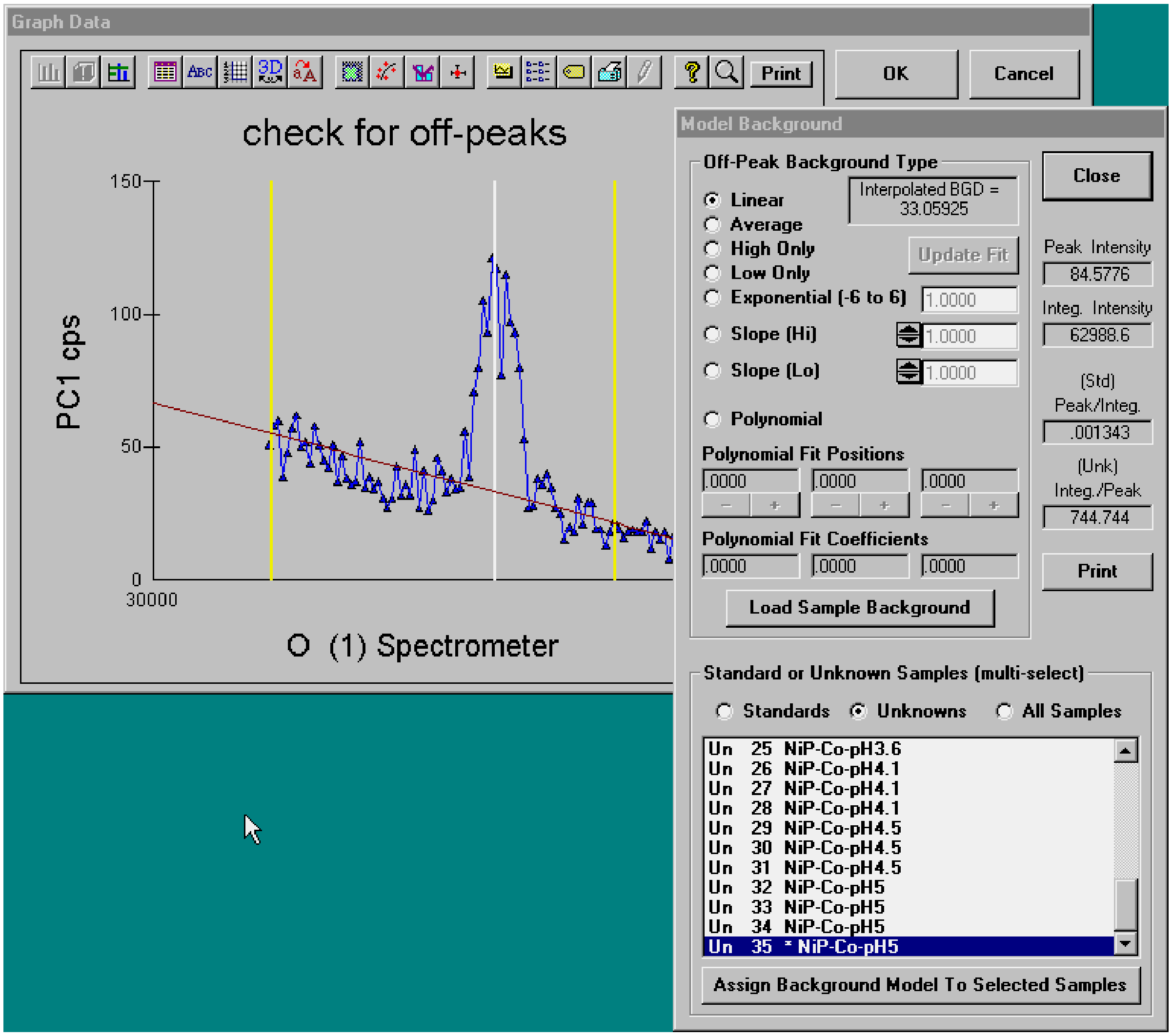
To move an off-peak (background) position for the next standard or unknown acquisition, click either the Low or High off-peak button. Position the cursor over the graph (note that the cursor changes to a cross-hair) and click where it is desired that the new off-peak position be located.

If the current sample contains no data, the off-peak position is updated for that sample, otherwise a warning is given that the off-peak position selected will be applied to the next new sample that is created.

The new off-peak position is shown in yellow, while the original off-peak position for the displayed sample is shown in purple.

Model Background

To model the various off-peak background correction types, click the Model Background button. This option is only available when a wavescan sample is displayed.



Off-Peak Background Type

- ● Linear
- ○ Average
- ○ High Only
- ○ Low Only
- ○ Exponential (-6 to 6) 1.0000
- ○ Slope (Hi) 1.0000
- ○ Slope (Lo) 1.0000
- ○ Polynomial

Interpolated BGD = 33.05925

Polynomial Fit Positions: .0000 .0000 .0000

Polynomial Fit Coefficients: .0000 .0000 .0000

Peak Intensity: 84.5776

Integ. Intensity: 62988.6

(Std) Peak/Integ.: .001343

(Unk) Integ./Peak: 744.744

Standard or Unknown Samples (multi-select)

○ Standards ● Unknowns ○ All Samples

```
Un  25  NiP-Co-pH3.6
Un  26  NiP-Co-pH4.1
Un  27  NiP-Co-pH4.1
Un  28  NiP-Co-pH4.1
Un  29  NiP-Co-pH4.5
Un  30  NiP-Co-pH4.5
Un  31  NiP-Co-pH4.5
Un  32  NiP-Co-pH5
Un  33  NiP-Co-pH5
Un  34  NiP-Co-pH5
Un  35  * NiP-Co-pH5
```

To see the background model, click the specific background type and observe the plotted background curve in the Graph window.

For the exponential, slope and polynomial off-peak background types coefficients are required. The exponential, slope-high and slope-low coefficients are entered by hand. The exponential exponent may be –6 to +6. For high or low only background types, a slope of one (1.) will produce exactly the same result as the high-only or low-only off-peak background type. In situations where there is some curvature and exponential cannot be used, examination of backgrounds on similar phases that lack the element of interest can give an appropriate "slope" factor to yield a proper background at the peak position. For example, if the high-only offset had a value of 10 and the slope factor entered was 1.3, the on peak background used would be 13.

The polynomial background fit coefficients are calculated automatically as the three different fit positions are moved by clicking the minus (-) or plus (+) buttons. The slope or polynomial coefficients can be applied to selected standard or unknown samples for use with a sample specific slope or polynomial off-peak background correction. That is, the actual slope or polynomial background correction will be calculated for each sample based on the actual off-peak data for that sample using the fit coefficients from the fit model.

To make the assignment to the selected unknown samples, be sure to click Ok in the Model Background dialog AND ALSO in the Graph Data dialog.

Area Peak Factor Calculations

The Model Background dialog will also calculate the background corrected peak and integrated areas. These are useful for Area Peak Factor (APF) calculations. The program will calculate both the P/I (Peak/Integrated) and the I/P (Integrated/Peak) values. The one that is ultimately utilized for an APF calculation by the user depends on whether the wavescan represents the primary standard or the secondary standard. See the section of APF calculations in the Analytical menu section for details on how these values are used for the calculation of APFs.

The APF calculations are in units of counts per second for the peak intensities and counts per second multiplied by spectrometer range (between the low off-peak and high off-peak positions) for the integrated intensities. Both the peak and integrated intensities are background corrected using the currently selected background fit type.

Centroid Calculations

The Model Background dialog will also calculate the centroid of the displayed wavescan. The program will fit the wavescan intensities that are within the currently displayed x-axis zoom range (min to max) of the Graph dialog to a parabola (2nd order polynomial). Therefore the user should zoom the wavescan to display only the top portion of the wavescan peak for best results. The peak centroid is calculated using the following equation:

$$P_C = \frac{2A}{-B}$$

Where: P_C is the centroid of the peak
A is the first fit coefficient (intercept)
B is the second fit coefficient (slope)

Close

This button will close the Plot! Window, although since it is a modeless dialog it can be left open if enough screen space is available.

Probe Menu Details

File

The File menu can be used to create new Probe for Windows runs, open an existing run, save the current run to another name, close the current run, display the current probe database file information, print the current log window contents or log window selection or exit the program.

New

The New menu opens a dialog to select a **new** Probe for Windows database file. If the file already exists, the program will prompt the user whether to overwrite the existing file. After the new file has been created the program will display a file information dialog to allow the user the personalize the run title and description.

The program will automatically append a .MDB extension to the file name if one is not supplied by the user. The .MDB file name indicates Microsoft Database and is a valid Microsoft Access v. 1.1 database file.

Open

The Open menu allows the user to select an **existing** Probe for Windows database file to process previously acquired data or to append additional acquisition data. The program will check that the specified file is of the correct format and warn the user if not. Probe for Windows generally uses a file extension of .MDB for it's database file extension.

Probe for Windows performs a general initialization of the ZAF correction factors when it opens a Probe for Windows database. If a x-ray initialization error occurs during this procedure, the program will allow the user to continue to open the file anyway or not. If an error does occur, for example an x-ray overvoltage condition, the user should take whatever steps are necessary to correct the anomalous condition.

Save As

The Save As menu allows the user to save the currently open Probe for Windows database file to another file name.

This option allows the user considerable flexibility in how new runs are created and utilized. For example, one possibility is to create a number of generic Probe for Windows runs that contains only a standardization for certain elements (FELDSPAR.MDB for example). Then, at a later time, the user could open that run and use the Save As option to save the run to another file name. Doing so, will create a new run with only the previously acquired standardization, to which unknown can then be acquired without altering the original run containing only the standardization.

Of course, whether this procedure is applicable or not depends greatly on both the reproducibility of the spectrometers and the accuracy required by the user.

Compact

The Compact menu allows the user to compact the current Probe database file. This allows the database to be sorted for maximum efficiency and the indexes updated. If the database has become very fragmented this process can also save a significant amount of disk space for large database files.

Close

The Close menu allows the user to close the currently open Probe for Windows database file. This can be used to close the current file before opening a different Probe for Windows database file without re-starting the program. The program will ask the user to confirm the close operation and all parameters are automatically saved.

Find File

This menu allows the user to open an existing run by browsing the available runs on disk. This is useful when the filename itself is unknown to the user, but the run itself, might be recognized on another basis such as user name or title.

This dialog has a directory browser that can be used to load Probe run files from various sub-directories if desired. For example, each user could utilize a separate sub-directory or their own or the different types of analysis could be used to define a sub-directory structure to hold files.

File Information

This menu displays and allows the user to change the run title and/or description fields for the currently open run. The title and user fields are limited to 64 characters and the description field is limited to 255 characters.

Normally, the user should completely fill out these fields since the text is saved not only to the user's run database, but also the user log database (see USERWIN.EXE). It is often helpful to use the description field to list the sample numbers or designations. Click the Insert <cr> button to make a new line in the description field.

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 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. The program will ask the user to confirm the exit procedure if an analytical run is open.

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.

Standard

Standard Database
This menu invokes a shell process to launch the Standard for Windows database application (STANDARD.EXE) as an asynchronous process. The standard database is used to maintain the database of standard compositions and also includes a number of features for exploring analytical conditions based on various standard compositions.

Since the shell process runs independently, it can be accessed during an automation or analysis procedure.

Add Standards To Run
This menu allows the user to specify additional standards to be used in the currently open Probe for Windows run.

Note that if the run is closed before any data is acquired for these newly added standards, then they will have to be added again, if the run is re-opened later to acquire data for them unless they are saved as the probe database is closed by clicking Yes when asked whether to save them for the next session. This is because Probe for Windows updates the list of standards in the run each time a database file is opened based on the standard samples that have been actually created.

All standards that need to be digitized, acquired or assigned, must be first added to the run using this window dialog.

Standards may also be removed from the standard list with some reservations. First, a standard cannot be removed from the standard list if it references a standard sample already created in the current probe database. Second, even if a standard does not reference a standard sample, it may still itself be referenced by a standard, interference standard or MAN (mean atomic number) background standard assignment, especially if a sample setup was loaded from another probe database using the Load File Setup option. It is strongly suggested that the user check that all assignments do not reference the standard number that is to be removed.

In the case of MAN standard assignments, it may be useful to use the Clear All MAN Assignments menu item under the Analytical menu to remove all standard references. These assignments can be easily reloaded by default the next time the MAN Fits menu is selected.

X-Ray

X-Ray Database

This menu allows the user the view specified ranges of the NIST x-ray wavelength database. This database covers the wavelength range from approximately 0.5 to 100.0 angstroms and includes higher order reflections as well. Higher order reflections are reduced in intensity by 25% for each subsequent order to simulate the effect of PHA analysis.

The x-ray list range (Start Angstroms and Stop Angstroms) and minimum search intensity (Minimum Intensity) of the x-ray list can be specified by the user. Note that since the display is limited to about 1000 items, the program will automatically increase the minimum intensity until the returned list of x-ray lines is less than 1000. To view x-ray lines of lesser intensity, simply reduce the x-ray range and click the Re-Load button.

Description of the X-ray Database (adapted from NIST documentation by C. Fiori)

The NIST x-ray database is based on 4985 (1st order) entries and includes all the measurable x-ray lines, satellites and absorption edges from under 100 eV to over 120 keV. Additionally, most of the x-ray lines and satellites are assigned a relative intensity (relative to the alpha-1 line in each family). The data base was assembled primarily from four sources:

1.) B.L. Doyle, W.F. Chambers, T.M. Christensen, J.M. Hall and G.H. Pepper "SINE THETA SETTINGS FOR X-RAY SPECTROMETERS", Atomic Data and Nuclear Data Tables Vol. 24, No 5, 1979.

2.) E.W. White, G.V. Gibbs, G.G. Johnson Jr. and G.R. Zechman "X-RAY WAVELENGTHS AND CRYSTAL INTERCHANGE SETTINGS FOR WAVELENGTH GEARED CURVED CRYSTAL SPECTROMETERS" Report of the Pennsylvania State Univ., 1964.

3.) J.A. Bearden "X-RAY WAVELENGTHS AND X-RAY ATOMIC ENERGY LEVELS" Rev. Mod. Phys., Vol. 39, No. 78, 1967.

4.) J.A Bearden and A.F. Burr,"REEVALUATION OF X-RAY ATOMIC ENERGY LEVELS", Rev. Mod. Phys., Vol. 31, No. 1, 1967.

Each x-ray line or edge series as a function of atomic number was fit to a fourth degree polynomial. The fit was subtracted from the appropriate data and the residuals plotted and examined. In this way rogue entries could be identified and corrected. The resulting data base is considered to be sufficiently accurate for any application involving the Si (Li) x-ray detector and single crystal wavelength spectrometers.

Note that the last entry in the x-ray database window gives a code for the source of the entry. If the column is blank the source is reference 2. If the column contains the letter "C" the source is reference 1. If the letters "BB" appear, the source is reference 4. The letters "W,F" mean that reference 2 was used but the relative transition probability has been adjusted by Fiori. Reference 3 was used as a check since it is the source of many of the entries of reference 1.

In column 3 the notation KA1,2 means the entry is the weighted sum of the KA1 and KA2 in the ratio 2 to 1. For low atomic number the entries are not self consistent since the data is from different sources. If the column begins with the capital letter S then the entry is a satellite line due to doubly ionized atoms. The relative transition values for these entries are only valid for electron excited specimens, and are, at best, estimates.

Th following are Siegbahn to shell-transition notation conversions:

```
KA   = KA1+KA2+KA3
KA1,2 = (2*KA1+KA2)/3
KA1  = K-L3
```

```
KA2  = K-L2
KA3  = K-L1
KB   = SUM(KBn)
KBX  = Metal
KB1  = K-M3
KB1' = KB1+KB3+KB5
KB2  = (K-N3)+(K-N2)
KB2' = K-N3
KB2'' = K-N2
KB3  = K-M2
KB4  = (K-N4)+(K-N5)
KB5  = (K-M4)+(K-M5)
KB5' = K-M5
KB5'' = K-M4
Kd1  = K-O3
Kd2  = K-O2
LA   = LA1+LA2
LA1  = L3-M5
LA2  = L3-M4
LB1  = L2-M4
LB10 = L1-M4
LB15 = L3-N4
LB17 = L2-M3
LB2  = L3-N5
LB3  = L1-M3
LB4  = L1-M2
LB5  = (L3-O4)+(L3-O5)
LB6  = L3-N1
LB7  = L3-O1
LB9  = L1-M5
LG1  = L2-N4
LG11 = L1-N5
LG2  = L1-N2
LG3  = L1-N3
LG4  = L1-O3
LG4' = L1-O2
LG6  = L2-O4
LG8  = L2-O1
Ll   = L3-M1
Ln   = L2-M1
Ls   = L3-M3
Lt   = L3-M2
Lu   = (L3-N6)+(L3-N7)
Lv   = L2-N6
MA1  = M5-N7
MA2  = M5-N6
MB   = M4-N6
MG   = M3-N5
MG2  = M3-N4
MZ1  = M5-N3
MZ2  = M4-N2
Md   = M2-N4
Me   = M3-O5
```

Spectrometer Table

This menu item outputs a table of spectrometer positions for all elements based on the crystals configured for the current microprobe setup in the SCALERS.DAT file in the Probe for Windows sub directory.

Both the alpha and beta series lines are listed. This table is especially useful when printed out and used as a reference when setting up an analytical setup to determine which spectrometers and crystal combinations can be used for the elements of interest.

Emission Table

This menu lists a table of emission energies (or angstroms) for all elements and their major analytical x-ray lines. Note that these values are stored in a binary data file. Although not recommended, it is possible to edit individual data entries use the CalcZAF program.

Edge Table

This menu lists a table of absorption edge energies (or angstroms) for all elements and their major analytical x-ray lines.

Note that these values are stored in a binary data file. Although not recommended, it is possible to edit individual data entries use the CalcZAF program.

Fluorescent Yield Table

This menu lists a table of fluorescent yield fractions for all elements and their major analytical x-ray lines.

Note that these values are stored in a binary data file. Although not recommended, it is possible to edit individual data entries use the CalcZAF program.

MAC Table

This menu lists a table of MACs (mass absorption coefficients) for the specified element and it's major analytical x-ray lines.

Note that these values are stored in a binary data file. Although not recommended, it is possible to edit individual data entries use the CalcZAF program.

The program will automatically load the values based on the selected default MAC table. See the Analytical | ZAF Selection section for a description of the MAC table choices.

Analytical

Analysis Options

The Analysis Options dialog allows 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 :

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

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 :

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

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 (where beam integration time is taken into account) :

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

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

However, since Probe for Windows stores and utilizes x-ray intensities in counts per second (already normalized to time), the actual beam drift correction, for direct reading faraday cup microprobes, is quite a bit more simple than the rigorous example above, and is instead shown here:

$$I_C = I_U \frac{B_N}{B_U}$$

Where : I_C is the beam drift corrected unknown intensity

I_U is the uncorrected unknown intensity

B_N is the nominal beam current

B_U is the beam current for the unknown intensity

This means that if the actual measured beam current for your unknown decreases over time, the value of the fraction $\frac{B_N}{B_U}$, increases and therefore the corrected x-ray intensity is adjusted upwards. If on the other hand, the actual measured beam current for your unknown increases over time, then the value of the fraction $\frac{B_N}{B_U}$, decreases and therefore the corrected x-ray intensity is adjusted downwards.

The beam drift correction essentially normalizes the x-ray intensities to the x-ray intensity that would be expected at the nominal beam current. For example, if most of the x-ray measurements are made at a beam current of 20 nA, then setting the nominal beam current to 20 nA will ensure that the x-ray intensities will appear scaled to readings taken at 20 nA (even if the measurement is taken at a different beam current). In an alternative usage, the x-ray intensities may be expressed in counts per second per nA by setting the nominal beam current to 1.0. See the Count Times dialog in the Acquire! Window to manually change the nominal beam current.

Use Automatic Drift Correction on Standard Intensities

Probe for Windows uses a sophisticated automatic drift correction to correct the counts on the standard, interference and MAN standard intensities. This standard drift correction should not be confused with the beam drift correction described previously. With the automatic standard drift correction, when Probe for Windows 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 are 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

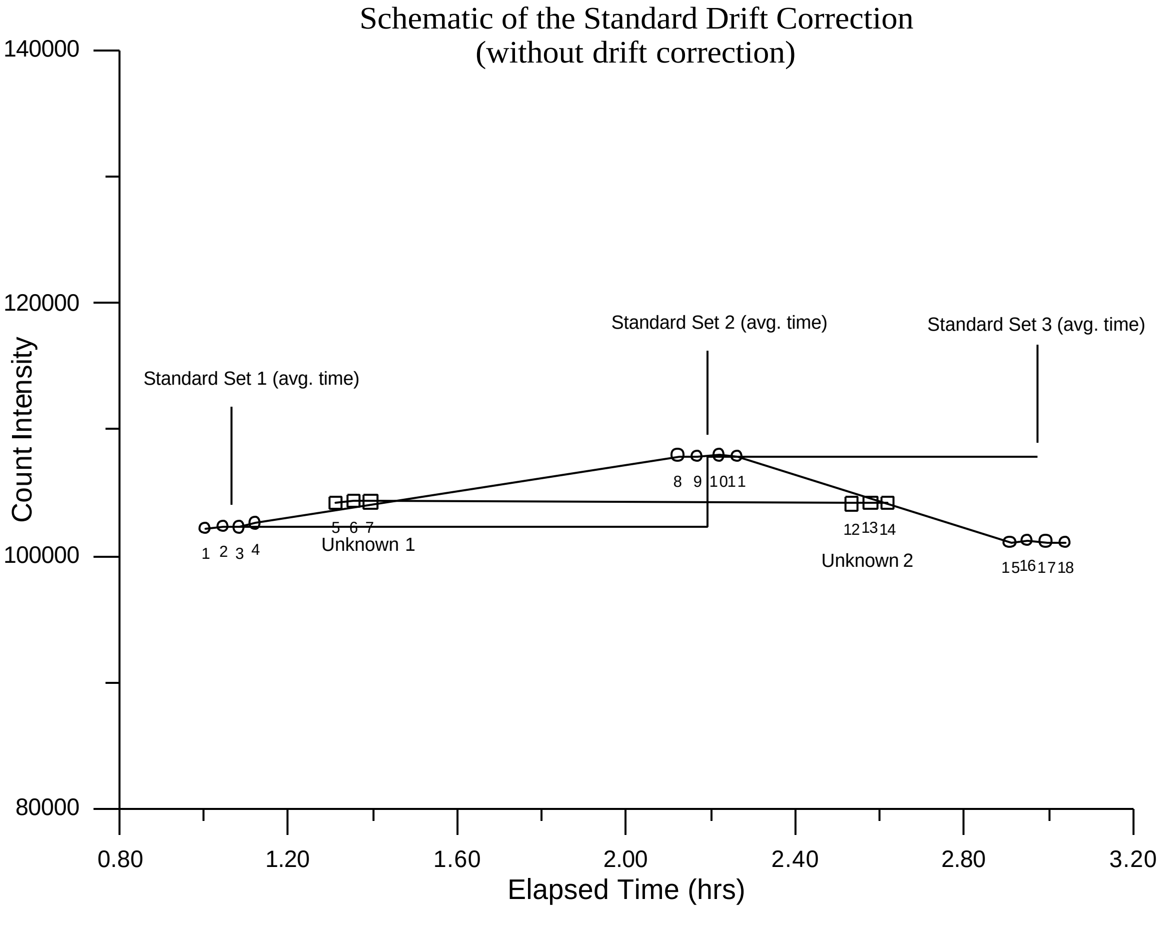
T'_S is the real time of the preceding standardization

T_S'' is the real time of the following standardization

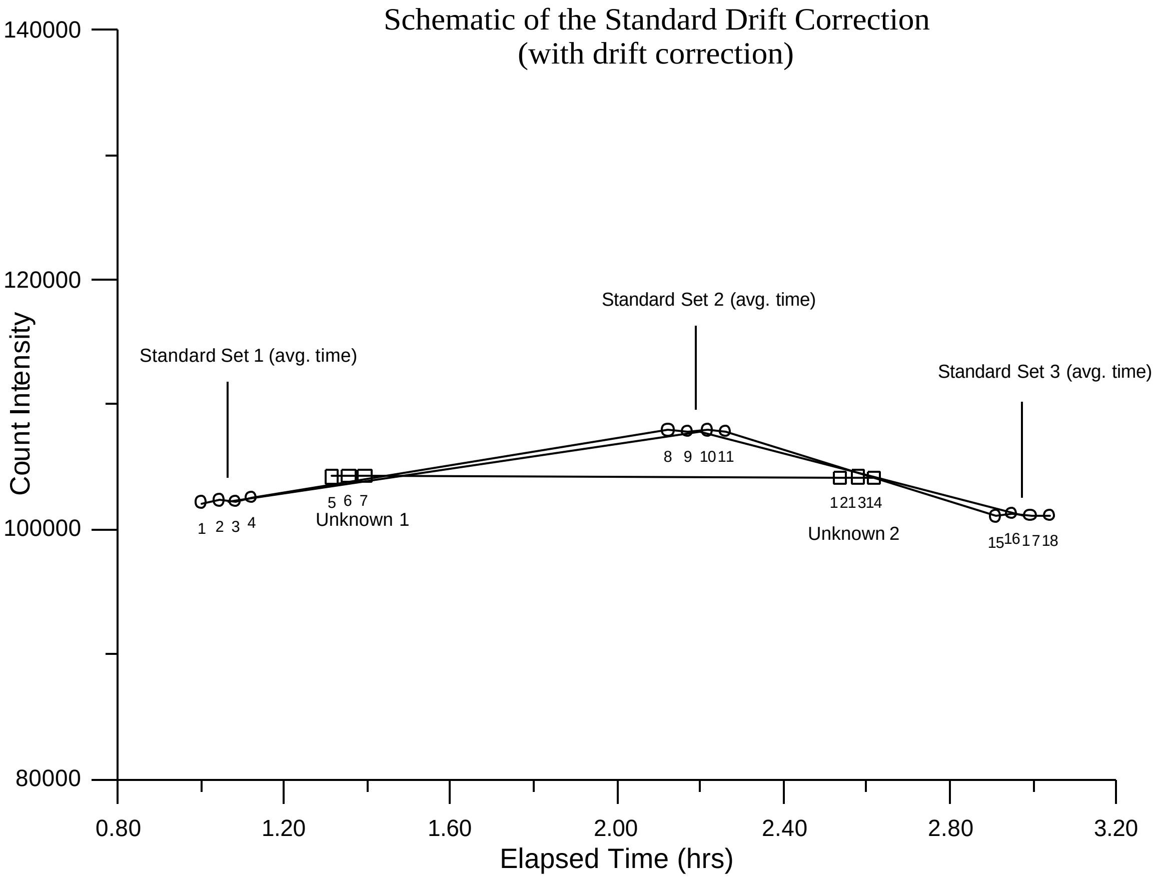
The following explanation will demonstrate how the standard drift correction is actually implemented in Probe for Windows. The example data shown here consists of four standard data points (set 1), followed by three unknown data points (points 5, 6 and 7), followed by four more standard data points (set 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 that the program would calculate in the absence of a drift correction. In other words, the standard intensity is always based on the last standardization and remains constant until the next standardization.

Note that each unknown data point actually uses the average intensity of the previous standardization. In a situation where drift has occurred, significant errors will result for the unknown analyses without a drift correction for the standard intensity.



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 that the program will calculate when a standard drift correction is used. 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.



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.

Use Assigned Volatile Corrections on Unknowns

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

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 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.

Use Empirical APF Values

This option will either enable or disable the use of empirical APFs (Area Peak Factors) for subsequent quantitative analysis. 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.

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.

Use Automatic Format For Results

This option will allow the program to use maximum precision or only the statistically significant digits when formatting numbers for output rather then 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 or when it is desirable to easily ascertain exactly how sensitive the quantitative analysis is, based on the counting statistics.

If the statistically significant automatic format output option is selected, then the program will calculate the percent error (precision) and the detection limit for each element and use this information to first format the number so that only statistically significant digits are displayed and finally it will check the value against the calculated detection limit and set the value to "n.d." (not detected) if the value is below the detection limit. This is scaled for each data type output (elemental, oxide, atomic percent and formula).

The calculation for significant digits is based on the percent analytical error as follows:

Percent Analytical Error	Number of Significant Digits
> 10	1
> 1	2
> 0.1	3
> 0.01	4
> 0.001	5
> 0.0001	6

Print Analyzed (Acquired) and Specified On Same Line

This option will allow both analyzed (acquired or 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.

Calculate Electron and X-ray Ranges

This option will cause the program to calculate both 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).

The expression:

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

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:

$$transmission\ fraction = e^{-m\,r\,t}$$

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/phi-rho(z), Bence-Albee and calibration curve matrix correction calculations. This option applies only to samples where oxygen is calculated by stoichiometry and contain acquired 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 it's 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 Probe for Windows.

For example, the following standard composition is entered with the assumption that all cations have a full complement of stoichiometric oxygen (and no correction for F or Cl):

```
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 (in the header), 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 (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 or another variable valence oxide is also present and reported, then that concentration needs to be added to the actual oxygen concentration (in Elements/Cations stoichiometry, e.g. Fe:O of 2:3 rather than 1:1) after subtraction of the oxygen equivalent from the halogens.

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

This analysis option is only applicable when using the Empirical Calibration Curve (multi-standard) option in the ZAF Selections dialog.

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 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.

Assign MAN Fits

This menu allows the user to display or modify the MAN (mean atomic number) background assignments and fits used for the background correction of elements in the currently open Probe for Windows database. The user has the option of using absorption corrected intensities and constant, linear or polynomial fits. An interactive graphical display is provided to facilitate the assignment process.

These MAN assignments are based on the element, x-ray, spectrometer number and crystal (and kilovolts and take-off angle) conditions and are applied globally to all quantitative samples in the run. If an element is analyzed on more then 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.

Be sure to click the Update 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.

MAN background corrections can be utilized when the P/B is sufficiently high or when the use of fixed spectrometers are required. The MAN Fits menu allows the user to enter which MAN (mean atomic number) background samples will be used to calculate the background fit for the polynomial MAN iteration of an analyzed sample. The MAN background correction scheme is valid, because the primary factor of background or continuum variation (aside from trace contamination and peak over-lap interferences) is the average atomic number of the sample. If a number of pure samples of known atomic number are measured, then a function can be fit to the data and applied to the unknown sample. However, since the atomic number depends on the composition of the unknown and that is not known, then the MAN background must be applied during the ZAF iteration calculation.

Again, remember that MAN backgrounds can be used whenever the ratio of x-ray peak to background is high (>10:1), and this is usually the case with WDS microanalysis. Note that MAN backgrounds must be used for any fixed spectrometers. When measuring trace quantities be sure to use the off-peak measurements instead of the MAN correction.

MAN Backgrounds

There are two common methods for performing a background correction on WDS X-ray fluorescence data. The method most familiar to many probe users is the Off-Peak background correction method. Probe for Windows uses this method and another called the MAN (for Mean Atomic Number) background correction.

This latter method is based on the fact that most of the background (continuum) production in a sample is directly proportional to the average atomic number of the sample. If the average atomic number of the sample is low (for example, silicates) and the peak to background ratio is high, 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.

The advantage of the MAN method is that it requires only a simple calibration of the analyzing channel over a range of atomic number that includes the atomic number range of the standards and samples. If many samples are to be measured for their major and even minor element concentrations, then substantial time may be saved using the MAN method. In addition, the use of fixed monochromators, requires MAN backgrounds for those channels, since they can not be adjusted off-peak.

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. See below for more on off-peak background corrections. Note that if no fixed spectrometers are used and only off-peak standards or unknown samples are acquired, then it is unnecessary to acquire or assign MAN background samples at all.

The Mean Atomic Number (MAN) background correction is an empirical calibration curve correction for background. Probe for Windows uses an iterated linear or polynomial fit of up to 10 background measurements to provide quantitative correction over a wide range of sample atomic numbers.

The technique is based on the fact that background is essentially a function of the average atomic number of a sample often referred to as "Z-bar". You can determine the Z-bar of any composition by using the "data" command in program Standard for Windows to print out a standard composition. You can of course also create a dummy composition for reference purposes and delete it later, or simply view the average atomic number values for standards with a similar composition to the one of interest in Standard for Windows.

The program uses a graphical display of the measured counts on the background standards versus their Z-bars for each analyzed element to allow the user to select individual points for the calibration curve. Once the curves are fit the program can then calculate the background of any sample during the ZAF iteration based on the composition of the sample for a quantitative background correction.

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 heard (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 (known) 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.

To begin manually collecting data on a MAN background (let's say MgO, which was given a standard number of 12 in the standard database), create a new unknown sample from the Acquire! window. Click OK and the sample will display in the log window.

Note that "Set 1" means the first time you have collected data for this standard sample in this run. You can now manually start the counters, and collect a series of lines or points of data. Each data line or point of data represents a single unit of counting time. These lines or points are grouped together into samples each containing 50 "lines" or less. All lines are numbered sequentially, and these line numbers are used frequently for reference purposes.

The line number, "status" of each line, beam counts and the x-ray counts on each channel are typed on the screen as the data is collected. The status of every line is initially "G" for good. If you see a bad line (epoxy, etc.) you can delete it at any time from the Analyze! window. This will change the status of that line to "B" for bad, and it will be ignored in all calculations. It may later be undeleted if you change your mind.

When you have collected a sufficient number (5-10) of good lines for this background sample, proceed to the next one. Note that as each point is acquired, the program will print out a summary of the current sample. The summary includes average counts, the standard deviation and the one sigma (predicted standard deviation) of the average counts on successive lines. If the scatter in the counts is due totally to counting randomness, the standard deviation of the number of counts should equal to or less than the one sigma values. If the standard deviation is much larger it indicates scatter due to other causes, such as sample inhomogeneity etc.

Continue collecting data on the MAN background samples until you are done. Although the background due to the continuum usually drifts very little, the program will automatically correct the MAN background correction for drift, if more than one set of MAN backgrounds are acquired. If it is suspected that the background is drifting, possibly due to a change in the P-10 gas purity for instance, simply acquire an additional set of MAN background samples and the program will automatically calculate a linear drift correction before each quantitative analysis. For a description on the form of the drift correction see the section above titled "Automatic Standard Drift Correction".

MAN Background Assignments

Once you have collected all the MAN (Mean Atomic Number) background samples you must decide which MAN backgrounds to use on each channel. MAN background corrections are made by assuming that background counts are a linear function of the mean atomic number of the sample. For each channel you may give the program up to 10 different backgrounds to fit. It will compute a second order polynomial (default) or force a straight line fit between background counts and MAN for these samples. These coefficients are then used to determine background counts on your unknowns, based on iterative approximations of the composition of the unknowns.

Be sure to click the Update 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.

You will find that the MAN background corrections in PROBE work quite well down to approximately 200-300 ppm (0.02-0.03 weight percent) levels in silicate samples (z-bar ~10 - 15) using 10 to 20 second count times. Higher atomic number samples will of course be more difficult and may require longer count times or the use of off-peak background measurements.

Correction for Absorption of the Continuum

Probe for Windows will also automatically perform an absorption correction for the continuum background counts if it is specified. 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.

Graphical Plot of Background vs. Z-bar

To tell the program which MAN backgrounds you want to use on which channels, click the MAN Fits under the Analytical menu. The program will load the standard count data and graphically plot the acquired MAN background samples using a default assignment. After selecting or deselecting (hold down the <ctrl> key while clicking) standards in the standard list box click the Update Fit button 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 is also displayed on the graph. You should avoid using samples which contain the channel element or produce an interference. These samples will show up as high points on the graph.

Note that the default selection of MAN standards by Probe for Windows is somewhat intelligent; if the standard database composition for the standard contains more than 0.01 weight percent of the element in question, then the program will not assign that standard in the initial plot. Of course, the user can still specify the standard explicitly by clicking it in, but remember, if the element is present then you are not actually measuring the background for that element. The "force linear fit" option can be used when you feel that the program is over-fitting the data.

You can assign the MAN fits as soon as you finish collecting data for the backgrounds, or just before you begin your first analysis. You can change the MAN assignments you have made at any time. If additional MAN backgrounds are necessary, add them to the run and acquire the additional data.

Clear All MAN Assignments

This menu will clear the current probe database of all MAN (mean atomic number) background assignments. 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 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 standard 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 dataset 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.

Empirical MACs

This menu allows the user to selectively load empirical MACs (mass absorption coefficients) from a supplied ASCII file or data entry.

Empirical MAC (Mass Absorption Coefficients) are stored in a file called EMPMAC.DAT in the Probe for Windows directory (usually **C:\Program Files\Probe for Windows-E**). If the user obtains any new empirical MAC data the file can be edited using any text editor such as NotePad or TextPad. Be careful to avoid adding any <tab> characters when editing the file (use space or comma delimited values only). The values can then be accessed using from the Analytical | Empirical MACs menu for runs that contains a matching emitter and absorber binary. Any changes to the default MAC values will be stored in your .MDB database file. Note that the elements may be in any order although they have been sorted to facilitate editing.

The format of the EMPMAC.DAT file is shown below :

```
"b"     "ka"    "b"        3471         "Pouchou (1992)"
"b"     "ka"    "c"        6750         "Pouchou (1992)"
"b"     "ka"    "n"        11000        "Pouchou (1992)"
"b"     "ka"    "o"        16500        "Pouchou (1992)"
"b"     "ka"    "al"       64000        "Pouchou (1992)"
"b"     "ka"    "si"       80000        "Pouchou (1992)"
"b"     "ka"    "ti"       15000        "Pouchou (1992)"
"b"     "ka"    "v"        18000        "Pouchou (1992)"
"b"     "ka"    "cr"       20700        "Pouchou (1992)"
"b"     "ka"    "fe"       27800        "Pouchou (1992)"
"b"     "ka"    "co"       32000        "Pouchou (1992)"
"b"     "ka"    "ni"       37000        "Pouchou (1992)"
"b"     "ka"    "zr"       4400         "Pouchou (1992)"
"b"     "ka"    "nb"       4500         "Pouchou (1992)"
"b"     "ka"    "mo"       4600         "Pouchou (1992)"
"b"     "ka"    "la"       2500         "Pouchou (1992)"
"b"     "ka"    "ta"       23000        "Pouchou (1992)"
"b"     "ka"    "w"        21000        "Pouchou (1992)"
```

```
"b"     "ka"    "u"        7400         "Pouchou (1992)"
"c"     "ka"    "b"        39000        "Pouchou (1992)"
"c"     "ka"    "c"        2170         "Pouchou (1992)"
"c"     "ka"    "si"       35000        "Pouchou (1992)"
"c"     "ka"    "ti"       8097         "Pouchou (1992)"
"c"     "ka"    "v "       8850         "Pouchou (1992)"
"c"     "ka"    "cr"       10700        "Pouchou (1992)"
"c"     "ka"    "fe"       13150        "Pouchou (1992)"
"c"     "ka"    "zr"       25000        "Pouchou (1992)"
"c"     "ka"    "nb"       24000        "Pouchou (1992)"
"c"     "ka"    "mo"       20500        "Pouchou (1992)"
"c"     "ka"    "hf"       18000        "Pouchou (1992)"
"c"     "ka"    "ta"       17000        "Pouchou (1992)"
"c"     "ka"    "w"        18000        "Pouchou (1992)"
"n"     "ka"    "b"        15800        "Pouchou (1992)"
"n"     "ka"    "n"        1640         "Pouchou (1992)"
"n"     "ka"    "al"       13800        "Pouchou (1992)"
"n"     "ka"    "si"       17000        "Pouchou (1992)"
"n"     "ka"    "ti"       4270         "Pouchou (1992)"
"n"     "ka"    "v "       4950         "Pouchou (1992)"
"n"     "ka"    "cr"       5650         "Pouchou (1992)"
"n"     "ka"    "fe"       7190         "Pouchou (1992)"
"n"     "ka"    "zr"       24000        "Pouchou (1992)"
"n"     "ka"    "nb"       25000        "Pouchou (1992)"
"n"     "ka"    "mo"       25800        "Pouchou (1992)"
"n"     "ka"    "hf"       14000        "Pouchou (1992)"
"n"     "ka"    "ta"       15500        "Pouchou (1992)"
"o"     "ka"    "li"       1600         "Bastin  (1992)"
"o"     "ka"    "b"        8550         "Bastin  (1992)"
"o"     "ka"    "b"        1200         "Bastin  (1992)"
"o"     "ka"    "f"        1850         "Love et al. (1974)"
"o"     "ka"    "ne"       2750         "Love et al. (1974)"
"o"     "ka"    "na"       3630         "Love et al. (1974)"
"o"     "ka"    "mg"       5170         "Bastin  (1992)"
"o"     "ka"    "al"       6720         "Bastin  (1992)"
"o"     "ka"    "si"       8790         "Bastin  (1992)"
"o"     "ka"    "p"        9820         "Love et al. (1974)"
"o"     "ka"    "s"        12400        "Love et al. (1974)"
"o"     "ka"    "cl"       14300        "Love et al. (1974)"
"o"     "ka"    "ar"       16100        "Love et al. (1974)"
"o"     "ka"    "k"        20500        "Love et al. (1974)"
"o"     "ka"    "ca"       24600        "Love et al. (1974)"
"o"     "ka"    "sc"       26800        "Love et al. (1974)"
"o"     "ka"    "ti"       19900        "Bastin  (1992)"
"o"     "ka"    "cr"       2900         "Bastin  (1992)"
"o"     "ka"    "mn"       3470         "Bastin  (1992)"
"o"     "ka"    "fe"       4000         "Bastin  (1992)"
"o"     "ka"    "co"       4500         "Bastin  (1992)"
"o"     "ka"    "ni"       5120         "Bastin  (1992)"
"o"     "ka"    "cu"       5920         "Bastin  (1992)"
"o"     "ka"    "zn"       6350         "Bastin  (1992)"
"o"     "ka"    "ga"       7090         "Bastin  (1992)"
"o"     "ka"    "y"        15100        "Bastin  (1992)"
"o"     "ka"    "zr"       16200        "Bastin  (1992)"
"o"     "ka"    "nb"       17100        "Bastin  (1992)"
"o"     "ka"    "mo"       18000        "Bastin  (1992)"
"o"     "ka"    "ru"       19700        "Bastin  (1992)"
"o"     "ka"    "sn"       15050        "Bastin  (1992)"
"o"     "ka"    "ba"       4560         "Bastin  (1992)"
"o"     "ka"    "la"       3600         "Bastin  (1992)"
"o"     "ka"    "ta"       10600        "Bastin  (1992)"
```

```
  "o"     "ka"    "w "       11300        "Bastin  (1992)"
  "o"     "ka"    "pb"       11000        "Bastin  (1992)"
  "o"     "ka"    "bi"       12100        "Bastin  (1992)"
  "f"     "ka"    "xe"       27300        "Henke et al. (1982)"
  "na"    "ka"    "zn"       10500        "Henke et al. (1982)"
  "na"    "ka"    "pm"       7920         "Henke et al. (1982)"
  "mg"    "ka"    "tb"       8240         "Henke et al. (1982)"
  "al"    "ka"    "tm"       4730         "Henke et al. (1982)"
  "cr"    "la"    "te"       39500        "Henke et al. (1982)"
  "co"    "la"    "co"       1920         "Henke et al. (1982)"
  "ge"    "ka"    "ta"       265          "Henke et al. (1982)"
  "ge"    "la"    "gd"       8500         "Henke et al. (1982)"
  "mo"    "la"    "hg"       951          "Henke et al. (1982)"
```

The first column ("b" in the example equals Boron) is the atomic symbol of the emitting element. The second column ("ka" in the example equals Kα) is the x-ray line of the emitting element. The third column is the atomic symbol of the absorber element. The element and x-ray symbols must be enclosed in double quotes. The fourth column is the actual mass absorption coefficient (MAC) that has been experimentally measured. The last parameter is a comment string that may contain a comment, usually the experimenter or attribution. The comment string must be in double quotes.

The first and third columns (emitting atomic number and absorber atomic number) must be integer values from 1 to 94. The second column (x-ray line type) must be a valid x-ray line (ka, kb, la, lb, ma, or mb). The fourth column (MAC value) must be a real (or integer) number greater than zero.

See Appendix C below for a large set of empirical mass absorption coefficients from a number of sources that indicates some of the variation among MACs from various sources.

Empirical APFs

This menu allows the user to selectively load empirical APFs (Area Peak Factors) from a supplied ASCII file or data entry.

A powerful feature in Probe for Windows allows the user to select an Area-Peak-Factor (APF) correction for use in correcting x-ray intensities for peak shift and shape changes between the standard and the unknown. This can occur especially with Kα lines of the light elements such as oxygen, nitrogen, carbon and boron. With these elements, differences in the bond energies between say TiC and SiC will produce significantly different peak shapes resulting in systematic errors in the analysis of these materials when only the peak x-ray intensities are used.

For example, when analyzing oxygen and using MgO or Fe2O3 as an oxygen standard, analyses of SiO2 will produce errors up to about 4.5%. This effect is independent of the matrix correction and can be corrected for only by the use of the appropriate APFs.

The APF concept was proposed by Bastin and Heijligers (Bastin and Heijligers, 1986) to provide a simple correction scheme for this effect. It basically requires measuring the ratio of the peak intensity to the integrated intensity between a primary standard and a number of secondary standards on the light element spectrometer used. The wavelength scan feature in Probe for Windows can be used to acquire the peak shape profiles. After correcting for background and removal of extraneous peaks from interfering lines (requires use of an off-line peak stripping program), the APF can be calculated. The calculation of the APF factor is shown below :

$$\mathrm{APF} = \frac{\mathrm{I}_{\mathrm{U}}^{\mathrm{I}} \cdot \mathrm{I}_{\mathrm{S}}^{\mathrm{P}}}{\mathrm{I}_{\mathrm{U}}^{\mathrm{P}} \cdot \mathrm{I}_{\mathrm{S}}^{\mathrm{I}}}$$

Where : $\mathrm{I}_{\mathrm{U}}^{\mathrm{I}}$ is the integrated intensity of the secondary standard (unknown)

I_S^P is the peak intensity of the primary standard

I_U^P is the peak intensity of the secondary standard (unknown)

I_S^I is the integrated intensity of the primary standard

The peak shape and shift of light element peaks can be easily demonstrated using MgO and SiO_2 standard samples. First select a suitable layered dispersive element (LDE) analyzing crystal for oxygen Kα analysis. Tune the spectrometer using the MgO standard and acquire a standard sample for MgO. Assign MgO as the calibration standard for oxygen. Then move to the SiO_2 standard and acquire another quantitative standard sample on the SiO_2 sample. Note that the analysis of SiO_2 using MgO as a calibration standard will result in a low total for the SiO_2, somewhere around 96-97 %. This is not an error in the mass absorption coefficient (MAC), and no attempt should be made to correct this problem by entering an arbitrary MAC value.

Instead, the proper APF correction will need to be applied as shown below. Although the values below are relative to Fe_2O_3, you will note that the APF for MgO is 1.000, which means that these correction factors apply equally well relative to MgO. In the Oxygen Area Peak Factor table below you will note that oxygen in the presence of SiO_2 needs to be corrected by a factor of 1.0444 when MgO or Fe_2O_3 is used as a calibration standard. After entering this APF correction factor for the oxygen channel and re-analyzing, note that the total is now close to 100 %.

It is very important to note that the APF values selected or entered are always measured relative to some standard sample. For example, if measuring C Kα and using Fe_3C as the primary standard for carbon, then any C Kα APF values used must be those measured relative to Fe_3C. For the same reason, if using APF values for a particular (light) element and one decides to re-assign the standard for that element, the APF values for that element must also be changed to reflect the standard re-assignment. See the section above for information on re-calculating the APF values relative to another standard.

For the above reason it is usually most efficient to simply always use the same standard for each light element analyzed. Typically (in order to utilize the APF values in the supplied EMPAPF.DAT file) these will be :

- Oxygen : MgO or Fe2O3
- Nitrogen : AlN
- Carbon : Fe3C
- Boron : B metal

The APF correction in **Probe for Windows Enterprise** will allow the user to enter empirical APF values in each run at the bottom of the Element dialog from the Elements/Cations button in the Analyze! window. The user may enter one or more APF factors for each emitting element although they are generally applied to soft x-ray lines. Note however that even S Kα exhibits peak shift and shape changes when comparing sulfide and sulfate peaks and there is well documented shifts and peak shape changes for Si Kα and Al Kα from metallic to oxides or silicate compounds. The APF for each absorber will be summed according to it's weight fraction in the composition and applied to the emitting element counts during the ZAF or Phi-Rho-Z iteration.

If it is desired to correct a complete unknown for peak shape changes, simply perform a wavelength scan on the standard being used for the light element emitter (oxygen, carbon, etc.) and also on the unknown. Calculate the APF using the expression above and then from the Analytical | Empirical APFs menu, enter the same APF for all absorbers in the unknown. The program will then sum the APFs which will be the same as the single measured APF. Note that this APF may only apply to a single composition. One can perform additional wavelength scans on other samples to confirm this however. Alternatively one can enter the single empirical APF in the APF field in the Elements/Cations dialog as described above.

The APF correction values are defined in the EMPAPF.DAT file in the Probe for Windows directory (usually **C:\Program Files\Probe for Windows-E**). The file contains some 50 or 60 values that may or may not be applicable, depending on the analyzing crystals and standards available. The user may edit the file using any ASCII text editor such as NotePad or TextPad to insert their own measurements. Be careful to avoid adding any <tab> characters when editing the file (use space or comma delimited values only). Note that the elements may be in any order although they have been sorted to facilitate editing.

The format of the EMPAPF.DAT file is shown below :

```
  "b"     "ka"    "c"       1.02         "B4C/B/STE"
  "b"     "ka"    "n"       1.2          "BN/B/STE"
  "b"     "ka"    "al"       1.12         "AlB2/B/STE"
  "b"     "ka"    "al"       1.01         "AlB12/B/STE"
  "b"     "ka"    "si"       1            "SiB3/B/STE"
  "b"     "ka"    "si"       .92          "SiB6/B/STE"
  "b"     "ka"    "ti"       .75          "TiB/B/STE"
  "b"     "ka"    "ti"       .88          "TiB2/B/STE"
  "b"     "ka"    "v"       1            "VB2/B/STE"
  "b"     "ka"    "cr"       .9           "CrB/B/STE"
  "b"     "ka"    "cr"       1.1          "CrB2/B/STE"
  "b"     "ka"    "fe"       1.1          "FeB/B/STE"
  "b"     "ka"    "fe"       1.25         "Fe2B/B/STE"
  "b"     "ka"    "co"       1.2          "CoB/B/STE"
  "b"     "ka"    "co"       1.02         "Co2B/B/STE"
  "b"     "ka"    "ni"       1.2          "NiB/B/STE"
  "b"     "ka"    "ni"       1.06         "Ni2B/B/STE"
  "b"     "ka"    "ni"       .98          "Ni3B/B/STE"
  "b"     "ka"    "zr"       .8           "ZrB2/B/STE"
  "b"     "ka"    "nb"       .8           "NbB/B/STE"
  "b"     "ka"    "nb"       .9           "NbB2/B/STE"
  "b"     "ka"    "mo"       .94          "MoB/B/STE"
  "b"     "ka"    "la"       .9           "LaB6/B/STE"
  "b"     "ka"    "ta"       .88          "TaB/B/STE"
  "b"     "ka"    "ta"       1.1          "TaB2/B/STE"
  "b"     "ka"    "w"       .98          "WB/B/STE"
  "b"     "ka"    "u"       1.04         "UB4/B/STE"
  "c"     "ka"    "b"       1.01         "B4C/Fe3C/WSi/59.8"
  "c"     "ka"    "si"       .933         "SiC/Fe3C/WSi/59.8"
  "c"     "ka"    "ti"       .868         "TiC/Fe3C/WSi/59.8"
  "c"     "ka"    "v"       .873         "V2C/Fe3C/WSi/59.8"
  "c"     "ka"    "v"       .873         "VC/Fe3C/WSi/59.8"
  "c"     "ka"    "cr"       .8           "Cr7C3/Fe3C/STE"
  "c"     "ka"    "cr"       .83          "Cr3C2/Fe3C/STE"
  "c"     "ka"    "cr"       .8           "Cr23C6/Fe3C/STE"
  "c"     "ka"    "zr"       .88          "ZrC/Fe3C/WSi/59.8"
  "c"     "ka"    "nb"       .79          "NbC/Fe3C/STE"
  "c"     "ka"    "mo"       .82          "Mo2C/Fe3C/STE"
  "c"     "ka"    "hf"       .83          "HfC/Fe3C/STE"
  "c"     "ka"    "ta"       .96          "TaC/Fe3C/STE"
  "c"     "ka"    "w"       .97          "WC/Fe3C/STE"
  "c"     "ka"    "w"       1.02         "W2C/Fe3C/STE"
  "n"     "ka"    "si"      1.103          "Si3N4/AlN/WSi/59.8"
  "n"     "ka"    "ti"       .997          "TiN/AlN/WSi/59.8"
  "n"     "ka"    "v"       1.0226         "VN/AlN/WSi/59.8"
  "n"     "ka"    "cr"      1.018          "Cr2N/AlN/WSi/59.8"
  "n"     "ka"    "fe"      1.012          "Fe2N/AlN/WSi/59.8"
  "n"     "ka"    "zr"       .9952         "ZrN/AlN/WSi/59.8"
  "n"     "ka"    "hf"      1.002          "HfN/AlN/WSi/59.8"
  "o"     "ka"    "b"       1.0628       "B6O/Fe2O3/WSi/59.8"
  "o"     "ka"    "mg"       1            "MgO/Fe2O3/WSi/59.8"
  "o"     "ka"    "al"       1.0213       "Al2O3/Fe2O3/WSi/59.8"
  "o"     "ka"    "si"       1.0444       "SiO2/Fe2O3/WSi/59.8"
  "o"     "ka"    "ti"       .9796        "TiO2/Fe2O3/WSi/59.8"
  "o"     "ka"    "cr"       .993         "Cr2O3/Fe2O3/WSi/59.8"
  "o"     "ka"    "mn"       1.0121       "MnO/Fe2O3/WSi/59.8"
```

```
"o"     "ka"    "fe"      .9962       "Fe3O4/Fe2O3/WSi/59.8"
"o"     "ka"    "co"      1.0133      "CoO/Fe2O3/WSi/59.8"
"o"     "ka"    "ni"      1.0153      "NiO/Fe2O3/WSi/59.8"
"o"     "ka"    "cu"      .9946       "Cu2O/Fe2O3/WSi/59.8"
"o"     "ka"    "cu"      .9943       "CuO/Fe2O3/WSi/59.8"
"o"     "ka"    "zn"      .9837       "ZnO/Fe2O3/WSi/59.8"
"o"     "ka"    "ga"      1           "Ga2O3/Fe2O3/WSi/59.8"
"o"     "ka"    "zr"      .9823       "Y3Fe5O12/Fe2O3/WSi/59.8"
```

The first column (in the example is "b" for Boron) is the atomic symbol of the emitting element. The second column ("ka" in the example equals Kα) is the x-ray line of the emitter. The third column is the atomic symbol of the absorber element. The fourth column is the actual area peak factor (APF) that has been experimentally measured. The last parameter is a string that contains the conditions under which the APF was measured. For example, the comment "B4C/B/STE" indicates that the peak and integrated intensities for the APF were measured on a B_4C (boron carbide) sample, relative to a B (elemental Boron) primary standard, using a Pb Stearate analyzer. The reason that this information is needed is because the APF is a relative measurement (to a standard) and the value is dependent on the resolution (crystal type) used. If a LDE (layered dispersive element) analyzer is used, the 2d of the analyzer should be indicated also as seen in the example file above.

The first and third columns (emitting atomic symbol and absorber atomic symbol) must be valid element symbols. The second column (x-ray line) must be "ka", "kb", "la", "lb", "ma" or "mb". All element and x-ray symbols must be enclosed in double quotes. The fourth column (APF value) must be a real number greater than 0.0. The comment string must be enclosed in double quotes.

These values can then be loaded from the Analytical | Empirical APFs menu item in Probe for Windows. Note that the comments listed after each APF value can be used to indicate the experimental conditions under which the APF was measured. For consistency sake, the formula of the compound measured is listed first, then the primary reference standard used and finally the analyzing crystal type (and 2d spacing if desired) used. Edit the EMPAPF.DAT file in the Probe for Windows directory to add additional APFs from your own measurements.

The following is a short listing of some typical APFs taken from Bastin and Heijligers (1986). Because the factors are spectrometer and crystal dependent these should be used as a guide only.

Oxygen Area Peak Factors (APF)

Relative to Fe_2O_3 or MgO using W/Si LDE (2d = 59.8)

Oxide	Area-Peak Factor (APF)
B_6O	1.0628
MgO	1.0000
Al_2O_3	1.0213
SiO_2	1.0444
TiO_2	0.9796
Cr_2O_3	0.9930
Mn_3O_4	1.0121
Fe_3O_4	0.9962
CoO	1.0133
NiO	1.0153
Cu_2O	0.9946

CuO	**0.9943**
ZnO	**0.9837**
Ga_2O_3	**1.0000**
$Y_3Fe_5O_{12}$	**0.9823**

Carbon Area-Peak Factors

Relative to Fe_3C using W/Si LDE (2d = 59.8):

Carbide	Area-Peak-Factor (APF)
B_4C	**1.010**
SiC	**0.933**
TiC	**0.868**
V_2C	**0.873**
VC	**0.873**
ZrC	**0.880**

Nitrogen Area-Peak Factors

Relative to AlN using W/Si LDE (2d = 59.8):

Carbide	Area-Peak-Factor (APF)
AlN	**1.000**
Si3N4	**1.103**
TiN	**.997**
VN	**1.0226**
Cr2N	**1.018**
Fe2N	**1.012**
ZrN	**.9952**
HfN	**1.002**

ZAF Selections

This menu allows the user to modify or display the ZAF or Phi-Rho-Z quantitative matrix correction options for all samples. 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.

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 (e.g., quantitative x-ray images).

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 :

$$C_A^u = \frac{C_A^s}{\mathrm{Beta}_{\lambda_A}^s} \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} \mathrm{Beta}_{\lambda_A}^u$$

where : $\mathrm{Beta}_{\lambda_A}^u$ is the unknown beta-factor

$\mathrm{Beta}_{\lambda_A}^s$ is the standard beta-factor

Use of Empirical Alpha-Factors

To utilize empirically determined Alpha-Factor terms, simply edit the EMPFAC.DAT file in the Probe for Windows directory (usually **C:\Program Files\Probe for Windows-E**). If an Alpha-factor entry in the file matches the run conditions of the current run, it can be used to overwrite the previously internally 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 Probe for Windows only supports the use of elemental alpha-factors, i.e., 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).

Calibration Curve

In addition, Probe for Windows 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. Probe for Windows 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. Probe for Windows 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.

In the analysis printout the program will display the three polynomial fit coefficients for the standard intensity fit for each element (in cps/nominal beam units), "FIT1:", "FIT2:" and "FIT3:" and the average relative deviation in percent.

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.

ZAF Matrix Corrections

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, but for modern CPU's this is a non-issue, except possibly when analyzing extremely large numbers 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 : $\frac{C_A^s}{[ZAF]_{\lambda_A}^s}\,\frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}$ is the unknown k-ratio and

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

and : $I^{u}_{A}(\lambda_A)$ is the unknown intensity for element A at λ
$I^{s}_{A}(\lambda_A)$ is the standard intensity for element A at λ
C^{s}_{A} is the concentration of the element in the standard
$[\ ZAF\ ]^{s}_{\lambda_A}$ is the ZAF correction for the element in the standard

Probe for Windows 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)
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 :

1. Choice of mean ionization potentials:

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.

2. Choice of 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.

3. Choice of 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 (1983 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.

4. Choice of Phi(0) expressions: (Not applicable if one of the ZAF corrections (#1-6) or PAP was selected for the absorption correction)

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

Both #1 and #2 give similar results. The default selection is #2.

5. Choice of 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.

6. Choice of backscatter loss 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.

Fluorescence Correction

Probe for Windows 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.

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.

Mass Absorption Coefficients

Probe for Windows provides four 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.

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.

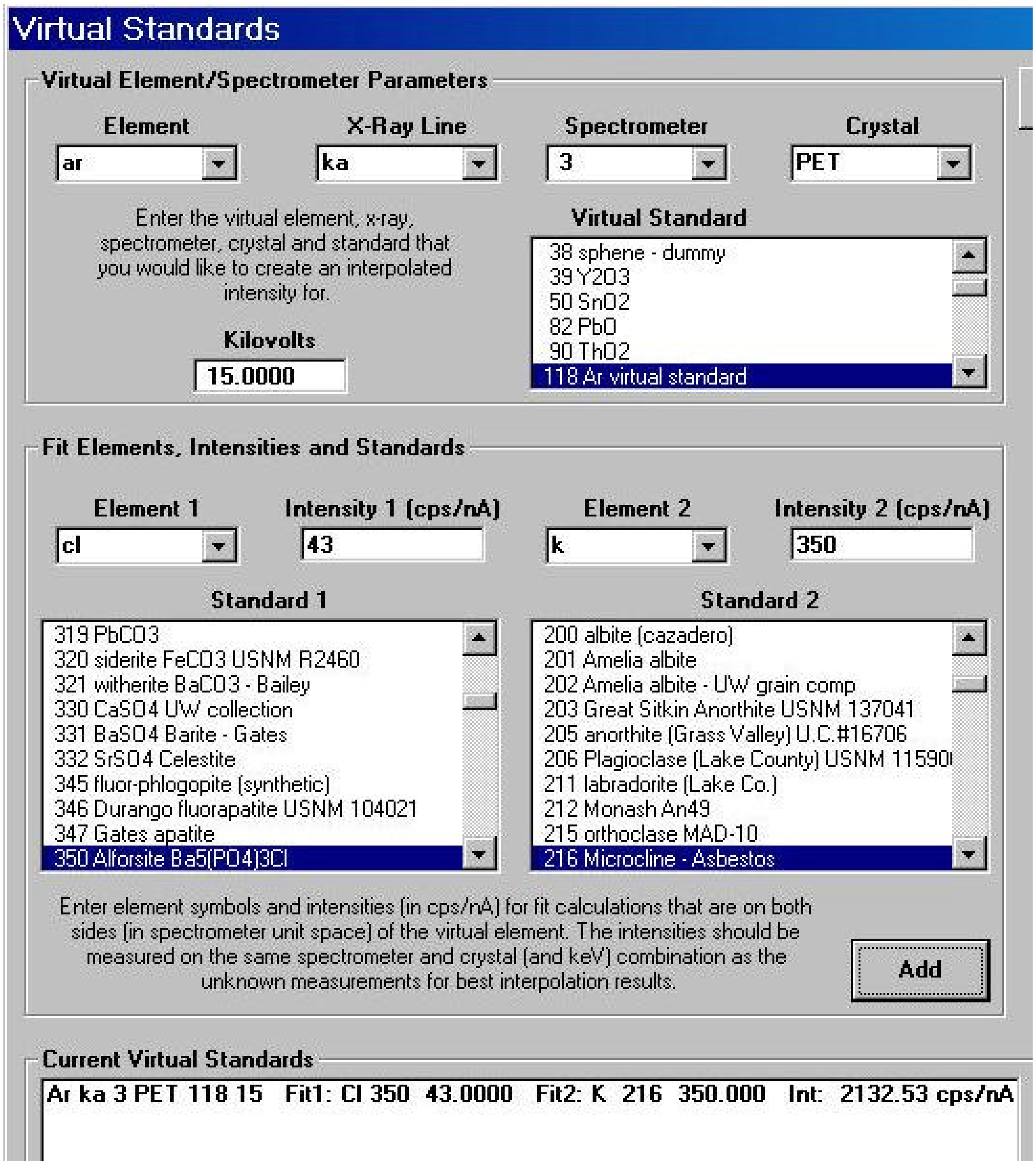
Create Virtual Standard Intensity

A new option is the use of "virtual" standard intensities. These are calculated intensities based on interpolation and matrix corrected similar (atomic numbers) elements measured on the same crystal, spectrometer and voltage as the unknowns. This may be useful in cases where a physical standard is not available (e.g., Ar).

To calculate a virtual standard intensity, first decide on the element and create a "virtual" standard composition using the Standard database application. This will be a composition that does not physically exist in the microprobe laboratory (e.g., pure iodine). Then decide what x-ray line, spectrometer, crystal and kilovolts to use for the unknown measurement. These will be used for the actual measurements on the unknown (usually trace concentrations). If it is not possible to peak the spectrometer properly without a major concentration of the element in a standard, so the use of a multiple peaks calibration procedure is suggested (see program StartWin for details) for getting the spectrometer position calibrated. Set the PHA parameters as for x-ray lines of similar energy.

Enter these parameters into the Virtual Element/Spectrometer Parameters frame. Then using the same x-ray line, spectrometer, crystal, and kilovolts, measure an available element on either side (in atomic number space) of the element that is used for the virtual standard intensity. For example if creating a virtual Ar intensity, it might useful to measure Cl and K since they are close to Ar.

Enter the chosen fit elements, intensities and standards in the Fit Elements, Intensities and Standards dialog and click the Add button. The program will calculate the virtual intensity and store it in a table in the database file. To utilize this intensity for standardizing an unknown, go to the Analyze window and click the Standard Assignments button, click the virtual element and select the virtual standard from the standard list and check the Use Virtual Standard for Virtual Intensity Calculation checkbox.



Element: ar
X-Ray Line: ka
Spectrometer: 3
Crystal: PET

Enter the virtual element, x-ray, spectrometer, crystal and standard that you would like to create an interpolated intensity for.

Kilovolts: 15.0000

Virtual Standard:
38 sphene - dummy
39 Y2O3
50 SnO2
82 PbO
90 ThO2
118 Ar virtual standard

Element 1: cl
Intensity 1 (cps/nA): 43
Element 2: k
Intensity 2 (cps/nA): 350

Standard 1:
319 PbCO3
320 siderite FeCO3 USNM R2460
321 witherite BaCO3 - Bailey
330 CaSO4 UW collection
331 BaSO4 Barite - Gates
332 SrSO4 Celestite
345 fluor-phlogopite (synthetic)
346 Durango fluorapatite USNM 104021
347 Gates apatite
350 Alforsite Ba5(PO4)3Cl

Standard 2:
200 albite (cazadero)
201 Amelia albite
202 Amelia albite - UW grain comp
203 Great Sitkin Anorthite USNM 137041
205 anorthite (Grass Valley) U.C.#16706
206 Plagioclase (Lake County) USNM 11590
211 labradorite (Lake Co.)
212 Monash An49
215 orthoclase MAD-10
216 Microcline - Asbestos

Enter element symbols and intensities (in cps/nA) for fit calculations that are on both sides (in spectrometer unit space) of the virtual element. The intensities should be measured on the same spectrometer and crystal (and keV) combination as the unknown measurements for best interpolation results.

```
Ar ka 3 PET 118 15   Fit1: Cl 350  43.0000   Fit2: K  216  350.000   Int:  2132.53 cps/nA
```

Student's "t" Table

This menu item provides a listing for typical confidence levels of Student's "t" values. William Gossett (1876-1937) worked for the Guiness Brewing Company on quality control issues. He developed a number of statistical tools for situations where it was not always feasible to measure a large enough number of replicate samples. Student's "t" or test table is one of these. He was not allowed to use his own name so he published then under the name "Student". These values are used in many statistical calculations to this day. See Calculate Detection Limits and Homogeneity above for an example of this parameter in use.

Run

This menu will output a variety of run information in summary format to the log window. This information can then be cut and pasted to another application or simply selected and printed using the File | Print Log menu.

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 Sample Names

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.

List Standard Counts

This menu will output a summary of all standard counts in the order acquired to the log window. This includes all standards, whether or not they are actually assigned as a standard for primary, interference or MAN calibrations. The date and average time of acquisition is also listed in the output.

To see a listing of the standard intensities that are applicable to a specific quantitative sample, see the List Report in the Analyze! window.

List Standard Compositions

This menu item will list the compositions of all standards in the current run based on the current values in the standard composition database.

List Current MACs

This menu item will list the currently loaded MACs (mass absorption coefficients) from the last quantitative analysis. Note that any empirical MACs listed from this menu will be used to overwrite table based MACs automatically during calculations.

List Current APFs

This menu item will list the currently loaded APFs (area peak factors) from the last quantitative analysis.

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.

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.

Load Custom Position Format #1

This menu will load a custom position file format (#1). This format is a fixed length field, comma delimited ASCII file that contains off-line digitized data from an automated light microscope. This format is intended for use with Canadian Geological Survey laboratory .LEP position files only.

See additional information on the "Import From ASCII File" button in the Automate! window and also the PositionImportExportFileType parameter in the PROBEWIN.INI file.

Save Custom Analysis Format #1

This menu will automatically create a custom file format (C.G.S. format). This format is a fixed length field, comma delimited ASCII file that contains unknown weight percent data only. The data will be output to a different file based on the analytical setup used to create the sample (if one was used). The file naming convention is based on the file setup name used to create the sample. For example, samples created using a setup file called FELDSPAR.MDB, will be output to FELDSPAR.DAT, and so on.

The first column contains an eight character wide field containing the sample name for each data point. The final column contains the totals. All elements, analyzed and specified will be output. The column labels are not enclosed in double quotes but the sample names are. The oxide or elemental basis for calculating the data is based on the first sample of a particular setup file for ensure that the data type is consistent within a single output file.

This format is intended for use with the Canadian Geological Survey MREPORT mineral recalculation program set which has been published as a open file report. An short example is shown here:

```
  SAMPLE   ,      BI,      SB,   TOTAL
 "mabisb06", 99.7657, .207527, 99.9733
 "mabisb06", 99.4798, .185703, 99.6655
 "mabisb06", 99.1180, .298709, 99.4167
 "mabisb75", 99.4394, .978249, 100.418
 "mabisb75", 98.2293, 1.69337, 99.9227
 "mkbisb06", 98.0328, 1.69929, 99.7321
 "mkbisb06", 97.5753, 1.45358, 99.0289
 "mkbisb06", 98.8127, 1.78520, 100.598
 "msbisb25", 89.4619, 10.3681, 99.8300
 "msbisb25", 99.6894, 1.03415, 100.724
 "msbisb25", 82.0337, 18.5264, 100.560
 "msbisb25", 80.8562, 17.6338, 98.4900
 "msbisb25", 85.7570, 13.9368, 99.6939
 "mabisb06", 99.4645, .463434, 99.9279
 "mabisb06", 99.2842, .682973, 99.9671
 "mabisb06", 99.4594, .567973, 100.027
 "mabisb25", 26.0476, 73.0580, 99.1056
 "msbisb25", 98.9069, .576286, 99.4832
 "msbisb25", 98.9150, .624202, 99.5392
 "msbisb25", 99.4395, .368290, 99.8078
 "msbisb25", 94.9391, 4.22091, 99.1600
 "mabisb75", 98.6824, .741002, 99.4234
 "mabisb75", 100.201, .230280, 100.431
 "mabisb75", 99.5045, .514928, 100.019
 "mabisb75", 99.3453, .749748, 100.095
 "mabisb75", 98.2343, .853120, 99.0874
```

Save Custom Analysis Format #2

This menu will automatically create a custom file format (H.T. format). This format is a tab delimited ASCII file and contains extensive information including elemental, oxide, atomic weight percents, raw, background and net counts, k-ratios and one sigma calculations for several data types, stage positions, count times, and ZAF correction factors.

A separate output file is created for each unknown based on each position sample. In addition, an option is available to have each output file automatically imported into an excel spreadsheet. This file format was specified by Haldor Topsoe Ltd. and cannot be modified for other applications.

A short explanation of the various column labels used for this custom output format is given here, but note that in reality, the symbol (El) will be replaced by the actual element symbol:

LINE	Line number
El AT%	Atomic weight percent
El WT%	Elemental weight percent
El (O2)	Oxide weight percent
TOTAL	Total weight percent
El OX/CA	Oxide to cation ratio
El ONTIM	On-peak counting time

El HITIM	High off-peak counting time
El LOTIM	Low off-peak counting time
El DETIM	Deadtime correction factor
X-POS	X stage position
Y-POS	Y stage position
Z-POS	Z stage position
RELDIST	Relative distance (in microns)
BEAMCUR	Beam current
El ONCNT	On-peak count intensity (cps/nominal beam)
El OFCNT	Off-peak count intensity (cps/nominal beam)
El NECNT	Net (off-peak corrected) count intensity (cps/nominal beam)
El +-CNT	One sigma standard deviation count intensity (cps/nominal beam)
El KRAT	Raw k-ratio
El +-RAT	One sigma standard deviation raw k-ratio
El Z-COR	Atomic number correction factor
El A-COR	Absorption correction factor
El F-COR	Fluorescence correction factor
El ZAF	Z*A*F correction factor

The elemental raw k-ratios and x-ray intensities are corrected for deadtime, beam current and normalized to cps in addition to background, volatile, area peak factors and spectral interference corrections.

Save Custom Analysis Format #3

This menu will automatically create a custom file format (J.H. format). This format is a tab delimited ASCII file and contains extensive information including elemental, oxide, atomic weight percents, detection limits, analytical error (percent error), raw k-ratios, raw and corrected x-ray intensities, background and net counts, count times, deadtimes, beam current, stage positions, relative distance (in microns) and standard counts.

This file format was specified by John Hanchar at George Washington University and cannot be modified for other applications. A short explanation of the various column labels used for this custom output format is given here, but note that in reality, the symbol (El) will be replaced by the actual element symbol:

LINE	Line number
El AT%	Atomic weight percent
El WT%	Elemental weight percent
El (O2)	Oxide weight percent
TOTAL	Total weight percent
El CDL99	Detection limit in elemental weight percent at 99% confidence
El %ERR	Analytical error in percent
El K-RAW	Elemental raw k-ratio (unk counts/standard counts)
El ONCNT	On-peak count intensity (cps/nominal beam)
El OFCNT	Off-peak count intensity (cps/nominal beam)
El NECNT	Net (off-peak corrected) count intensity (cps/nominal beam)
El ONTIM	On-peak counting time
El HITIM	High off-peak counting time
El LOTIM	Low off-peak counting time
El DETIM	Deadtime correction factor (in secs)
BEAMCUR	Beam current (in nA)
X-POS	X stage position
Y-POS	Y stage position
Z-POS	Z stage position
RELDIST	Relative distance (in microns)
El STDCTS	Standard counts (cps/nominal beam)

The elemental raw k-ratios and x-ray intensities are corrected for deadtime, beam current and normalized to cps in addition to background, volatile, area peak factors and spectral interference corrections.

Save Custom Analysis Format #4

This menu (J.J.D. format) will create an output file of standard or unknown average weight, oxide and atomic percents along with average detection and analytical sensitivity. The user can select averages only, standard deviations only, or averages and standard deviations (x.xxx +/- x.xxx) output.

Save Custom Analysis Format #5

This menu (J.J.D.-2 format) will create an output file of standard or unknown x, y, z coordinates and relative distance in microns, elemental weight percents, along with average detection and analytical sensitivity and raw k-ratios. Each sample in the data file will automatically be output to an ASCII file (*.DAT extension) with a unique filename based on the probe database file name and the sample type, sample set and name. The directory will be the same one that the database file resides in.

LINE	Data file line number
X-POS	X stage position
Y-POS	Y stage position
Z-POS	Z stage position
RELDIST	Relative stage distance in microns
WT%	Elemental weight percent
TOTAL	Total weight percent
CDL99	Single line detection limit (99% confidence) in weight percent
%ERR	Percent error based on unknown and standard count rates, Goldstein
K-RAW	Raw k-ratio (corrected)

This format is especially useful when it is desired to plot multiple (or duplicate) datasets in a graph with similar or separate axes for each dataset. The elemental raw k-ratios and x-ray intensities are corrected for deadtime, beam current and normalized to cps in addition to background, volatile, area peak factors and spectral interference corrections.

Save Custom Analysis Format #6

This menu (H.W. format) will create an output file of standard or unknown atomic, elemental and oxide weight percents, along with average detection and analytical sensitivity and raw k-ratios, count times, beam current and x, y, z coordinates and relative distance in microns.

	Sample description text (no column label)
LINE	Line number
El AT%	Atomic weight percent
El WT%	Elemental weight percent
El (O2)	Oxide weight percent
TOTAL	Total weight percent
El CDL99	Detection limit in elemental weight percent at 99% confidence
El %ERR	Analytical error in percent
El K-RAW	Elemental raw k-ratio (unk counts/standard counts)
El ONTIM	On-peak counting time
El HITIM	High off-peak counting time
El LOTIM	Low off-peak counting time
BEAMCUR	Beam current (in nA)
X-POS	X stage position
Y-POS	Y stage position

Z-POS	Z stage position
RELDIST	Relative distance (in microns)

This file format was specified by Heather Wright at the University of Oregon and cannot be modified for other applications. In addition the first column of tab delimited data will contain any sample description text as separate strings enclosed in double quotes. **This is the only output format in PFW that will output the sample description field text.**

Save Custom Analysis Format #7

This menu (NIST format) will create an output file of raw (uncorrected, un-normalized) intensities for standard or unknown samples and count times, deadtimes, beam current and x, y, z coordinates and relative distance in microns, raw k-ratios and corrected unknown and standard intensities. These last three items are corrected for deadtime, beam current and normalized to cps in addition to background, volatile, area peak factors and spectral interference corrections.

This file format was specified by The National Institute of Standards and Technology and cannot be modified for other applications.

LINE	Data file line number
RAWONCNT	Raw on-peak intensity (no correction)
RAWHICNT	Raw high off peak intensity (no correction)
RAWLOCNT	Raw low off peak intensity (no correction)
RAWOFCNT	Raw background intensity (no correction)
ONTIM	Actual on peak count time
HITIM	Actual high off peak count time
LOTIM	Actual low off peak count time
DETIM	Deadtime in micro-seconds
BEAMCUR	Faraday or beam current reading in nano-amps
X-POS	Stage x axis position
Y-POS	Stage x axis position
Z-POS	Stage x axis position
RELDIST	Stage distance in relative microns
K-RAW	Raw k-ratio (corrected)
UNCNT	Unknown count intensity (corrected)
STCNT	Standard count intensity (corrected)

Save CalcZAF Format

This menu will output x-ray intensity raw k-ratio data for all unknown samples in the current run to a CalcZAF compatible format. Each line in each sample will be output to the file. Import in CalcZAF using the File | Open menu and click the Load Next Dataset From File button to load the next data line.

Save StrataGem Format

This menu will open a dialog that allows the user to select samples of different voltage conditions for use in thin film calculations in the StrataGem application. The format includes the raw k-ratios for all samples and the standard compositions assigned in the last selected sample. The user has the choice of exporting all data in a sample or just the average of each sample.

Once the file is exported, from StrataGem select File | Import | StrataGem Import and the program will prompt the user whether to import or skip each k-ratio. The program will average all imported values for each element that have the same voltage.

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 to both the StartWin and ProbeWin applications for sending both intensity and quantitative data to an Excel spreadsheet. This feature requires Excel 8 (Office 97) or higher.

From StartWin, each time intensity data is acquired, it will be automatically sent to an Excel spreadsheet along with the column labels. From ProbeWin, the analysis line number and elemental weight percents and totals are sent to an Excel spreadsheet after an analysis is performed and the user clicks the ">>Excel" button in the Analyze! window. In the ProbeWin application the column labels will be sent if they differ from the previous sample.

Close Link To Excel

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

Help

About Probe for Windows

This menu displays the copyright notice, acknowledgments and contact information for users of **Probe for Windows Enterprise**.

Help On Probe for Windows

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 anytime during a run. Each help topic may be printed. To obtain a complete printout of the help file, ask for an updated copy of the PROBEWIN.PDF file, which is an Adobe Acrobat portable document file that may be viewed and/or printed using the free Acrobat Reader.

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.

Appendix A

Importing Databases from Probe for Windows (16 bit)

The following instructions can be used to import certain database information from the previous version of Probe for Windows (16 bit) to the current Probe for Windows (32 bit) file formats.

The following data may be imported using from the 16 bit version of Probe for Windows and using the instructions described below:

Standard Composition Data

Create a standard composition export file (STANDARD.DAT) in Probe for Windows (16 bit) using the File | Export menu. Copy the file to the new Probe for Windows application directory (usually Program Files\Probe for Windows\). Run the new Probe for Windows (32 bit) Standard application and click Cancel when asked for a database file to open. Then create a new standard database from the File | New menu. Finally, use the File | Import menu to import the previously created standard composition export file.

Element Setup Data

Create a element setup export file (SETUP.DAT) in Probe for Windows (16 bit) using the Export button in the Element setup dialog. Copy the file to the new Probe for Windows application directory (usually Program Files\Probe for Windows\). Run the new Probe for Windows (32 bit) ProbeWin application and open the Element Setup Dialog. Using the Import button, import the previously created element setup export file.

Note that the older 16 bit version of the element setup database did not include fields for wavescan and peaking information. Therefore, those element records that have been imported from the 16 bit version will contain zeros and blanks for those fields, however the program will load the current defaults from the run when those element setups are loaded.

Position Data

Position data is normally imported from ASCII .POS files which should already exist from the 16 bit Probe for Windows files. Simply copy all .POS files from the C:\PROBEWIN directory to new Probe for Windows application directory (usually Program Files\Probe for Windows\) and import them as usual from the Automate! window.

Probe Data

Probe for Windows (16 bit) data can simply be opened by the 32 bit version of Probe for Windows, no conversion is necessary if the standard database file has been converted as specified above.

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Appendix B

Problems with Light Element Analysis

The analysis of light elements (fluorine - beryllium) present special problems for the microprobe analyst. Some of these problems are technical in substance, relating to the measurement procedure, while others are inherent and are due to physical and chemical effects. The following is just an overview of these concerns. For a more complete treatment the reader is referred to (Bastin and Heijligers, 1986) and (Goldstein, et. al., 1981, and 1992).

Physical and Chemical Effects

1. Low fluorescence yields from these k-lines, compounded by significant matrix absorption at "normal" accelerating voltages (15-20 keV), the relatively poor reflectivity of traditional analyzing crystals (e.g., STE), and the low sensitivity of detector systems, can result in extremely low count rates. Increasing the beam current can produce unacceptably high deadtime corrections for any metal lines being measured, although Probe for Windows now can accommodate "combined conditions" where certain low intensity elements are run at high beam currents, and other high intensity elements are run at low beam currents. Count rates can be enhanced by use of layered dispersive element (LDE) reflectors as well as decreasing the absorption path length by running at lower operating voltages.

2. Errors in the estimation or accuracy of the take off angle or operating voltage of the microprobe. While slight variations in these parameters normally have a little effect on a typical analysis, due to the very high absorption corrections of low energy x-rays, the effect on the ZAF correction can be much larger for the light elements and can sometimes result is large systematic errors.

3. Errors in the mass absorption coefficients (or MACs) for the x-ray absorption cross sections for these elements are considerable. See Appendix C for a table of MACs for the light elements from a variety of sources. There is considerable disagreement among investigators. Probe for Windows allows the user to enter MACs from any source for re-calculation purposes.

4. Chemical bonding effects can results in large peak shift and/or shape changes to the analytical x-ray lines. In fact the degree of shift and/or shape changes in light element K lines and transition metal L lines can sometimes be related to the degree of oxidation in the compound. But normally these effects are a nuisance to the analyst. In a few instances there has even been documented cases of particular lines being strongly enhanced (Ni Lα in NiAl) or reduced (B Kα in nickel borides) (Pouchou and Pichoir, 1988).

5. Mobilization toward or away from the beam ("volatilization") in some glasses and a few minerals of certain light elements such as fluorine and oxygen as well as alkali elements such as sodium and potassium to a lesser extent is often the case. This requires special attention, either by operating a lower current, defocusing the beam, using a cold stage (not common), or using a robust software correction. See the section on the Volatile element correction in this document.

6. Crystallographic orientation can play a role for analysis of certain phases. This has been well documented for some crystalline borides, and also when measuring fluorine in apatites.

Problems with the Measurement Techniques

1. Higher order interferences from metal lines are everywhere and must be avoided when possible or corrected for in software when not. The elements Ti, Cr, Mn, Zr and Nb are well known in this respect. See Donovan et al (1993). These interferences are especially severe for minor and trace level measurements. Use of pulse height analysis to reduce those interferences that are caused by high order interferences (>1) is a logical choice; however it can introduce further problems if not used with care. In particular, narrow windows required for discrimination of second order peaks may be so narrow that a shift in pulse location ("pulse height depression", as pulse voltage drops with high count rate) will produce significant errors. Similarly, the pulse location may shift between the standard (pure element) and the unknown in extreme cases.

2. Carbon contamination is a serious problem for quantitative analysis of light elements, especially of course carbon, but also other light elements. Contamination is produced by the polymerization of hydrocarbons at the point of impact of the electron beam. Carbon compounds present may include mainly rotary but also some diffusion pump oils, polishing agents, cleaning solvents, and "canned air" propellants, among others. The use of an air jet and cold finger has been shown to dramatically reduce carbon contamination, though the use of a Freon chilled baffle at the top of the diffusion pump will completely eliminate back streaming of oil from a diffusion pump. A turbo pumped system is expensive but also eliminates oil contamination from the pumping system. It is suggested that the analyst perform measurements to ascertain the actual carbon contamination rate in their microprobe for each element being analyzed.

3. Trace analysis of light elements is particularly difficult, especially oxygen and carbon. Keeping a metallic sample surface from oxidizing is not a trivial matter. The use of an ion mill inside the probe to remove the very top layer of the sample, just prior to the analysis, if available, would be ideal. Note that the increase in temperature of non-thermally conducting samples can be significant enough to cause additional oxidation of the surface. Trace carbon analyses can be difficult without the use of an air jet to reduce the carbon contamination at the point of impact of the beam; however, it has been found to be counterproductive for oxygen analysis (i.e., it enhances oxidation under the beam).

4. Another problem which has not been adequately addressed is x-ray production in non-conductive samples. Effects on x-ray production are seen even when a conductive coating has been applied, possibly due to internal charge buildup below the conductive layer. This effect may also be implicated in the "volatile element" behavior observed in glasses and some minerals.

5. The selection of standards is also critical due to the already mentioned peak shift and/or shape changes for light element x-rays. The use of Area Peak Factors (APFs) (Bastin and Heijligers, 1986) can provide the analyst with a practical method for treatment of these effects. Program Probe for Windows supports the use of APF factors for analysis of light elements. See the previous sections on using APFs for correcting for peak shape and shift effects when analyzing light elements.

Many analysts use high purity metals as standards for various elements, without realizing that many metals develop oxide skins, which will reduce the actual number of x-rays of the particular element of interest (e.g., Al, Ti, Mn being among the worst). One either needs to repolish immediately prior to probing, or spend some time estimating the oxide content, or find an alloy that doesn't oxidize as quickly.

6. Be aware also that carbide, boride and nitride standards are often pressed and sintered powders and are not 100% dense, resulting in significant errors in the analysis. If single crystals, or arc-melted pieces (e.g., boron) can be obtained, so much the better.

Appendix C

Use of Empirical MACs

The following is a small compilation of mass absorption coefficients (MACs) from a number of investigators. Some of these MACs may be selected for use in the quantitative calculations in Probe for Windows, from the Analytical | Empirical MACs menu item. Up to MaxEmp% empirical mass absorption coefficients may be defined for each run. These MACs will be saved to the .MDB file for subsequent re-processing and can be added to, changed or deleted again.

Empirical Mass Absorption Coefficients (MACs)

Emitter	Absorber	Henke Ebisu	Ruste	Henke et al.	Bastin Heijligers	Heinrich	Frazer	Pouchou Pichoir
B ka	B	3353		3350	3500			3471
B ka	C	6456		6350	6500			6750
B ka	N	10570		11200	11200			11000
B ka	O							16500
B ka	Al	65170		64000	64000			64000
B ka	Si	74180		84000	84000			80000
B ka	Ti	15280		15300	14700			15000
B ka	V	16710		16700	17700			18000
B ka	Cr	20670		20700	20200			20700
B ka	Fe	25780		27600	27300			27800
B ka	Co	28340		30900	33400			32000
B ka	Ni	33090		35700	42000			37000
B ka	Zr	38410[1]		8270	4000			4400
B ka	Nb	4417		6560	4600	3822		4500
B ka	Mo	4717		5610	4550	4208		4600
B ka	La	3826		3730	2500	11654		2500
B ka	Ta	20820		20800	22500			23000
B ka	W	19660		19700	21400			21000
B ka	U	2247		9020	8200			7400
C ka	B	37020	37020	37000	41000			39000
C ka	C	2373	2373	2350	2373	2147		2170
C ka	Si	36980	36980	36800	37000			35000
C ka	Ti	8094	8094	8090	9400	8290		8097
C ka	V	8840	9236	8840	10100			8850
C ka	Cr	10590	10482	10600	10950			10700
C ka	Fe	13300	13300	13900	13500	14103		13150
C ka	Zr	31130	31130	21600	24000	31304		25000
C ka	Nb	33990[1]	24203	19400	23200	29760		24000
C ka	Mo	32420[1]	15500	16400	19200			20500
C ka	Hf							18000
C ka	Ta	18390	20000	18400	16000			17000
C ka	W	18750	21580	18800	17000			18000
N ka	B							15800
N ka	N							1640
N ka	Al							13800
N ka	Si							17000
N ka	Ti							4270
N ka	V							4950
N ka	Cr							5650
N ka	Fe							7190
N ka	Zr							24000
N ka	Nb							25000

N ka	Mo	23220		20200		26458		25800
N ka	Hf							14000
N ka	Ta							15500
O ka	Li	1602		1600	1600			
O ka	B	7416		7420	8550			
O ka	O	1200		1200	1200			
O ka	Mg	5174		5170	5170			
O ka	Al	6715		6720	6720			
O ka	Si	8790		8790	8790			
O ka	Ti	22140		22100	19900			
O ka	Cr	3143		3140	2900			
O ka	Mn	3468		3470	3470			
O ka	Fe	4001		4000	4000			
O ka	Co	4407		4410	4500			
O ka	Ni	5245		5120	5120			
O ka	Cu	5920		5920	5920			
O ka	Zn	6548		6550	6350			
O ka	Ga	7086		7090	7090			
O ka	Y	15140		15100	15100			
O ka	Zr	16140		14800	16200			
O ka	Nb	17850		15300	17100			
O ka	Mo	18660		16700	18000			
O ka	Ru	19680		19700	19700			
O ka	Sn	23090		23100	15050			
O ka	Ba	4560		4560	4560			
O ka	La	4690		4690	3600			
O ka	Ta	10560		10600	10600			
O ka	W	10990		11000	11300			
O ka	Pb	12470		12500	11000			
O ka	Bi	12690		12700	12100			
Al ka	Al			403		397	404	393
Al ka	Cu			4550		4764	5410	4588
Si Ka	Si			350		347	332	356
Si ka	Ta			3760		1698		1500
S ka	Au					3380	3203	2200
S ka	Hg					1499	932	850
Sc la	Sc							4750
Ti la	Ti							4550
V la	V							4370
Cr la	Cr							3850
Mn la	Mn							3340
Fe la	Fe							3350
Co la	Co							3260
Ni la	Ni							3560
Cu la	Al			1450		1421	1494	1464

Cu la	Ni			11700		11776	12106	11879
Cu la	Cu							1755
Zn la	Zn			1520		1485	1581	1500
Ge la	Ge			1260		1262	1278	1240
As la	Ga							7000
Nb la	Nb			726		718	726	779
Mo la	Au			3680		3437		2200
W la	W					1215	1458	1258
Au ma	Au					1061	1101	1103

[1] extrapolated across absorption edge

Appendix D

Problems With the Analysis

Quantitative analysis is always beset with many difficulties and it is often difficult to pinpoint the cause of "bad" analyses. What is a bad analysis? This is usually based upon one or two tests: is the weight percent elemental (or oxide) totals very close to 100%? And if the material should have a certain stoichiometry, does it?

More often than not, the effect is the sum of more than one problem. Several things need to be checked. First of all, start by examining the standards.

Are the standards really "good" standards (both on their own, and for your particular suite of unknowns). Have their compositions been determined by a reliable analytical method? Traditionally, major element concentrations of standards have been determined using a bulk chemical technique, commonly "wet chemistry". The greatest problem is with natural minerals and glasses, which may be somewhat heterogeneous, and may have a sample "split" that is of a slightly different composition compared to the "official" composition. It is in situations like this, the use of secondary standards can really be helpful in determining what is going on. If the primary and secondary standards do not agree with each other, there is a problem: which is correct?

Traditionally, analysts have run analyses of several standards, using another as the standard for a particular element, and then repeat with different standards, to see which gives the "most correct" values the most times. The Probe for Windows "Evaluate" application takes this one step further and plots up all standards for one element against each other (stated composition vs ZAF corrected intensity), giving a clear indication of which standards are "good" (consistent with each other) and which are not (i.e., off the 1:1 line).

Also, are the concentrations entered in the Standard.mdb database correct and without typographical errors? And were counts acquired on the actual intended standard? It is easy to get lost at 300-400 magnification when using a standard mount which contains many standards (EDS helps here).

> Some other things to consider :
>
> 1. Is the operating voltage correctly specified? Is the correct x-ray line tuned for each element? Check the on-peak position offsets from the Peak/Scan Option dialog and see if they are reasonable. The program will usually type a warning if the actual and calculated peak positions are very different. Be sure that the spectrometer is not tuned on a nearby line of another element if using multi-element standards.
>
> 2. Be sure that no "bad" data points are in the standards samples used for the quantitative calibration. The best way to check for this is to analyze each standard and examine the results to look for points with obviously bad or low totals (epoxy, bad surface polish, bad carbon coat, etc.). If a bad point is found, one can delete it. Remember, one can always undelete data later on. A deleted point is simply not used in calculating the analytical

calculations but is still present. A good rule of thumb is to only delete points that have low totals since generally most of the problems mentioned above will result in fewer x-ray counts. Avoid deleting points just to get better agreement between the primary and secondary standards. Points that have high totals should not be arbitrarily deleted. It may be necessary to look for other problems such as points with low totals in the primary standards.

3. Look for interferences on the analyzed elements. One easy way to do this is to use the Interferences menu item in the Standard for Windows program. One can also perform a wavelength scan and display possible interfering peak markers. If the element causing the interference is present in significant concentrations in your unknowns, and is not being analyzed for, it may be necessary to add the interfering element to the run by creating a new sample with the interfering element as an analyzed element. Be sure that the proper standards are available to use for the interference correction.

4. It would be useful to examine the precise choices for x-ray peaks; did the software/firmware routine choose the best peak position? Sometimes the algorithm doesn't. You want to use the center of the peak quasi-plateau where either any small spectrometer drift or peak/shape effects will be minimized. Probe for Windows has a "post-scan" confirmation option where you can verify this. This issue would be for the main elements in a multi-element phase, and not that important for minor or trace elements where the determination of the background is the critical endeavor.

5. If none of the above suggestions seem to help, try acquiring the standards again. Probe for Windows uses an automatic standard drift corrections which can make a significant difference in situations where one or more of your analytical channels is drifting. Note that since the program will perform an automatic drift correction not only on the standards, but also the interference standards and the MAN background standards, it might be also be necessary to run additional sets of those standards or MAN standards.

6. In the case of trace or minor elements, also check to see that none of the off-peak positions are interfered with by another peak. This can cause a reduction in the on-peak counts, sometimes enough to result in a negative k-ratio. Always run at least one wavelength scan on a sample, using the same count time as your quantitative analyses, and if a peak is seen interfering with the off-peak marker, use the Low and/or High buttons in the Graph Data window to select a new off-peak position that is not interfered with.

In addition, to solve problems with trace analysis, it is always useful to run at least one "blank" that is similar to your unknown sample, at least in terms of average atomic number, if not actual chemistry. For example, when analyzing trace elements in quartz, try to run an unknown analysis on a "pure" synthetic quartz sample, one that is known to contain known concentrations of the trace elements. The point is to try to determine how closely one can measure "zero" concentrations.

Glossary of Terms

ALPHA-FACTOR

Early EPMA workers did not have the luxury of high speed computers, and the complex rigorous physics-based matrix corrections could not be easily performed in an applications-oriented probe lab. Alpha factors or coefficients for matrix correction in binary compounds (e.g., Fe on Ni Ka, Ni on Fe Ka) were initially conceived of by Castaing in his 1951 Ph.D. dissertation. Ziebold and Ogilive (1964) revisited alpha factors in the popular scientific literature as the development of commercial electron microprobes took off. Shortly thereafter, efforts to consider phases of more than 2 elements spurred the development of beta-factors. This was applied to geological EPMA by Bence and Albee (1968) who developed oxide alpha factors; this paper is one of the most frequently cited references in geology (over 1800 citations between 1982-2001). Several decades later, it was recognized that the alpha-factor approach could be fine-tuned for improved quantitative results using additional fit coefficients (linear and polynomial) (Rivers, pers. comm., 1990, and 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:

$$C_A^u = \frac{C_A^s}{\mathrm{Beta}_{\lambda_A}^s}\,\frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)}\,\mathrm{Beta}_{\lambda_A}^u$$

where :	$\mathrm{Beta}_{\lambda_A}^u$	is the unknown beta-factor

$\mathrm{Beta}^{s}_{\lambda_A}$ is the standard beta-factor

ANALYTICAL ERROR

This calculation is for analytical sensitivity of each line (= one measurement), considering _both_ peak and background count rates (Love and Scott, 1974). It is a similar type of statistic as the 1 sigma counting precision figure, but it is presented as a percentage in the Probe for Windows statistical printout.

$$e_{P-B} = \frac{\sqrt{\dfrac{N_P}{t_P^2} + \dfrac{N_B}{t_B^2}}}{\left(\dfrac{N_P}{t_P} - \dfrac{N_B}{t_B}\right)}$$

Where :

N_P is the total peak counts

N_B is the total background counts

t_P is the peak count time

t_B is the background count time

ANGSTROM

Unit of measure for x-ray wavelengths. Wavescan intensities and KLM markers may be displayed in spectrometer or angstrom units.

The conversion of spectrometer to angstrom units is by default based on the calculated spectrometer offset from the theoretical peak position compared to the actual or measured peak position using the following expression:

$$\Delta P = P_T - P_A$$

where: P_T = the theoretical spectrometer peak position

P_A = the actual or measured spectrometer peak position

This assumes that any inaccuracy in spectrometer position from the exact theoretical position is a constant offset regardless of the spectrometer position. Usually this is sufficient for most purposes, where the spectrometers are not too far out of alignment. Of course, you will determine the exact peak positions in practice; the accuracy discussed here affects the initial locating of spectrometers and labeling of peaks in the Plot! displays.

.For ultimate accuracy in initial spectrometer locating and peak labels in Plot!, use of the multiple peak calibration option in the StartWin application will produce a calibration table that will be used by Probe for Windows in calculating a variable spectrometer offset based on the spectrometer position for each spectrometer and crystal combination and for each Ka, Kb, La, Lb, Ma or Mb family. See the PROBEWIN.INI keyword "UseMultiplePeakCalibrationOffset" for more information on the use of this variable spectrometer offset feature.

ATOMIC PERCENT

The atomic percent is calculated based of the fraction of the atomic weight of the element. Also called "elemental mole" percent. Since the calculation normalizes the data to a 100 % total, it is recommended that the calculation be only performed on samples which total close to 100 % (e.g., 98-102). The calculation is as follows :

$$A.P. = \frac{100}{\sum_{i=1}^{n} \left(\frac{W}{A} \right)} \bullet \frac{W_i}{A_i}$$

where : W is the elemental weight percent of the element

A is the atomic weight of the element

AVERAGE

Also known as the mean or arithmetic mean. The average is calculated by simply dividing the sum by the number of values. The calculation is shown below.

$$A = \frac{\sum_{i=1}^{n} X_i}{n}$$

where : X are the values to be averaged

n is the number of values to be averaged

AVERAGE ATOMIC NUMBER

Also known as Z-bar or Mean Atomic Number (MAN). The sum of the elemental weight or atomic fractions of the element atomic numbers of a sample.

The sum of the weight fractions of the atomic numbers of a sample is applicable for modeling the background continuum and is used in the MAN background correction iterated polynomial calculation by Probe for Windows to approximate the average z-bar (electron fractions are actually more rigorous).

On the other hand, the sum of the atomic fractions of the atomic numbers of a sample is applicable to stopping power calculations and is used in Monte Carlo calculations of electron trajectories.

The weight fraction calculation is quite simply :

$$\bar{Z} = \sum_{i=1}^{n} \left(\frac{W}{\sum_{i=1}^{n} W} \right) \bullet Z$$

where : Z is the atomic number of the element

	W	is the elemental weight or atomic percent of the element

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.

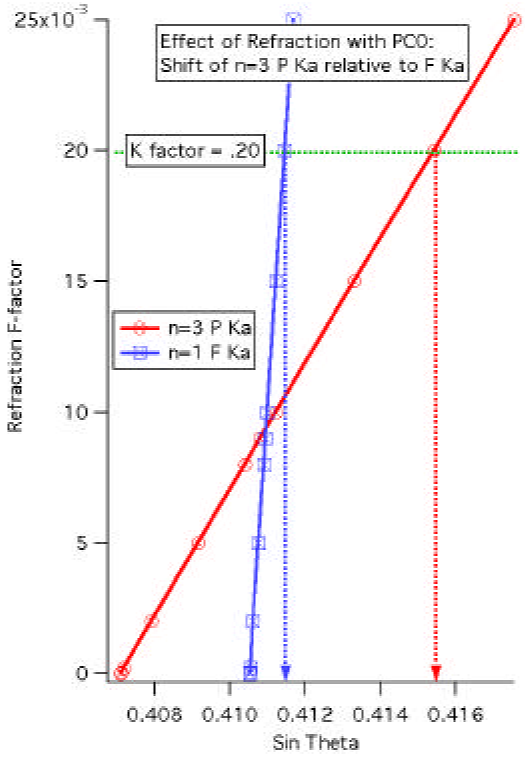
BRAGG'S LAW

In 1913, the father-son team of William H + William L Bragg built an X-ray spectrometer, using NaCl to resolve Pt X-rays. For this they received the Nobel Prize in 1915.

$$n\lambda = 2d \sin \phi$$

where :	n	is the order of the x-ray (1st, 2nd, etc.)
	λ	is the wavelength in angstroms
	$2d$	is the analyzing crystal 2d spacing in angstroms
	ϕ	is the angle of diffraction

There is a more precise form of Bragg's Law that allows for refraction of x-rays by the crystal or diffractor; this can be shown as a modification of the 2d such that d' = d[1-(k/n^2)] where n is the order of reflection and k is a constant for each crystal. These constants range from 6x10-5 for LiF to 2.2x10-3 for TAP (Reed, 1993). They can cause higher order lines to "cross over" and appear on the opposite side of a peak, such as the 3rd order P Ka upon the F Ka for LDEs. Probe for Windows automatically uses this precise calculation.



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 stoichiometry (ratio) for Silicon to Oxygen is 1 to 2 and the subscript for Silicon is 1 and for oxygen is 2.

CHARACTERISTIC X-RAY

Inner shell electrons can be knocked out by high energy electrons, with an electron from a higher shell taking its place. The excess energy of the second electron is emitted as a photon which either is converted internally into an Auger electron or an x-ray with a characteristic energy/wavelength. See Fluorescence Yield

CONTINUUM

The continuum is the background radiation produced during the production of the characteristic x-rays. It is generated as the high energy electrons from the gun interact with the nuclei of the target atoms, and their trajectories are altered by the positive charge of the nuclei. When the electron trajectory bends, x-ray radiation is emitted at an energy level that ranges on a continuous scale (hence continuum) from a minimal low value, up to a maximum of the acceleration voltage value. Also known as Bremstrahlung (literally "braking radiation").

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 (and be sure that the nominal current is set at the actual value used to obtain the unnormalized intensity data).

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:

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

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 Probe for Windows supports the use of a hardware "enforced" deadtime for rigorous correction of the deadtime effect if available on the microprobe (e.g. Cameca SX-50/51/100). 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 the NASA Marshall Flight center is available from Advanced MicroBeam.

Detection Limit

The lowest concentration that can reliably be detected above the level of the background. To achieve low (10-100 ppm) detection level requires a large number of counts which means running at maximum currents (hundreds of nA), long times (100s of seconds) and the highest accelerating voltage possible. It has been shown that (P^2/B) is the "figure of merit" for trace element analysis, and it increases for many elements with increasing accelerating voltage.

Probe for Windows offers two versions of the detection limit calculation. The first is for each line ("single line") which means that in a heterogeneous material, it is the detection limit for each measured spot. Alternatively, if many counts are acquired on a homogeneous material, then they can be averaged, yielding a lower detection limit. The software provides such a detection limit for an average sample at a variety of confidence levels (normal level is 99%) utilizing a T-test. (see T-test)

EDS

Energy Dispersive Spectrometry. This method utilizes a solid state detector that operates similarly to the gas-filled detector in the electron microprobe spectrometer, with important distinctions. In the solid state detector, the x-rays knock out electrons (specifically the photoelectric effect), producing electron-hole pairs, each part migrating to + or - surface of the voltage biased Si(Li) or Ge crystal. The number of electron-hole pairs is directly proportional to the x-ray energy, and a small pulse is generated. This is immediately amplified in an adjacent FET (field effect transistor), and then the signal proceeds to a pre-amp, and then to the processing and counting electronics. The result is a histogram of energy levels, or spectrum.

Many electron microprobes also have EDS detectors that are used to "fingerprint" materials prior to WDS analysis. EDS is also combined with WDS on some instruments for increasing the number of elements that can be elementally mapped.

Probe for Windows offers additional options for both acquiring elements for quantitative analysis, as well as acquiring and storing EDS spectra when each WDS measurement is made (useful for off-line data processing).

EPMA

Electron Probe Micro Analysis. Differentiated from SEM/EDS analysis by the use of high precision, high resolution, high sensitivity vertical WDS spectrometers.

ESCAPE PEAK

In both the EDS detector and the WDS gas-filled proportional counter, there is the statistically probability that besides photoelectrons (and holes in EDS, and Ar cations in P10-filled WDS detector), there may be some secondary fluorescence. That is, the incident x-ray (let's say Fe ka for example) could knock out an inner shell electron and produce another x-ray (Si ka in typical Si-Li detector; Ar ka in P10-filled detector). Most of these x-rays will be "consumed" within the detector, yielding photoelectrons, but some will find a means to escape the detector. Their characteristic energy will be lost to the detector for this one x-ray, resulting in one pulse that is at a lower energy level than is expected, which will then show up as a small peak at a lower voltage.

Taking the Fe Ka X-ray as an example, in the Si-Li EDS spectra, there will be a small peak at 4.66 keV, 1.74 keV below the Fe Ka peak of 6.40 keV. In the WDS detector using P10 gas (90% Ar, 10% CH4), Ar-escape peaks will occur on the PHA energy display at a proportionally lower value, i.e., if the Fe Ka pulse is centered at 2.5 volts, then there will be a small Ar-escape peak at around 1.3 volts, because Ar Ka = 2.96 keV, so the escape peak will be 6.40 - 2.96 = 3.44 keV; 3.44/6.40 =0.54; 0.54 * 2.5 volts = 1.34 volts.

In WDS, sometimes it is impossible to acquire the complete Ar-escape peak, because the lower part is too low in energy and falls below the baseline cutoff. In that case, it is recommended that the baseline be raised to cut off all of the escape peak; either acquire all of it, or none of it. See section on PHA for more details.

FIDUCIAL

Refers to the physical marking of a sample mount with a number of reference marks, so that all data can be referenced directly to those marks on the sample surface. This is used to provide a method of re-locating specific positions even after the sample has been removed from the sample holder. This method can also be used to relocate coordinates from an entirely different coordinate system such as a digitizing microscope stage. In the Probe for Windows software package all samples using this feature must have 3 fiducial marks. This is because the program assumes that the positions are digitized in three dimensions (fixed to x, y and x).

FLUORESCENCE YIELD

The fraction of inner shell ionizations that yield characteristic x-rays; the remaining ionizations yield Auger electrons of very low energy.

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.

HI PEAK COUNTS

Hi Peak counts are one background (continuum) measurement usually above the peak position, although the "high" adjective is strictly relative to the "low peak", so in practice could be below the peak position, but higher than the "low peak" position.

In Probe for Windows the "high" peak position is always measured first, following the on-peak measurement.

INTERFERENCE

An analytical situation when a peak from another element overlaps a primary analytical line or background measurement position used in the data acquisition. Ignoring this interference will often result in an incorrect analysis. This is sometimes seen as a high total when the on-peak interference is large or as a negative raw k-ratio (KRAW) when the off-peak position is interfered with. 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 for Windows. 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.

In some cases where one has the choice between use of two diffracting crystals, the one with the lowest 2d will provide the maximum spectral resolution available for minimizing overlap of peaks.

INTERFERENCE STANDARD

A standard used for the quantitative interference correction in Probe for Windows. 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 (this is done automatically if the interference is declared in the Analyze! | Standard Assignments). To use the quantitative interference corrections in Probe for Windows you must acquire counts on 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 Probe for Windows 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. Probe for Windows 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

Initial probe work by Castaing was metallurgical and the standards were pure elements, and so the K-ratio was defined relative to a pure element standards. In the situations where the standard is not the pure element, a means to use the normal form K-ratio is to normalize the standard, using the standard k-factor. This is the concentration of the element in the standard (as a fraction) 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.

LOW PEAK COUNTS

Low Peak counts are one background (continuum) measurement usually below the peak position, although the "low" adjective is strictly relative to the "hi peak" position, so could be above the peak position, but lower than the "hi peak" position.

In Probe for Windows the "high" peak position is always measured first, following the on-peak measurement, followed by the "low" peak measurement.

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. An additional option has been added whereby the background count rates at the characteristic peaks in samples containing the element of interest are found using the measured off-peak backgrounds, and similarly utilized.

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

This is an algorithmic calculation to correct for the absorption, fluorescence and atomic number effects of other elements upon the element of interest in the material. In his 1951 Ph.D. thesis, Raymond Castaing laid out the two approaches that could be used to apply matrix corrections to the data: an empirical "alpha factor" correction for binary compounds, where each pair of elements has a pair of constant a-factors representing the effect that each element has upon the other for measured X-ray intensity; and a more rigorous physical model explicitly accounting for absorption and fluorescence in the specimen. This later approach also includes atomic number effects and became known as ZAF correction. Probe for Windows supports the various matrix corrections, i.e., alpha, Bence Albee, and several types of both ZAF and Phi-Rho-Z algorithms. See those terms.

MULTI-SELECT

Multi-select means that the list box supports the selection of more than one item. To select a range of items click the first item in the list and then holding the <shift> key, select the last item to be selected. To select individual items, click while holding the <ctrl> key down.

NOMINAL

Nominal is defined in the Oxford American Dictionary as "in name only" or "a token fee". However, in the Probe for Windows 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.

OFF COUNTS

Off Counts are the values used for the background (continuum) at the characteristic peak position. They are the measured at the peak position (if MAN background) or calculated from one or two off-peak positions (if off peak method).

ON COUNTS

On Counts are the net or background-corrected counts at the peak position, and result from the characteristic x-ray intensity minus the background intensity.

ON PEAK COUNTS

On Peak Counts are the total or gross counts at the peak position, and are composed of x-rays of the continuum (background) upon which the characteristic x-ray intensity rides.

ONE SIGMA

This is a statistical value giving precision based upon counting statistics, i.e. count rate and counting time and is calculated from the square root of the total counts. It is sometimes also referred to as a "standard deviation" even though one can calculate a value based upon only one measurement (see Poisson Statistics) Use the one sigma value to evaluate whether a given average count rate represents a homogeneous set of sample data.

Standard deviations (SDEV) larger than the one sigma value (1SIG), i.e., SIGR >1, indicate the possibility of actual compositional variation within the data set. The 1 sigma value is the predicted standard deviation based on the count rate and counting time. It is calculated by dividing the square root of the count rate by the square root of the average counting time.

$$s = \frac{\sqrt{i_{cps}}}{\sqrt{t_s}}$$

where : i_{cps} = intensity in counts per second

t_s = count time in seconds

OXIDE

Geologists and geochemists typically report their data in wt% oxides, as oxygen is the dominant element in earth materials and many elements in nature are bonded with oxygen in crystal lattices or glass. Thus, silicon (Si) is reported as silicon dioxide or silica (SiO_2), Ca as CaO, Na as Na_2O, phosphorus as P_2O_5. These are discrete, stoichiometric ratios with charge balance.

Some elements can easily exist in different valence states (e.g. Fe, Cr) but for convenience sake are nominally assumed to exist in one form (e.g., FeO, Cr_2O_3). They can be easily "translated" to elemental weight values; simply create a fraction using atomic weights from the periodic table, with numerator the element wt % and denominator the oxide wt% summed up. Thus to determine Si from SiO_2, one would divide 28.09 by (28.09 + [2 x 16.00]), yielding the fraction 0.4675. Thus, something at is 100 wt% SiO_2 is actually 46.75 wt% Si and the balance oxygen by weight. And elemental wt% values can be converted to oxide wt% by the inverse. In a Probe for Windows run, the sample compositions are reported as oxides if the Display As Oxides option is selected for that sample.

P/B

Peak to Background Ratio. Strictly the total counts at the peak position (which will also include the continuum contribution in addition to the characteristic x-ray counts). A measure of the sensitivity of the analysis. To improve your detection limit, you will want to increase the peak to background ratio. This can be accomplished by using the analyzing crystal with the highest theta available (for example run K $K\alpha$ on LiF rather than PET) by using the highest accelerating voltage reasonably feasible, and using lower noise flow detectors rather than sealed detectors. The P/B is calculated as :

$$P / B = \frac{I_P + I_B}{I_B}$$

where : I_P is the background corrected peak intensity

I_B is the background continuum intensity

PHOTOELECTRIC EFFECT

The photoelectric effect was discovered in 1887: light (photon of energy > metals absorption edge) falling on metal surface ejects electrons from the metal. X-rays hitting a metal, a semi-conductor, or a gas will similarly eject electrons from the materials, and the electrons are therefore called photoelectrons.

PHOTOELECTRONS

The electrons knocked out of materials (e.g., SiLi detector, Ar molecules in P10 gas) are photoelectrons.

POISSON

X-ray production is a random process, where each repeated measurement represents a sample of the same specimen volume (for a homogeneous specimen). The expected distribution can be described by Poisson statistics, which for large number of counts is closely approximated by the "normal" Gaussian distribution ("bell curve"). For these distributions, 1 sigma = square root of the counts, and 68.3% of the sampled counts should fall within ±1 sigma, 95.4% within ±2 sigma, and 99.7 within ±3 sigma.

PHA

Pulse Height Analysis (or Analyzer). The x-rays that satisfy Braggs Law reach the detector inside the spectrometer housing, where they ionize the gas (produce photoelectrons and Ar cations) and create a small analog electronic signal. This signal passes to a pre-amp and then through an electronic circuit that shapes it into a digital pulse for input to the x-ray counter scalers. In a properly configured detection system, the bias in the detector is set so that the ionization occurs in the "proportional range", and higher order (n>1) diffractions that also satisfy Braggs Law (and are discrete fractions of the wavelength of the desired element), will have discrete multiples of the pulse energy. Thus, if the first order peak has a peak at 2.0 volts, the 3rd order peak would have a peak at 6.0 volts. This provides one way to reduce or eliminate higher order interferences: setting a window so that the desired element's x-rays are passed through, but that the higher energy interfering x-rays are rejected. This is known as "differential" mode, whereas under "integral" mode there is no window. Also, a lower limit or baseline (e.g. 0.5 volts) is set to filter low energy electronic noise. Use of differential mode PHA should be used with care, as there are possible serious errors that can occur to the unwary (see discussion of energy shifts in the manual). Probe for Windows offers a sophisticated interference correction which in many situation eliminates the need to use differential mode PHA (which can only reduce higher order interferences in any case).

PHI-RHO-Z

In developing models of x-ray generation, analytical scientists decided that the easiest way was to consider "mass depth" or Rho-Z, the product of the sample density and the linear depth Z. The function that describes the relative intensity of x-ray generation with mass depth, is call Phi. The expression is often written as $\rho\phi(z)$ Phi (Rho-z). At the surface there is a moderate amount of x-rays produced, but it rapidly increases as the electrons scatter laterally, and then quickly reaches a maximum, and trails off to zero. Some matrix corrections use this explicitly, combining the absorption and atomic number corrections. This is an alternative method to the ZAF matrix correction, which can be more easily verified using so called tracer and wedge experiments.

POLYGON

An enclosed shape consisting of a number of line segments. **Probe for Windows Enterprise** supports the automated acquisition of data from within user defined polygon boundaries. The digitized polygon coordinates are automatically saved to the run file as they are acquired and are automatically output when the Surfer .BAS option is selected.

POLYNOMIAL

A mathematical expression of the form : $Y = A + BX + CX^2 + ...$ The MAN background correction used in **Probe for Windows Enterprise** 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.

PPM

Parts per million, can be either elemental or oxide. To convert wt % to ppm, multiply by 10000. Thus 0.1 wt% = 1000 ppm; 0.01 wt% = 100 ppm; etc.

PRIMARY STANDARD

An analytical standard which is ***assigned*** as the calibration standard for one or more analyzed elements in a quantitative run. Elements in standards not assigned as the primary calibration, but which contain an acquired element can be considered secondary standards.

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 a 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

If the standard were a pure element, then the K(raw) would be a fraction less than or equal to 1, and very roughly equivalent to the elemental fraction in the unknown. This approximation has become known as "Castaing's first approximation", after the founder of EPMA.

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.

Unlike other EPMA software programs that write or store the user's data in "normal" computer files, Probe for Windows uses a robust industry standard (Microsoft Access) file format based on transactional processing, guaranteeing the preservation of the data regardless of power failures, computer crashes, etc.

SCANNING SPECTROMETER

A spectrometer that can be tuned to a range of analytical x-ray lines. Usually contains two to four analyzing crystals. Scanning spectrometers are required for off-peak background corrections. MAN background corrections can be used for either fixed or scanning spectrometers.

SECONDARY STANDARD

A standard which is not assigned as a primary standard for a given element (that is, not directly used in the quantitative calculation of unknowns). However, it is useful, if the secondary standard contains a known quantity of the analyzed element, to check the quality of the secondary analysis can be judged by observing the "%VAR" line when an analysis is performed. The "%VAR" is calculated as follows :

$$\%\ \mathrm{VAR} = \frac{W_{AVER} - W_{PUBL}}{W_{PUBL}} \bullet 100$$

where : W_{PUBL} is the published concentration of the element

W_{AVER} is the measured average concentration of the element

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 Probe for Windows. Standards which contain elements which are not being measured, 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 measuring, 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 present in the specimen but is not being measured (reasons: difficult or impossible to measure; concentration is known; stoichiometry is known). It is included to account for its effect on atomic number effects, absorption and fluorescence in the sample matrix, as well as to yield an analytical total more accurately representative of the sample.

STANDARD DEVIATION

A calculation that essentially describes the error for a single point of a sample. It can only be rigorously calculated when more than one data point has been measured. The calculation is :

$$\mathrm{S.D.} = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \mu)^2}{n-1}}$$

where : X_i is the data observations

μ is the mean of the data

n is the number of observations

When only a few points have been measured and it is necessary to know the confidence that one can assign to the precision, the use of the Student's "t" factor is often applied.

STANDARD ERROR

A calculation that essentially describes the error for the average of a sample. It is calculated by dividing the standard deviation by the square root of the number of data points. The calculation is :

$$S.E. = \frac{\sqrt{\dfrac{\sum_{i=1}^{n} (X_i - m)^2}{n-1}}}{\sqrt{n}}$$

where : X_i is the data observations

μ is the mean of the data

n is the number of observations

STOICHIOMETRY

A fixed atomic ratio between elements. For example the mineral olivine has a stoichiometry of (Fe,Mg):Si:O of 2:1:4 (atomic). A test for a "good" analysis would be to calculate (Analyze!|Calculation Options) the stoichiometry on the basis of 4 oxygens. Values for Si of .997 and sum for Fe and Mg of 1.995 would be generally considered very good.

STUDENT'S T

The general problem relevant to WDS EPMA of having some level of confidence that a measure is equivalent to another, or larger/smaller than another, is that the sample size is small and the population variance is unknown. This type problem was first treated in 1905 by W.S. Gossett, who published his analysis under the pseudonym "Student". His employer, the Guinness Breweries of Ireland, had a policy of keeping all their research as proprietary secrets. The importance of his work argued for its being published, but it was felt that anonymity would protect the company.

In statistical evaluation of x-ray count data, an exacting criterion is that of calculating a precise range (in wt%) and level (in %) of homogeneity. These calculations utilize the standard deviation of measured values and the degree of statistical confidence in the determination of the average.

The degree of confidence means that we wish to avoid a risk (alpha) of rejecting a good result a large per cent of the time (95 or 99%) of the time. Student's t distribution gives various confidence levels for evaluation of data, i.e. whether a particular value could be said to be within the expected range of a population -- or more likely, whether two similar compositions could be confidently said to be the same. The degree of confidence is given as 1- a, usually .95 or .99. This means we can define a range of homogeneity, in wt%, where on the average only 5% or 1% of repeated random points would be outside this range.

TIFF

(Tagged Image File Format) An image file format consisting of rasterized pixel color information. Probe for Windows can create an OLE script that will automatically create .GRD files that can be imported by Micro-Image for Windows for fully registered TIFF images.

TUNABLE SPECTROMETER

A spectrometer that can be tuned to a range of analytical x-ray lines. Usually contains two to four analyzing crystals. See SCANNING SPECTROMETER above.

UNKNOWN K-RATIO

The unknown k-ratio is defined as the product of the raw k-ratio and the standard k-factor. It is always a fraction, since the pure element is 1.0. See also raw k-ratio, k-factor and ZAF. The expression is :

$$K_{unk} = \frac{C^s_A}{[ZAF]^s_{l_A}} \frac{I^u_A(l_A)}{I^s_A(l_A)}$$

where :	$I^u_A(\lambda_A)$	is the unknown intensity for element A at λ
	$I^s_A(\lambda_A)$	is the standard intensity for element A at λ
	C^s_A	is the concentration of the element in the standard
	$[\,ZAF\,]^s_{\lambda_A}$	is the ZAF correction for the element in the standard

WDS

(Wavelength Dispersive Spectrometry) X-ray analysis based on Bragg's law of x-ray diffraction.

$$n\lambda = 2d \sin \phi$$

where :	n	is the order of the x-ray (1st, 2nd, etc.)
	λ	is the wavelength in angstroms
	$2d$	is the analyzing crystal 2d spacing in angstroms
	ϕ	is the angle of diffraction

ZAF

A method for the matrix correction of emitted (as opposed to generated) x-rays from a samples. The method calculates the effects of atomic number (Z), absorption (A) and characteristic (and sometimes continuum) 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 :

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

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

$[ZAF]^u_{\lambda_A}$	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
$[ZAF]^s_{\lambda_A}$	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.

Z-BAR

See Average Atomic Number.

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