Probe for EPMA v. 12.8.0

Advanced Topics

Xtreme Edition

Probe For EPMA

Acquisition, Automation and Analysis

Xtreme

Distributed by Probe Software, Inc.

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Edited by Karsten Goemann for
Probe Software, Inc.

Contents

Acknowledgements

Many people have aided the author both directly and indirectly in the preparation of this Advanced Topics manual. First and foremost, John Donovan and Paul Carpenter, they have freely given their time, expertise, and even data files for incorporation into this manual. Their technical discussions as well as their friendship over the years have made this manual better.

Disclaimer

Conventions Used in this Guide

The following conventions are used in this document; **Menu Commands** and **Dialog Box (Windows) Names and buttons** are bold-faced whenever they occur in the text. *Dialog Box Options* are italicized and FILE NAMES are capitalized.
Several tips for saving time/steps include:

Context sensitive HELP is available in any window by pressing the F1 key.
Pressing <Enter> (or <Return> <↵ > on international keyboards) on the keyboard is identical to clicking the **OK** button.
Pressing the <Esc> key on the keyboard is identical to clicking the **Cancel** command.
To select a range of items in *Multi-Select* list boxes, click on the first item, move to the last and hold the <Shift> key down while clicking on the last item.
To select individual items in *Multi-Select* list boxes, hold down the <Ctrl> key down while clicking on the item.
De-select items in *Multi-Select* list boxes by holding the <Ctrl> key down and clicking the item.

Introduction

PROBE FOR EPMA is a very versatile and powerful acquisition, automation and analysis package for WDS and EDS electron microprobe analysis running under Microsoft Windows operating systems.

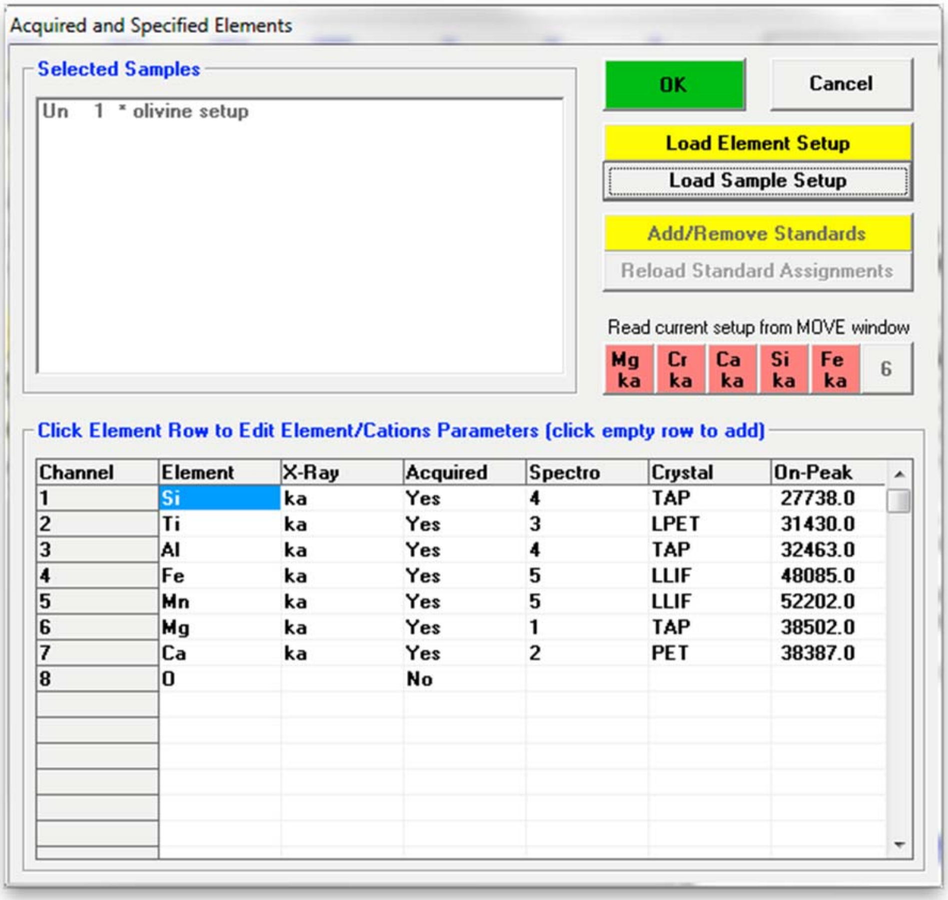
One of the strengths of PROBE FOR EPMA is the wide variety of options and features for many different tasks that are available to the probe operator. The aim of this manual then is to document some of the more advanced features usually skipped over in an introductory text. And as always, the path taken to cover a feature may not be the only avenue to approach the subject.

This manual was originally produced on the Washington University (Earth and Planetary Sciences) JEOL 733 Superprobe equipped with three wavelength dispersive spectrometers and updated using PROBE FOR EPMA in demo mode in the configuration of the Cameca SX100 at University of Tasmania.

Element Setups

Individual element analytical configurations for a specific element, x-ray, spectrometer, and diffraction crystal may be saved to the SETUP.MDB database for use in creating new sample setups within a probe run, for use in future runs or for documentation and performance evaluation purposes. The example below will illustrate how to create element setups from within a typical eight-element olivine routine and store them in a new SETUP.MDB database.

Open a new PROBE FOR EPMA run in the usual manner. From the **Acquire!** window, create a new unknown sample from the **New Sample** dialog box, then click the **Elements/Cations** button. Next, enter the elements of interest into the **Acquired and Specified Elements** window in the usual manner. Below is the completed **Acquired and Specified Elements** window after the entry of all seven elements plus oxygen.

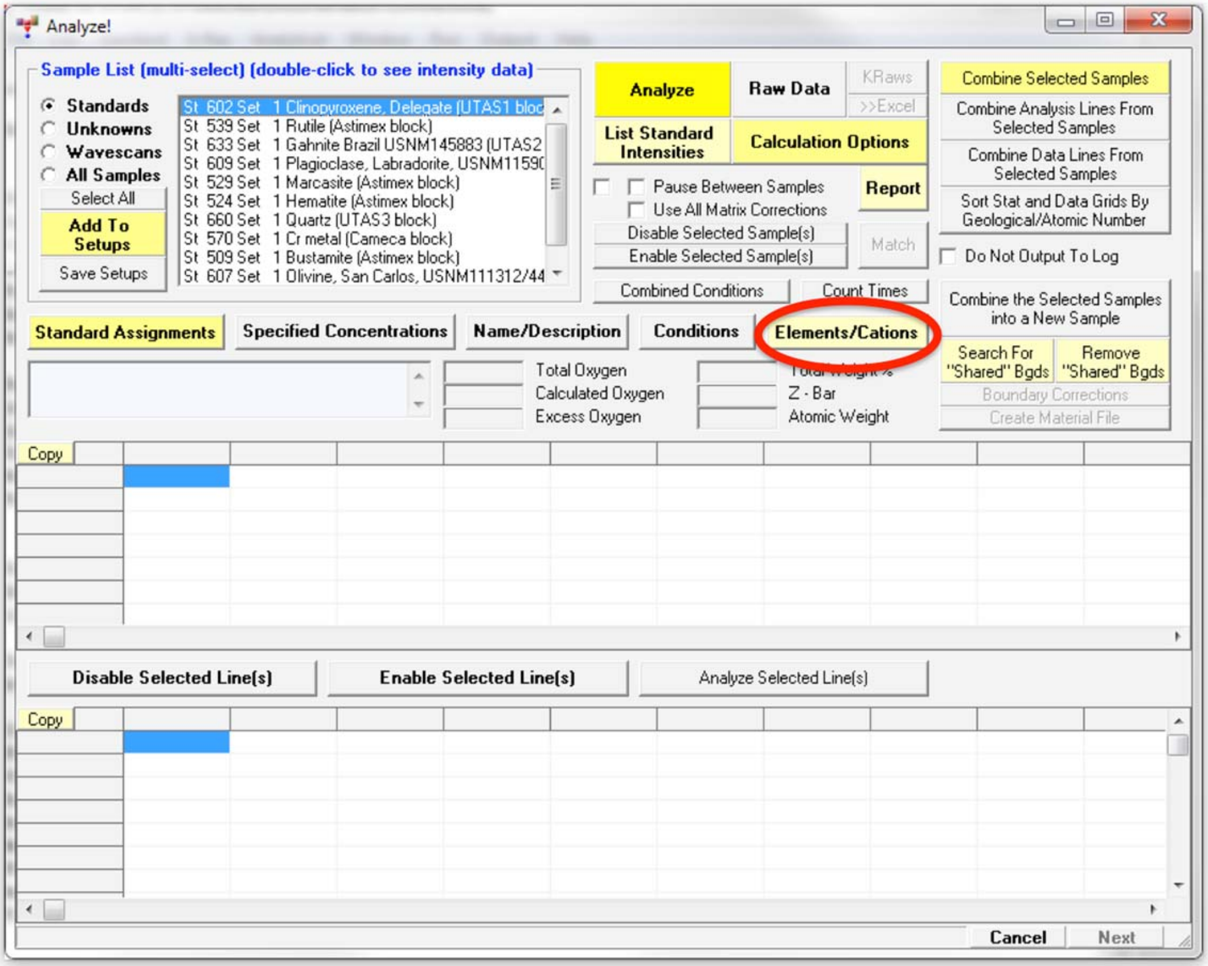


Un 1 * olivine setup

Channel	Element	X-Ray	Acquired	Spectro	Crystal	On-Peak
1	Si	ka	Yes	4	TAP	27738.0
2	Ti	ka	Yes	3	LPET	31430.0
3	Al	ka	Yes	4	TAP	32463.0
4	Fe	ka	Yes	5	LLIF	48085.0
5	Mn	ka	Yes	5	LLIF	52202.0
6	Mg	ka	Yes	1	TAP	38502.0
7	Ca	ka	Yes	2	PET	38387.0
8	O		No			

Go through the calibration process; find new peak positions and standardize to acquire intensity data on each standard. Normally one should save the element setup of an element that is assigned as the standard for that element. This is done because in that case the x-ray intensity data, P/B data, PHA parameters, and other information will also be saved in the SETUP.MDB database. This information is very useful for documentation and evaluation purposes.

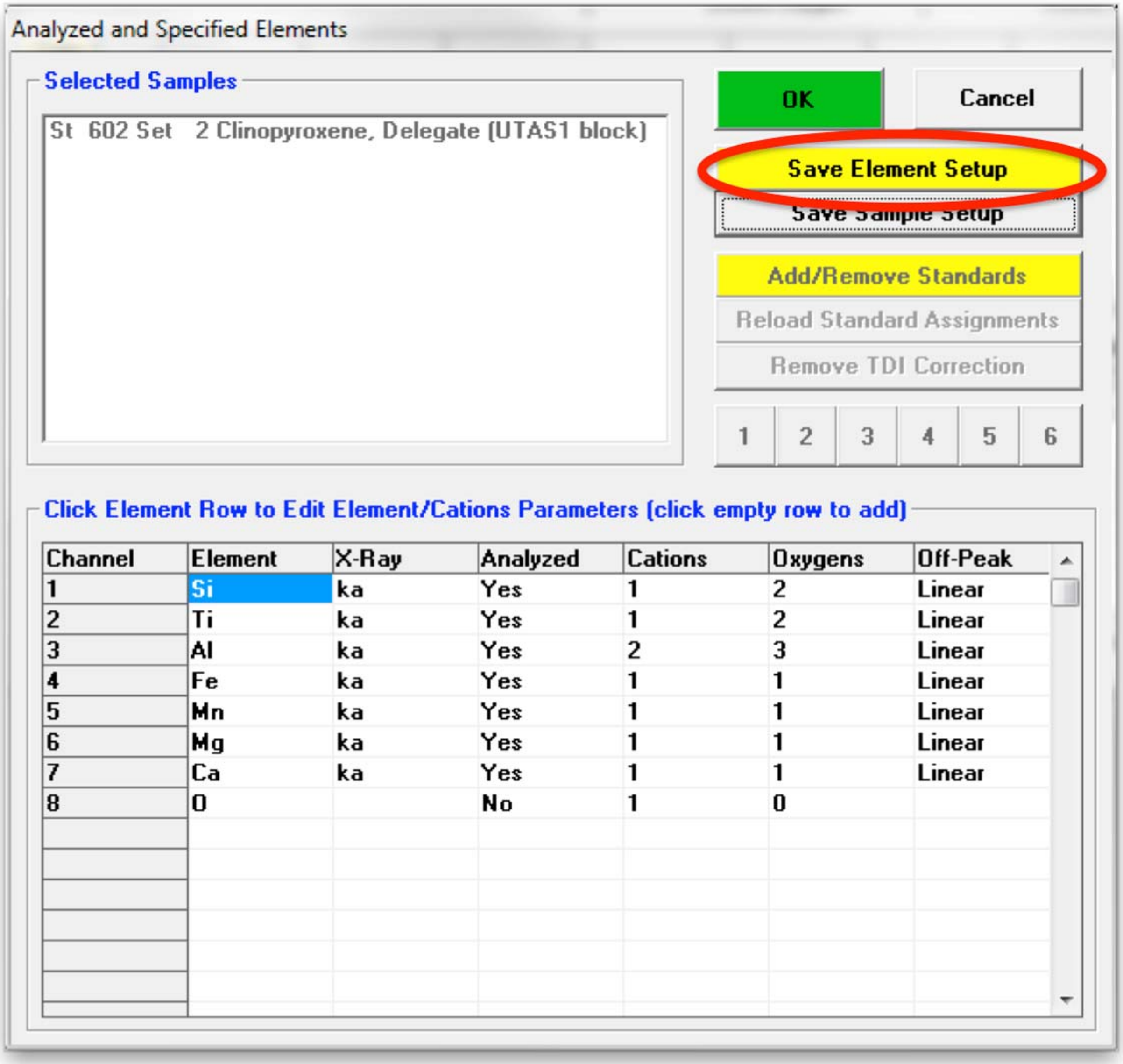
After completing the calibration and standardization process, open the **Analyze!** window. Choose the element setup to be stored and highlight the standard (calcium in clinopyroxene, in this example).



St 602 Set 1 Clinopyroxene, Delegate (UTAS1 bloc
St 539 Set 1 Rutile (Astimex block)
St 633 Set 1 Gahnite Brazil USNM145883 (UTAS2
St 609 Set 1 Plagioclase, Labradorite, USNM11590
St 529 Set 1 Marcasite (Astimex block)
St 524 Set 1 Hematite (Astimex block)
St 660 Set 1 Quartz (UTAS3 block)
St 570 Set 1 Cr metal (Cameca block)
St 509 Set 1 Bustamite (Astimex block)
St 607 Set 1 Olivine, San Carlos, USNM111312/44

Click the **Elements/Cations** button.

This opens the **Analyzed and Specified Elements** window.

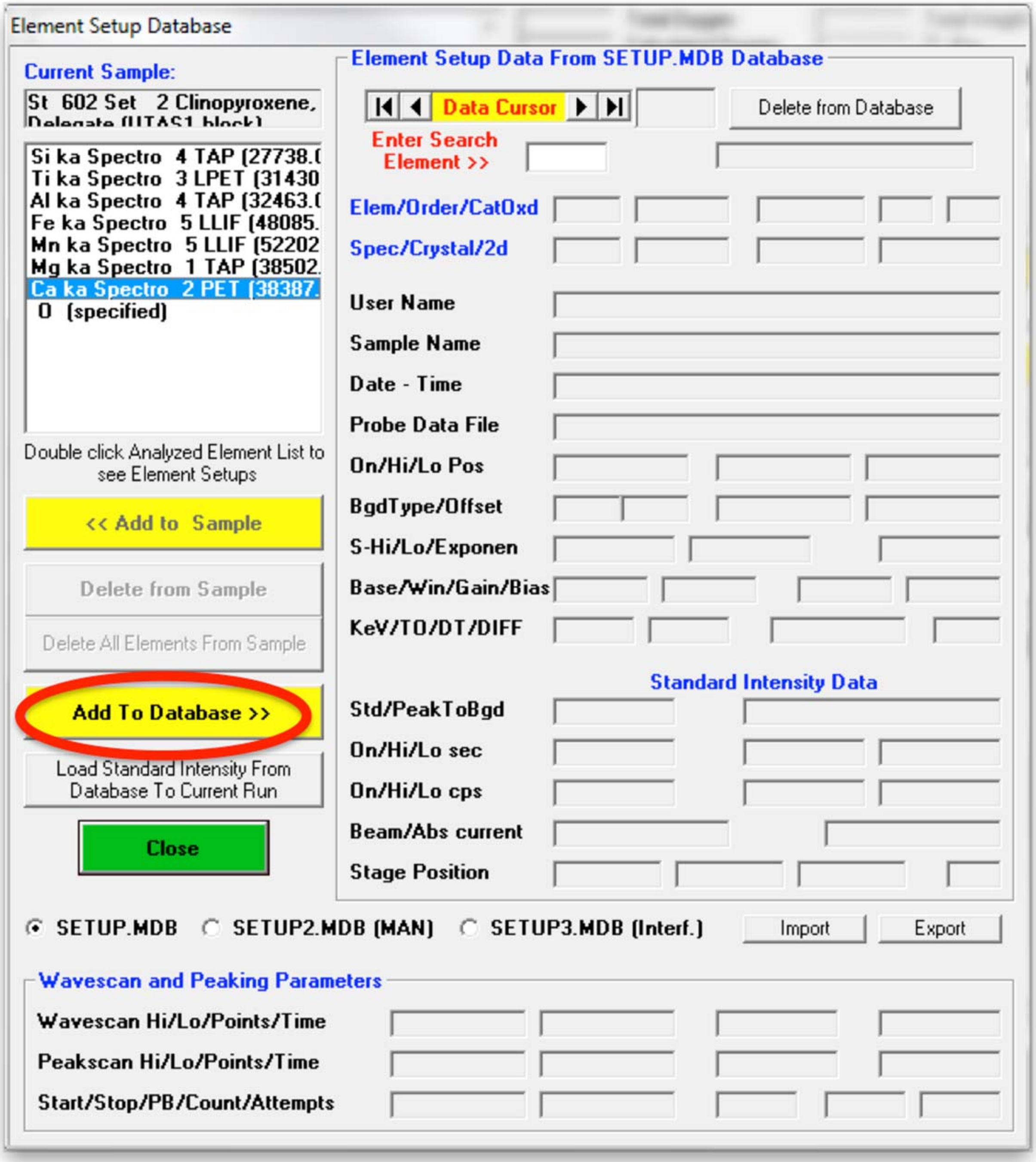


St 602 Set 2 Clinopyroxene, Delegate (UTAS1 block)

Channel	Element	X-Ray	Analyzed	Cations	Oxygens	Off-Peak
1	Si	ka	Yes	1	2	Linear
2	Ti	ka	Yes	1	2	Linear
3	Al	ka	Yes	2	3	Linear
4	Fe	ka	Yes	1	1	Linear
5	Mn	ka	Yes	1	1	Linear
6	Mg	ka	Yes	1	1	Linear
7	Ca	ka	Yes	1	1	Linear
8	O		No	1	0	

Click the **Save Element Setup** button.

The **Element Setup Database** opens.

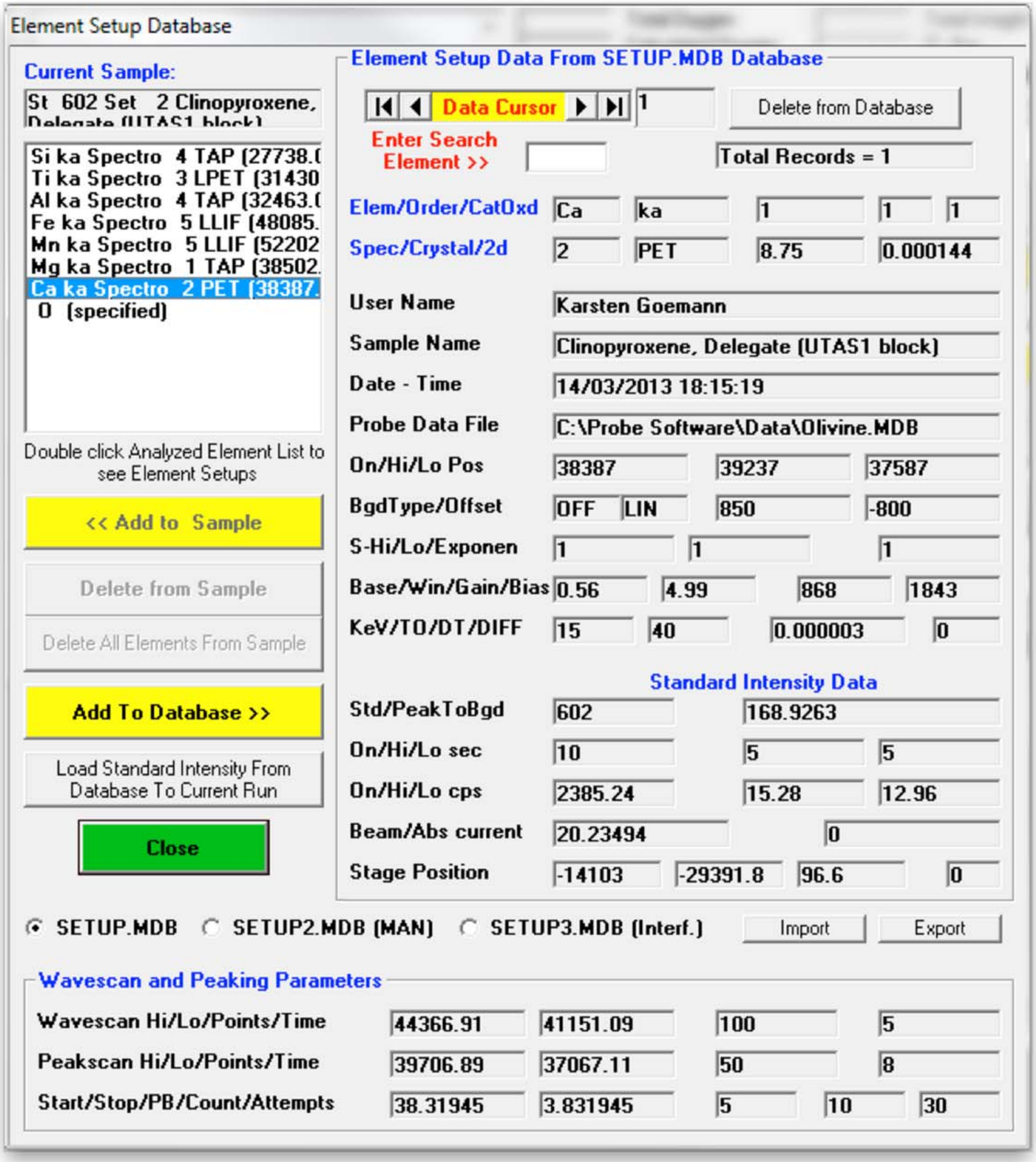


St 602 Set 2 Clinopyroxene, Delegate (UTAS1 block)

Si ka Spectro 4 TAP (27738.
Ti ka Spectro 3 LPET (31430
Al ka Spectro 4 TAP (32463.
Fe ka Spectro 5 LLIF (48085.
Mn ka Spectro 5 LLIF (52202
Mg ka Spectro 1 TAP (38502.
Ca ka Spectro 2 PET (38387.
O (specified)

Highlight the specific element to save and click the **Add To Database**>> button.

Record number 1 has been stored as illustrated below. Note that the *Standard Intensity Data* and *Wavescan and Peaking Parameters* are stored as well.



Current Sample: St 602 Set 2 Clinopyroxene, Delegate (UTAS1 block)

Si ka Spectro 4 TAP (27738.
Ti ka Spectro 3 LPET (31430
Al ka Spectro 4 TAP (32463.
Fe ka Spectro 5 LLIF (48085.
Mn ka Spectro 5 LLIF (52202
Mg ka Spectro 1 TAP (38502.
Ca ka Spectro 2 PET (38387.
O (specified)

Element Setup Data From SETUP.MDB Database

Data Cursor: 1
Total Records = 1
Elem/Order/CatOxd: Ca ka 1 1 1
Spec/Crystal/2d: 2 PET 8.75 0.000144
User Name: Karsten Goemann
Sample Name: Clinopyroxene, Delegate (UTAS1 block)
Date - Time: 14/03/2013 18:15:19
Probe Data File: C:\Probe Software\Data\Olivine.MDB
On/Hi/Lo Pos: 38387 39237 37587
BgdType/Offset: OFF LIN 850 -800
S-Hi/Lo/Exponen: 1 1 1
Base/Win/Gain/Bias: 0.56 4.99 868 1843
KeV/TO/DT/DIFF: 15 40 0.000003 0

Standard Intensity Data

Std/PeakToBgd: 602 168.9263
On/Hi/Lo sec: 10 5 5
On/Hi/Lo cps: 2385.24 15.28 12.96
Beam/Abs current: 20.23494 0
Stage Position: -14103 -29391.8 96.6 0

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time: 44366.91 41151.09 100 5
Peakscan Hi/Lo/Points/Time: 39706.89 37067.11 50 8
Start/Stop/PB/Count/Attempts: 38.31945 3.831945 5 10 30

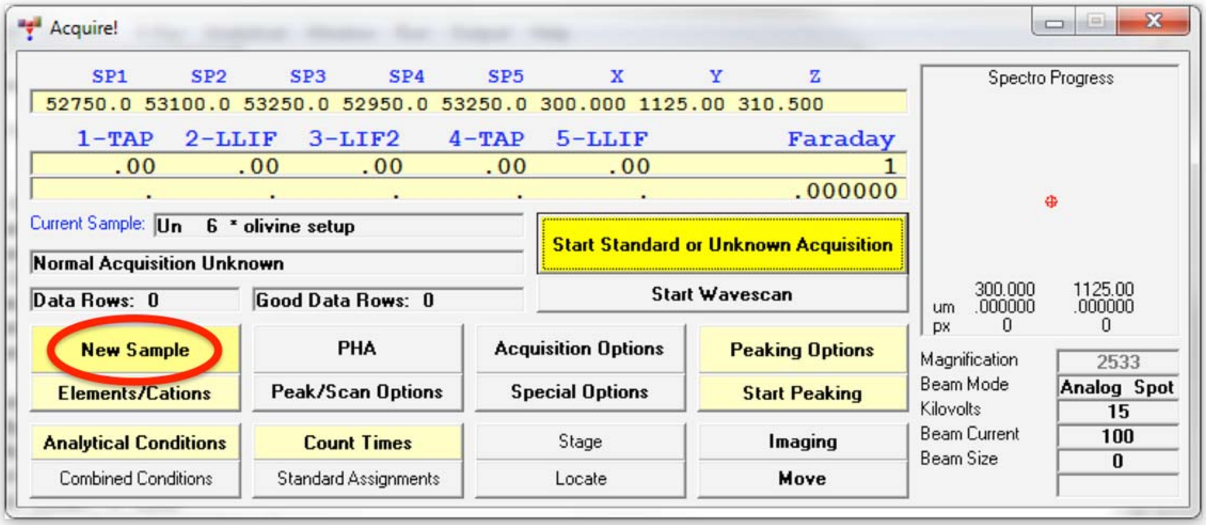
Click the **Close** button. The **Analyzed and Specified Elements** window reappears. Click the **OK** button. The **Analyze!** window returns.

The other element setups from this calibrated and standardized run or other probe runs may be entered into the database in a similar manner for future use.

The **Save Setups** button in the **Analyze!** window will allow the user to save all element setups in the selected sample (highlighted in the *Sample List*) to the element database (SETUP.MDB).

To recall an element setup from the SETUP.MDB database for a new sample setup follow the procedure outlined below. Open a new PROBE FOR EPMA run. This process will also be applicable if the user simply wants to add an element to an existing sample setup. This example will illustrate recalling elements from the database for the setup of a new pyroxene run.

From the **Acquire!** window, click the **New Sample** button.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 6 * olivine setup

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

um	300.000 .000000	1125.00 .000000
px	0	0

Magnification: 2533

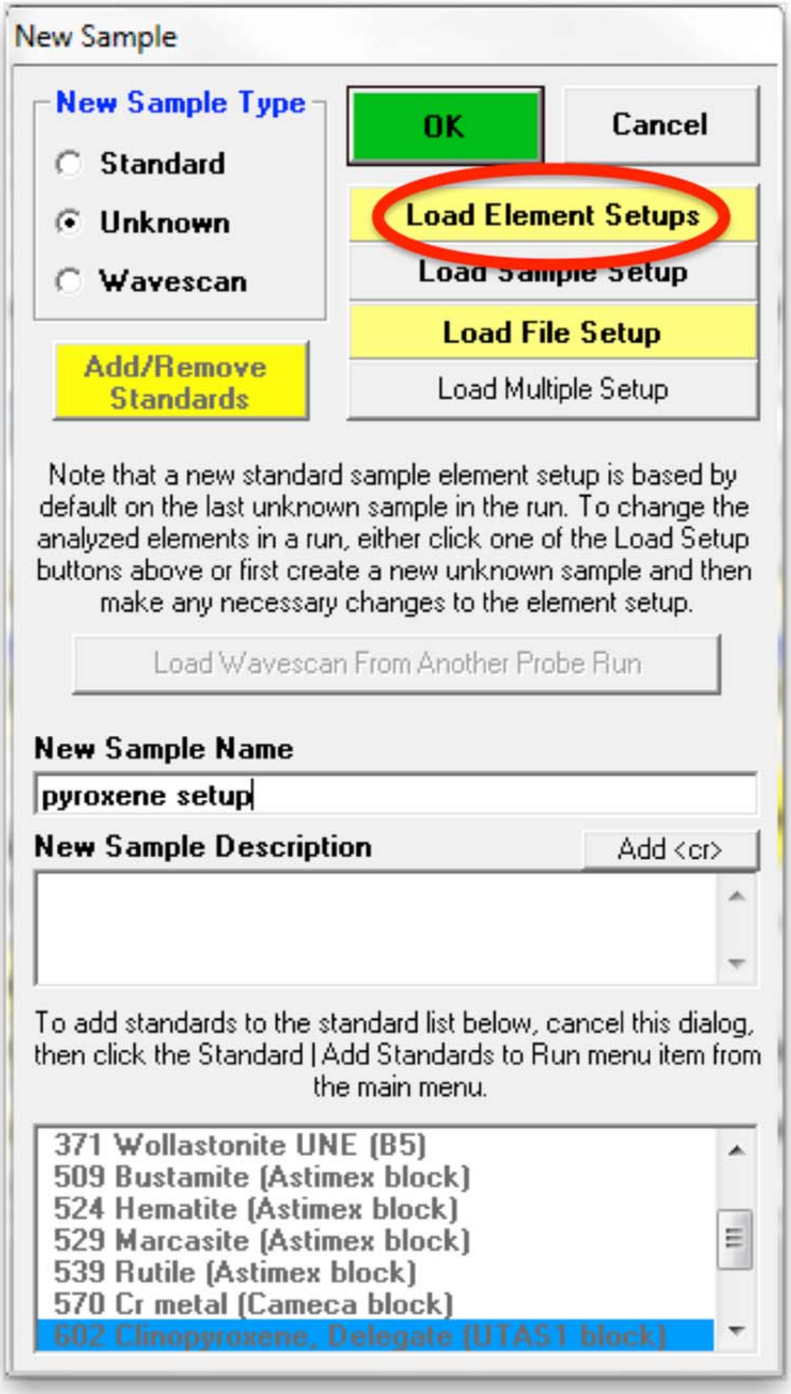
Beam Mode: Analog Spot

Kilovolts: 15

Beam Current: 100

Beam Size: 0

This opens the **New Sample** window. Edit the *New Sample Name* text field.



New Sample Type
○ Standard
● Unknown
○ Wavescan

Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: pyroxene setup

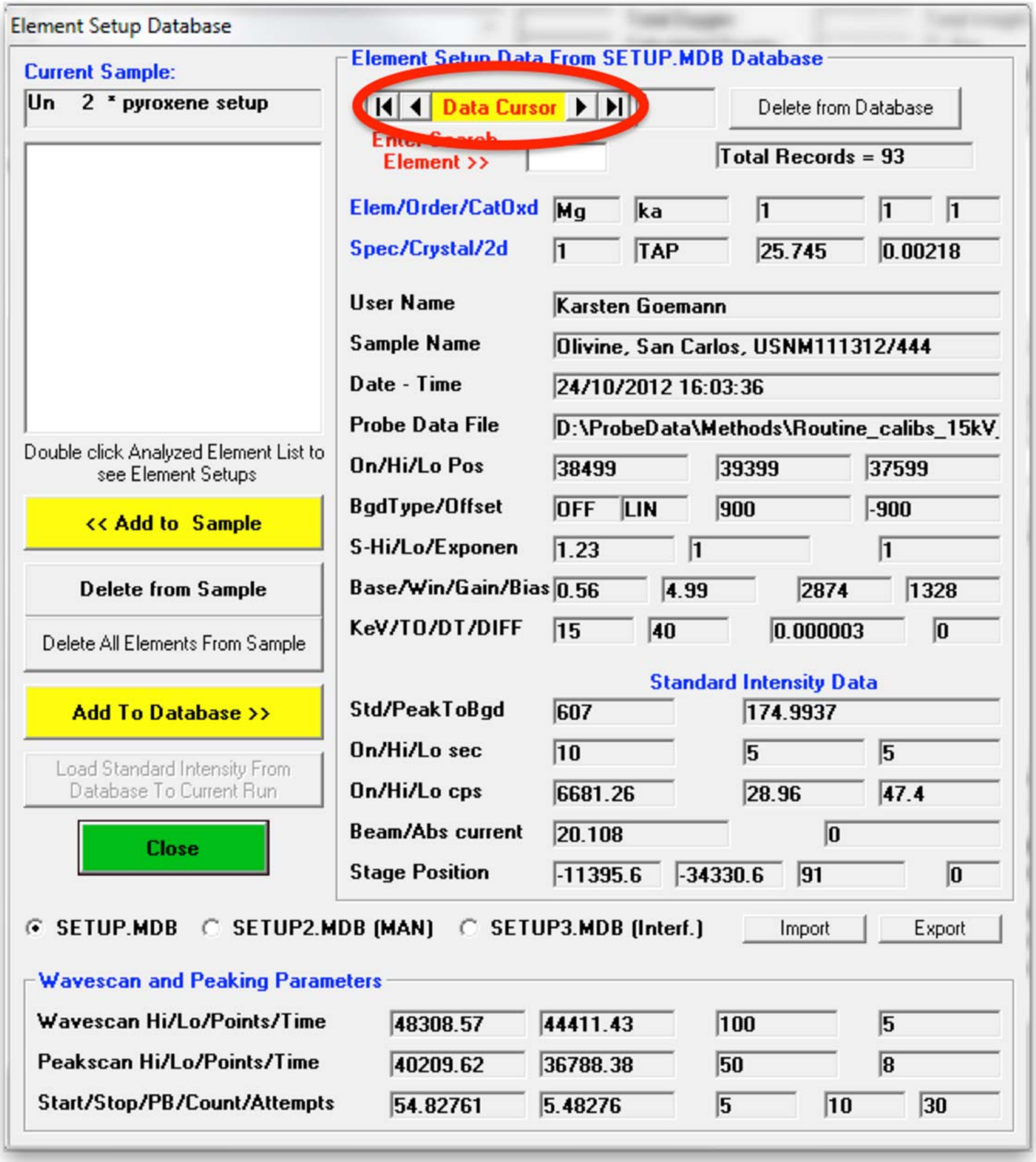
New Sample Description:

To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

- 371 Wollastonite UNE (B5)
- 509 Bustamite (Astimex block)
- 524 Hematite (Astimex block)
- 529 Marcasite (Astimex block)
- 539 Rutile (Astimex block)
- 570 Cr metal (Cameca block)
- 602 Clinopyroxene, Delegate (UTAS1 block)

Click the **Load Element Setups** button in the **New Sample** window.

This opens the **Element Setup Database**.



Current Sample: Un 2 * pyroxene setup

Element Setup Data From SETUP.MDB Database

Enter Search Element >>

Total Records = 93

Elem/Order/CatOxd: Mg, ka, 1, 1, 1

Spec/Crystal/2d: 1, TAP, 25.745, 0.00218

User Name: Karsten Goemann

Sample Name: Olivine, San Carlos, USNM111312/444

Date - Time: 24/10/2012 16:03:36

Probe Data File: D:\ProbeData\Methods\Routine_calibs_15kV_

On/Hi/Lo Pos: 38499, 39399, 37599

BgdType/Offset: OFF, LIN, 900, -900

S-Hi/Lo/Exponen: 1.23, 1, 1

Base/Win/Gain/Bias: 0.56, 4.99, 2874, 1328

KeV/TO/DT/DIFF: 15, 40, 0.000003, 0

Standard Intensity Data

Std/PeakToBgd: 607, 174.9937

On/Hi/Lo sec: 10, 5, 5

On/Hi/Lo cps: 6681.26, 28.96, 47.4

Beam/Abs current: 20.108, 0

Stage Position: -11395.6, -34330.6, 91, 0

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

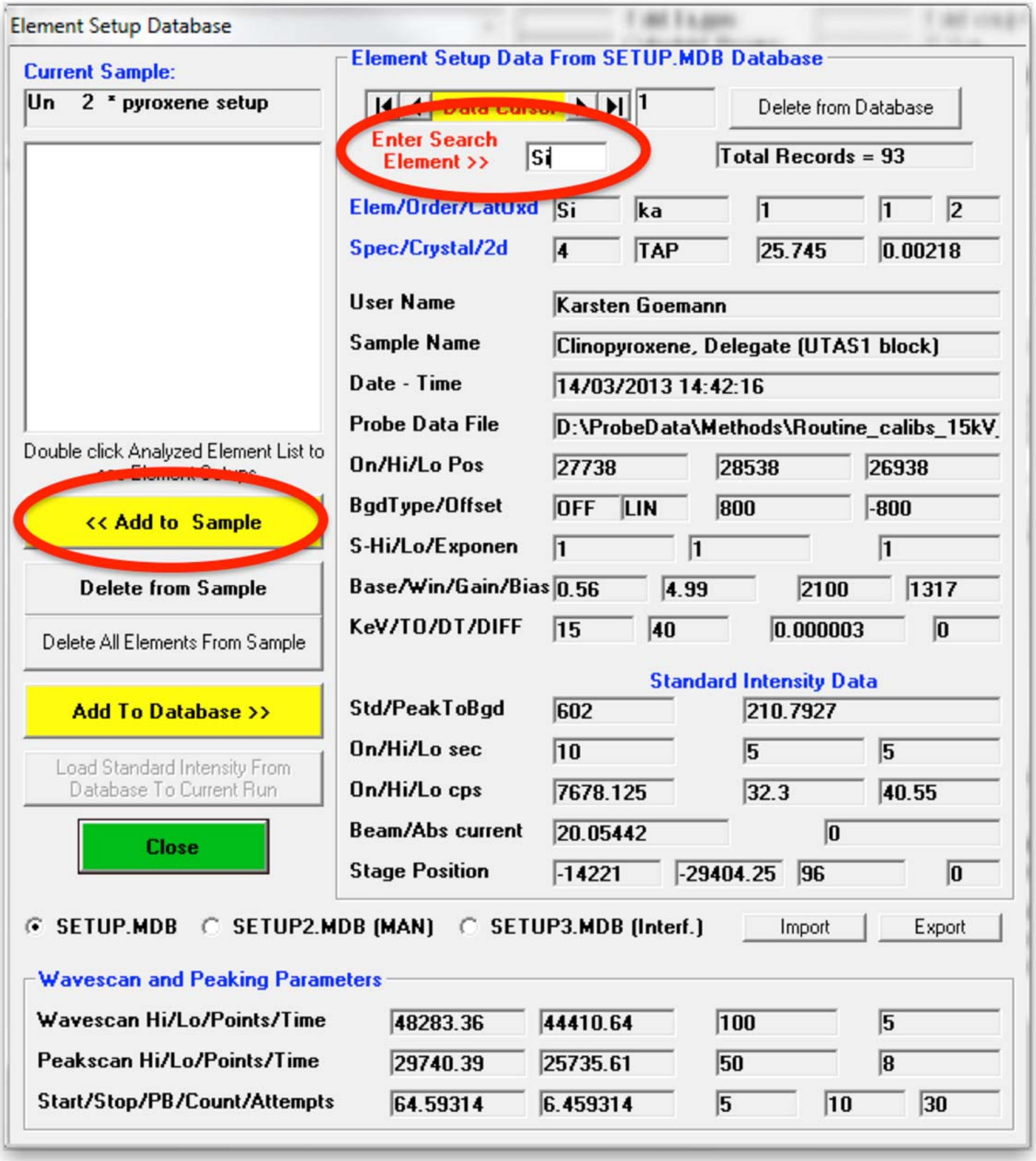
Wavescan Hi/Lo/Points/Time: 48308.57, 44411.43, 100, 5

Peakscan Hi/Lo/Points/Time: 40209.62, 36788.38, 50, 8

Start/Stop/PB/Count/Attempts: 54.82761, 5.48276, 5, 10, 30

Scroll through the list of elements (records) and find the desired element and setup using the data cursor. Use the left, right arrows (top, center) to move through the database. To see all the setups for a particular element, enter the element symbol into the *Search Element* text field and use the arrow keys as before. To see all element setups again, simply clear the *Search Element* text field. To view the most recent addition(s) to the SETUP database, click the ⏭ button on the data cursor.

Here, the user browses through the records and selects the appropriate silicon (si) entry as the first element setup to load. The output list order of elements will follow this list.



Current Sample: Un 2 * pyroxene setup

Data Cursor: 1

Total Records = 93

Enter Search Element >> Si

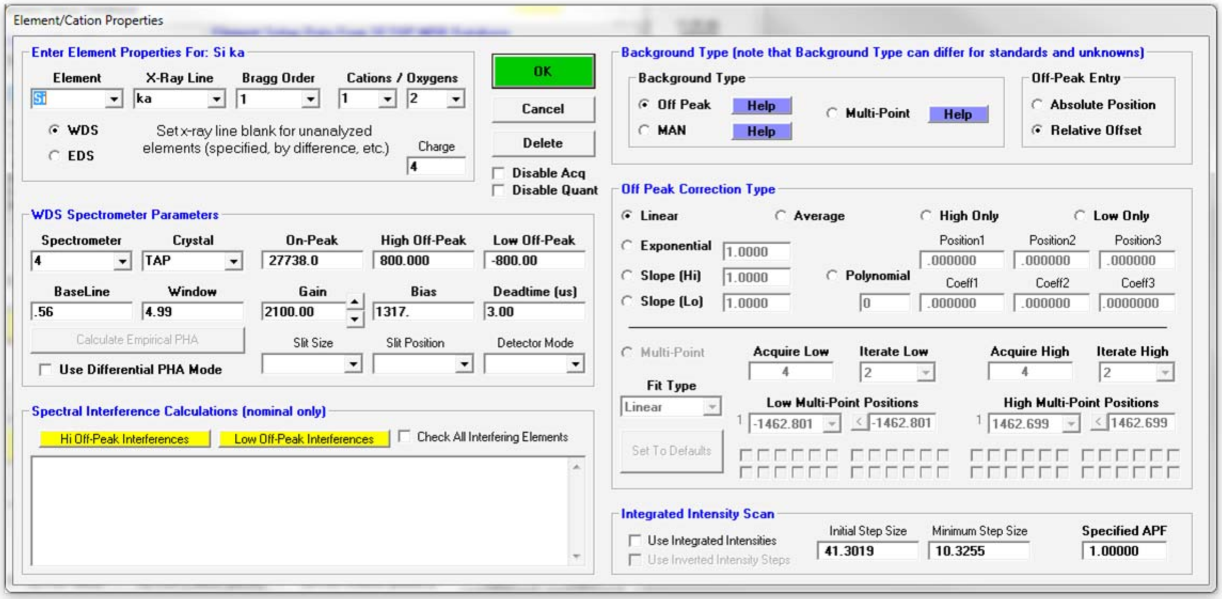
Elem/Order/CatOxd	Si	ka	1	1	2
Spec/Crystal/2d	4	TAP	25.745	0.00218	
User Name	Karsten Goemann				
Sample Name	Clinopyroxene, Delegate (UTAS1 block)				
Date - Time	14/03/2013 14:42:16				
Probe Data File	D:\ProbeData\Methods\Routine_calibs_15kV_				
On/Hi/Lo Pos	27738	28538	26938		
BgdType/Offset	OFF	LIN	800	-800	
S-Hi/Lo/Exponen	1	1	1		
Base/Win/Gain/Bias	0.56	4.99	2100	1317	
KeV/TO/DT/DIFF	15	40	0.000003	0	
Std/PeakToBgd	602	210.7927			
On/Hi/Lo sec	10	5	5		
On/Hi/Lo cps	7678.125	32.3	40.55		
Beam/Abs current	20.05442	0			
Stage Position	-14221	-29404.25	96	0	

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan Hi/Lo/Points/Time	48283.36	44410.64	100	5	
Peakscan Hi/Lo/Points/Time	29740.39	25735.61	50	8	
Start/Stop/PB/Count/Attempts	64.59314	6.459314	5	10	30

Click the << **Add to Sample** button to add the element setup to the current sample.

The **Element Properties** window for silicon appears.



Element/Cation Properties

Enter Element Properties For: Si ka

Element: Si
X-Ray Line: ka
Bragg Order: 1
Cations / Oxygens: 1 / 2
● WDS
○ EDS
Set x-ray line blank for unanalyzed elements (specified, by difference, etc.)
Charge: 4
☐ Disable Acq
☐ Disable Quant

WDS Spectrometer Parameters

Spectrometer: 4
Crystal: TAP
On-Peak: 27738.0
High Off-Peak: 800.000
Low Off-Peak: -800.00
BaseLine: .56
Window: 4.99
Gain: 2100.00
Bias: 1317.
Deadtime (us): 3.00
☐ Use Differential PHA Mode

Spectral Interference Calculations (nominal only)

☐ Check All Interfering Elements

Background Type (note that Background Type can differ for standards and unknowns)

Background Type: ● Off Peak ○ MAN ○ Multi-Point
Off-Peak Entry: ○ Absolute Position ● Relative Offset

Off Peak Correction Type

● Linear ○ Average ○ High Only ○ Low Only
○ Exponential: 1.0000
○ Slope (Hi): 1.0000
○ Slope (Lo): 1.0000
○ Polynomial: 0
Position1: .000000 Position2: .000000 Position3: .000000
Coeff1: .000000 Coeff2: .000000 Coeff3: .0000000

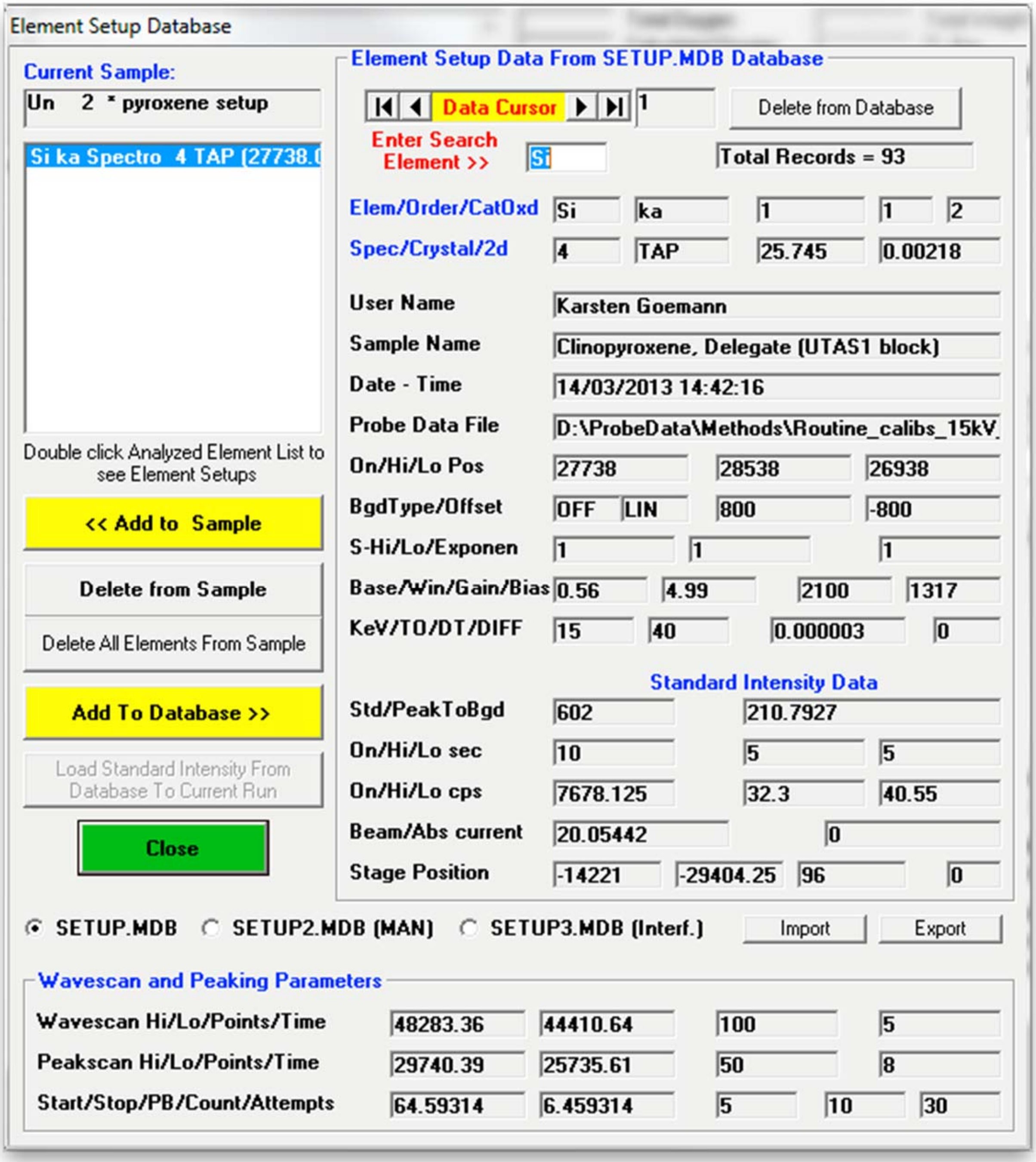
○ Multi-Point
Acquire Low: 4
Iterate Low: 2
Acquire High: 4
Iterate High: 2
Fit Type: Linear
Low Multi-Point Positions: 1 -1462.801 -1462.801
High Multi-Point Positions: 1 1462.699 1462.699

Integrated Intensity Scan

☐ Use Integrated Intensities
☐ Use Inverted Intensity Steps
Initial Step Size: 41.3019
Minimum Step Size: 10.3255
Specified APF: 1.00000

Edit if required, then click the **OK** button to accept these values.

The silicon record is then listed in the text field under the previously defined sample name.



Current Sample: Un 2 * pyroxene setup

Si ka Spectro 4 TAP (27738.(

Element Setup Data From SETUP.MDB Database

Data Cursor: 1

Enter Search Element >> Si

Total Records = 93

Elem/Order/CatOxd: Si | ka | 1 | 1 | 2

Spec/Crystal/2d: 4 | TAP | 25.745 | 0.00218

User Name: Karsten Goemann

Sample Name: Clinopyroxene, Delegate (UTAS1 block)

Date - Time: 14/03/2013 14:42:16

Probe Data File: D:\ProbeData\Methods\Routine_calibs_15kV_

On/Hi/Lo Pos: 27738 | 28538 | 26938

BgdType/Offset: OFF | LIN | 800 | -800

S-Hi/Lo/Exponen: 1 | 1 | 1

Base/Win/Gain/Bias: 0.56 | 4.99 | 2100 | 1317

KeV/TO/DT/DIFF: 15 | 40 | 0.000003 | 0

Standard Intensity Data

Std/PeakToBgd: 602 | 210.7927

On/Hi/Lo sec: 10 | 5 | 5

On/Hi/Lo cps: 7678.125 | 32.3 | 40.55

Beam/Abs current: 20.05442 | 0

Stage Position: -14221 | -29404.25 | 96 | 0

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

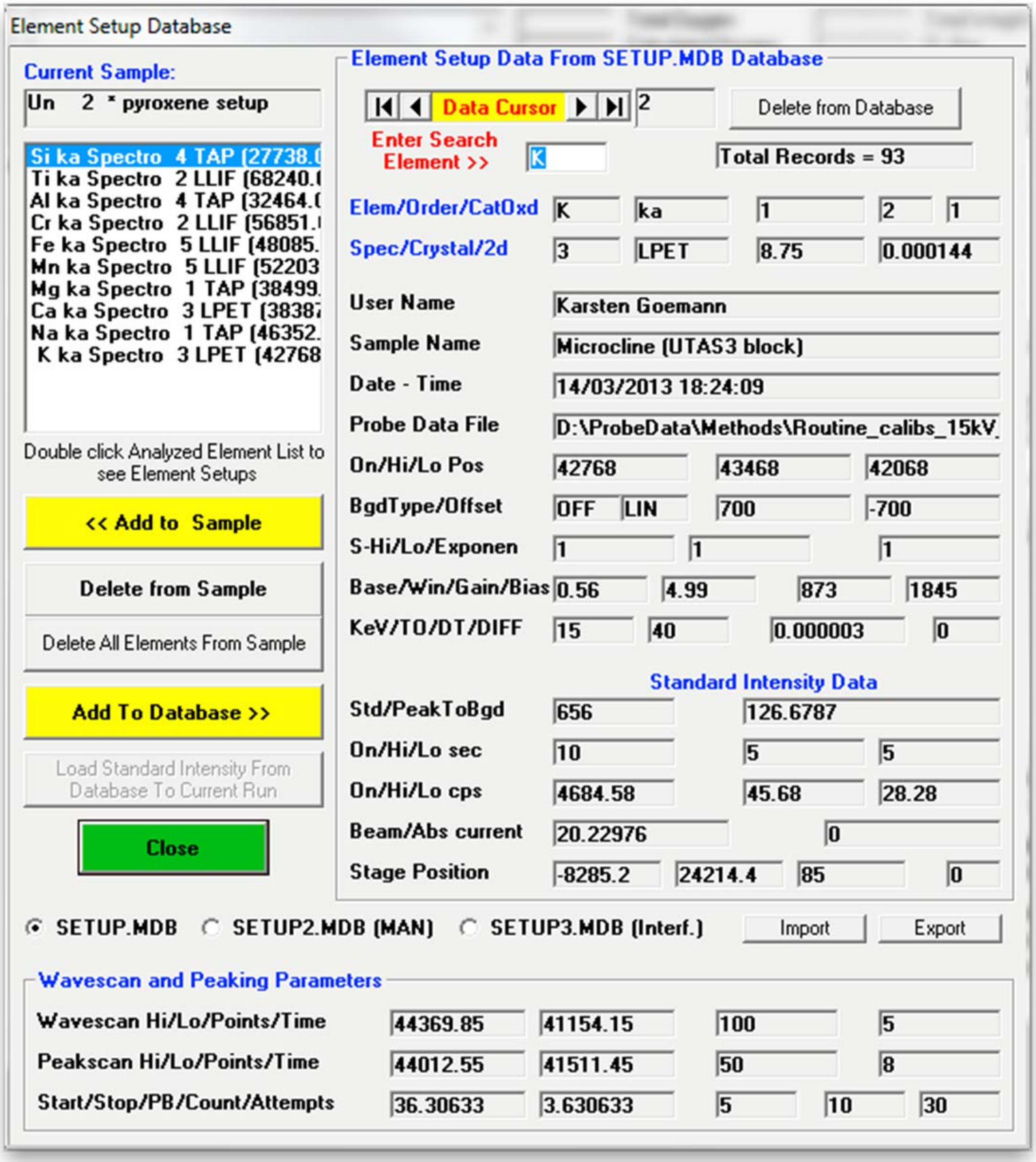
Wavescan Hi/Lo/Points/Time: 48283.36 | 44410.64 | 100 | 5

Peakscan Hi/Lo/Points/Time: 29740.39 | 25735.61 | 50 | 8

Start/Stop/PB/Count/Attempts: 64.59314 | 6.459314 | 5 | 10 | 30

Continue browsing the element setup database and add all required element setups desired to the sample.

A typical pyroxene element setup list is shown below.



Current Sample: Un 2 * pyroxene setup

Si ka Spectro 4 TAP (27738.
Ti ka Spectro 2 LLIF (68240.
Al ka Spectro 4 TAP (32464.
Cr ka Spectro 2 LLIF (56851.
Fe ka Spectro 5 LLIF (48085.
Mn ka Spectro 5 LLIF (52203
Mg ka Spectro 1 TAP (38499.
Ca ka Spectro 3 LPET (3838
Na ka Spectro 1 TAP (46352.
K ka Spectro 3 LPET (42768

Element Setup Data From SETUP.MDB Database

Data Cursor: 2
Enter Search Element >> K
Total Records = 93

Elem/Order/CatOxd	K	ka	1	2	1
Spec/Crystal/2d	3	LPET	8.75	0.000144	
User Name	Karsten Goemann				
Sample Name	Microcline (UTAS3 block)				
Date - Time	14/03/2013 18:24:09				
Probe Data File	D:\ProbeData\Methods\Routine_calibs_15kV_				
On/Hi/Lo Pos	42768	43468	42068		
BgdType/Offset	OFF	LIN	700	-700	
S-Hi/Lo/Exponen	1	1	1		
Base/Win/Gain/Bias	0.56	4.99	873	1845	
KeV/TO/DT/DIFF	15	40	0.000003	0	

Standard Intensity Data

Std/PeakToBgd	656	126.6787		
On/Hi/Lo sec	10	5	5	
On/Hi/Lo cps	4684.58	45.68	28.28	
Beam/Abs current	20.22976	0		
Stage Position	-8285.2	24214.4	85	0

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	44369.85	41154.15	100	5	
Peakscan Hi/Lo/Points/Time	44012.55	41511.45	50	8	
Start/Stop/PB/Count/Attempts	36.30633	3.630633	5	10	30

Click the **Close** button when finished. The **New Sample** window reappears.

Click the **OK** button, returning to the **Acquire!** window. Don't forget to add oxygen as a specified element to the list for stoichiometry and other calculations. Note specified elements cannot be saved to the SETUP.MDB database.

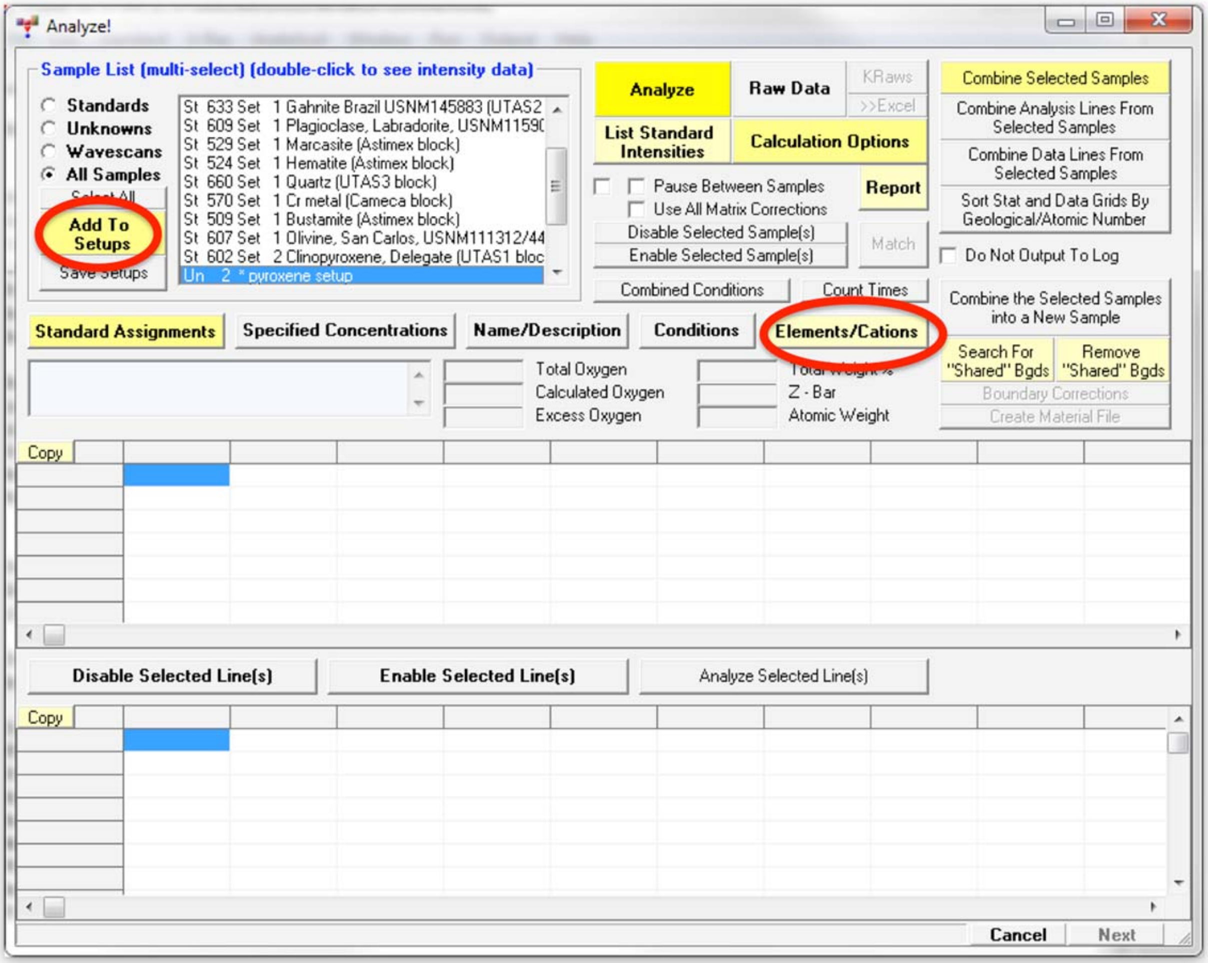
Sample Setups

Normally, PROBE FOR EPMA uses the sample setup from the last unknown (or standard if there are no unknown samples) to create the next new sample setup. Sample setups on the other hand are designed to allow the user to easily recall a previous sample setup within a current run. This allows the user to create and re-use multiple setups comprised of different groups of elements **within** a single run. In the example below, sample setups for pyroxene and olivine will be created, each with a different set of elements and conditions, that may be recalled at anytime during the current probe run.

The saving of a sample setup actually saves only a pointer to the sample selected. All of this sample's acquisition and calculation options, elements/cations, standard assignments, etc will be utilized when a new sample is created based on this sample setup.

A new PROBE FOR EPMA run is opened in the usual manner. Ten elements and appropriate standards for pyroxenes are loaded from the SETUP.MDB database and the STANDARD.MDB database, respectively. Each element is then calibrated and standardized. Count times, acquisition and calculation options are adjusted to optimize the analyses and output requirements.

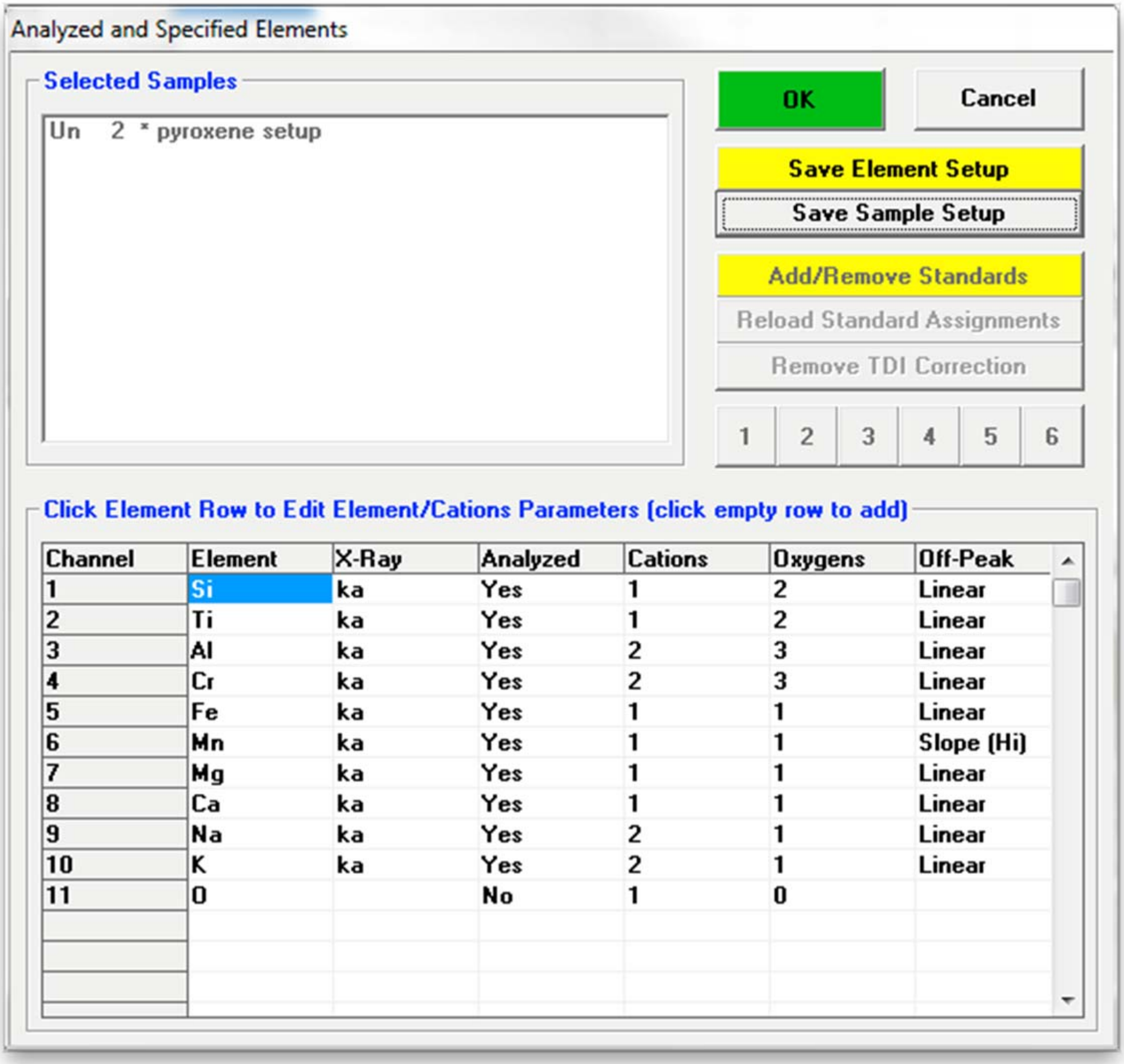
To save the just calibrated pyroxene sample as a sample setup, start by clicking the **Add To Setups** button from the **Analyze!** window.



St 633 Set 1 Gahnite Brazil USNM145883 (UTAS2
St 609 Set 1 Plagioclase, Labradorite, USNM1159(
St 529 Set 1 Marcasite (Astimex block)
St 524 Set 1 Hematite (Astimex block)
St 660 Set 1 Quartz (UTAS3 block)
St 570 Set 1 Cr metal (Cameca block)
St 509 Set 1 Bustamite (Astimex block)
St 607 Set 1 Olivine, San Carlos, USNM111312/44
St 602 Set 2 Clinopyroxene, Delegate (UTAS1 bloc
Un 2 * pyroxene setup

To review the saved sample setup, click the **Elements/Cations** button.

The **Analyzed and Specified Elements** dialog box appears.

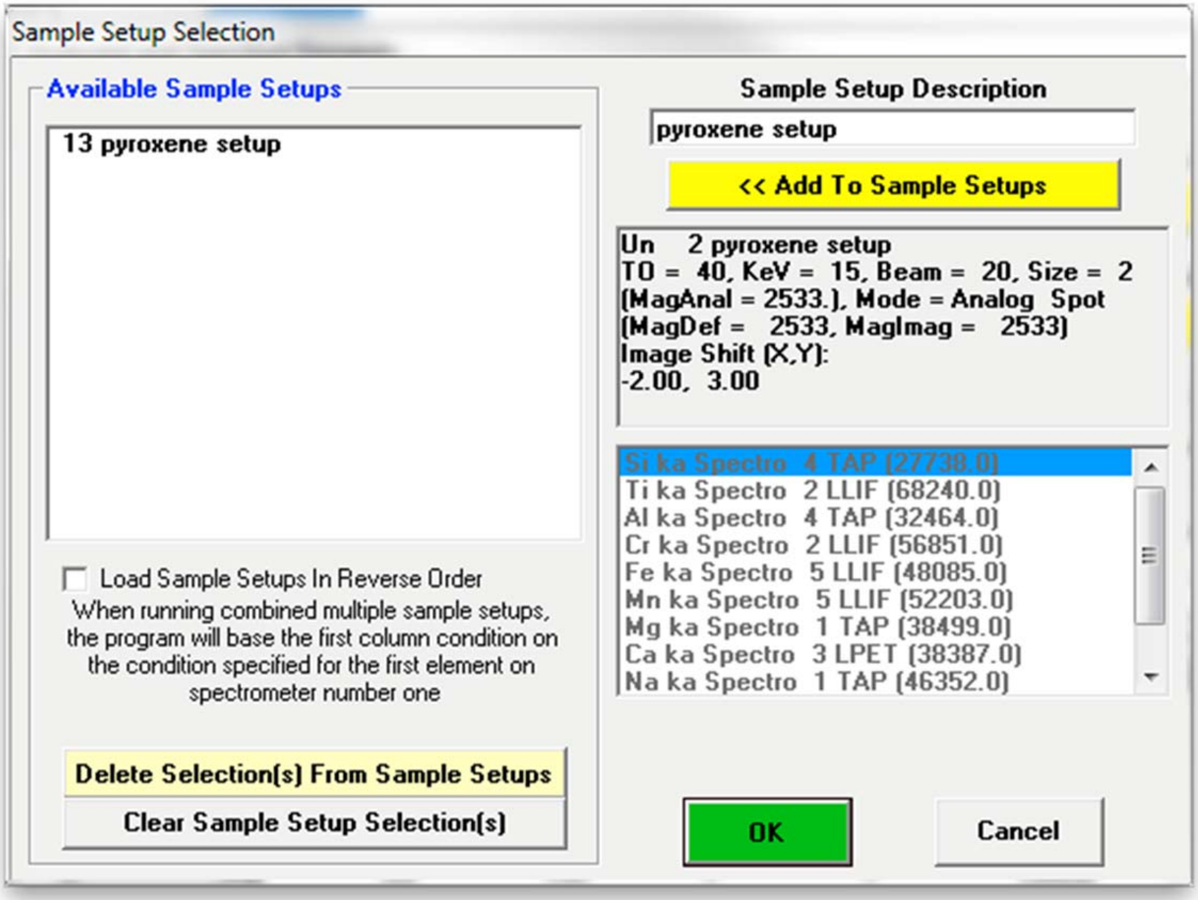


Un 2 * pyroxene setup

Channel	Element	X-Ray	Analyzed	Cations	Oxygens	Off-Peak
1	Si	ka	Yes	1	2	Linear
2	Ti	ka	Yes	1	2	Linear
3	Al	ka	Yes	2	3	Linear
4	Cr	ka	Yes	2	3	Linear
5	Fe	ka	Yes	1	1	Linear
6	Mn	ka	Yes	1	1	Slope (Hi)
7	Mg	ka	Yes	1	1	Linear
8	Ca	ka	Yes	1	1	Linear
9	Na	ka	Yes	2	1	Linear
10	K	ka	Yes	2	1	Linear
11	O		No	1	0	

Click the **Save Sample Setup** button.

The **Sample Setup Selection** window opens.



13 pyroxene setup

pyroxene setup

```
Un    2 pyroxene setup
TO =  40, KeV =  15, Beam =  20, Size =  2
(MagAnal = 2533.), Mode = Analog  Spot
(MagDef =   2533, MagImag =   2533)
Image Shift (X,Y):
-2.00,  3.00
```

```
Si ka Spectro  4 TAP (27738.0)
Ti ka Spectro  2 LLIF (68240.0)
Al ka Spectro  4 TAP (32464.0)
Cr ka Spectro  2 LLIF (56851.0)
Fe ka Spectro  5 LLIF (48085.0)
Mn ka Spectro  5 LLIF (52203.0)
Mg ka Spectro  1 TAP (38499.0)
Ca ka Spectro  3 LPET (38387.0)
Na ka Spectro  1 TAP (46352.0)
```

☐ Load Sample Setups In Reverse Order

When running combined multiple sample setups, the program will base the first column condition on the condition specified for the first element on spectrometer number one

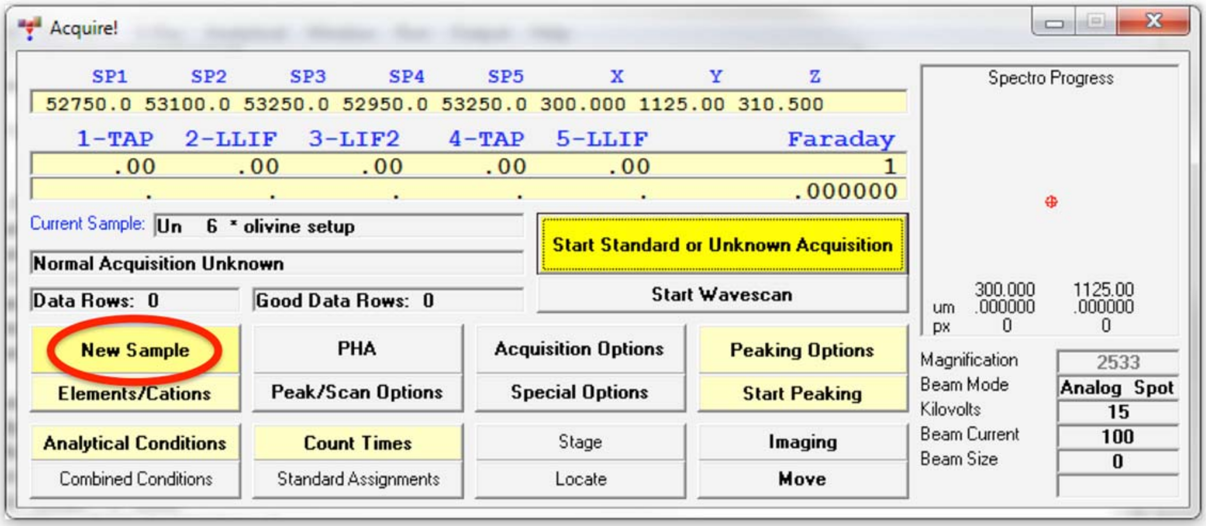
All saved sample setups are listed in the *Available Sample Setups* section. Note: the first number (13) represents the sample's row number and can be seen listed using the **Run | List Sample Rows, Names, Conditions** menu.

Use the **Delete Selection(s) From Sample Setups** button to remove sample setups if desired. If the sample setup has not been saved yet, it can also be saved here by clicking the **<< Add To Sample Setups** button. Before adding the sample setup, edit the *Sample Setup Description* text box to change the name as desired.

Click the **OK** button, returning to the **Analyzed and Specified Elements** window.

Click the **OK** button of the **Analyzed and Specified Elements** window returning to the **Analyze!** window.

Return to the **Acquire!** window to create a new sample.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 6 * olivine setup

Normal Acquisition Unknown

Data Rows: 0

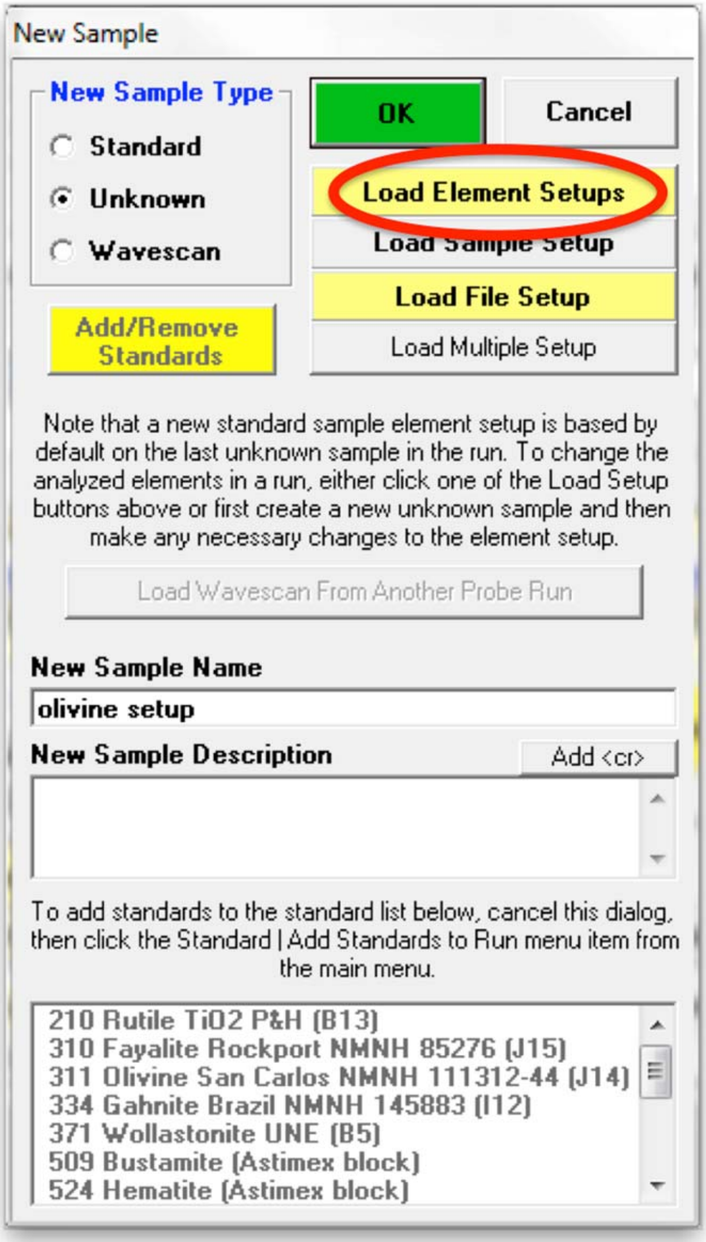
Good Data Rows: 0

um	300.000 .000000	1125.00 .000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	100
Beam Size	0

Click the **New Sample** button.

Edit the *New Sample Name* text field. Here, the user will establish an olivine sample setup.



Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: olivine setup

New Sample Description:

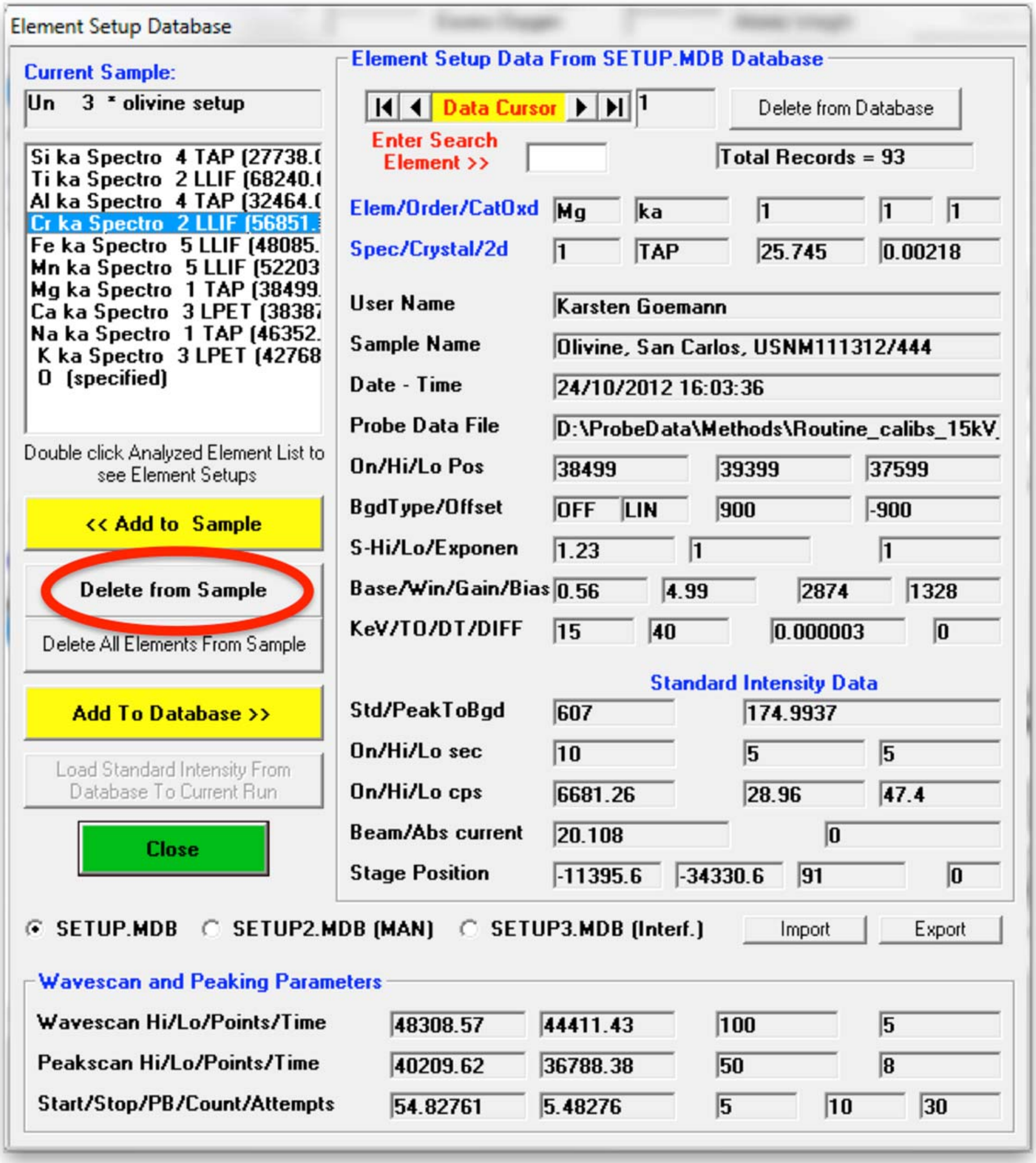
To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

210 Rutile TiO2 P&H (B13)
310 Fayalite Rockport NMNH 85276 (J15)
311 Olivine San Carlos NMNH 111312-44 (J14)
334 Gahnite Brazil NMNH 145883 (I12)
371 Wollastonite UNE (B5)
509 Bustamite (Astimex block)
524 Hematite (Astimex block)

Several paths may be taken from here to load new elements for the olivine sample. To enter an entirely new list of elements and parameters it might be easier to click the **OK** button and follow the **Element/Cations** button of the **Acquire!** window to the **Element Properties** dialog.

If (as in this example) only minor changes to a sample are required then from the **New Sample** window, click the **Load Element Setups** button.

The **Element Setup Database** opens.



Current Sample: Un 3 * olivine setup

Si ka Spectro 4 TAP (27738.
Ti ka Spectro 2 LLIF (68240.
Al ka Spectro 4 TAP (32464.
Cr ka Spectro 2 LLIF (56851.
Fe ka Spectro 5 LLIF (48085.
Mn ka Spectro 5 LLIF (52203
Mg ka Spectro 1 TAP (38499.
Ca ka Spectro 3 LPET (3838
Na ka Spectro 1 TAP (46352.
K ka Spectro 3 LPET (42768
O (specified)

Double click Analyzed Element List to see Element Setups

Element Setup Data From SETUP.MDB Database

Data Cursor: 1

Enter Search Element >>

Total Records = 93

Elem/Order/CatOxd	Mg	ka	1	1	1
Spec/Crystal/2d	1	TAP	25.745	0.00218	
User Name	Karsten Goemann				
Sample Name	Olivine, San Carlos, USNM111312/444				
Date - Time	24/10/2012 16:03:36				
Probe Data File	D:\ProbeData\Methods\Routine_calibs_15kV				
On/Hi/Lo Pos	38499	39399	37599		
BgdType/Offset	OFF	LIN	900	-900	
S-Hi/Lo/Exponen	1.23	1	1		
Base/Win/Gain/Bias	0.56	4.99	2874	1328	
KeV/TO/DT/DIFF	15	40	0.000003	0	

Standard Intensity Data

Std/PeakToBgd	607	174.9937		
On/Hi/Lo sec	10	5	5	
On/Hi/Lo cps	6681.26	28.96	47.4	
Beam/Abs current	20.108	0		
Stage Position	-11395.6	-34330.6	91	0

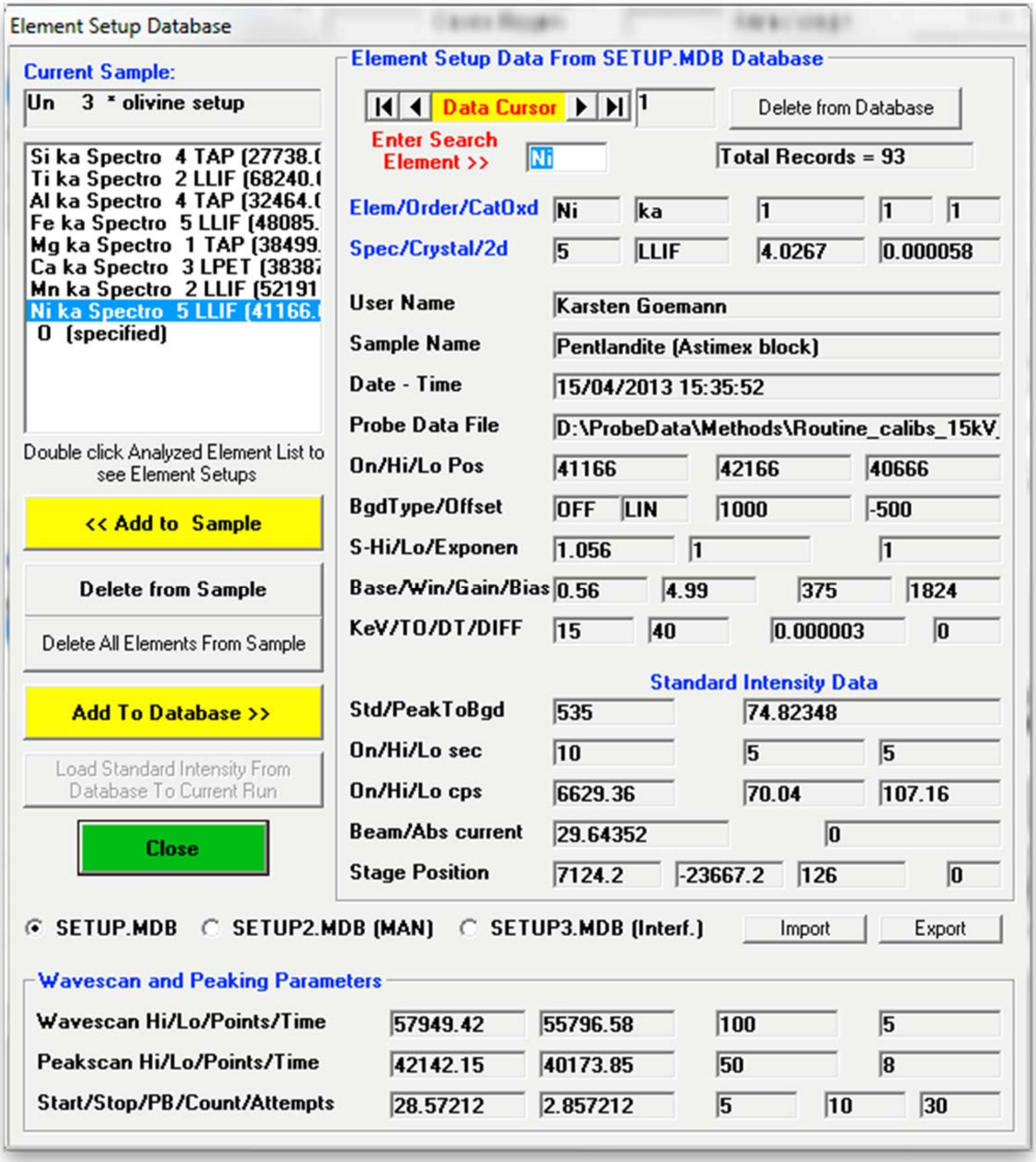
● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	48308.57	44411.43	100	5	
Peakscan Hi/Lo/Points/Time	40209.62	36788.38	50	8	
Start/Stop/PB/Count/Attempts	54.82761	5.48276	5	10	30

Edit the previous pyroxene list, in this example chromium, sodium, potassium are eliminated from the list by highlighting each element and clicking the **Delete from Sample** button. If additional elements are required, recall them at this time (nickel is added in this example). Manganese is moved to a different spectrometer (by deleting and adding) to balance counting times.

After editing, the window appears as below.



Current Sample: Un 3 * olivine setup

Si ka Spectro 4 TAP (27738.(
Ti ka Spectro 2 LLIF (68240.(
Al ka Spectro 4 TAP (32464.(
Fe ka Spectro 5 LLIF (48085.
Mg ka Spectro 1 TAP (38499.
Ca ka Spectro 3 LPET (38387
Mn ka Spectro 2 LLIF (52191
Ni ka Spectro 5 LLIF (41166.(
0 (specified)

Element Setup Data From SETUP.MDB Database

Data Cursor: 1
Enter Search Element >> Ni
Total Records = 93

Elem/Order/CatOxd: Ni | ka | 1 | 1 | 1
Spec/Crystal/2d: 5 | LLIF | 4.0267 | 0.000058
User Name: Karsten Goemann
Sample Name: Pentlandite (Astimex block)
Date - Time: 15/04/2013 15:35:52
Probe Data File: D:\ProbeData\Methods\Routine_calibs_15kV
On/Hi/Lo Pos: 41166 | 42166 | 40666
BgdType/Offset: OFF | LIN | 1000 | -500
S-Hi/Lo/Exponen: 1.056 | 1 | 1
Base/Win/Gain/Bias: 0.56 | 4.99 | 375 | 1824
KeV/TO/DT/DIFF: 15 | 40 | 0.000003 | 0

Standard Intensity Data

Std/PeakToBgd: 535 | 74.82348
On/Hi/Lo sec: 10 | 5 | 5
On/Hi/Lo cps: 6629.36 | 70.04 | 107.16
Beam/Abs current: 29.64352 | 0
Stage Position: 7124.2 | -23667.2 | 126 | 0

● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time: 57949.42 | 55796.58 | 100 | 5
Peakscan Hi/Lo/Points/Time: 42142.15 | 40173.85 | 50 | 8
Start/Stop/PB/Count/Attempts: 28.57212 | 2.857212 | 5 | 10 | 30

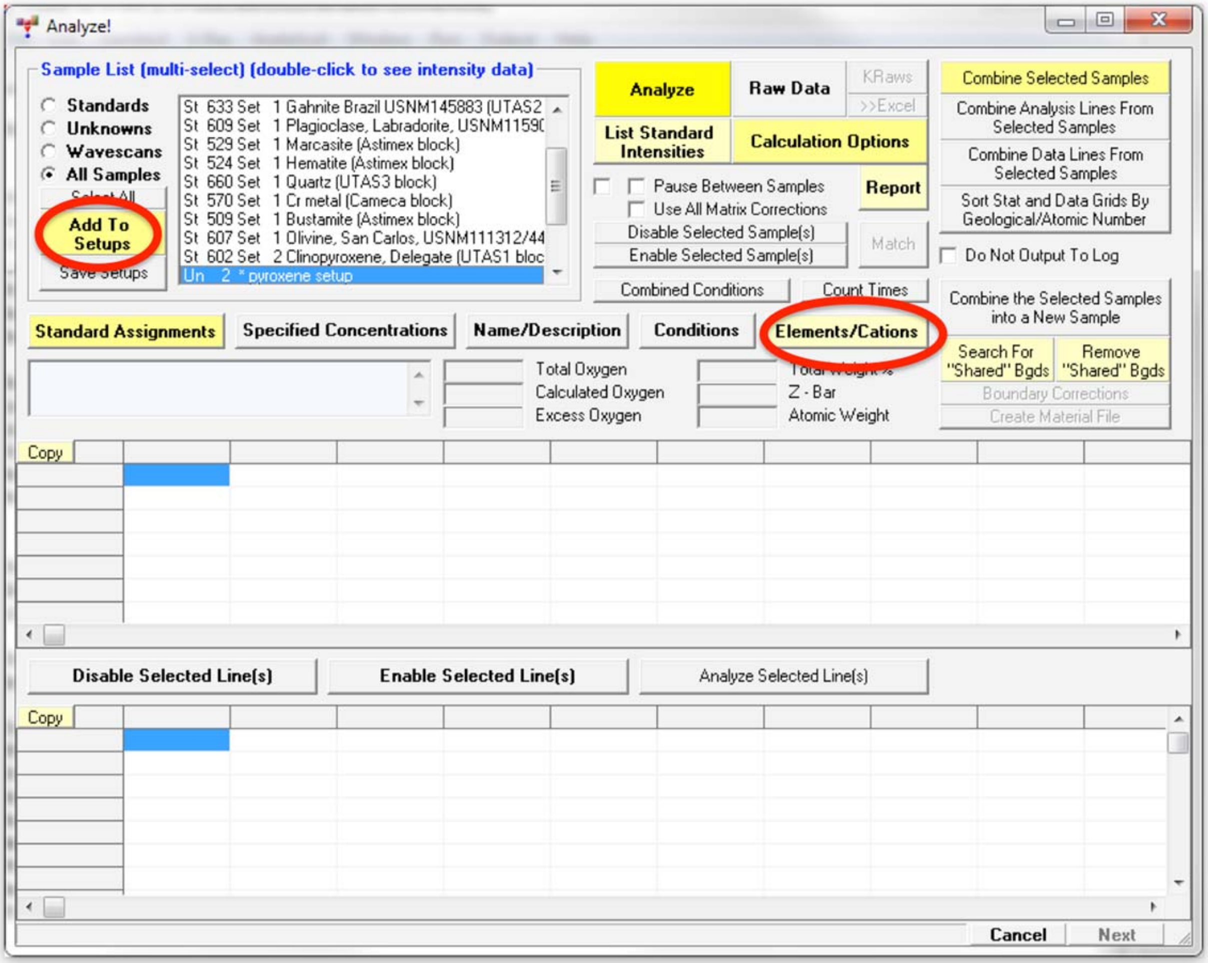
Click the **Close** button of the **Element Setup Database**, returning to the **New Sample** window.

Click the **OK** button in the **New Sample** window, returning to the **Acquire!** window.

If different standard choices are required they should be added from the STANDARD.MDB database at this point. Use the **Standard | Add/Remove Standards To/From Run** menu in the main PROBE FOR EPMA log window.

Recalibrate and standardize all new elements and adjust count times, acquisition, and calculation options to optimize for olivine analysis.

From the **Analyze!** window, click the **Add To Setups** button.

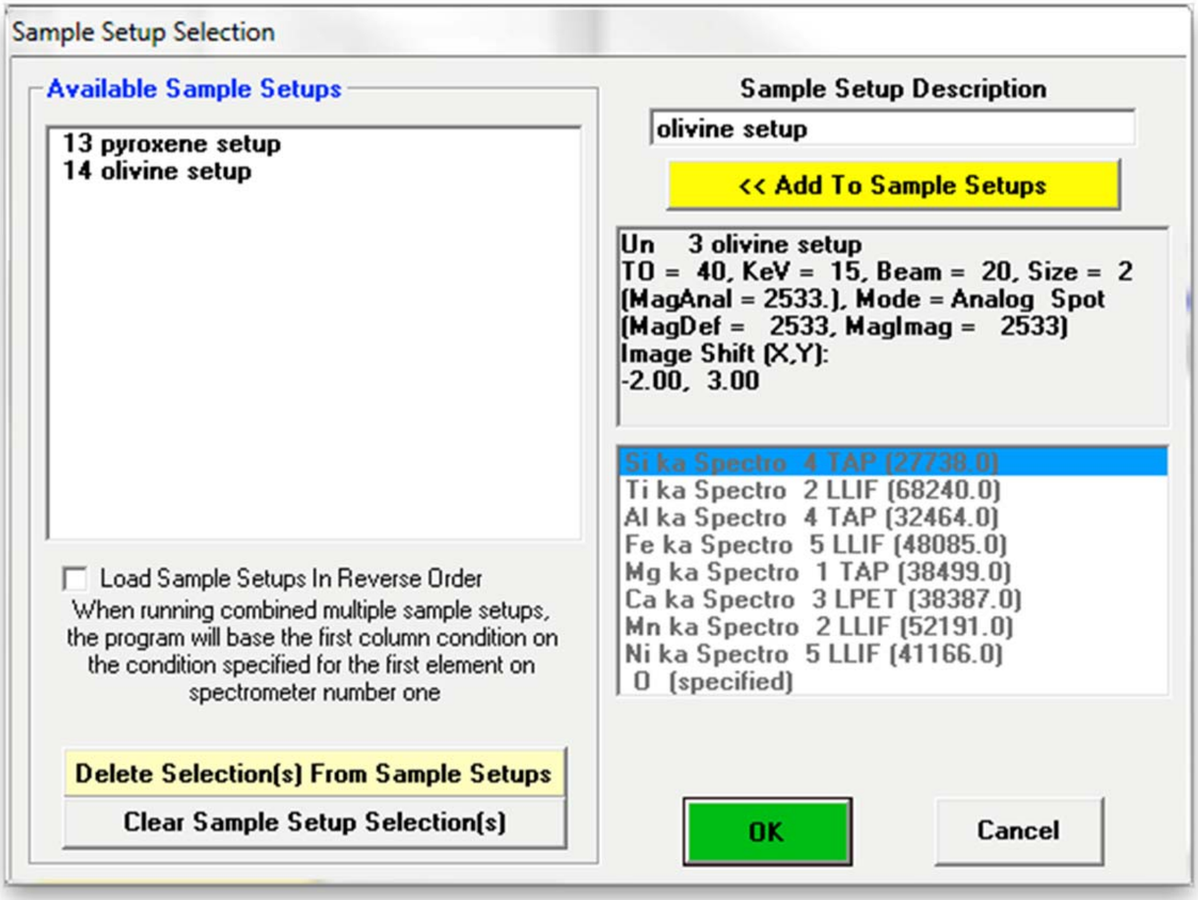


```
St  633 Set  1 Gahnite Brazil USNM145883 (UTAS2
St  609 Set  1 Plagioclase, Labradorite, USNM1159(
St  529 Set  1 Marcasite (Astimex block)
St  524 Set  1 Hematite (Astimex block)
St  660 Set  1 Quartz (UTAS3 block)
St  570 Set  1 Cr metal (Cameca block)
St  509 Set  1 Bustamite (Astimex block)
St  607 Set  1 Olivine, San Carlos, USNM111312/44
St  602 Set  2 Clinopyroxene, Delegate (UTAS1 bloc
Un    2  * pyroxene setup
```

To review the created sample setups, click the **Elements/Cations** button.

The **Analyzed and Specified Elements** window opens, click the **Save Sample Setup** button.

The **Sample Setup Selection** window appears. The olivine sample setup has been added to *Available Sample Setups* list box.



13 pyroxene setup
14 olivine setup

☐ Load Sample Setups In Reverse Order

When running combined multiple sample setups, the program will base the first column condition on the condition specified for the first element on spectrometer number one

Sample Setup Description: olivine setup

```
Un    3 olivine setup
TO =  40, KeV =  15, Beam =  20, Size =  2
(MagAnal = 2533.), Mode = Analog  Spot
(MagDef =   2533, MagImag =   2533)
Image Shift (X,Y):
-2.00,  3.00
```

```
Si ka Spectro  4 TAP (27738.0)
Ti ka Spectro  2 LLIF (68240.0)
Al ka Spectro  4 TAP (32464.0)
Fe ka Spectro  5 LLIF (48085.0)
Mg ka Spectro  1 TAP (38499.0)
Ca ka Spectro  3 LPET (38387.0)
Mn ka Spectro  2 LLIF (52191.0)
Ni ka Spectro  5 LLIF (41166.0)
 O  (specified)
```

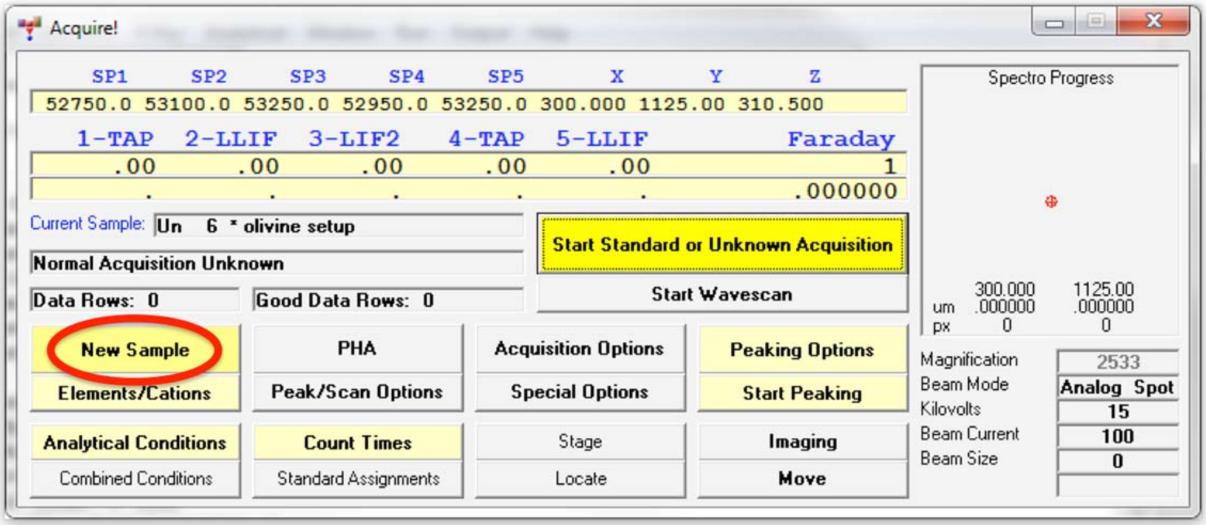
Click the **OK** button of the **Sample Setup Selection** window returning to the **Analyzed and Specified Elements** window.

Click the **OK** button to go back to the **Analyze!** window.

Any number of sample setups can be created as described above.

The user now has two calibrated sample setups available to analyze any pyroxene or olivine in the samples supplied for microprobe analysis. The olivine setup (last) is currently active however to recall any other sample setup, follow the steps outlined below.

Bring forward the **Acquire!** window. Move to the next unknown analysis spot, in this example the user wishes to analyze several pyroxene grains.



```
SP1     SP2     SP3     SP4     SP5     X       Y       Z
52750.0 53100.0 53250.0 52950.0 53250.0 300.000 1125.00 310.500
1-TAP   2-LLIF  3-LIF2  4-TAP   5-LLIF                  Faraday
.00     .00     .00     .00     .00                     1
.       .       .       .       .                       .000000
```

Current Sample: Un 6 * olivine setup

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

```
    300.000   1125.00
um  .000000   .000000
px  0         0
```

Magnification: 2533

Beam Mode: Analog Spot

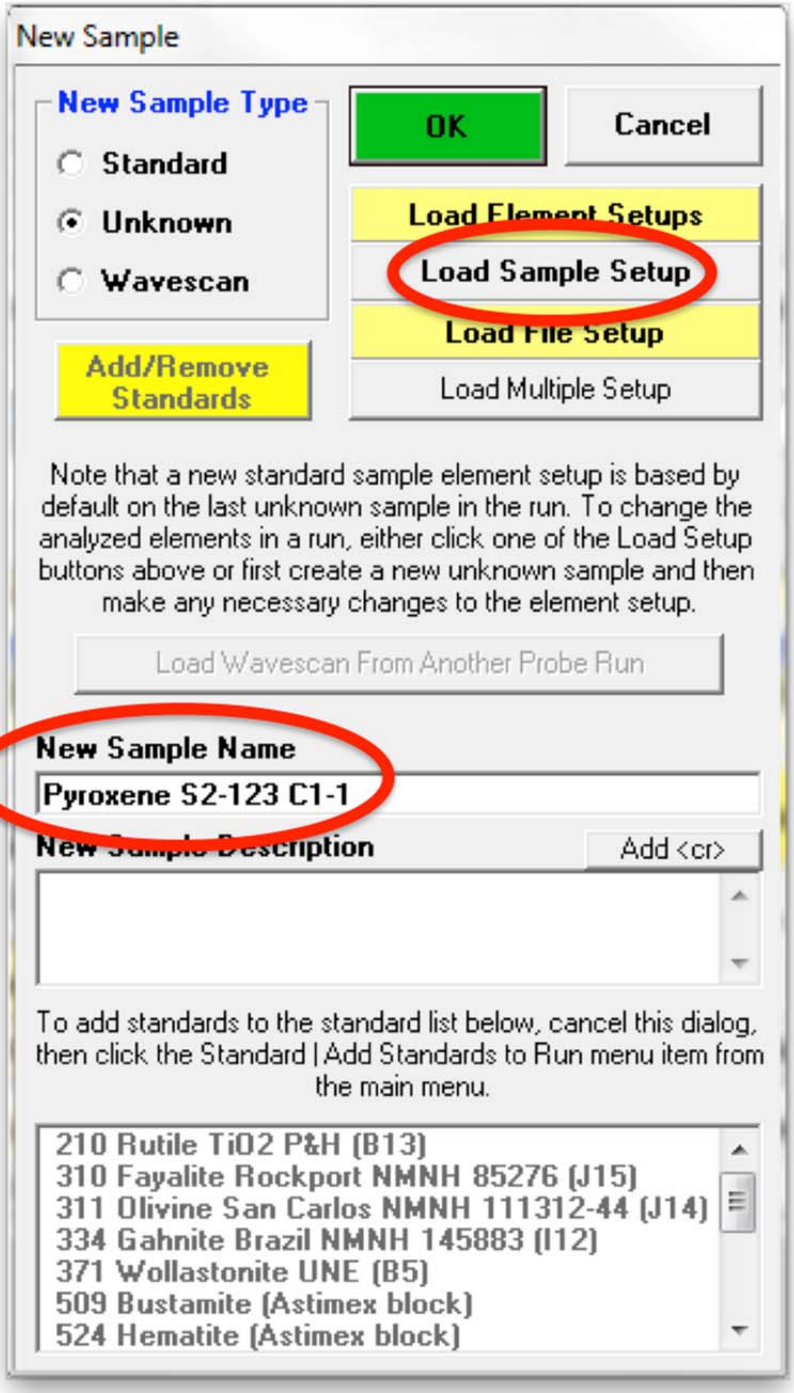
Kilovolts: 15

Beam Current: 100

Beam Size: 0

Click the **New Sample** button.

The **New Sample** window opens. Enter the appropriate text into the *New Sample Name* and *New Sample Description* fields.



Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: Pyroxene S2-123 C1-1

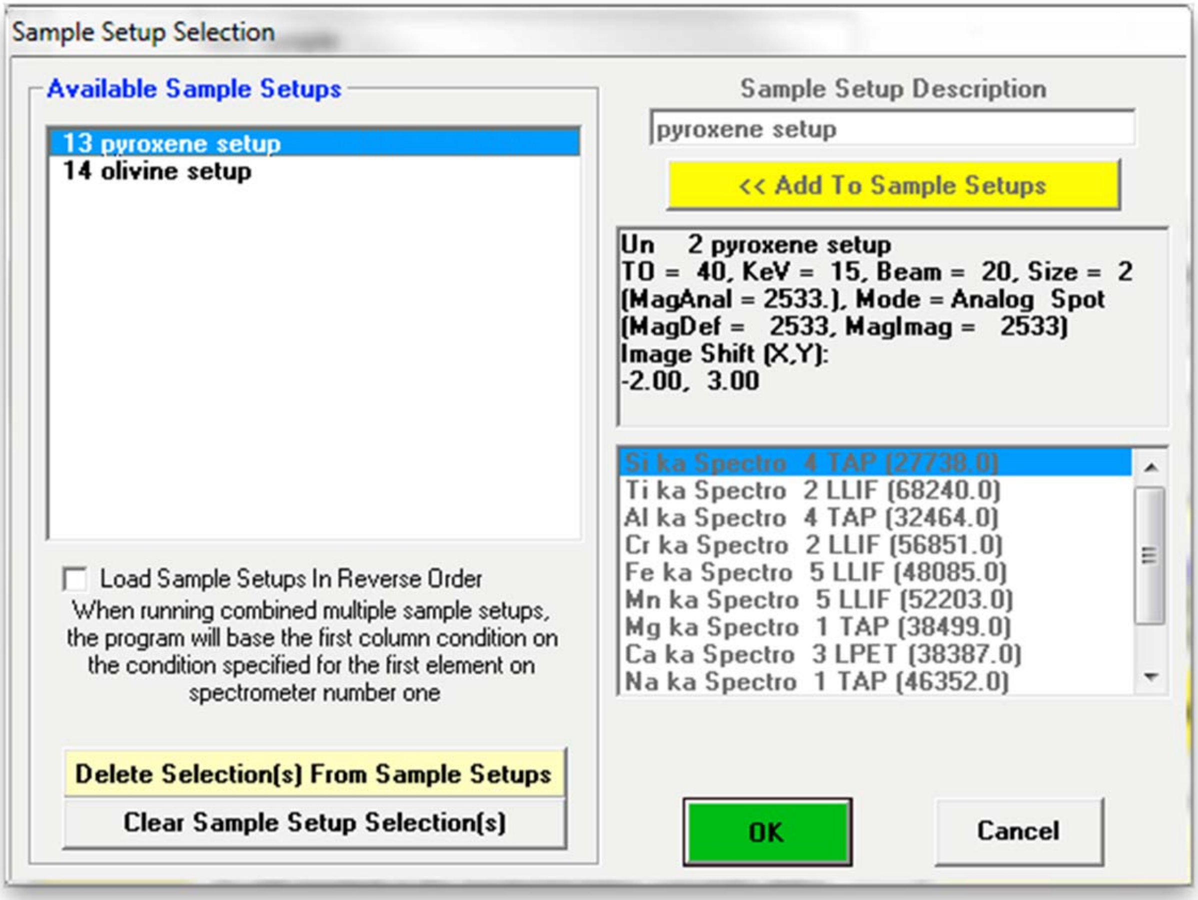
To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

210 Rutile TiO2 P&H (B13)
310 Fayalite Rockport NMNH 85276 (J15)
311 Olivine San Carlos NMNH 111312-44 (J14)
334 Gahnite Brazil NMNH 145883 (I12)
371 Wollastonite UNE (B5)
509 Bustamite (Astimex block)
524 Hematite (Astimex block)

Click the **Load Sample Setup** button.

This opens the **Sample Setup Selection** window.

Select the pyroxene setup, highlighting it allows the operator to view the element list.



13 pyroxene setup
14 olivine setup

pyroxene setup

```
Un    2 pyroxene setup
TO =  40, KeV =  15, Beam =  20, Size =  2
(MagAnal = 2533.), Mode = Analog  Spot
(MagDef =   2533, MagImag =   2533)
Image Shift (X,Y):
-2.00,  3.00
```

```
Si ka Spectro  4 TAP (27738.0)
Ti ka Spectro  2 LLIF (68240.0)
Al ka Spectro  4 TAP (32464.0)
Cr ka Spectro  2 LLIF (56851.0)
Fe ka Spectro  5 LLIF (48085.0)
Mn ka Spectro  5 LLIF (52203.0)
Mg ka Spectro  1 TAP (38499.0)
Ca ka Spectro  3 LPET (38387.0)
Na ka Spectro  1 TAP (46352.0)
```

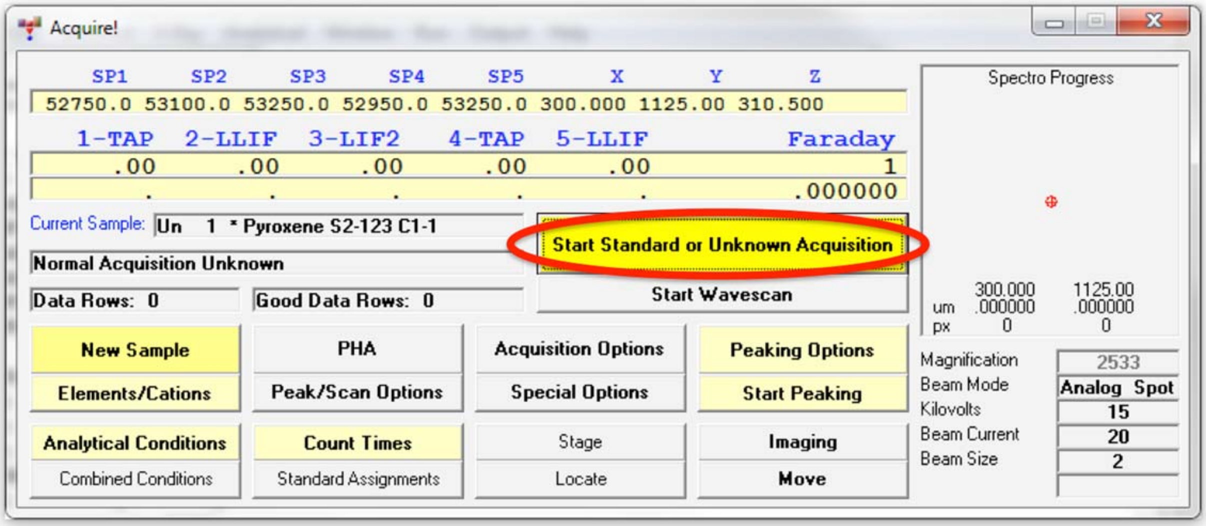
☐ Load Sample Setups In Reverse Order

When running combined multiple sample setups, the program will base the first column condition on the condition specified for the first element on spectrometer number one

Click the **OK** button of the **Sample Setup Selection** window to load the sample setup.

The program returns to the **New Sample** window. Click the **OK** button.

The **Acquire!** window reappears.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 1 * Pyroxene S2-123 C1-1

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

um	300.000 .000000	1125.00 .000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	20
Beam Size	2

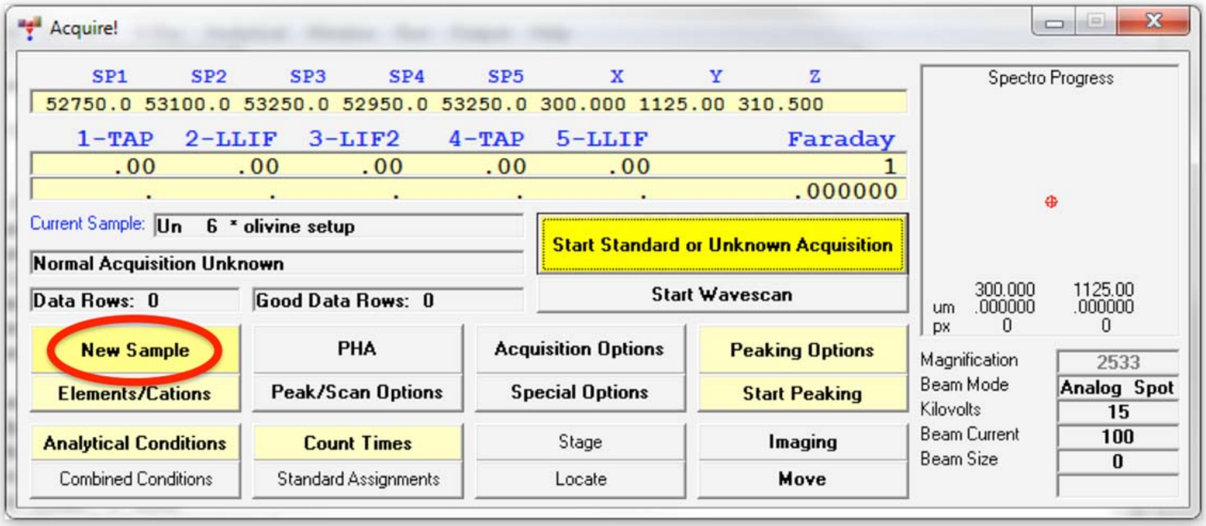
Double check your spot selection and focus and click the **Start Standard or Unknown Acquisition** button to initiate data acquisition.

The availability of multiple sample setups during the course of automated unknown analysis gives the user tremendous flexibility. Upon activation of the **Use Digitized Sample Setups** button in the **Automate!** window, each unknown analysis may be based on a different sample setup that was specified when the unknown sample position was digitized. See the User’s Guide and Reference documentation for more details.

File Setups

To load any sample setup from a previous probe run file, the file setup option is provided. These file setups are old Probe database files that contain old sample setups and may or may not contain standardization count intensity data.

The example below will illustrate how to use the file setup option to easily import two different (an olivine and a pyroxene) sample setups into the current new probe run. Open a new PROBE FOR EPMA run and click the **New Sample** button from the **Acquire!** window.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 6 * olivine setup

Normal Acquisition Unknown

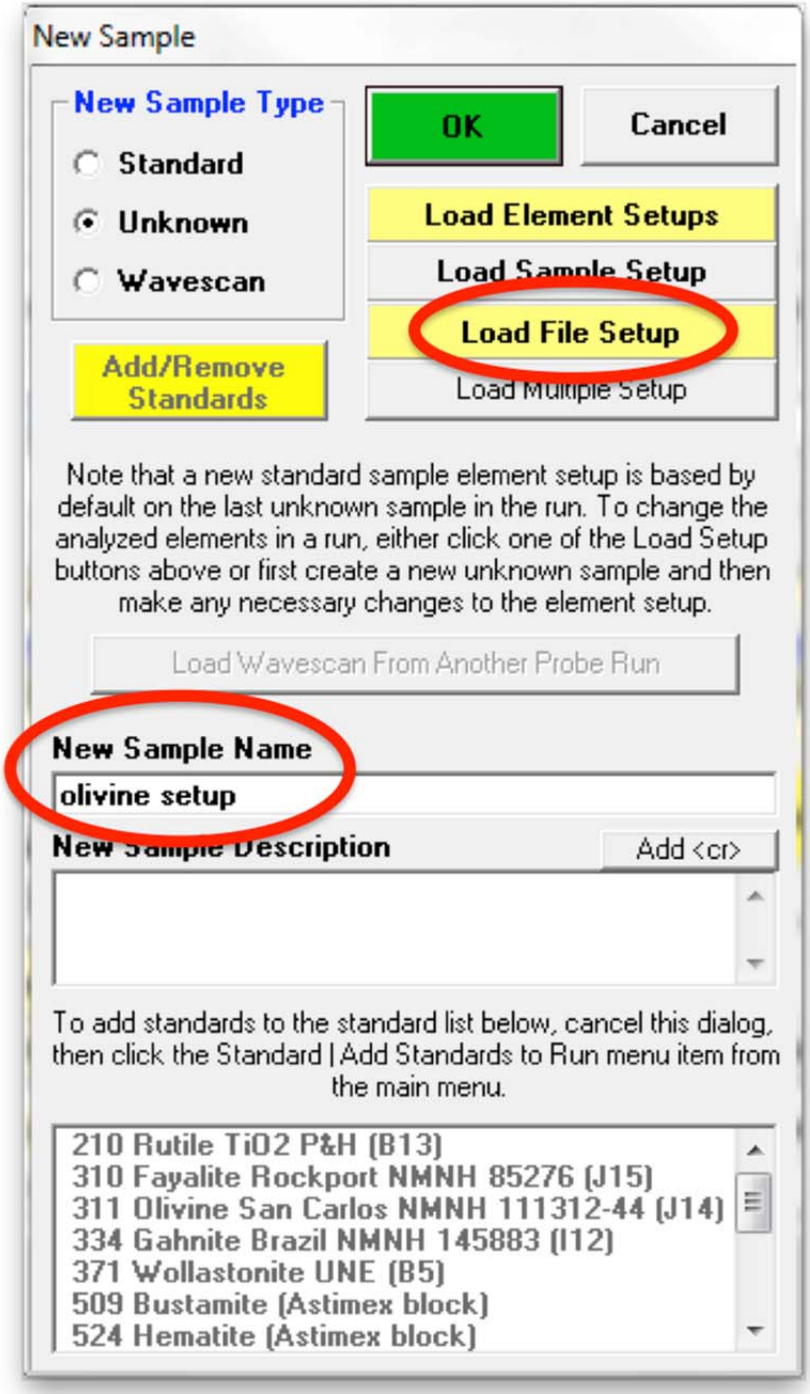
Data Rows: 0

Good Data Rows: 0

	X	Y
um	300.000 .000000	1125.00 .000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	100
Beam Size	0

The **New Sample** window appears. Edit the *New Sample Name* text box.



New Sample Type

○ Standard
● Unknown
○ Wavescan

Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: olivine setup

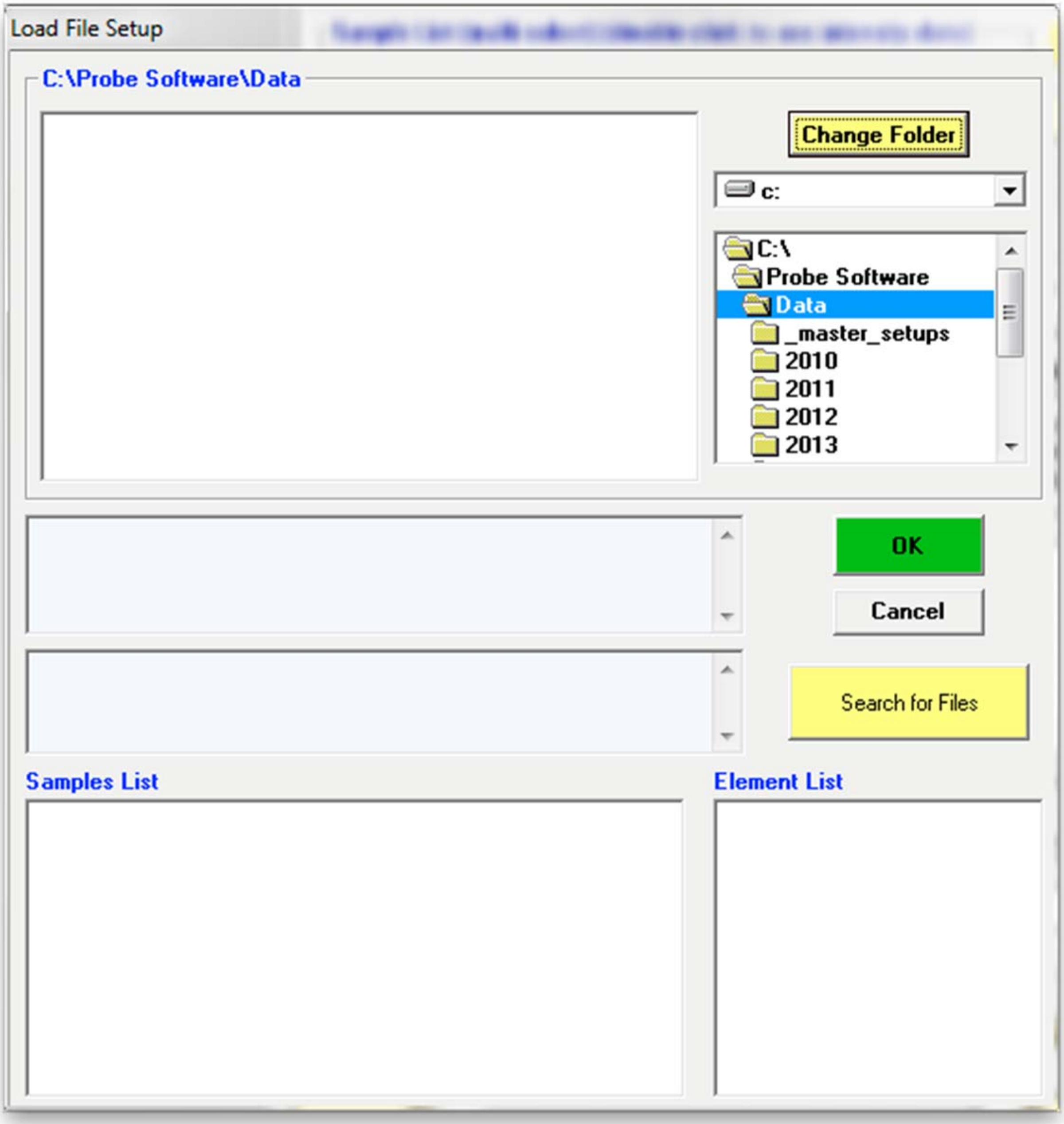
New Sample Description:

To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

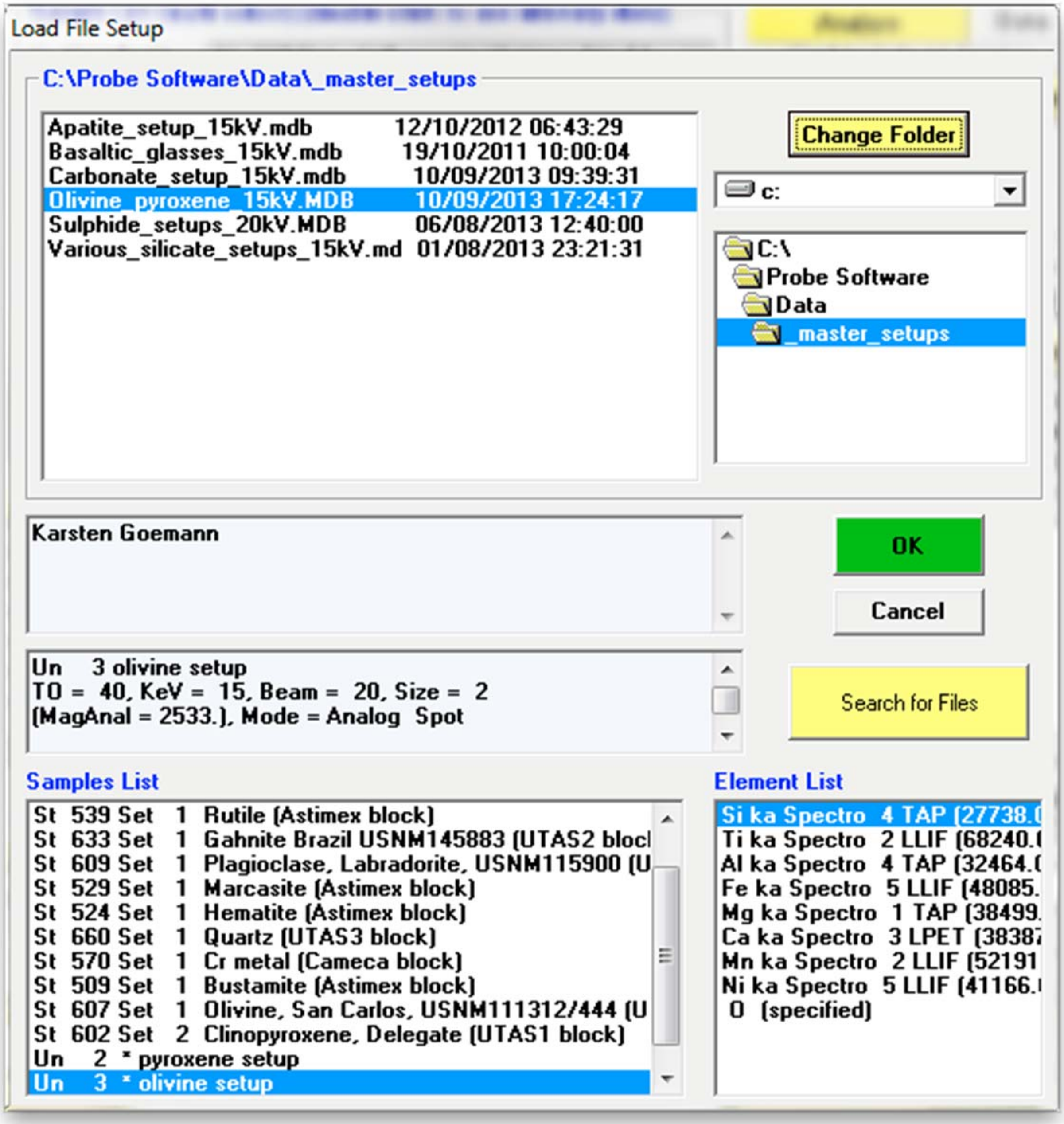
210 Rutile TiO2 P&H (B13)
310 Fayalite Rockport NMNH 85276 (J15)
311 Olivine San Carlos NMNH 111312-44 (J14)
334 Gahnite Brazil NMNH 145883 (I12)
371 Wollastonite UNE (B5)
509 Bustamite (Astimex block)
524 Hematite (Astimex block)

Click the **Load File Setup** button.

The **Load File Setup** window opens and will list all available PROBE FOR EPMA files that can be loaded. The initial available Probe Run Files directory pointer is the location specified when opening a new probe database file earlier. Move to another directory location if necessary. The last file listed in the available Probe Run Files along with the last entry in the *Samples List* will be shown by default.



Scroll through the available Probe Run Files list and highlight the file to load from. The last setup will be displayed in the *Samples List* and *Element List* text field. Next, select the sample setup that you wish to load into the new probe run. All of the run parameters and options for that sample setup will be loaded. The only parameters not loaded are the nominal beam current and the volatile element assignments since they are unknown sample specific.



C:\Probe Software\Data_master_setups

```
Apatite_setup_15kV.mdb              12/10/2012 06:43:29
Basaltic_glasses_15kV.mdb           19/10/2011 10:00:04
Carbonate_setup_15kV.mdb            10/09/2013 09:39:31
Olivine_pyroxene_15kV.MDB           10/09/2013 17:24:17
Sulphide_setups_20kV.MDB            06/08/2013 12:40:00
Various_silicate_setups_15kV.md     01/08/2013 23:21:31
```

```
Karsten Goemann
```

```
Un    3 olivine setup
TO =  40, KeV =  15, Beam =  20, Size =  2
(MagAnal = 2533.), Mode = Analog  Spot
```

Samples List

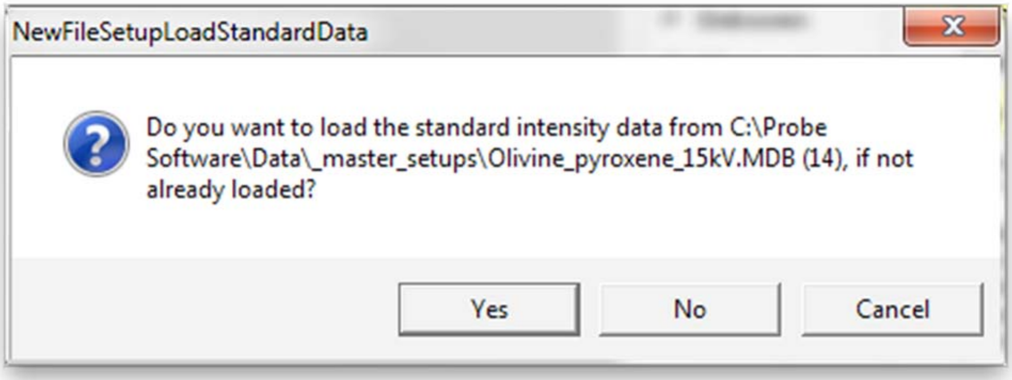
```
St  539 Set   1  Rutile (Astimex block)
St  633 Set   1  Gahnite Brazil USNM145883 (UTAS2 bloc
St  609 Set   1  Plagioclase, Labradorite, USNM115900 (U
St  529 Set   1  Marcasite (Astimex block)
St  524 Set   1  Hematite (Astimex block)
St  660 Set   1  Quartz (UTAS3 block)
St  570 Set   1  Cr metal (Cameca block)
St  509 Set   1  Bustamite (Astimex block)
St  607 Set   1  Olivine, San Carlos, USNM111312/444 (U
St  602 Set   2  Clinopyroxene, Delegate (UTAS1 block)
Un    2  * pyroxene setup
Un    3  * olivine setup
```

Element List

```
Si ka Spectro  4 TAP (27738.
Ti ka Spectro  2 LLIF (68240.
Al ka Spectro  4 TAP (32464.
Fe ka Spectro  5 LLIF (48085.
Mg ka Spectro  1 TAP (38499.
Ca ka Spectro  3 LPET (3838
Mn ka Spectro  2 LLIF (52191
Ni ka Spectro  5 LLIF (41166.
 O  (specified)
```

Click the **OK** button to load in this sample setup of interest.

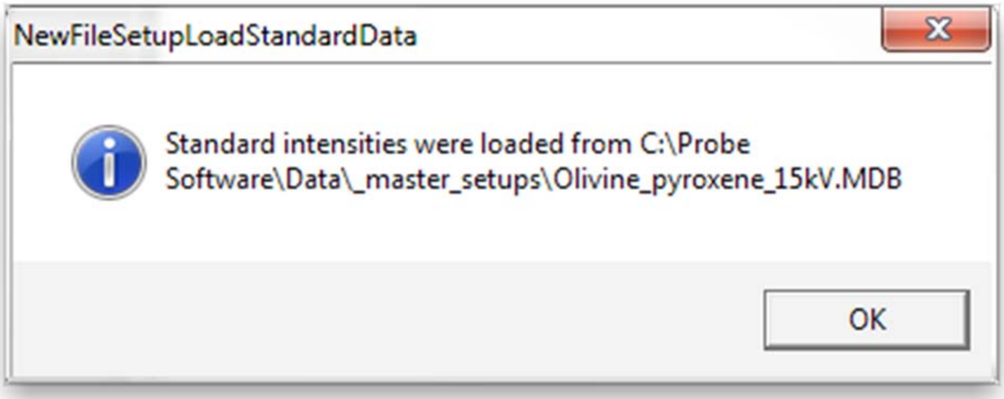
The **NewFileSetupLoadStandardData** window appears next, asking whether the user wants the previous standard intensity data to be loaded as well.



Do you want to load the standard intensity data from C:\Probe Software\Data_master_setups\Olivine_pyroxene_15kV.MDB (14), if not already loaded?

Selecting **Yes** would load the old standard intensity data from the file setup into this new run. Depending on the stability of your instrument, it may or may not be necessary to re-standardize some or all of the standards. In this case, the user chooses to load the standard intensity data, selecting the **Yes** button.

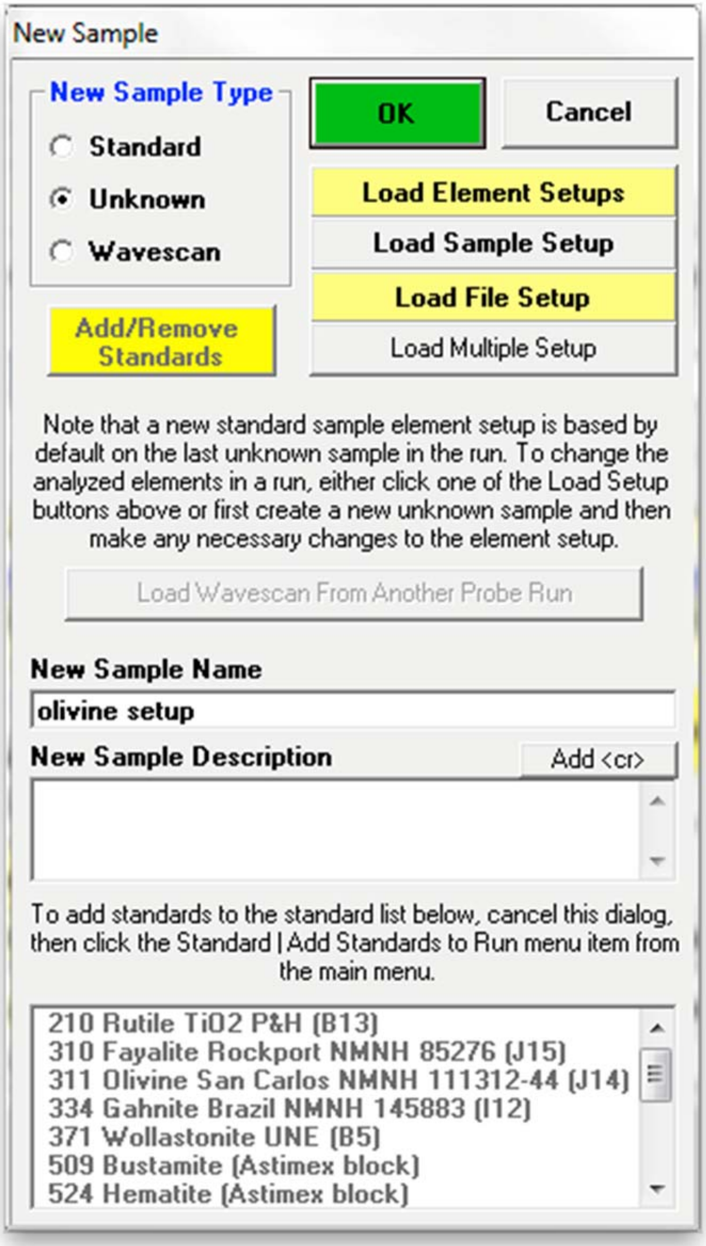
The **NewFileSetupLoadStandardData** window appears.



Standard intensities were loaded from C:\Probe Software\Data_master_setups\Olivine_pyroxene_15kV.MDB

Click the **OK** button.

The **New Sample** dialog box reappears.



New Sample Type
○ Standard
● Unknown
○ Wavescan

Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: olivine setup

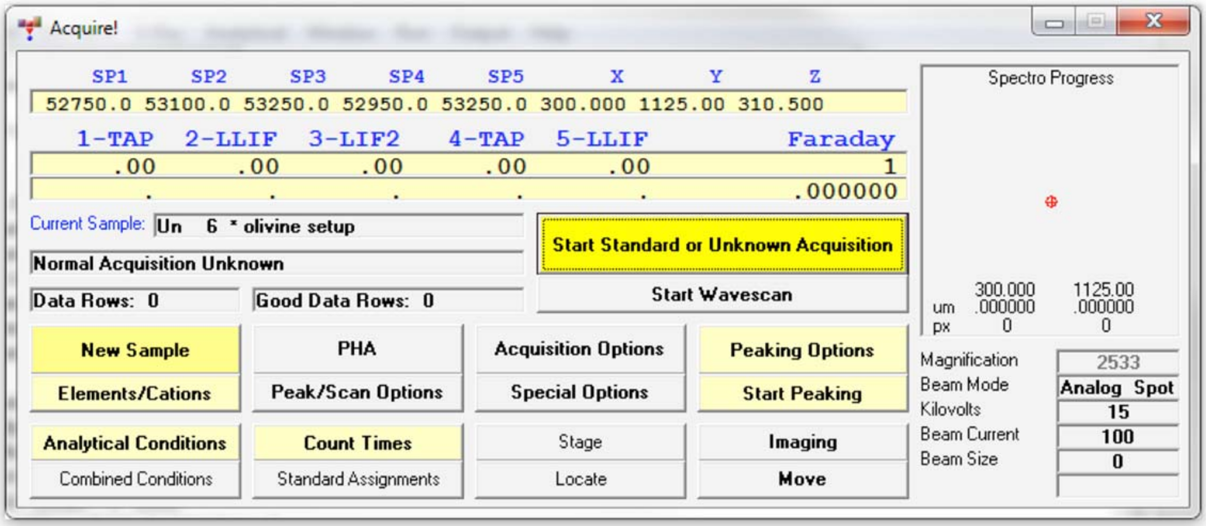
New Sample Description:

To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

210 Rutile TiO2 P&H (B13)
310 Fayalite Rockport NMNH 85276 (J15)
311 Olivine San Carlos NMNH 111312-44 (J14)
334 Gahnite Brazil NMNH 145883 (I12)
371 Wollastonite UNE (B5)
509 Bustamite (Astimex block)
524 Hematite (Astimex block)

Click the **OK** button to complete the loading of the olivine sample setup from the old probe run.

The program now returns to the fully active **Acquire!** window.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 6 * olivine setup

Normal Acquisition Unknown

Data Rows: 0

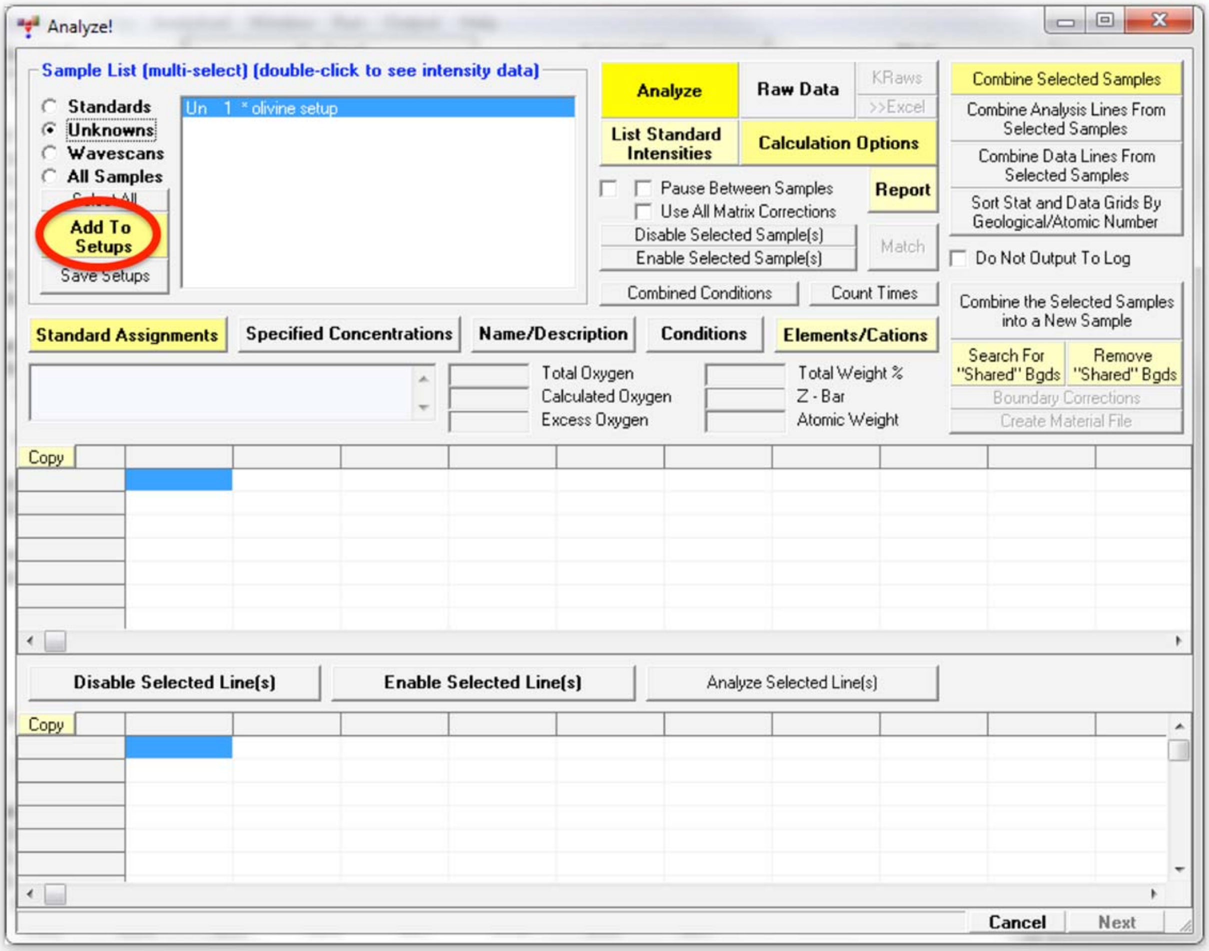
Good Data Rows: 0

	300.000	1125.00
um	.000000	.000000
px	0	0

Magnification: 2533
Beam Mode: Analog Spot
Kilovolts: 15
Beam Current: 100
Beam Size: 0

Normally the user would check the calibration by running a secondary standard or two to verify the composition, repeaking and/or collecting standard intensities as required.

The user then opens the **Analyze!** window to save this olivine setup as a sample setup in this current probe run.



Click the **Add To Setups** button.

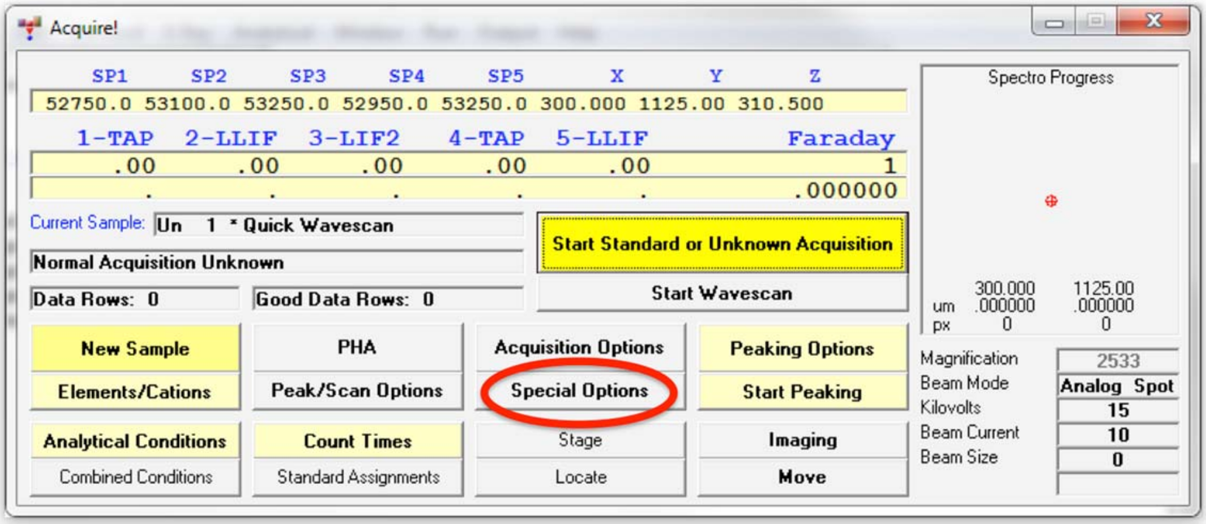
If another, previously created sample setup is needed for this current probe run, open the **New Sample** window and follow the instructions of the past eight pages.

Wavescans

Quick Wavescan Acquisition

This feature is useful if an EDS detector is not available or WDS resolution over the entire spectrometer range is required. The program will move each spectrometer currently assigned to it's upper limit and then continuously scan each spectrometer to it's lower travel limit while acquiring simultaneous count data. The count time used for the **Quick Wavescan Acquisition** is specified in the **Count Times** dialog box, opened from the **Acquire!** window. The current sample setup specifies which spectrometer and reflecting crystal to use. The program uses the spectrometer calibration of the first acquired element (order = 1) in the sample.

From an open PROBE FOR EPMA run, containing an unknown sample and the appropriate unknown under the crosshairs, click the **Special Options** button from the **Acquire!** window.



Acquire!

SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 1 * Quick Wavescan

Normal Acquisition Unknown

Data Rows: 0

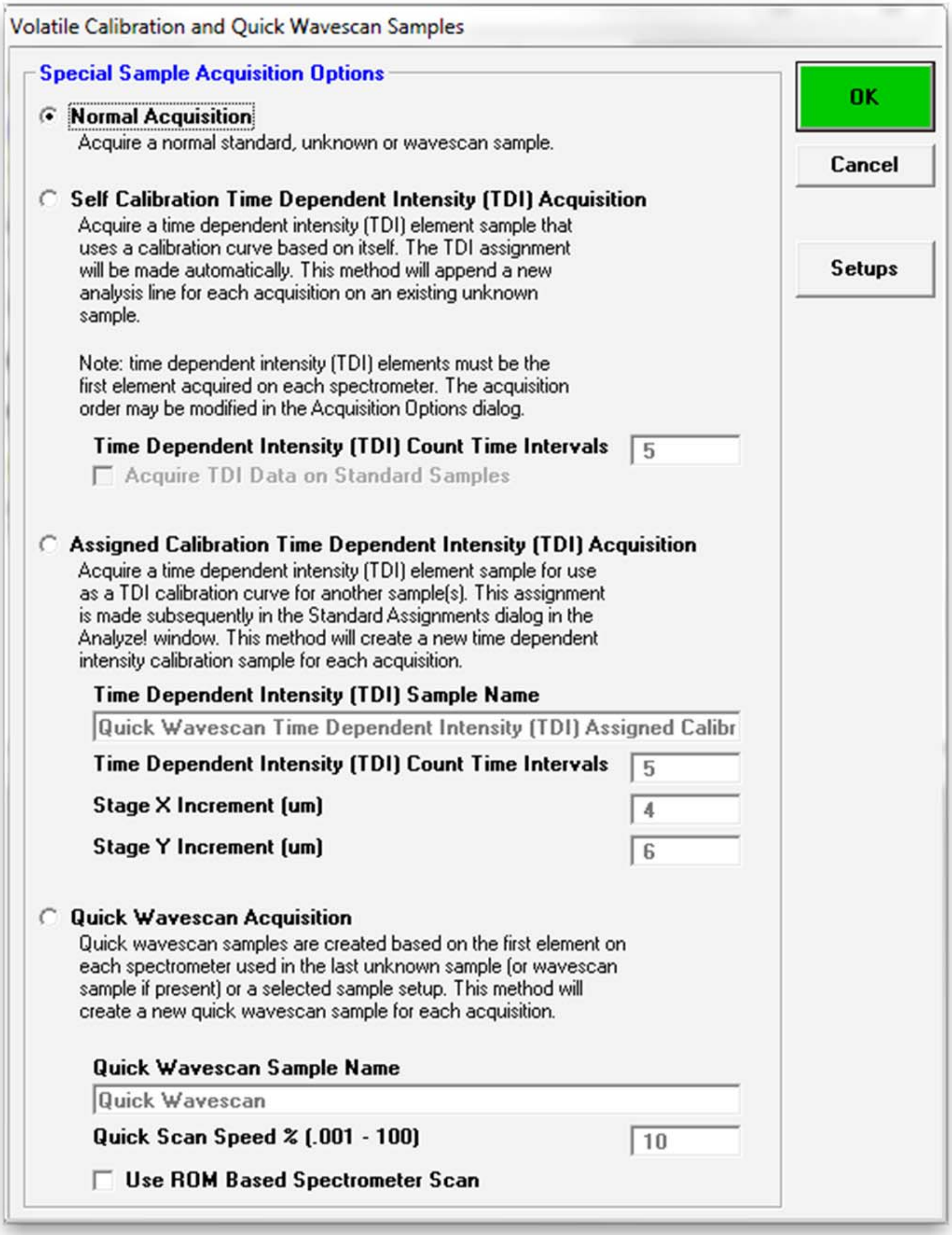
Good Data Rows: 0

Spectro Progress

	300.000	1125.00
um	.000000	.000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	10
Beam Size	0

This opens the **Volatile Calibration and Quick Wavescan Samples** window. Note the default acquisition option is *Normal Acquisition*.



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

○ **Self Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample that uses a calibration curve based on itself. The TDI assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing unknown sample.

Note: time dependent intensity (TDI) elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Time Dependent Intensity (TDI) Count Time Intervals 5
☐ Acquire TDI Data on Standard Samples

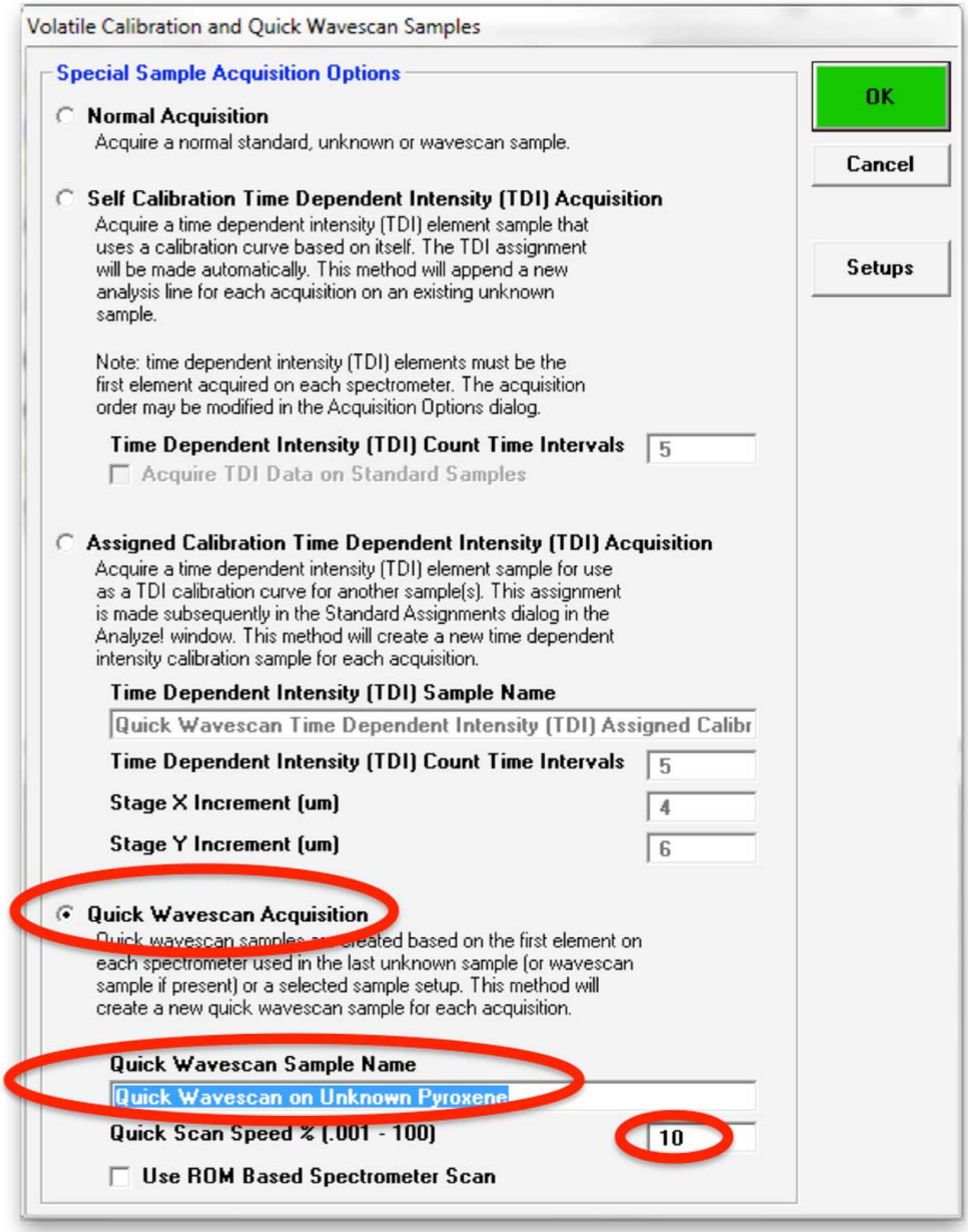
○ **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI calibration curve for another sample(s). This assignment is made subsequently in the Standard Assignments dialog in the Analyze! window. This method will create a new time dependent intensity calibration sample for each acquisition.

Time Dependent Intensity (TDI) Sample Name
Quick Wavescan Time Dependent Intensity (TDI) Assigned Calibr
Time Dependent Intensity (TDI) 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
Quick Wavescan
Quick Scan Speed % (.001 - 100) 10
☐ **Use ROM Based Spectrometer Scan**

Select the *Quick Wavescan Acquisition* dialog button. Enter a *Quick Wavescan Sample Name* and *Quick Scan Speed* into the text fields. The smaller the scan speed percentage the slower the spectrometer will travel per second and of course each instrument would require different settings. If ROM scanning is possible on your instrument, you can also check the *Use ROM Based Spectrometer Scan* tick box. This will usually make the scan faster, but is limited by the minimum and maximum speeds the spectrometers are capable of.



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

○ **Self Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample that uses a calibration curve based on itself. The TDI assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing unknown sample.

Note: time dependent intensity (TDI) elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Time Dependent Intensity (TDI) Count Time Intervals: 5
☐ Acquire TDI Data on Standard Samples

○ **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI 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 time dependent intensity calibration sample for each acquisition.

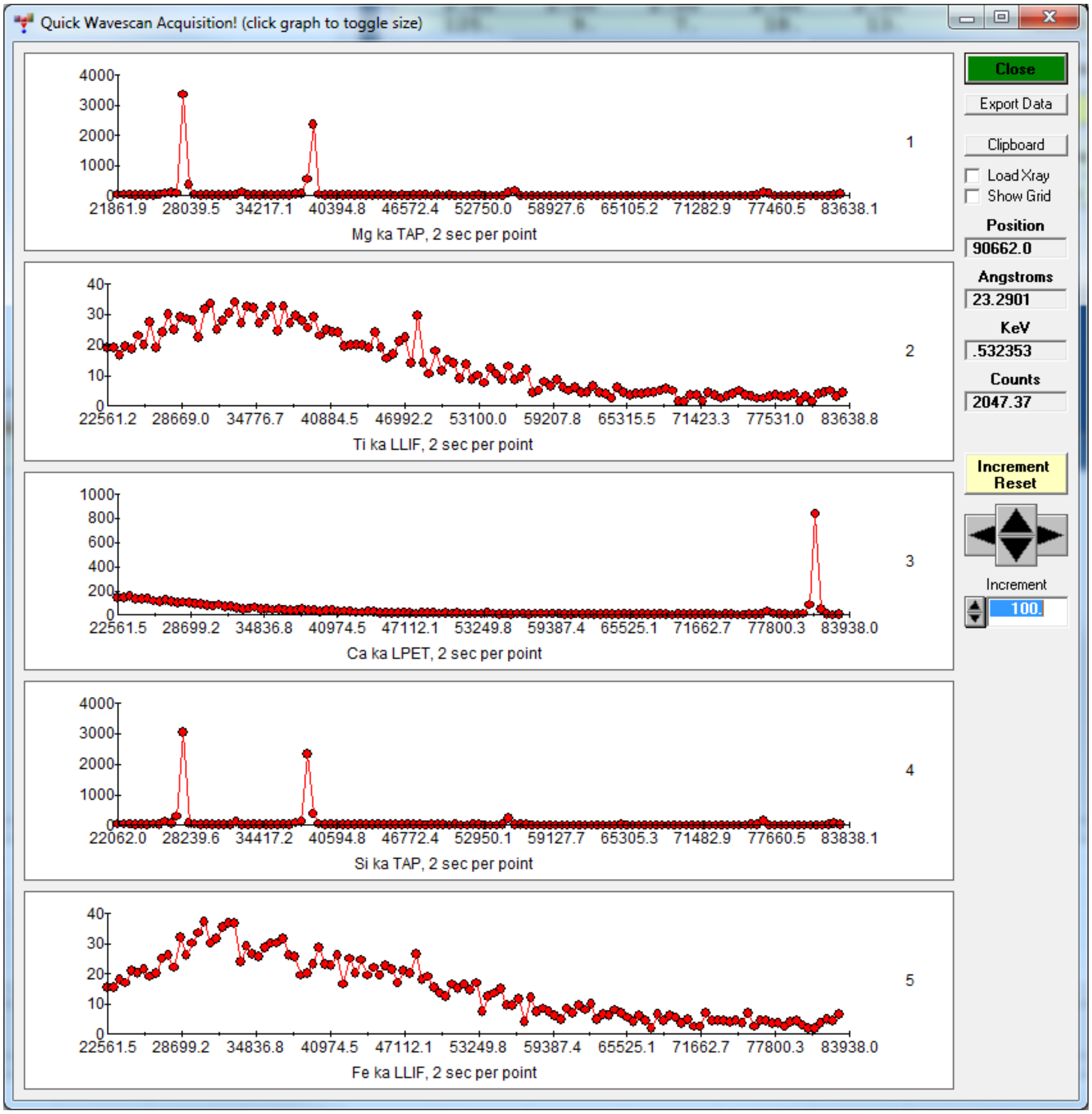
Time Dependent Intensity (TDI) Sample Name: Quick Wavescan Time Dependent Intensity (TDI) Assigned Calibr
Time Dependent Intensity (TDI) Count Time Intervals: 5
Stage X Increment (um): 4
Stage Y Increment (um): 6

● **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: Quick Wavescan on Unknown Pyroxene
Quick Scan Speed % (.001 - 100): 10
☐ Use ROM Based Spectrometer Scan

Click the **OK** button to return to the **Acquire!** window.

To initiate the quick wavescan acquisition, click the **Start Wavescan** button in the **Acquire!** window. A new wavescan sample is automatically started using the sample name just supplied. The spectrometers move to their respective upper or lower limits and proceed with the wavescan. The **Wavescan Acquisition** window opens and real time data display is viewable. A completed five-spectrometer **Wavescan Acquisition** window is shown below.



Position
90662.0
Angstroms
23.2901
KeV
.532353
Counts
2047.37
Increment
100.

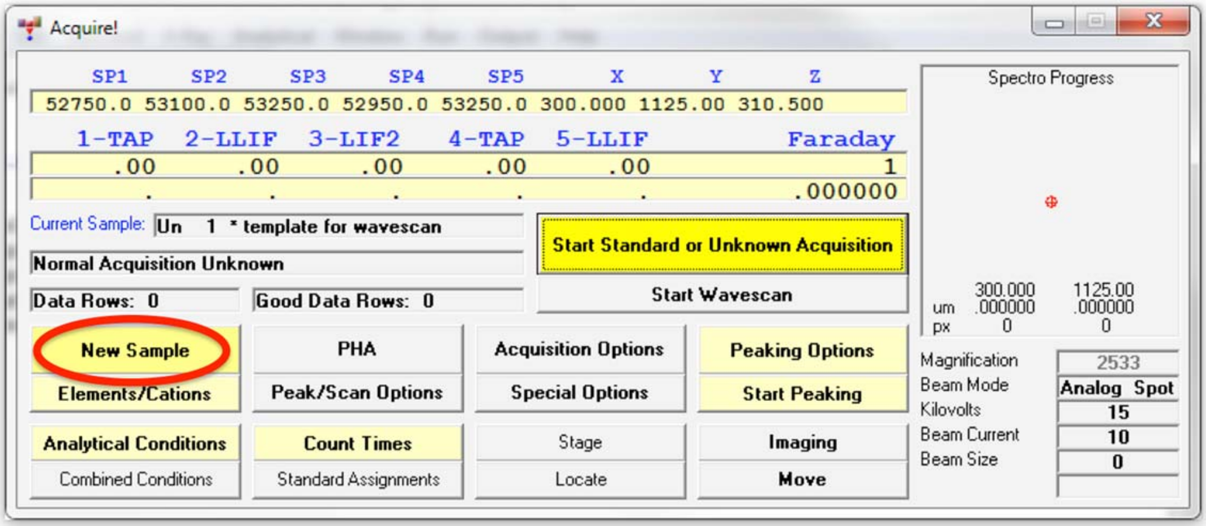
The size of each graph maybe expanded (not shown) by clicking on the relevant wavescan. Upon completion of the quick wavescan, the data may be exported via the **Export Data** button to an ASCII file or examined in more detail along with KLM marker overlay capabilities from the **Plot!** window. Printing of the quick wavescan is possible by selecting the **Print** option under the **Graph Data** window (see next section for a specific example).

Calibrated Multi-Element Wavescans

Another unique feature of PROBE FOR EPMA is the ability to acquire calibrated multi-element wavescans. This provides an easy and rapid method to scan **all** elements in a sample for off-peak interferences. The example below will illustrate calibrated wavescans on a ten-element pyroxene sample and the adjustment of off-peak background positions.

Open a new PROBE FOR EPMA run in the usual manner. Confirm motor and crystal positions as well as setting the beam current to the appropriate value. Click the **New Sample** button and create a sample using the elements of interest. Next, re-peak the elements using either manual or automatic peaking on the appropriate standards. This calibrates the spectrometer motors. And finally, move to the sample to perform the calibrated wavescan.

From the **Acquire!** window, click the **New Sample** button to create a wavescan sample.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 1 * template for wavescan

Normal Acquisition Unknown

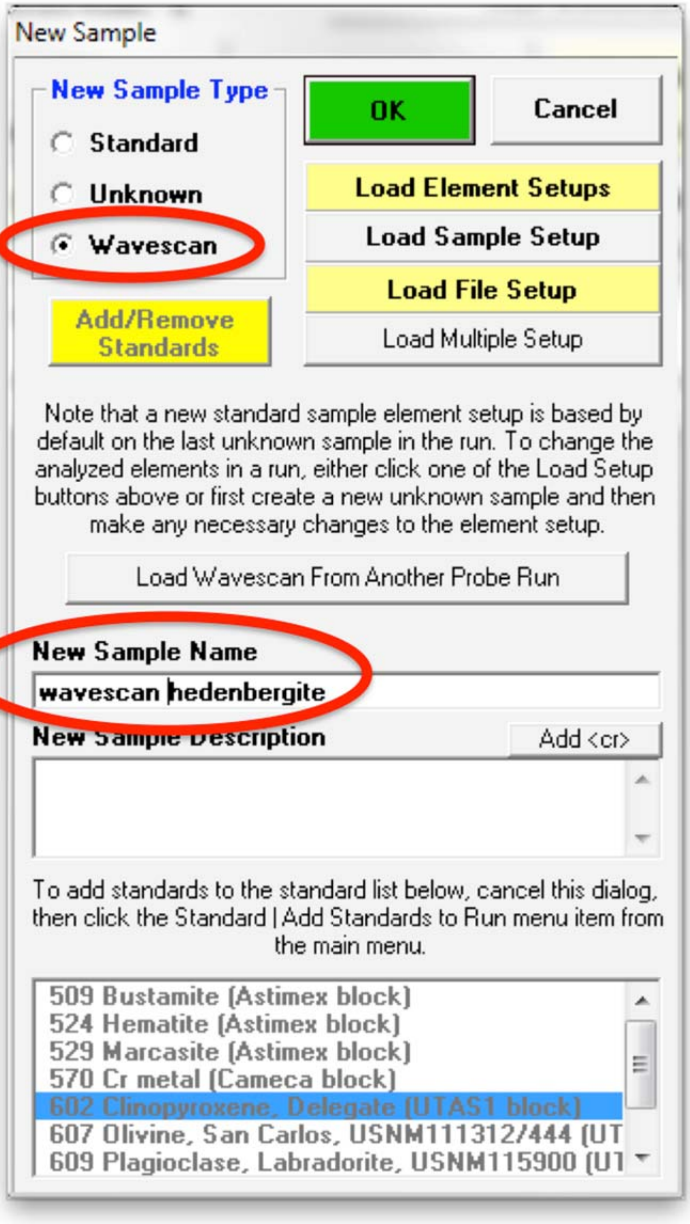
Data Rows: 0

Good Data Rows: 0

	300.000	1125.00
um	.000000	.000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	10
Beam Size	0

The **New Sample** window opens. Select the *Wavescan* check button as the *New Sample Type.* Edit the *New Sample Name* and *New Sample Description* text fields.



New Sample Type
○ Standard
○ Unknown
● Wavescan

Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: wavescan hedenbergite

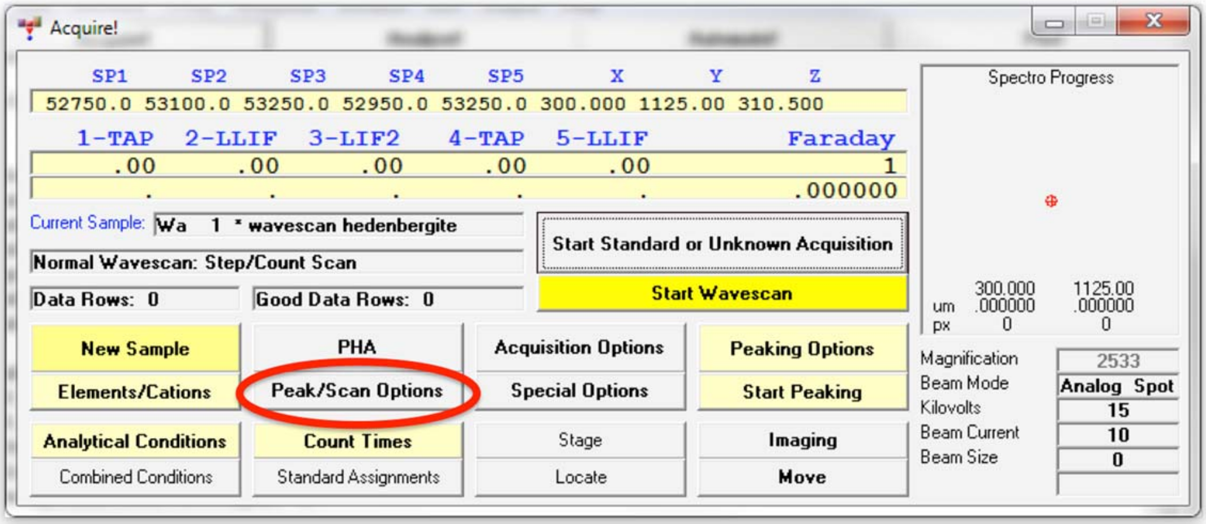
New Sample Description:

To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

509 Bustamite (Astimex block)
524 Hematite (Astimex block)
529 Marcasite (Astimex block)
570 Cr metal (Cameca block)
602 Clinopyroxene, Delegate (UTAS1 block)
607 Olivine, San Carlos, USNM111312/444 (UT
609 Plagioclase, Labradorite, USNM115900 (UT

Click the **OK** button.

The program returns to the **Acquire!** window.



Acquire!

```
  SP1      SP2      SP3      SP4      SP5       X        Y        Z
52750.0  53100.0  53250.0  52950.0  53250.0  300.000  1125.00  310.500
  1-TAP   2-LLIF   3-LIF2   4-TAP   5-LLIF                Faraday
   .00      .00      .00      .00      .00                      1
     .        .        .        .        .                .000000
```

Current Sample: Wa 1 * wavescan hedenbergite

Normal Wavescan: Step/Count Scan

Data Rows: 0

Good Data Rows: 0

Spectro Progress

```
     300.000   1125.00
um   .000000   .000000
px   0         0
```

Magnification: 2533

Beam Mode: Analog Spot

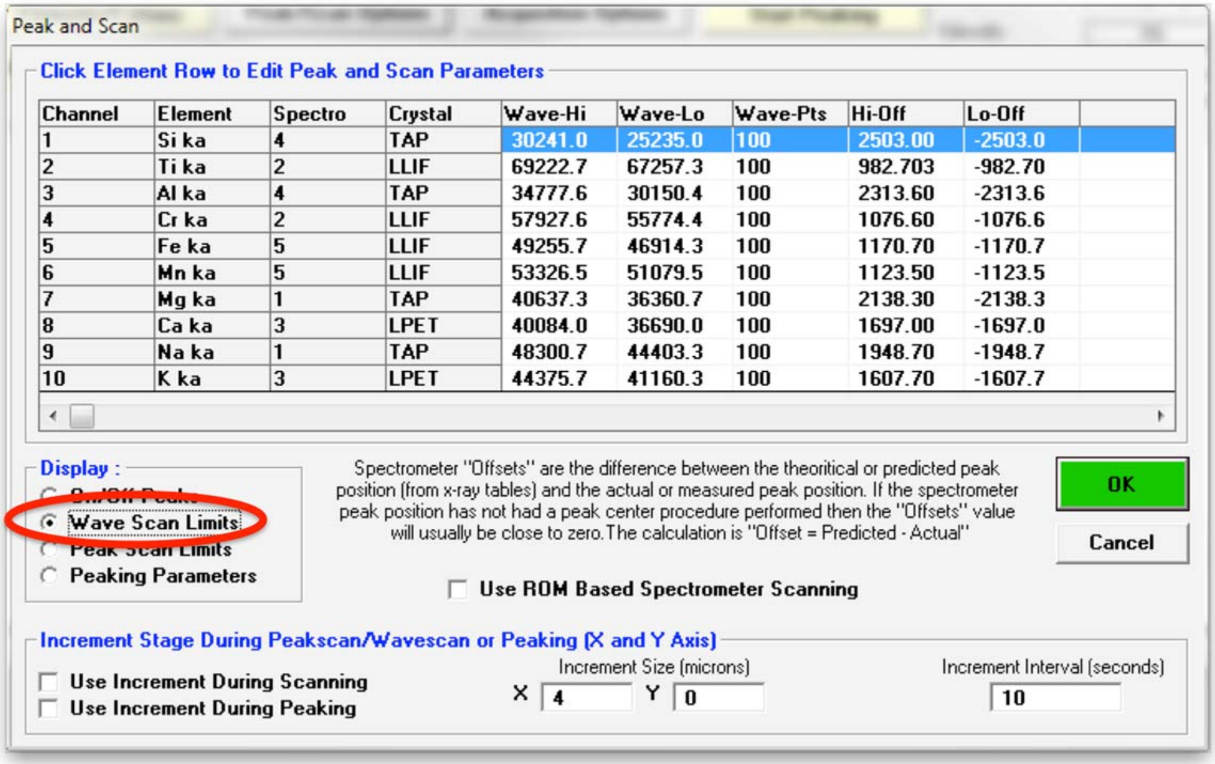
Kilovolts: 15

Beam Current: 10

Beam Size: 0

To modify the wavescan range and/or number of data points to be collected, click on the **Peak/Scan Options** button in the **Acquire!** window.

Select the *Wave Scan Limits* check button under *Display:* and click on the appropriate element row to edit the parameters. The stage may also be moved (incremented) during the acquisition using the *Stage Step During Peakscan/Wavescan or Peaking (X and Y Axis)* check box and *Increment Size (microns)* text field.



Peak and Scan

Click Element Row to Edit Peak and Scan Parameters

Channel	Element	Spectro	Crystal	Wave-Hi	Wave-Lo	Wave-Pts	Hi-Off	Lo-Off
1	Si ka	4	TAP	30241.0	25235.0	100	2503.00	-2503.0
2	Ti ka	2	LLIF	69222.7	67257.3	100	982.703	-982.70
3	Al ka	4	TAP	34777.6	30150.4	100	2313.60	-2313.6
4	Cr ka	2	LLIF	57927.6	55774.4	100	1076.60	-1076.6
5	Fe ka	5	LLIF	49255.7	46914.3	100	1170.70	-1170.7
6	Mn ka	5	LLIF	53326.5	51079.5	100	1123.50	-1123.5
7	Mg ka	1	TAP	40637.3	36360.7	100	2138.30	-2138.3
8	Ca ka	3	LPET	40084.0	36690.0	100	1697.00	-1697.0
9	Na ka	1	TAP	48300.7	44403.3	100	1948.70	-1948.7
10	K ka	3	LPET	44375.7	41160.3	100	1607.70	-1607.7

Display :

○ On/Off Peaks
● Wave Scan Limits
○ Peak Scan Limits
○ Peaking Parameters

Spectrometer "Offsets" are the difference between the theoritical or predicted peak position (from x-ray tables) and the actual or measured peak position. If the spectrometer peak position has not had a peak center procedure performed then the "Offsets" value will usually be close to zero. The calculation is "Offset = Predicted - Actual"

☐ Use ROM Based Spectrometer Scanning

Increment Stage During Peakscan/Wavescan or Peaking (X and Y Axis)

☐ Use Increment During Scanning
☐ Use Increment During Peaking

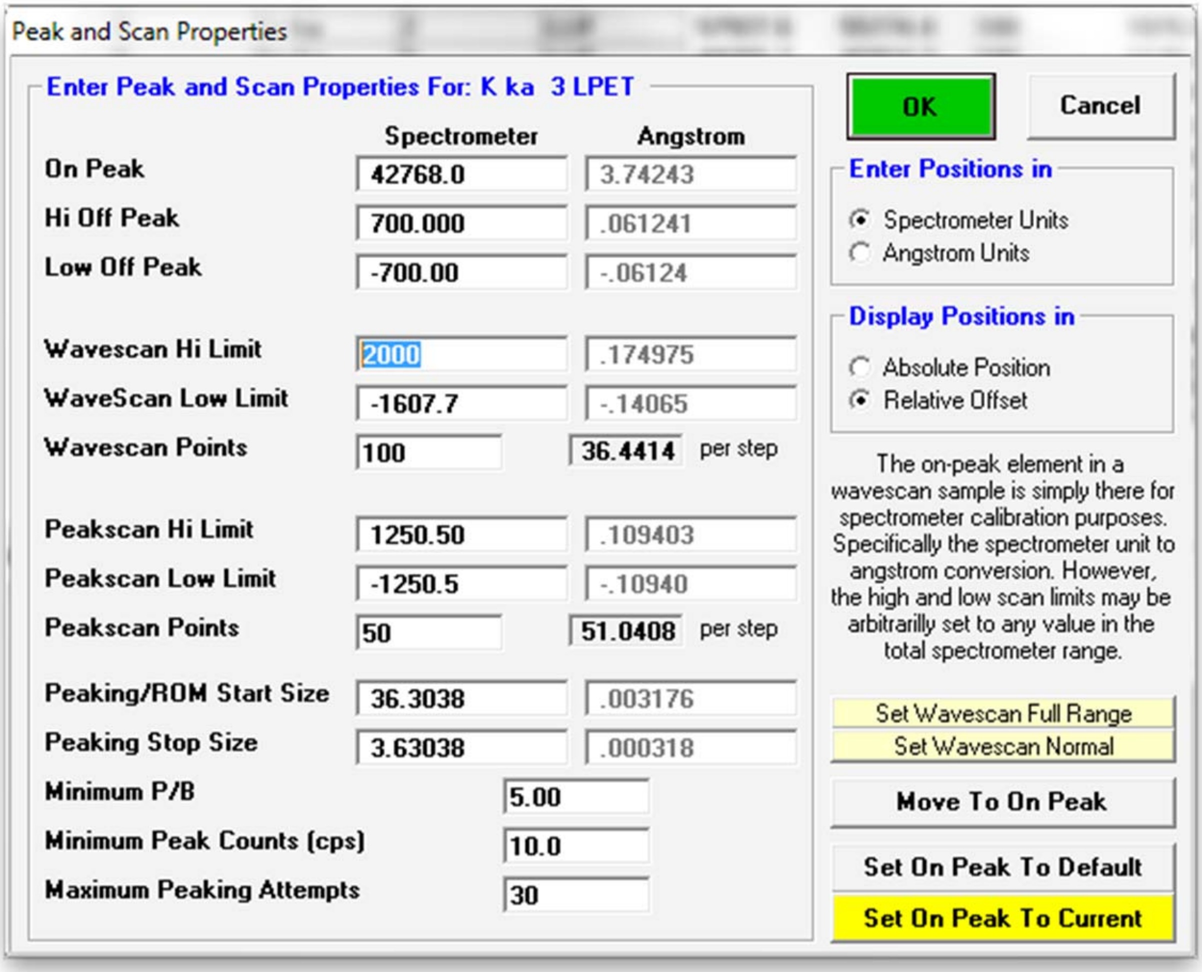
Increment Size (microns) X 4 Y 0

Increment Interval (seconds) 10

If ROM scanning is possible on your instrument (e.g. Cameca SX100), you can also check the *Use ROM Based Spectrometer Scan* tick box. This will usually make the scan faster, but is limited by the minimum and maximum speeds the spectrometers are capable of.

To adjust the spectrometer start and stop values for an element, click on the corresponding row, e.g. K Kα..

This opens the **Peak and Scan Properties** window. Adjust the values as desired:



Enter Peak and Scan Properties For: K ka 3 LPET

	Spectrometer	Angstrom
On Peak	42768.0	3.74243
Hi Off Peak	700.000	.061241
Low Off Peak	-700.00	-.06124
Wavescan Hi Limit	2000	.174975
WaveScan Low Limit	-1607.7	-.14065
Wavescan Points	100	36.4414 per step
Peakscan Hi Limit	1250.50	.109403
Peakscan Low Limit	-1250.5	-.10940
Peakscan Points	50	51.0408 per step
Peaking/ROM Start Size	36.3038	.003176
Peaking Stop Size	3.63038	.000318

Minimum P/B 5.00
Minimum Peak Counts (cps) 10.0
Maximum Peaking Attempts 30

Enter Positions in
● Spectrometer Units
○ Angstrom Units

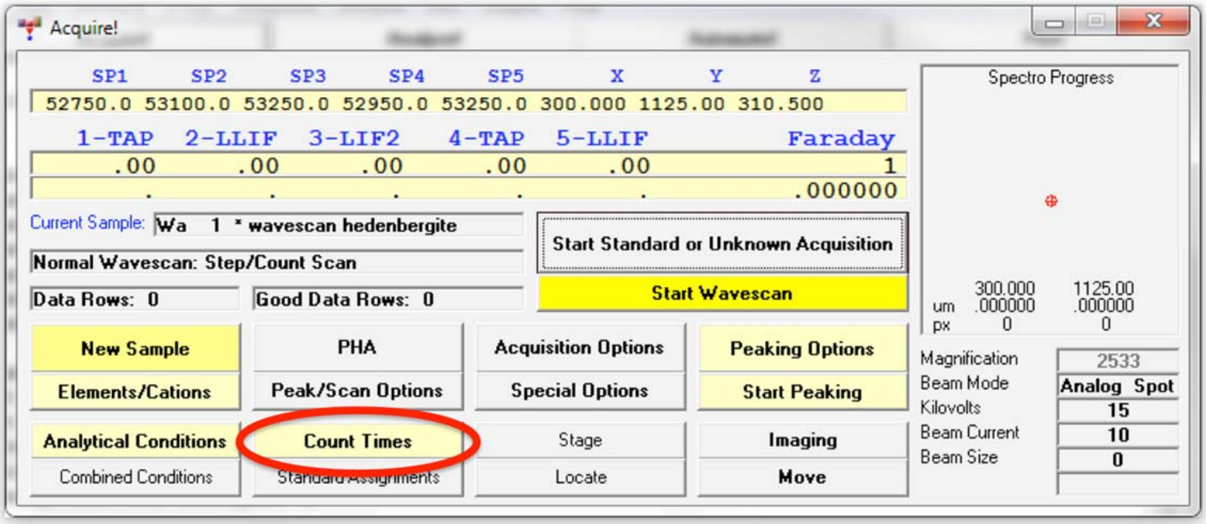
Display Positions in
○ Absolute Position
● Relative Offset

The on-peak element in a wavescan sample is simply there for spectrometer calibration purposes. Specifically the spectrometer unit to angstrom conversion. However, the high and low scan limits may be arbitrarilly set to any value in the total spectrometer range.

Click the **OK** button of the **Peak and Scan Properties** window when done editing.

Then click the **OK** of **Peak and Scan** window to close.

Wavescan count times for each element are adjusted via the **Count Times** button in the **Acquire!** window.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Wa 1 * wavescan hedenbergite

Normal Wavescan: Step/Count Scan

Data Rows: 0

Good Data Rows: 0

um	300.000 .000000	1125.00 .000000
px	0	0

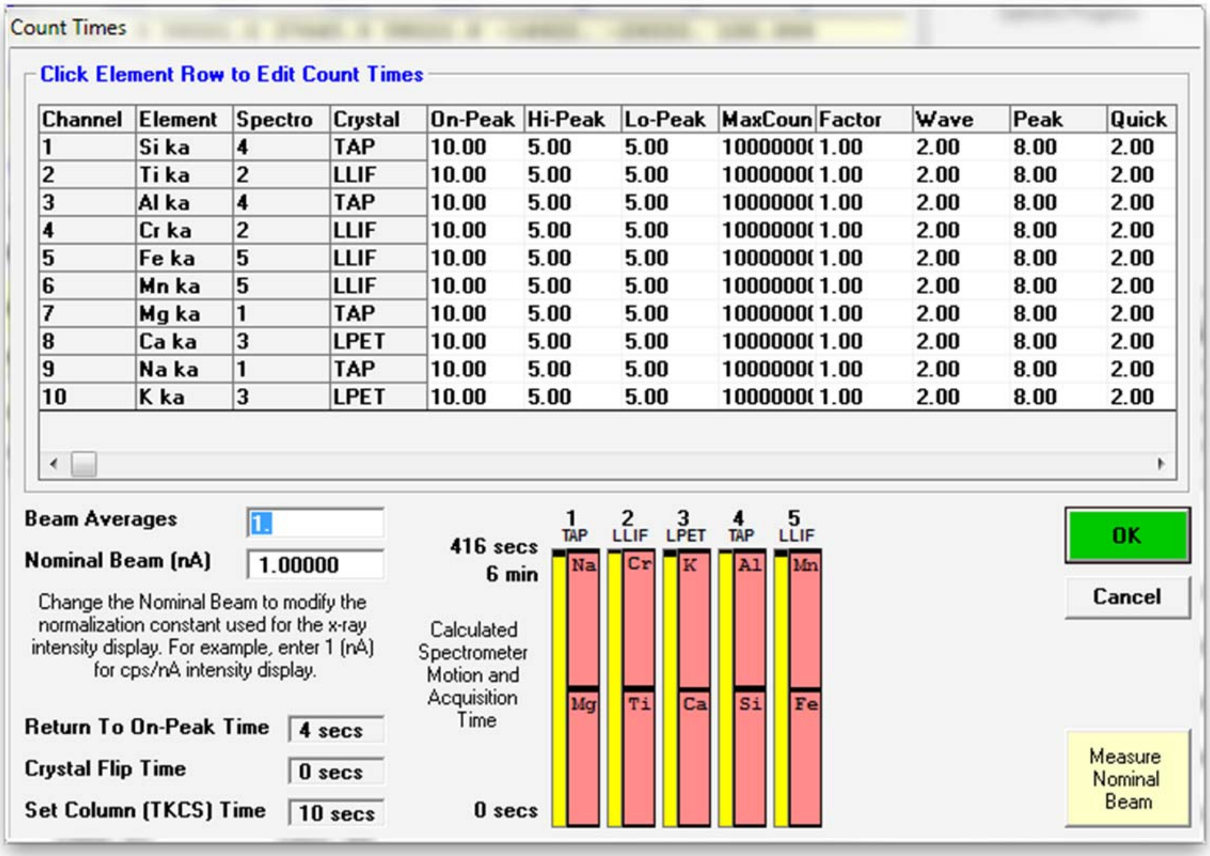
Magnification 2533

Beam Mode Analog Spot

Kilovolts 15

Beam Current 10

Beam Size 0



Channel	Element	Spectro	Crystal	On-Peak	Hi-Peak	Lo-Peak	MaxCoun	Factor	Wave	Peak	Quick
1	Si ka	4	TAP	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
2	Ti ka	2	LLIF	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
3	Al ka	4	TAP	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
4	Cr ka	2	LLIF	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
5	Fe ka	5	LLIF	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
6	Mn ka	5	LLIF	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
7	Mg ka	1	TAP	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
8	Ca ka	3	LPET	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
9	Na ka	1	TAP	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00
10	K ka	3	LPET	10.00	5.00	5.00	1000000(	1.00	2.00	8.00	2.00

Beam Averages 1.

Nominal Beam (nA) 1.00000

Change the Nominal Beam to modify the normalization constant used for the x-ray intensity display. For example, enter 1 (nA) for cps/nA intensity display.

Return To On-Peak Time 4 secs

Crystal Flip Time 0 secs

Set Column (TKCS) Time 10 secs

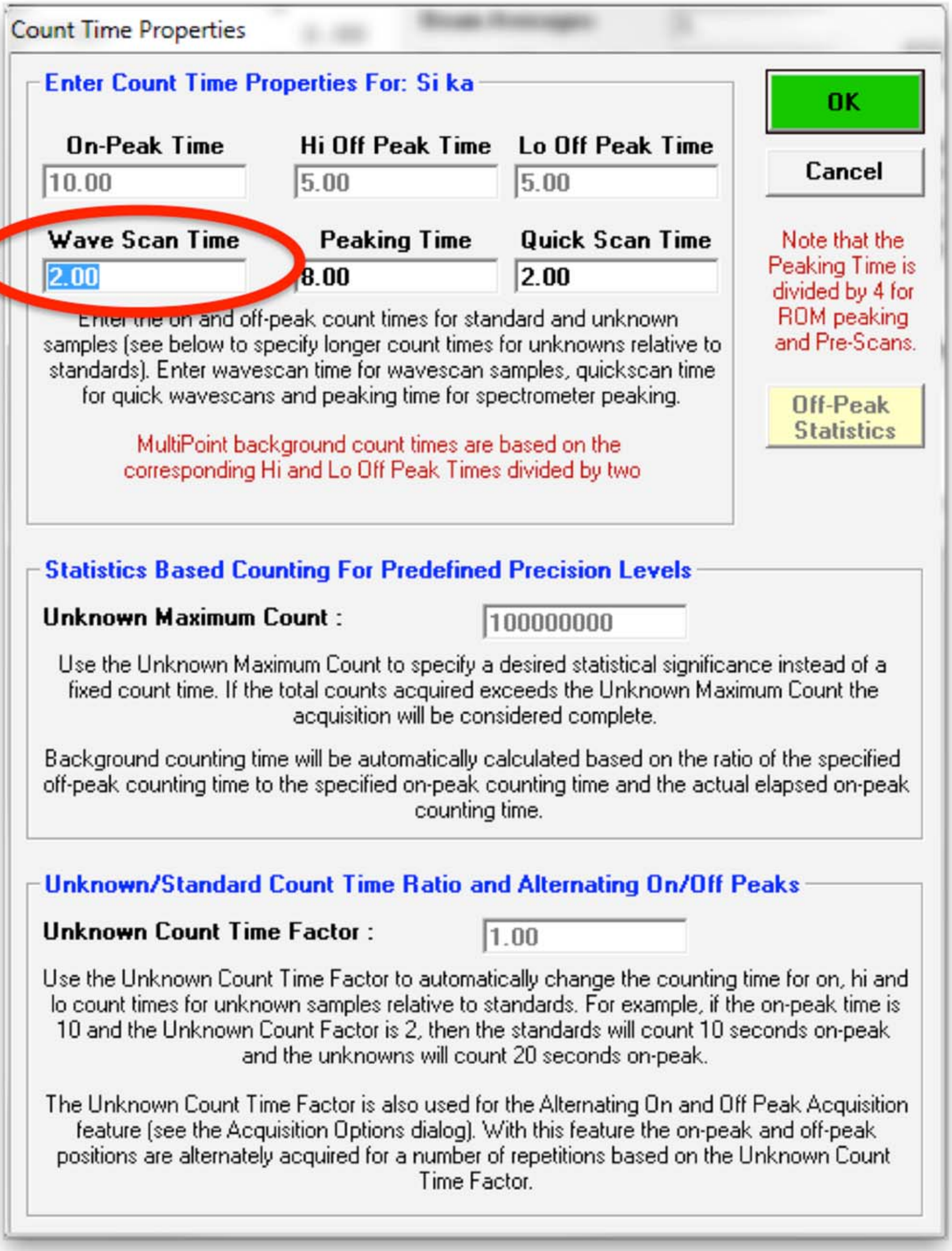
416 secs
6 min

Calculated Spectrometer Motion and Acquisition Time

0 secs

Click on the appropriate element row to open the **Count Time Properties** dialog box.

Edit the *Wave Scan Time* as desired and then click the **OK** button to close.



On-Peak Time: 10.00
Hi Off Peak Time: 5.00
Lo Off Peak Time: 5.00
Wave Scan Time: 2.00
Peaking Time: 8.00
Quick Scan Time: 2.00

Enter the on and off-peak count times for standard and unknown samples (see below to specify longer count times for unknowns relative to standards). Enter wavescan time for wavescan samples, quickscan time for quick wavescans and peaking time for spectrometer peaking.

MultiPoint background count times are based on the corresponding Hi and Lo Off Peak Times divided by two

Note that the Peaking Time is divided by 4 for ROM peaking and Pre-Scans.

Unknown Maximum Count : 100000000

Use the Unknown Maximum Count to specify a desired statistical significance instead of a fixed count time. If the total counts acquired exceeds the Unknown Maximum Count the acquisition will be considered complete.

Background counting time will be automatically calculated based on the ratio of the specified off-peak counting time to the specified on-peak counting time and the actual elapsed on-peak counting time.

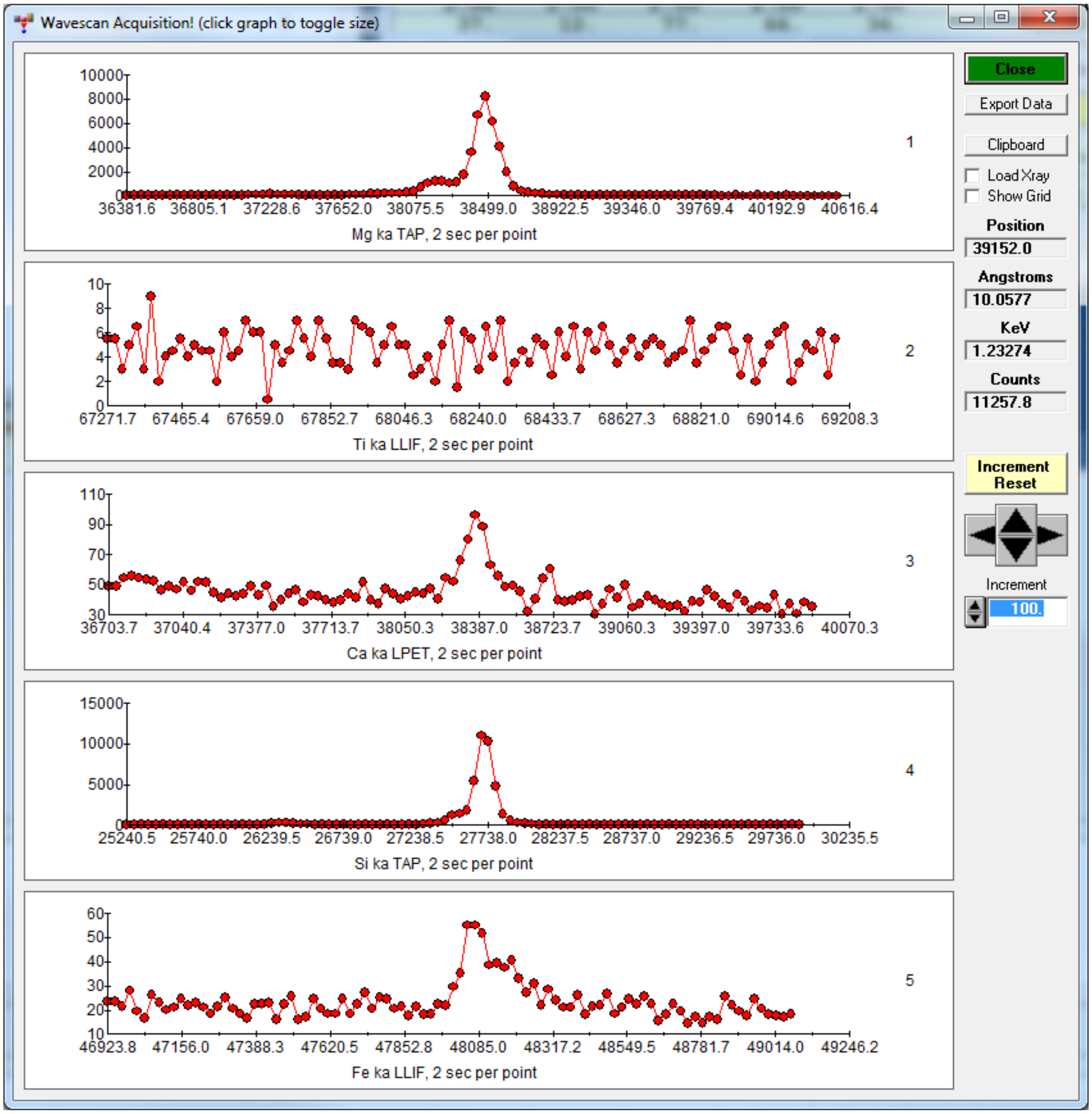
Unknown Count Time Factor : 1.00

Use the Unknown Count Time Factor to automatically change the counting time for on, hi and lo count times for unknown samples relative to standards. For example, if the on-peak time is 10 and the Unknown Count Factor is 2, then the standards will count 10 seconds on-peak and the unknowns will count 20 seconds on-peak.

The Unknown Count Time Factor is also used for the Alternating On and Off Peak Acquisition feature (see the Acquisition Options dialog). With this feature the on-peak and off-peak positions are alternately acquired for a number of repetitions based on the Unknown Count Time Factor.

Click the **OK** button to close the **Count Times** window.

Click the **Start Wavescan** button in the **Acquire!** window to initiate the calibrated multi-element wavescan. The **Wavescan Acquisition** window opens. The program will automatically start acquiring the wavescan ranges selected. If more than one element is assigned to a given spectrometer, the program will automatically go to the next element's wavescan range after the previous wavescan element range is completed. The order of acquisition is defined in the **Acquisition Options** window. Below illustrates a wavescan acquisition.



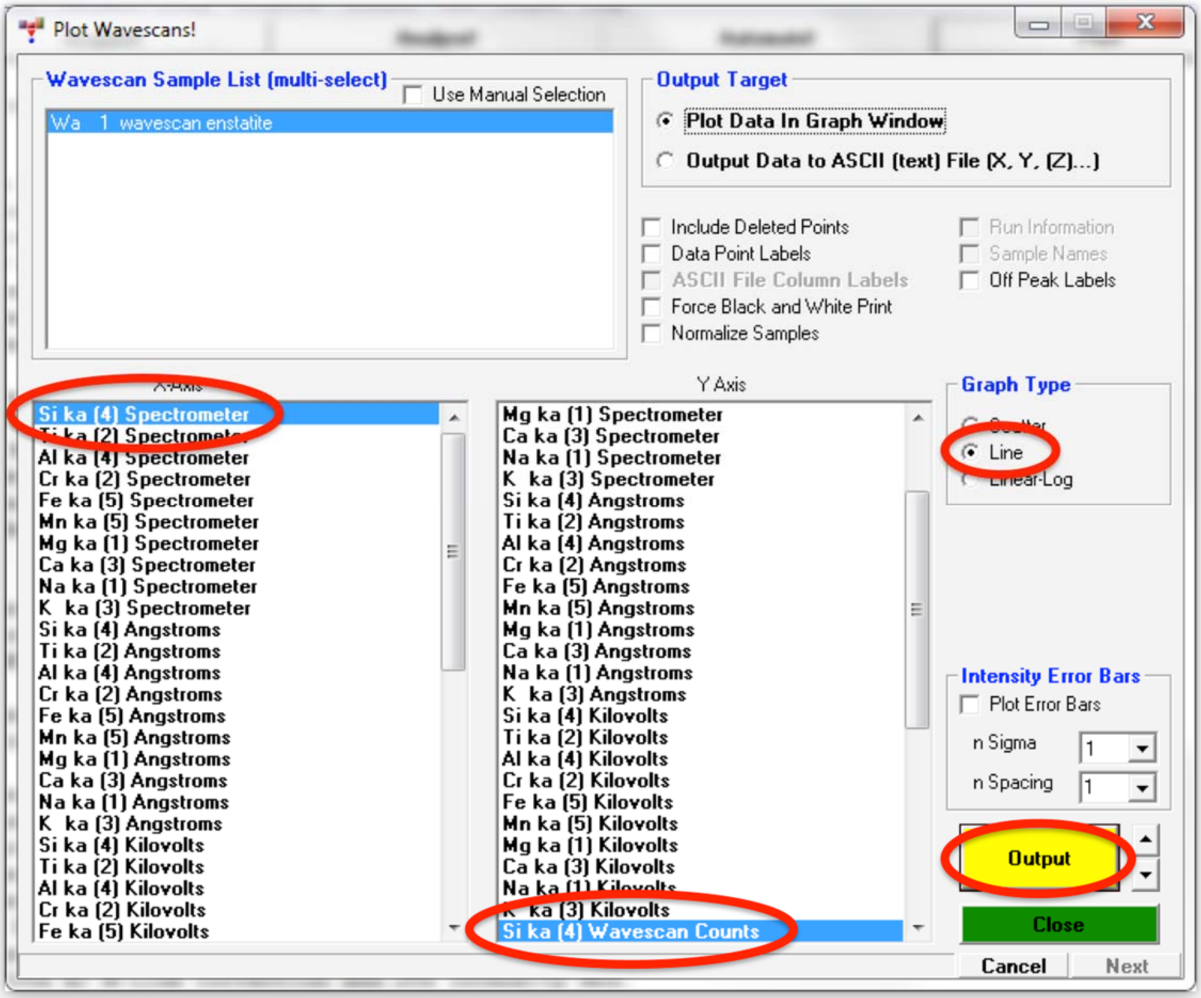
Position 39152.0
Angstroms 10.0577
KeV 1.23274
Counts 11257.8
Increment 100.

As the wavescan is acquiring data, the wavescan graph may be viewed in greater detail by clicking on the graph to toggle/expand the display size.

The *Position* (spectrometer units), *Angstroms*, and *Counts* in any channel may be read by placing the cursor on the graph. Selecting the *Load Xray* check box and clicking the graph, loads the NIST x-ray database.

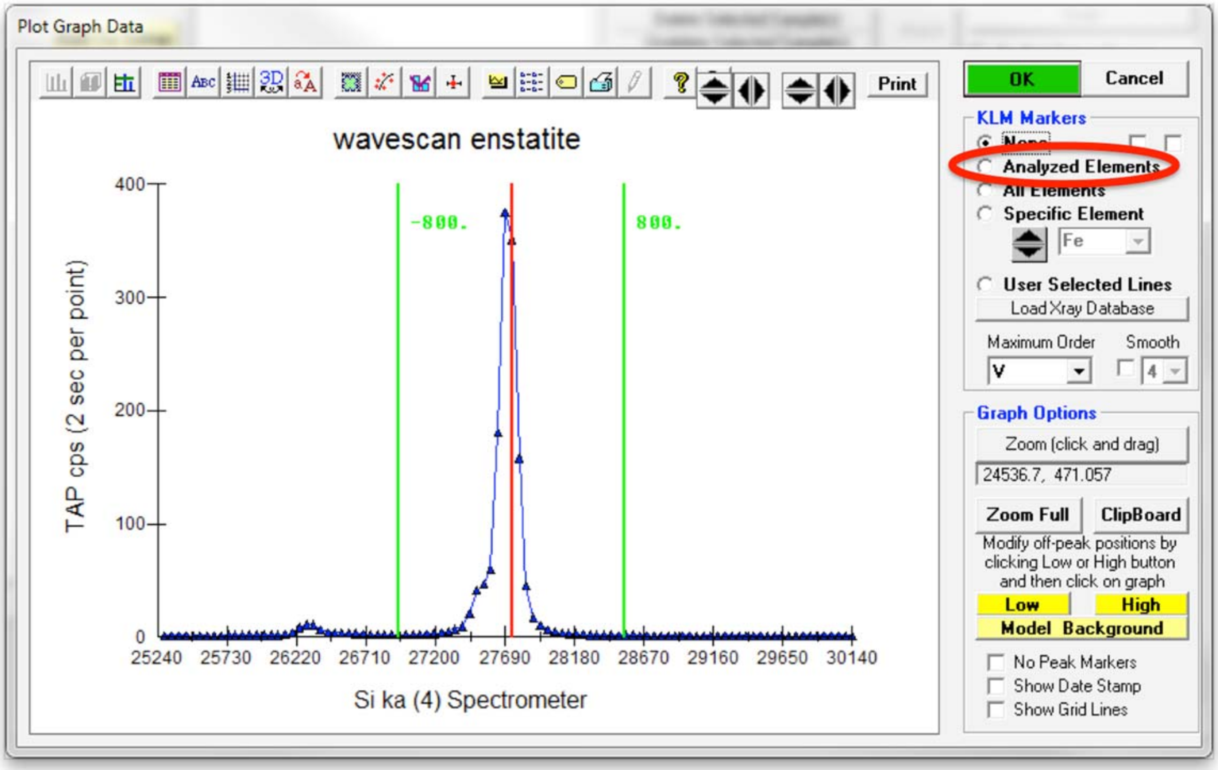
After all wavescans have been acquired on the sample, the user would typically inspect off-peak interferences and background locations by using the **Plot!** window. Note that if more than 100 points were acquired in a wavescan be sure to highlight all of the “continued” samples associated with the wavescan.

Select an *X-Axis* parameter (normally a specific spectrometer) and a *Y-Axis* parameter (normally the associated wavescan counts). The number (X) after the element in each *List* designates the spectrometer employed to collect the data. Finally, click the *Line* check button under *Graph Type*.



Click the **Output** button to graph the wavescan.

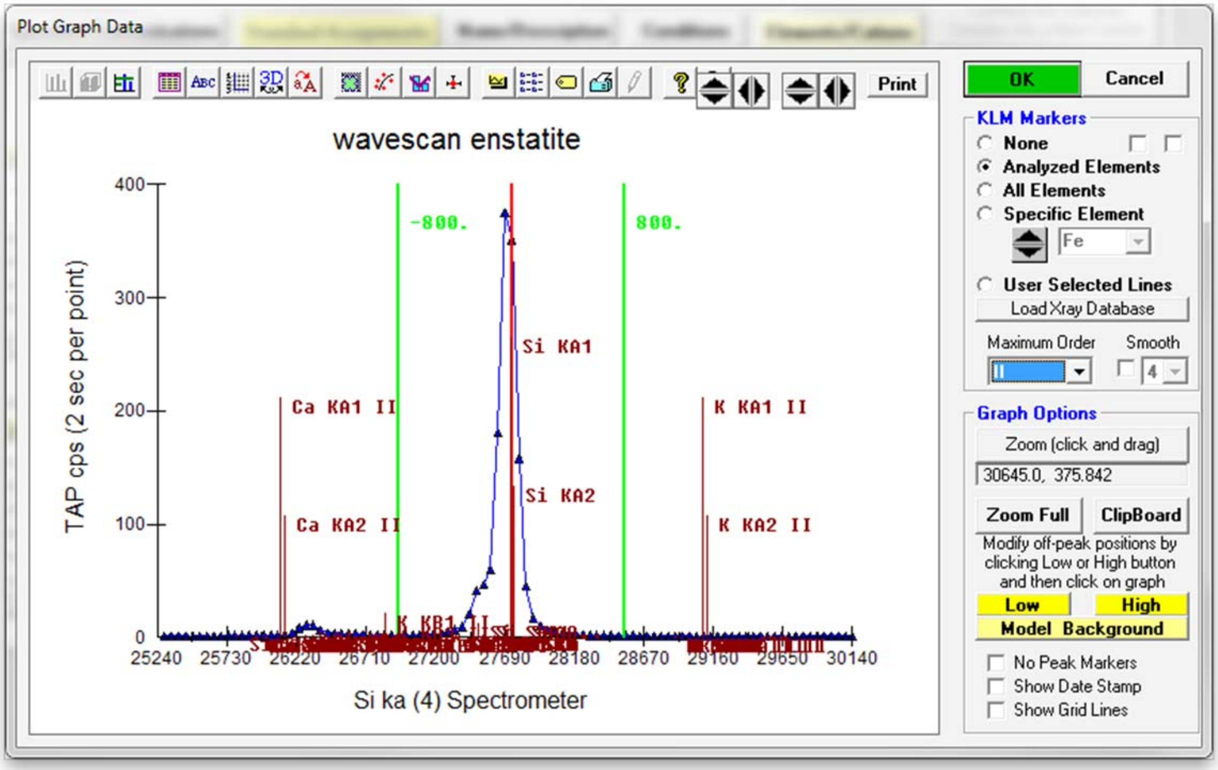
The **Plot Graph Data** window opens displaying the plotted components. The currently selected off-peak positions for background measurements are also indicated (green).



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

To evaluate potential interferences select a *KLM Markers* option (*Analyzed Elements* check button, for instance) to view the KLM markers or use the **Load Xray Database** button.

The **Plot Graph Data** window open below illustrates this powerful feature and the identification of the small x-ray peaks (satellite lines) to the high-energy side of the main silicon x-ray peak.



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

Maximum Order: II
Smooth: ☐ 4

Zoom (click and drag): 30645.0, 375.842

☐ No Peak Markers
☐ Show Date Stamp
☐ Show Grid Lines

The off-peak positions for background determinations for quantitative samples are adjusted with the **Low** and **High** buttons (located lower right of **Plot Graph Data** window).

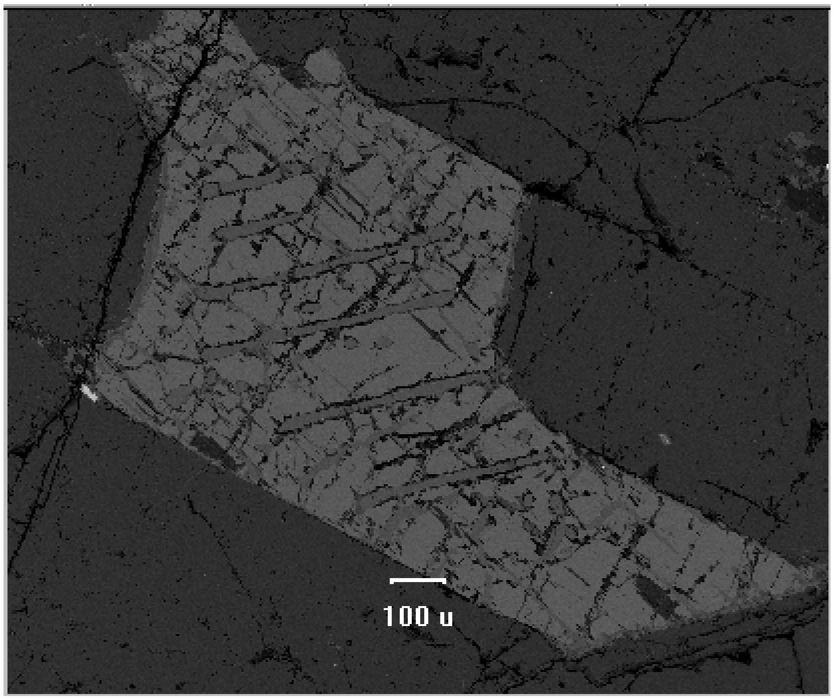
Click and drag the mouse to **Zoom** in on any portion of the graph.

This window can also be used to adjust off-peak positions, for example in case of spectral interferences. For more details, see the section on **Wavescan Acquisitions and Off-Peak Adjustments** in the **Probe For EPMA User's Guide to Getting Started** document.

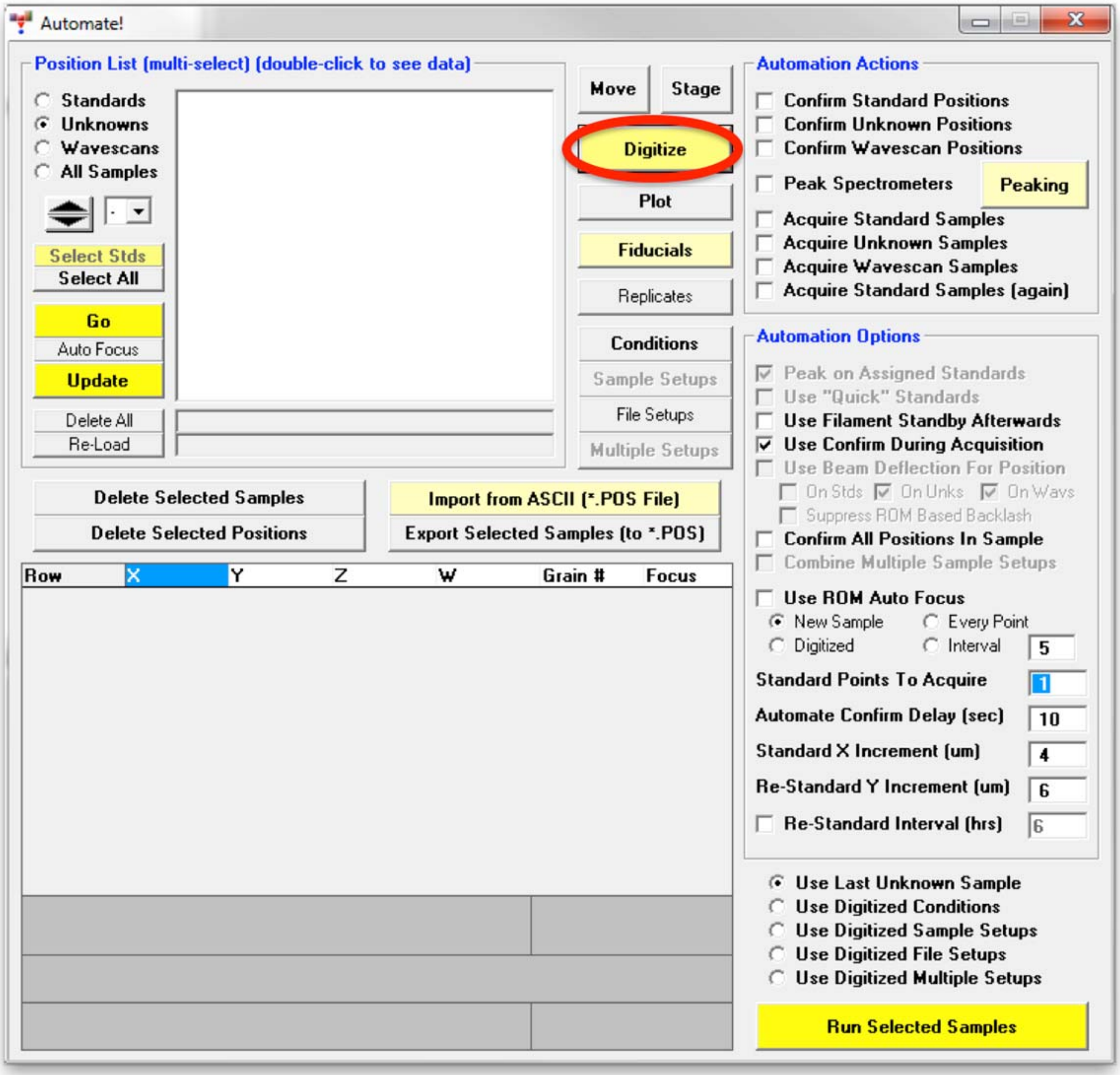
Polygon Gridding – Using Surfer Option

Another useful feature of PROBE FOR EPMA is the ability to perform automated polygon gridded analyses of unknowns. After acquiring the digitized data set, PROBE FOR EPMA can create a script file (if the SURFER.BAS file option is selected in the **Plot!** window) for use with Golden Software SURFER to automatically generate contour, surface and *.GRD concentration files of your data. These *.GRD files can be imported into the CALCIMAGE application for viewing in false color or further processing. The images will be quantitatively registered during the import process so that color represents elemental or oxide concentration.

In this example an unknown and complexly exsolved pyroxene (see image below) will be gridded and digitized, then run quantitatively. Move to the unknown grain location.



Click the **Digitize** button of the **Automate!** window.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

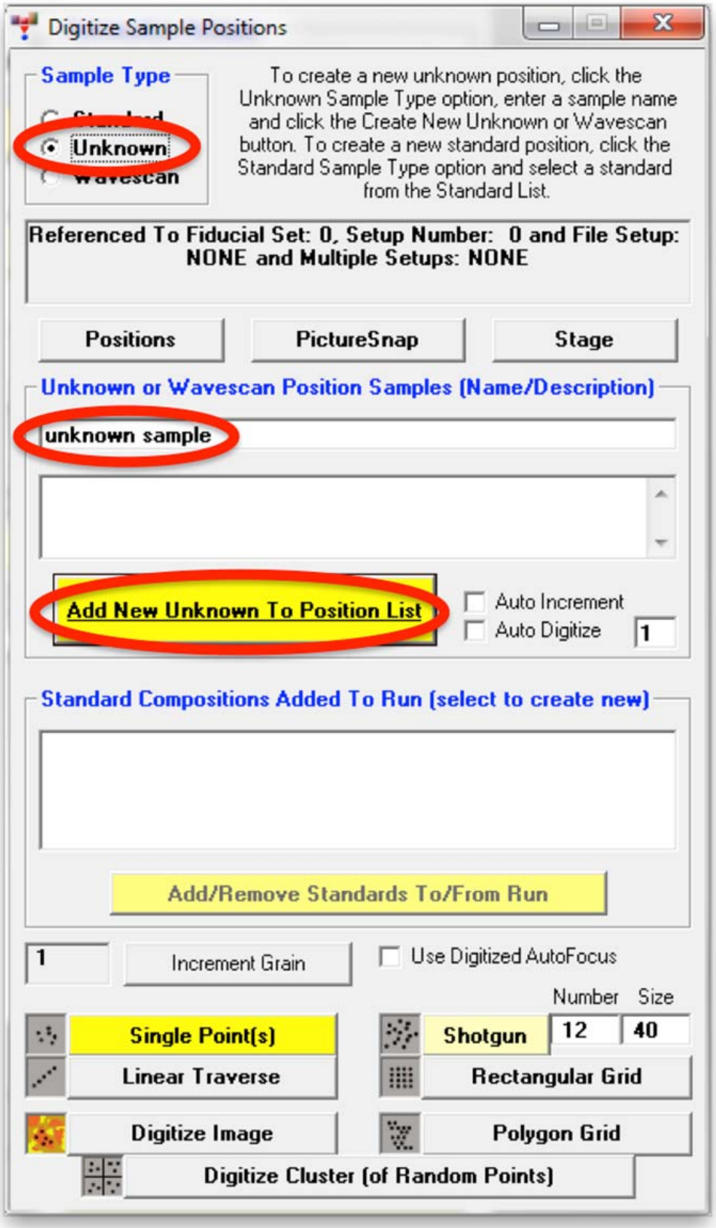
☐ Confirm Standard Positions
☐ Confirm Unknown Positions
☐ Confirm Wavescan Positions
☐ Peak Spectrometers
☐ Acquire Standard Samples
☐ Acquire Unknown Samples
☐ Acquire Wavescan Samples
☐ Acquire Standard Samples (again)

☑ Peak on Assigned Standards
☐ Use "Quick" Standards
☐ Use Filament Standby Afterwards
☑ Use Confirm During Acquisition
☐ Use Beam Deflection For Position
☐ On Stds ☑ On Unks ☑ On Wavs
☐ Suppress ROM Based Backlash
☐ Confirm All Positions In Sample
☐ Combine Multiple Sample Setups
☐ Use ROM Auto Focus
● New Sample ○ Every Point
○ Digitized ○ Interval 5

Standard Points To Acquire 1
Automate Confirm Delay (sec) 10
Standard X Increment (um) 4
Re-Standard Y Increment (um) 6
☐ Re-Standard Interval (hrs) 6

● Use Last Unknown Sample
○ Use Digitized Conditions
○ Use Digitized Sample Setups
○ Use Digitized File Setups
○ Use Digitized Multiple Setups

The **Digitize Sample Positions** window opens.



Digitize Sample Positions

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 or Wavescan Position Samples (Name/Description): unknown sample

☐ Auto Increment
☐ Auto Digitize: 1

Standard Compositions Added To Run (select to create new)

Increment Grain: 1

☐ Use Digitized AutoFocus

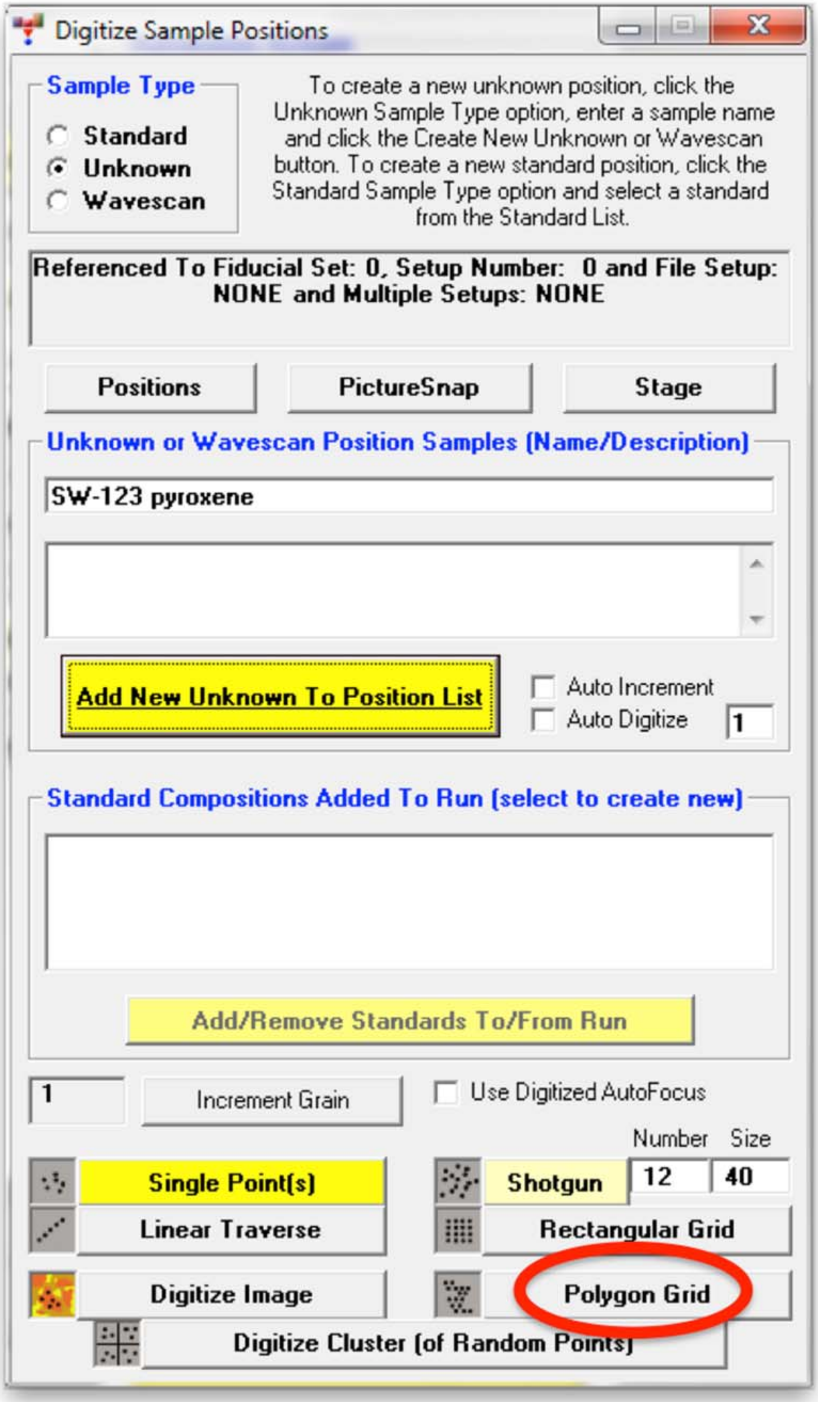
Shotgun: Number 12, Size 40

Select the *Unknown* check button from the *Sample Type* choices.

Enter a new sample name in the *Unknown or Wavescan Position Samples* text field, and click the **Add New Unknown To Position List** button.

A digitized polygon area grid will now be setup on the unknown grain.

Click the **Polygon Grid** button at the bottom of the **Digitize Sample Positions** window.



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

Sample Type: ○ Standard ● Unknown ○ Wavescan

Unknown or Wavescan Position Samples (Name/Description): SW-123 pyroxene

☐ Auto Increment

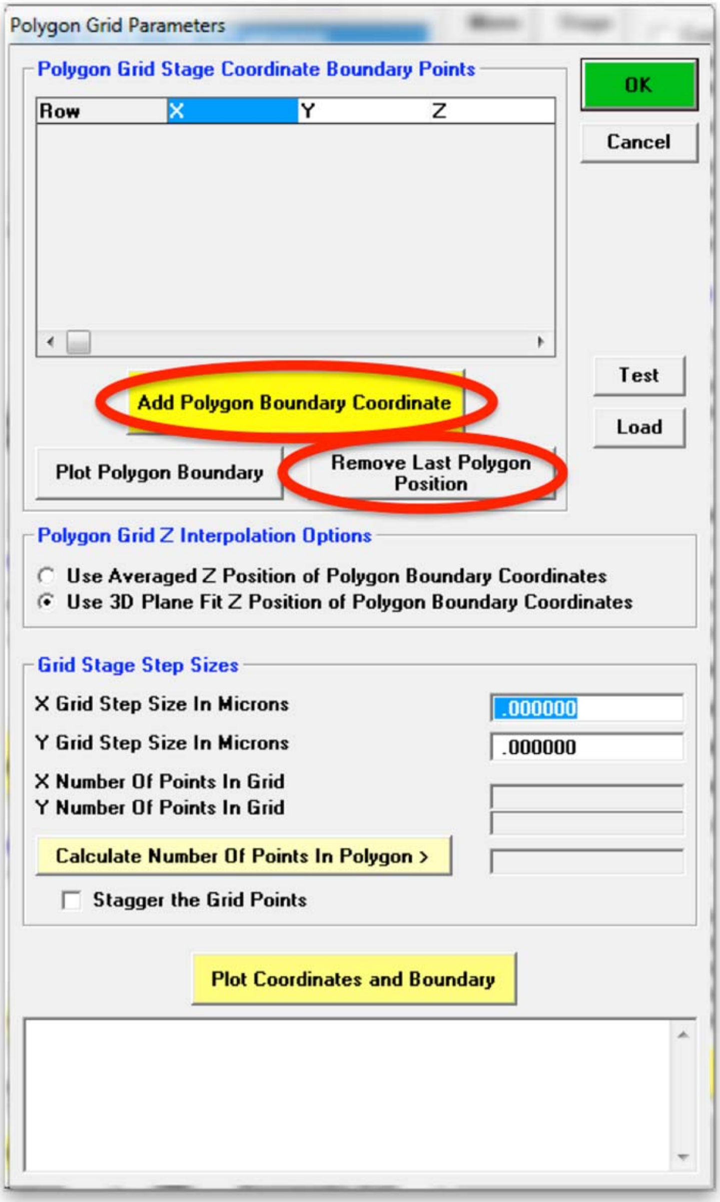
☐ Auto Digitize: 1

Increment Grain: 1

☐ Use Digitized AutoFocus

Shotgun: Number 12, Size 40

The **Polygon Grid Parameters** window opens.



Row	X	Y	Z

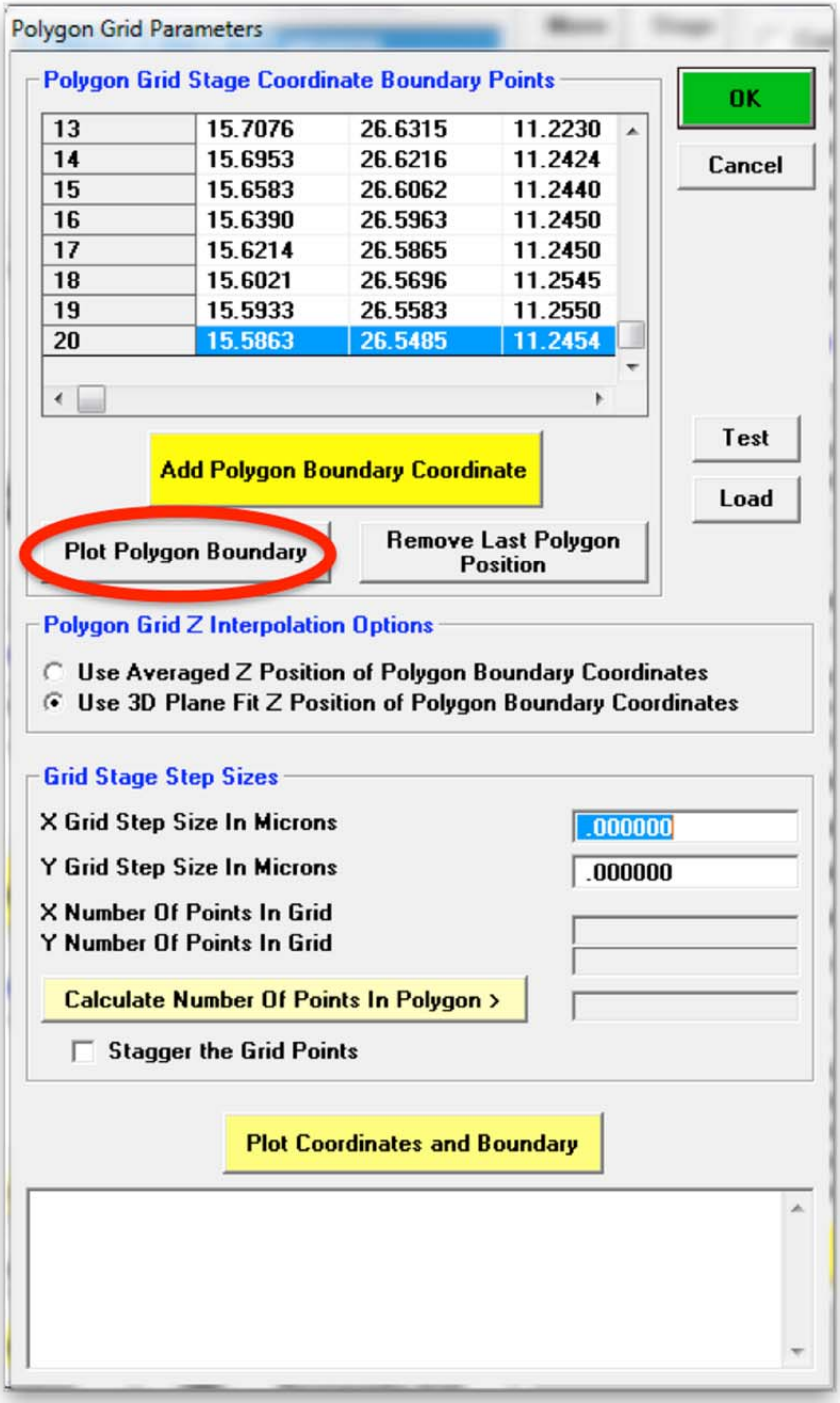
○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

X Grid Step Size In Microns: .000000
Y Grid Step Size In Microns: .000000

☐ Stagger the Grid Points

The user will outline the perimeter of the grain to be gridded. An easy way to accomplish this is to image the grain with backscattered electrons, at any magnification, and trace around the grain boundary. Start in one corner and on a recognizable feature, click the **Add Polygon Boundary Coordinate** button and then move linearly toward another feature or edge, clicking the **Add Polygon Boundary Coordinate** button to outline this portion of the grain. Continue to trace line segments around the grain, clicking the **Add Polygon Boundary Coordinate** button to enclose another portion of the grain. Eventually, returning to the starting point, completing the enclosure. If a mistake is made or you simply wish to remove the previous boundary point, click the **Remove Last Polygon Position** button.

In this example, twenty line segments were used to enclose the grain of interest. Each end point is listed in the *Polygon Grid Stage Coordinate Boundary Points* text box.



13	15.7076	26.6315	11.2230
14	15.6953	26.6216	11.2424
15	15.6583	26.6062	11.2440
16	15.6390	26.5963	11.2450
17	15.6214	26.5865	11.2450
18	15.6021	26.5696	11.2545
19	15.5933	26.5583	11.2550
20	15.5863	26.5485	11.2454

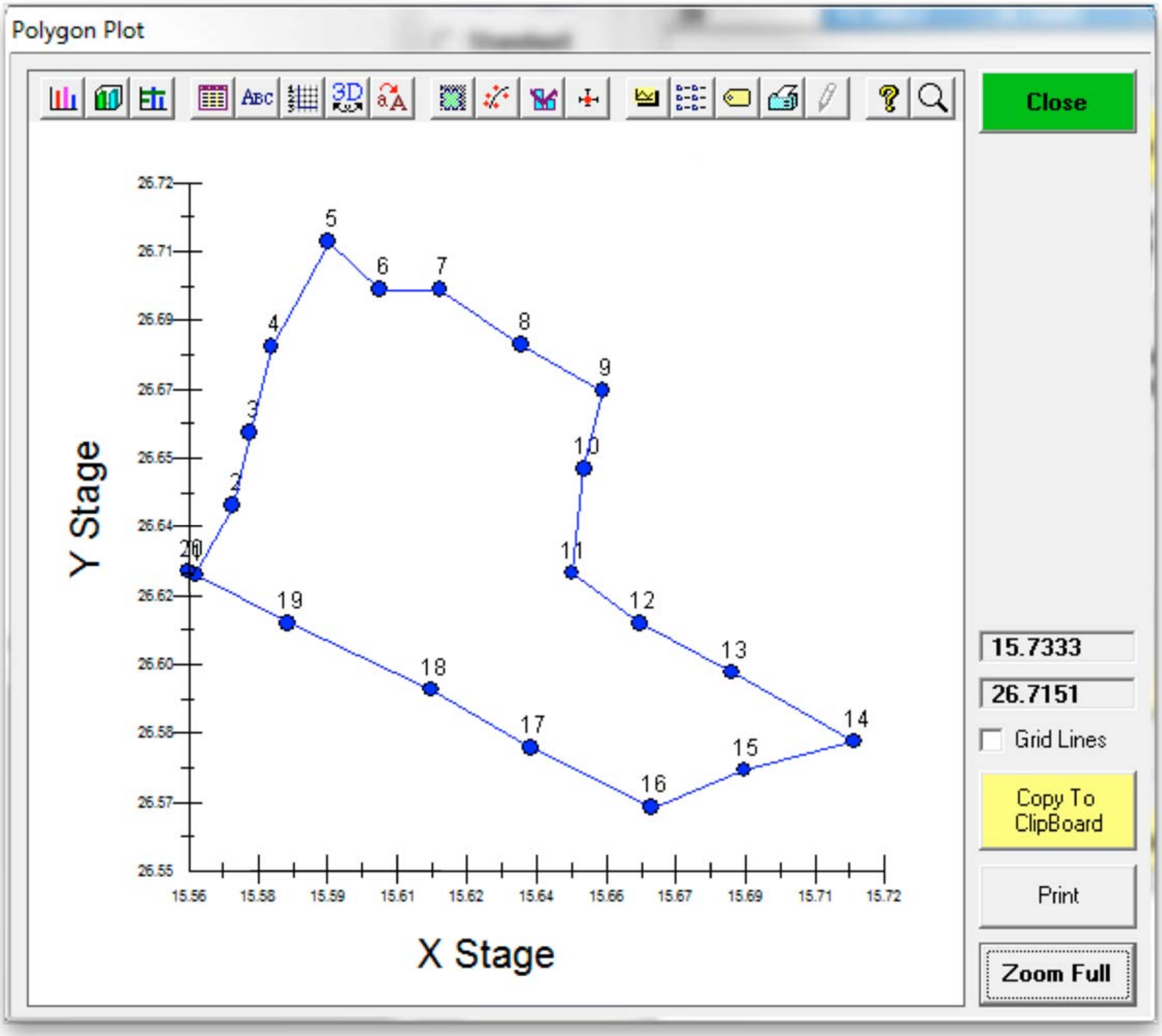
○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

X Grid Step Size In Microns .000000
Y Grid Step Size In Microns .000000
X Number Of Points In Grid
Y Number Of Points In Grid

☐ Stagger the Grid Points

Click the **Plot Polygon Boundary** button to inspect the perimeter just drawn.

To start over and re-draw the perimeter outline again, click the **Close** button on the **Polygon Plot** window, click the **Cancel** button of the **Polygon Grid Parameters** window, and the click the **Polygon Grid** button of the **Digitize Sample Positions** window.



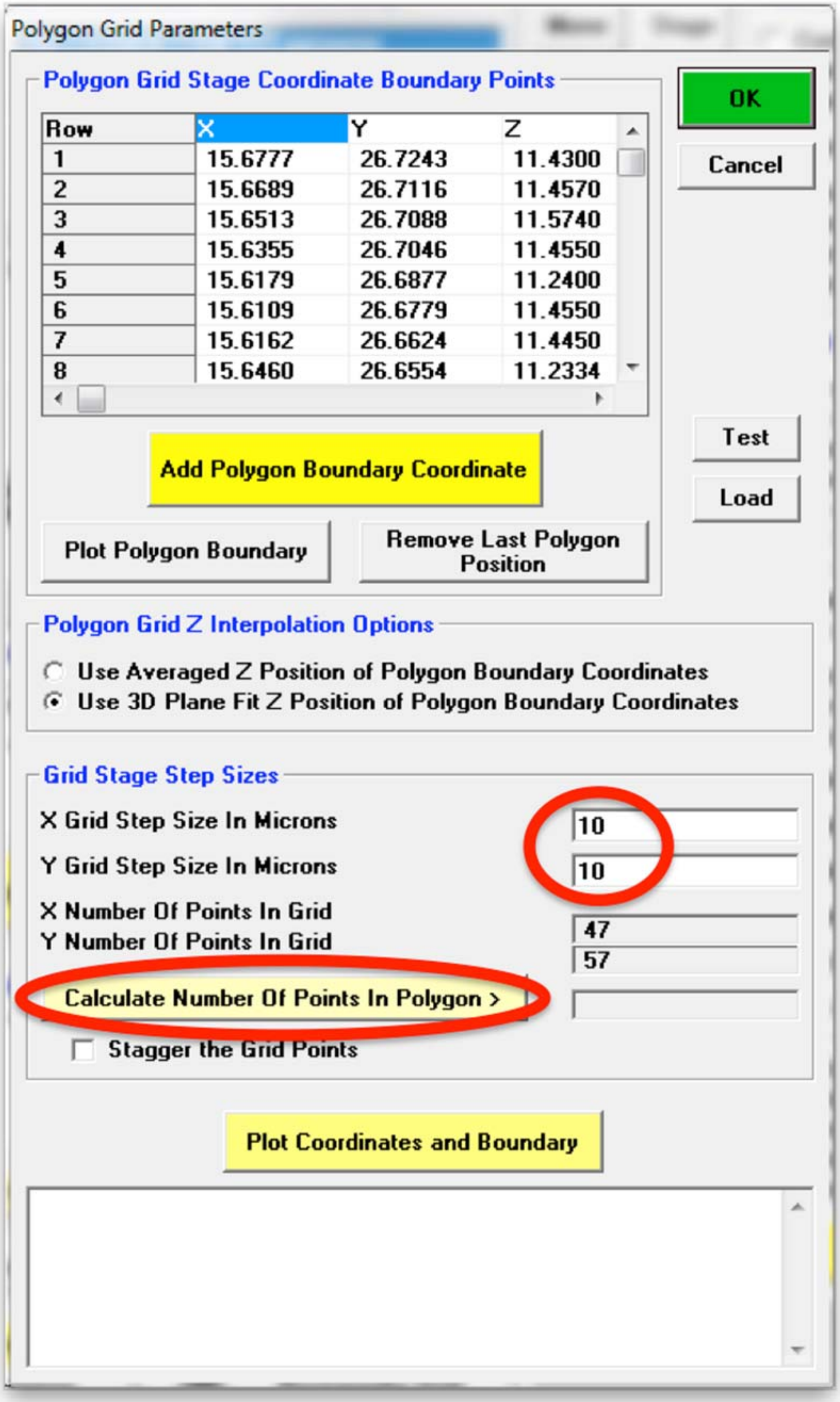
15.7333

26.7151

☐ Grid Lines

When satisfied with the outline of the grid, click the **Close** button of the **Polygon Plot** window.

Enter *Grid Stage Step Sizes* (in microns) for both X and Y.



Polygon Grid Stage Coordinate Boundary Points

Row	X	Y	Z
1	15.6777	26.7243	11.4300
2	15.6689	26.7116	11.4570
3	15.6513	26.7088	11.5740
4	15.6355	26.7046	11.4550
5	15.6179	26.6877	11.2400
6	15.6109	26.6779	11.4550
7	15.6162	26.6624	11.4450
8	15.6460	26.6554	11.2334

Polygon Grid Z Interpolation Options

○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

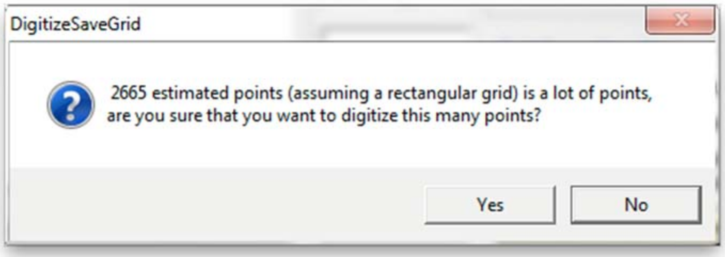
Grid Stage Step Sizes

X Grid Step Size In Microns: 10
Y Grid Step Size In Microns: 10
X Number Of Points In Grid: 47
Y Number Of Points In Grid: 57

☐ Stagger the Grid Points

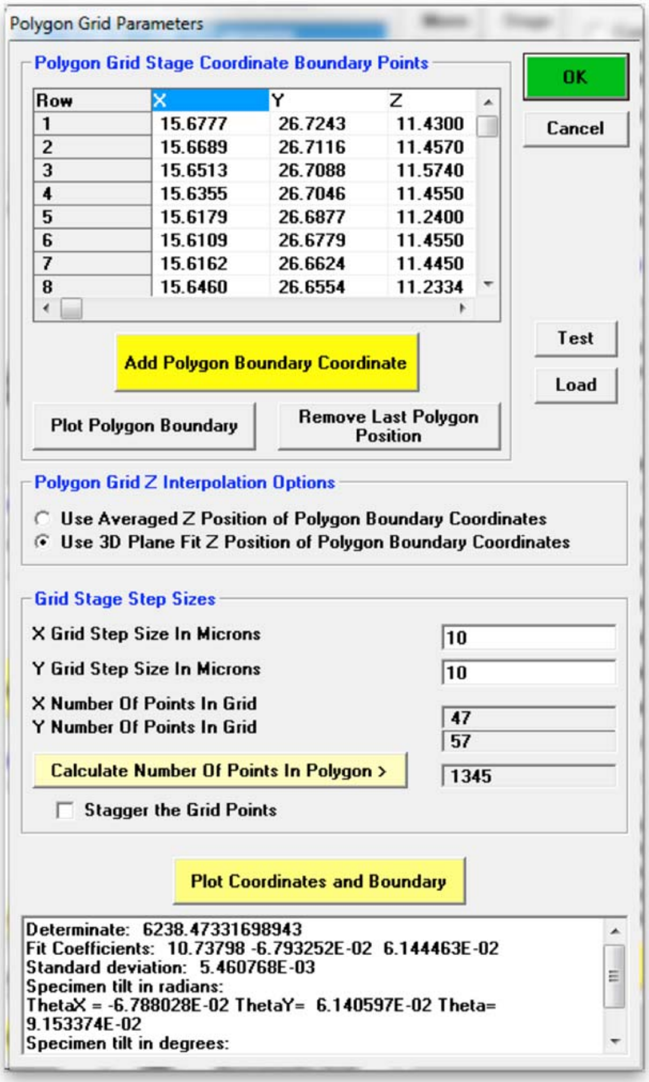
Click the **Calculate Number of Points in Polygon>** button to determine how many data points will be digitized. Readjust the *X and Y Grid Step Sizes* if necessary. Select a method of Z determination from the two option buttons under *Polygon Grid Z Interpolation Options*.

The **DigitizeSaveGrid** window appears with the number of points in an ideal rectangular grid.



2665 estimated points (assuming a rectangular grid) is a lot of points, are you sure that you want to digitize this many points?

Click the **Yes** button to calculate the total number of points.



Polygon Grid Stage Coordinate Boundary Points

Row	X	Y	Z
1	15.6777	26.7243	11.4300
2	15.6689	26.7116	11.4570
3	15.6513	26.7088	11.5740
4	15.6355	26.7046	11.4550
5	15.6179	26.6877	11.2400
6	15.6109	26.6779	11.4550
7	15.6162	26.6624	11.4450
8	15.6460	26.6554	11.2334

Polygon Grid Z Interpolation Options

○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

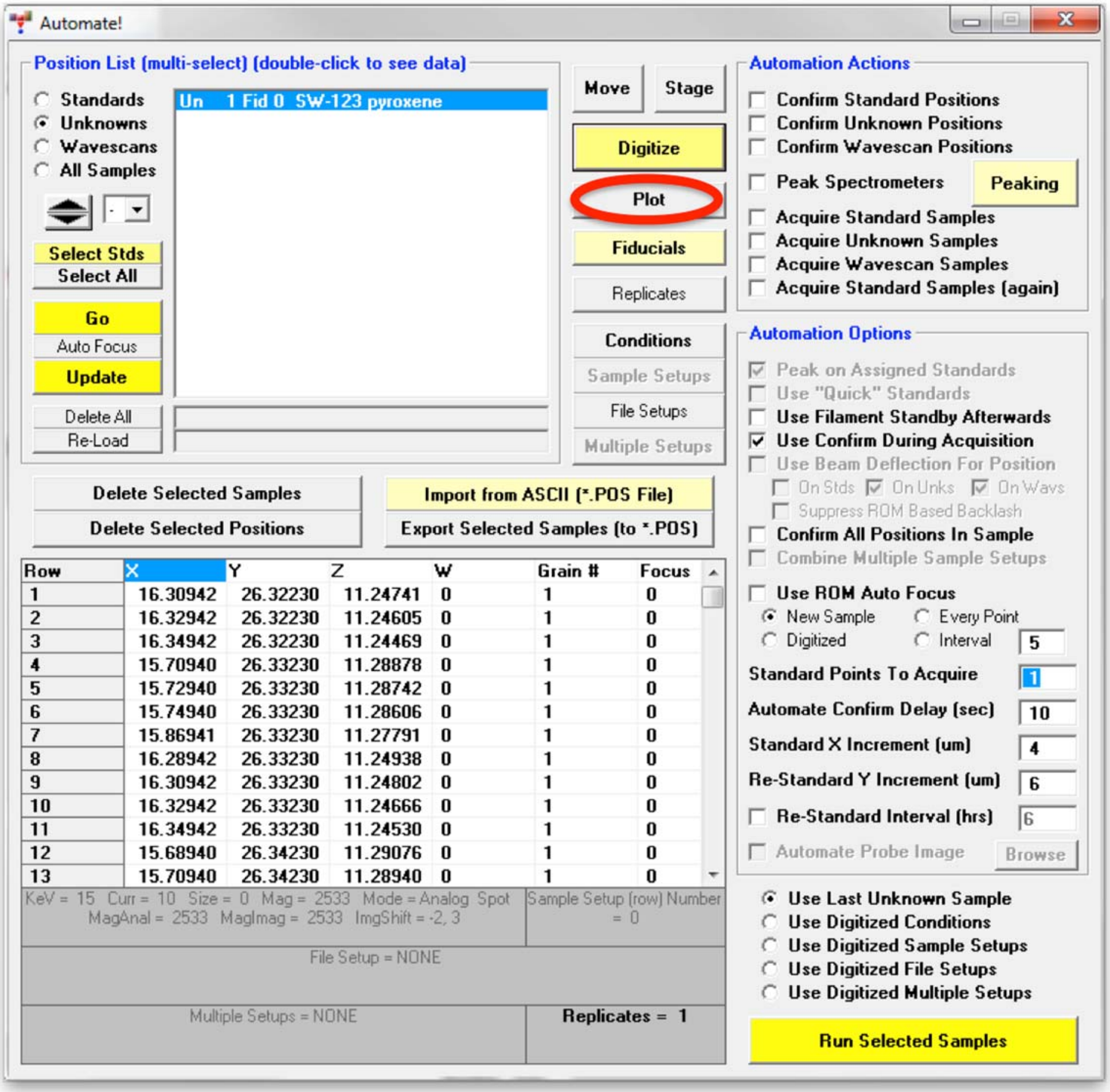
Grid Stage Step Sizes

X Grid Step Size In Microns: 10
Y Grid Step Size In Microns: 10
X Number Of Points In Grid: 47
Y Number Of Points In Grid: 57
Calculate Number Of Points In Polygon > 1345
☐ Stagger the Grid Points

```
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:
```

When the appropriate gridding parameters have been set, click the **OK** button, closing the **Polygon Grid Parameters** window. The **DigitizeSaveGrid** window re-appears, click the **Yes** button.

The program automatically digitizes each of the number of points in the polygon and returns to the **Automate!** window.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 Fid 0 SW-123 pyroxene

Row	X	Y	Z	W	Grain #	Focus
1	16.30942	26.32230	11.24741	0	1	0
2	16.32942	26.32230	11.24605	0	1	0
3	16.34942	26.32230	11.24469	0	1	0
4	15.70940	26.33230	11.28878	0	1	0
5	15.72940	26.33230	11.28742	0	1	0
6	15.74940	26.33230	11.28606	0	1	0
7	15.86941	26.33230	11.27791	0	1	0
8	16.28942	26.33230	11.24938	0	1	0
9	16.30942	26.33230	11.24802	0	1	0
10	16.32942	26.33230	11.24666	0	1	0
11	16.34942	26.33230	11.24530	0	1	0
12	15.68940	26.34230	11.29076	0	1	0
13	15.70940	26.34230	11.28940	0	1	0

KeV = 15 Curr = 10 Size = 0 Mag = 2533 Mode = Analog Spot MagAnal = 2533 MagImag = 2533 ImgShift = -2, 3

Sample Setup (row) Number = 0

File Setup = NONE

Multiple Setups = NONE

Replicates = 1

Automation Actions

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

Automation Options

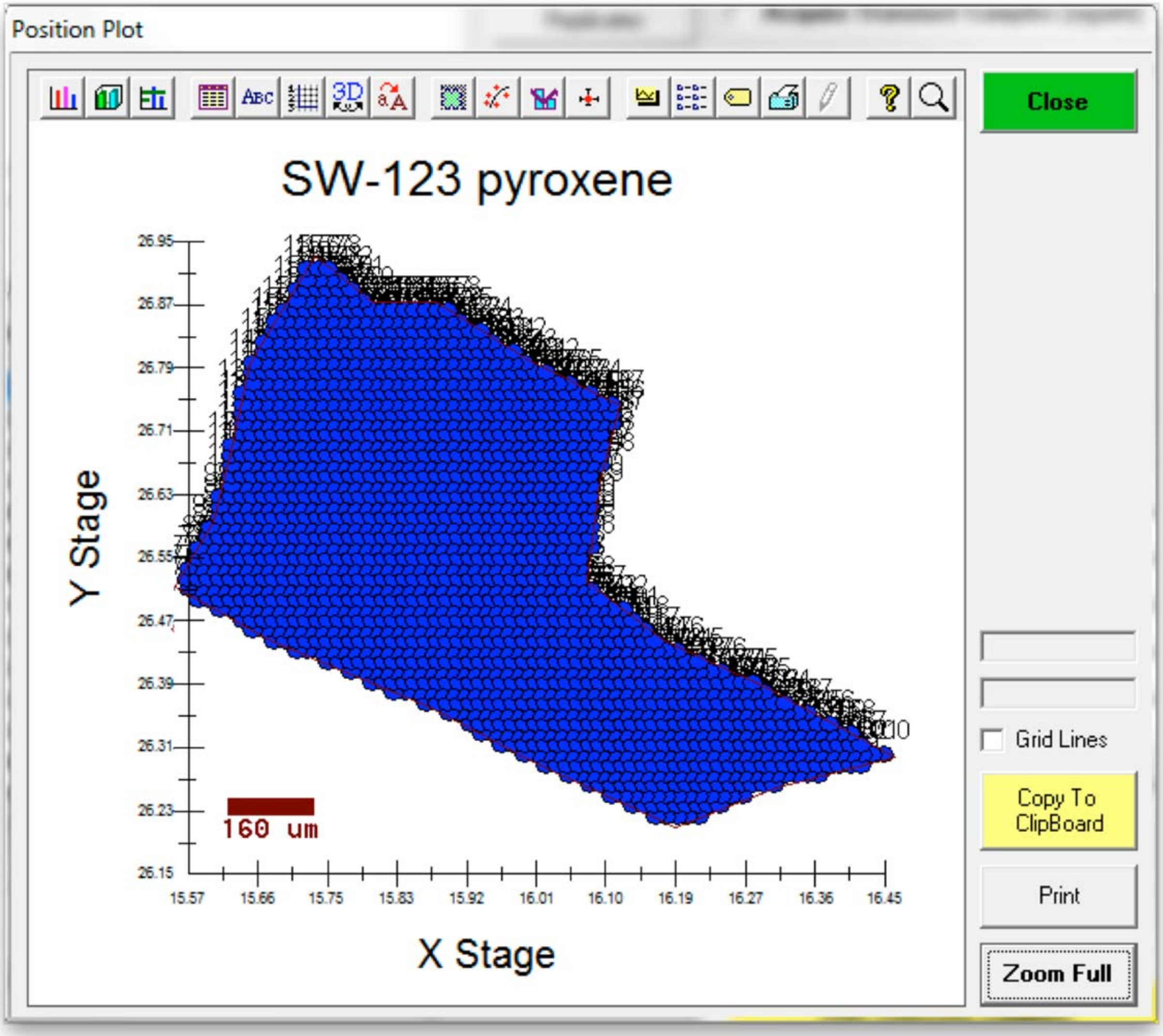
☑ Peak on Assigned Standards
☐ Use "Quick" Standards
☐ Use Filament Standby Afterwards
☑ Use Confirm During Acquisition
☐ Use Beam Deflection For Position
☐ On Stds ☑ On Unks ☑ On Wavs
☐ Suppress ROM Based Backlash
☐ Confirm All Positions In Sample
☐ Combine Multiple Sample Setups
☐ Use ROM Auto Focus
● New Sample ○ Every Point
○ Digitized ○ Interval 5

Standard Points To Acquire 1
Automate Confirm Delay (sec) 10
Standard X Increment (um) 4
Re-Standard Y Increment (um) 6
☐ Re-Standard Interval (hrs) 6
☐ Automate Probe Image

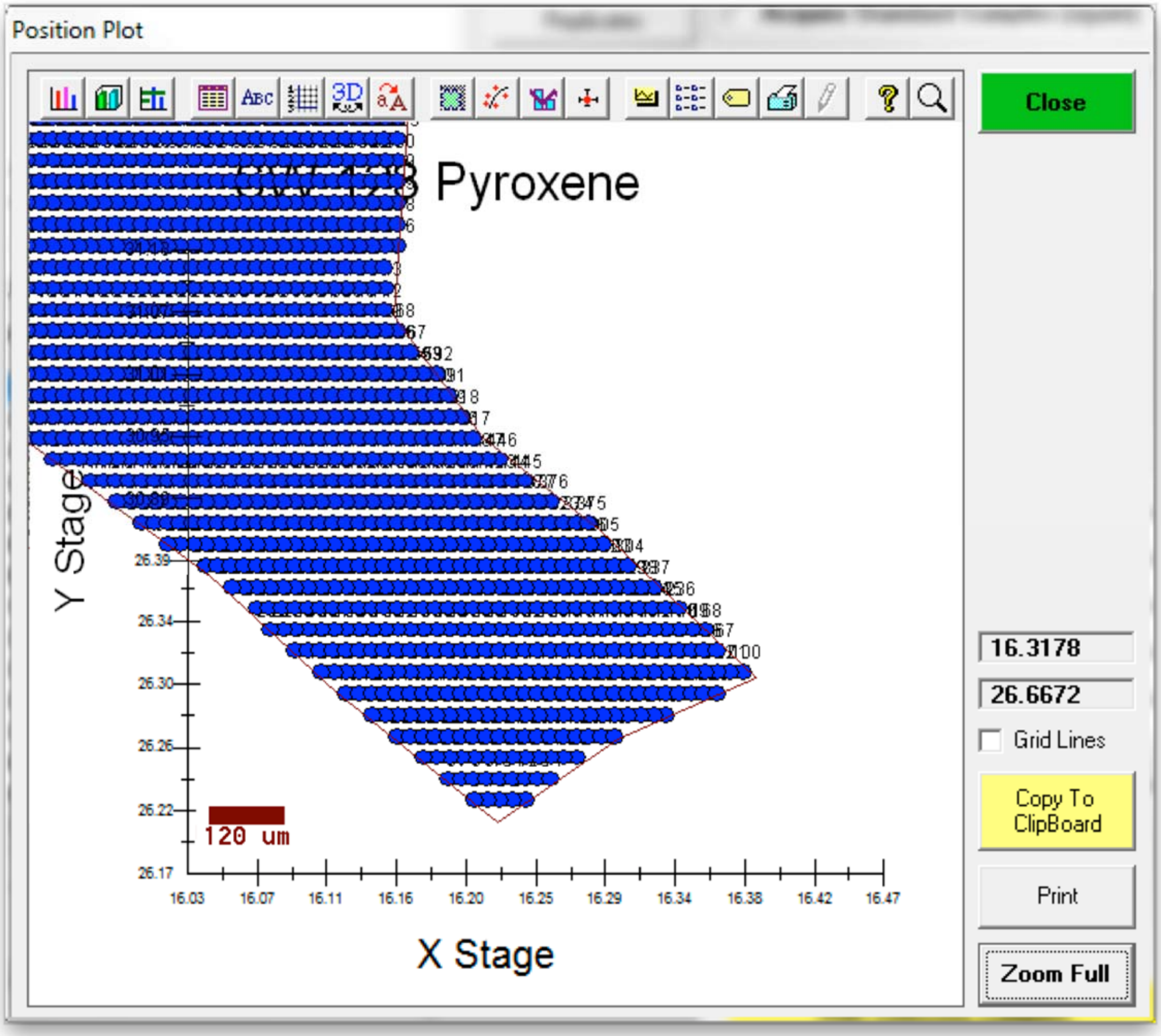
● Use Last Unknown Sample
○ Use Digitized Conditions
○ Use Digitized Sample Setups
○ Use Digitized File Setups
○ Use Digitized Multiple Setups

Click the **Plot** button in the **Automate!** dialog box to open the **Position Plot** window and view the locations of all of the digitized points in this sample.

Click the **Plot** button in the **Automate!** dialog box to open the **Position Plot** window and view the locations of all of the digitized points in this sample. In this example, the 10 micron spacing creates too many points to be individually visible on this view.



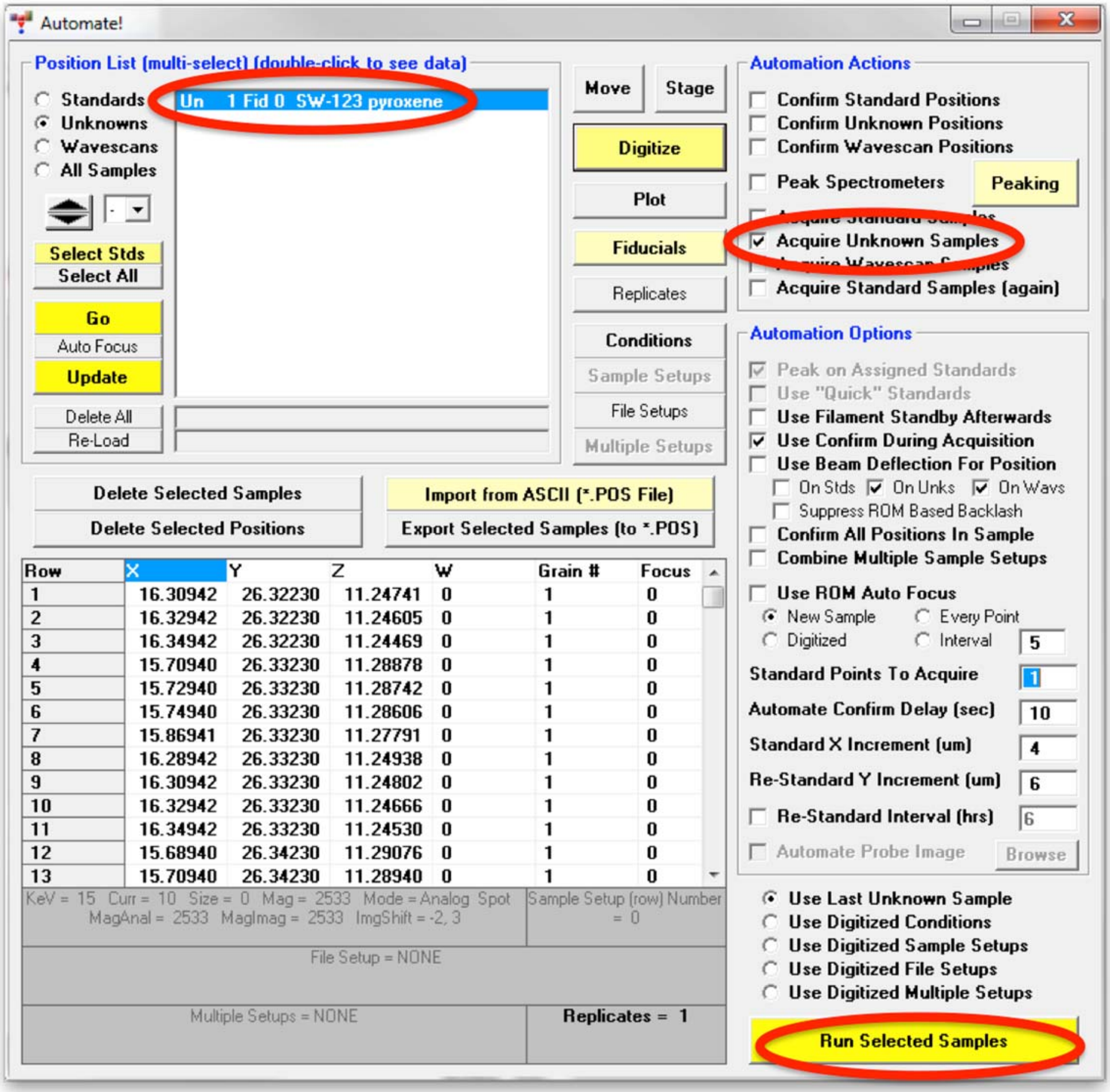
The user may click and drag the mouse to zoom on the plot to expand the scale.



Click the **Close** button of the **Position Plot** window to return to the **Automate!** dialog box.

The user should proceed with calibration and standardization of the elements in the probe run and checking the accuracy of the standardization.

Then, to run the just digitized polygon grid sample from the **Automate!** window, highlight it in the *Position List*. Under the *Automation Actions*, click the *Acquire Unknown Samples* check box. Finally, click the **Run Selected Samples** button.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 Fid 0 SW-123 pyroxene

Row	X	Y	Z	W	Grain #	Focus
1	16.30942	26.32230	11.24741	0	1	0
2	16.32942	26.32230	11.24605	0	1	0
3	16.34942	26.32230	11.24469	0	1	0
4	15.70940	26.33230	11.28878	0	1	0
5	15.72940	26.33230	11.28742	0	1	0
6	15.74940	26.33230	11.28606	0	1	0
7	15.86941	26.33230	11.27791	0	1	0
8	16.28942	26.33230	11.24938	0	1	0
9	16.30942	26.33230	11.24802	0	1	0
10	16.32942	26.33230	11.24666	0	1	0
11	16.34942	26.33230	11.24530	0	1	0
12	15.68940	26.34230	11.29076	0	1	0
13	15.70940	26.34230	11.28940	0	1	0

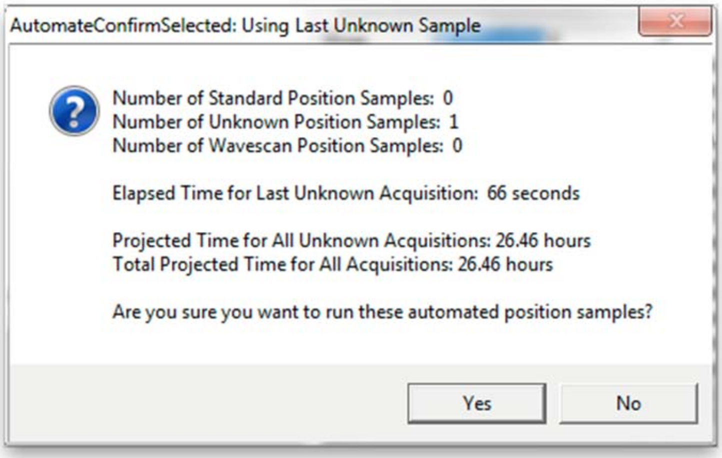
KeV = 15 Curr = 10 Size = 0 Mag = 2533 Mode = Analog Spot
MagAnal = 2533 MagImag = 2533 ImgShift = -2, 3
Sample Setup (row) Number = 0
File Setup = NONE
Multiple Setups = NONE
Replicates = 1

Automation Actions
☐ Confirm Standard Positions
☐ Confirm Unknown Positions
☐ Confirm Wavescan Positions
☐ Peak Spectrometers
☐ Acquire Standard Samples
☑ Acquire Unknown Samples
☐ Acquire Wavescan Samples
☐ Acquire Standard Samples (again)

Automation Options
☑ Peak on Assigned Standards
☐ Use "Quick" Standards
☐ Use Filament Standby Afterwards
☑ Use Confirm During Acquisition
☐ Use Beam Deflection For Position
☐ On Stds ☑ On Unks ☑ On Wavs
☐ Suppress ROM Based Backlash
☐ Confirm All Positions In Sample
☐ Combine Multiple Sample Setups
☐ Use ROM Auto Focus
● New Sample ○ Every Point
○ Digitized ○ Interval 5
Standard Points To Acquire 1
Automate Confirm Delay (sec) 10
Standard X Increment (um) 4
Re-Standard Y Increment (um) 6
☐ Re-Standard Interval (hrs) 6
☐ Automate Probe Image

● Use Last Unknown Sample
○ Use Digitized Conditions
○ Use Digitized Sample Setups
○ Use Digitized File Setups
○ Use Digitized Multiple Setups

The **AutomateConfirmSelected** window opens and the user clicks the **Yes** button to activate the acquisition. The acquisition time is now calculated.



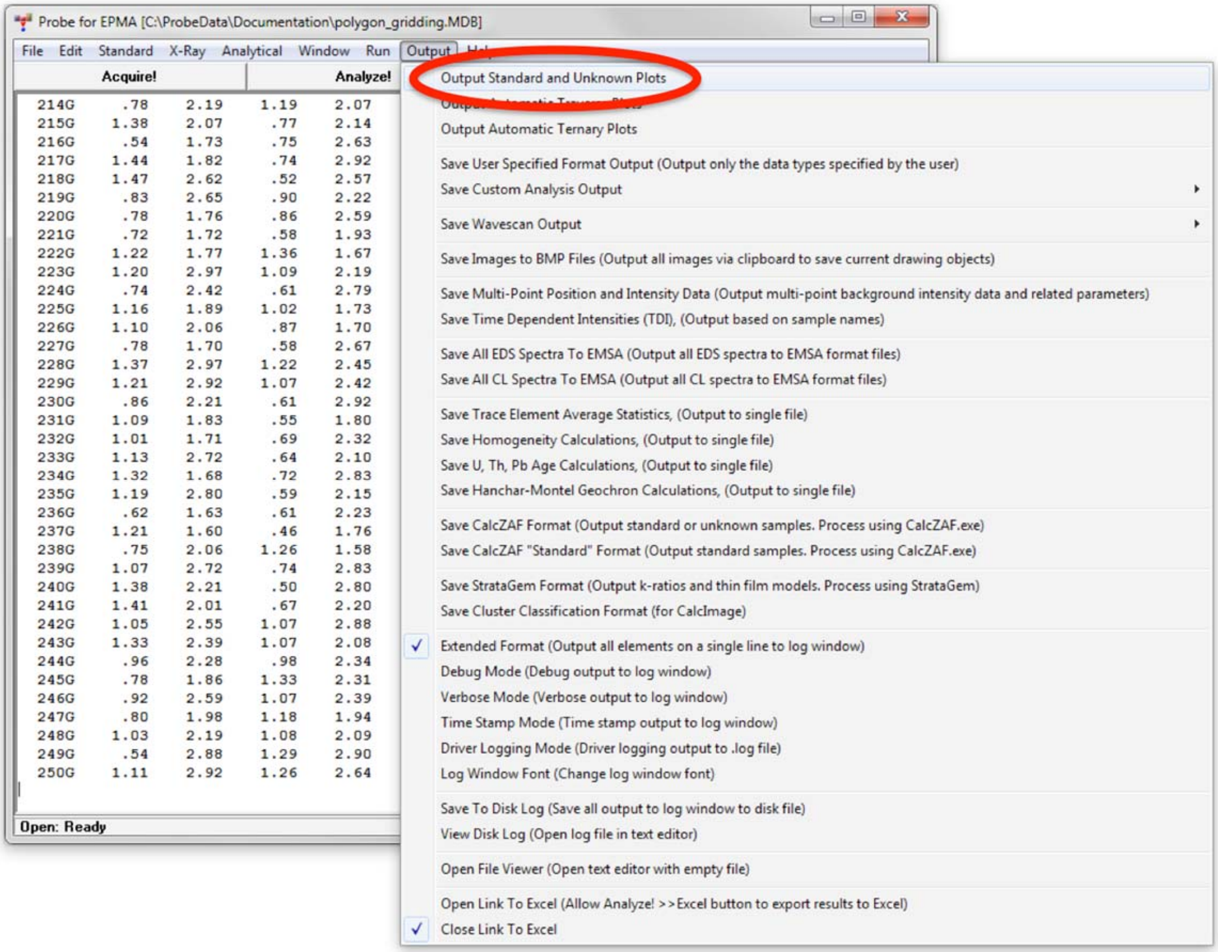
Number of Standard Position Samples: 0
Number of Unknown Position Samples: 1
Number of Wavescan Position Samples: 0

Elapsed Time for Last Unknown Acquisition: 66 seconds

Projected Time for All Unknown Acquisitions: 26.46 hours
Total Projected Time for All Acquisitions: 26.46 hours

Are you sure you want to run these automated position samples?

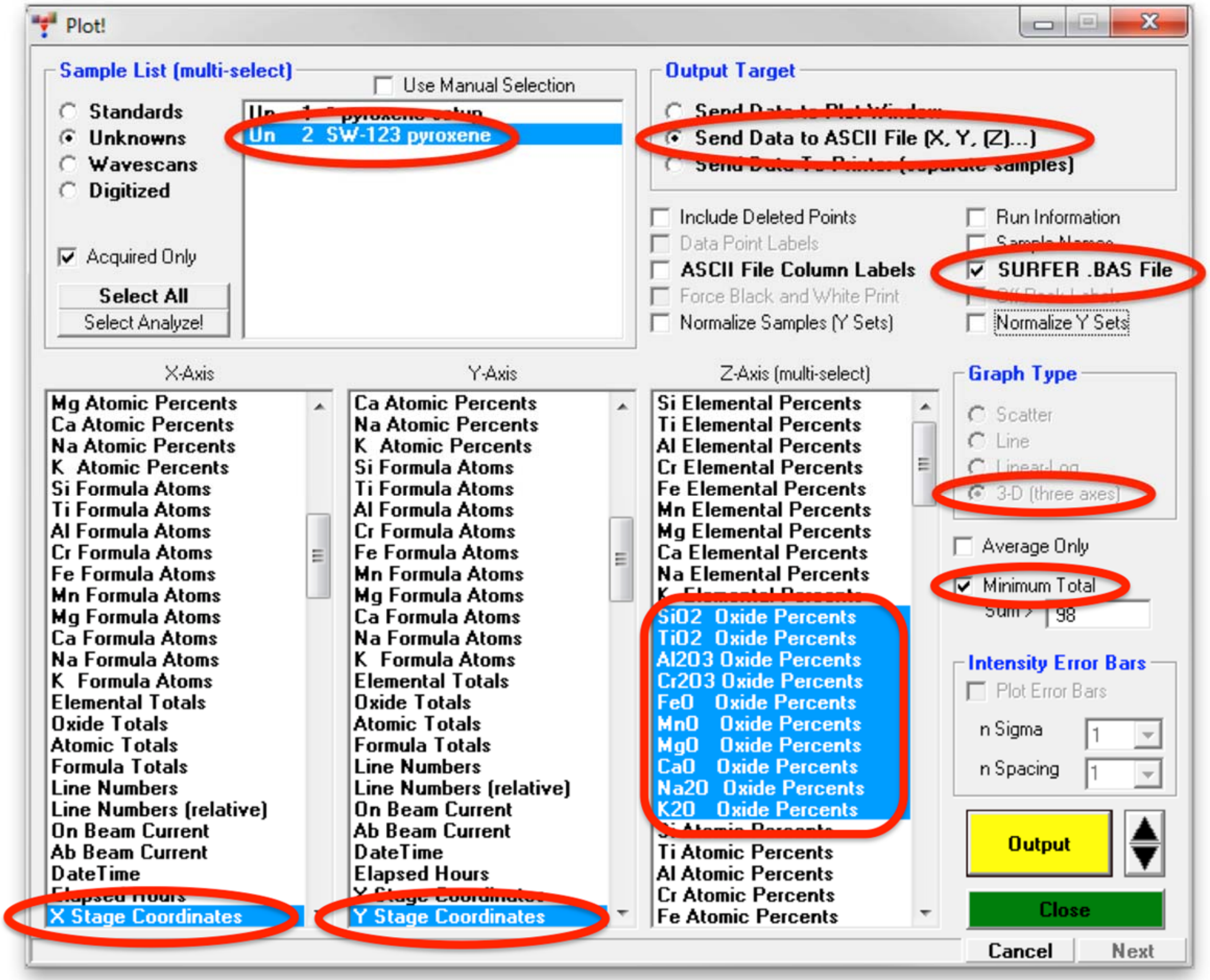
Upon completion of the data acquisition, return to the main window and select **Output Standard and Unknown Plots** in the **Output** menu:



```
  214G      .78     2.19     1.19     2.07
  215G     1.38     2.07      .77     2.14
  216G      .54     1.73      .75     2.63
  217G     1.44     1.82      .74     2.92
  218G     1.47     2.62      .52     2.57
  219G      .83     2.65      .90     2.22
  220G      .78     1.76      .86     2.59
  221G      .72     1.72      .58     1.93
  222G     1.22     1.77     1.36     1.67
  223G     1.20     2.97     1.09     2.19
  224G      .74     2.42      .61     2.79
  225G     1.16     1.89     1.02     1.73
  226G     1.10     2.06      .87     1.70
  227G      .78     1.70      .58     2.67
  228G     1.37     2.97     1.22     2.45
  229G     1.21     2.92     1.07     2.42
  230G      .86     2.21      .61     2.92
  231G     1.09     1.83      .55     1.80
  232G     1.01     1.71      .69     2.32
  233G     1.13     2.72      .64     2.10
  234G     1.32     1.68      .72     2.83
  235G     1.19     2.80      .59     2.15
  236G      .62     1.63      .61     2.23
  237G     1.21     1.60      .46     1.76
  238G      .75     2.06     1.26     1.58
  239G     1.07     2.72      .74     2.83
  240G     1.38     2.21      .50     2.80
  241G     1.41     2.01      .67     2.20
  242G     1.05     2.55     1.07     2.88
  243G     1.33     2.39     1.07     2.08
  244G      .96     2.28      .98     2.34
  245G      .78     1.86     1.33     2.31
  246G      .92     2.59     1.07     2.39
  247G      .80     1.98     1.18     1.94
  248G     1.03     2.19     1.08     2.09
  249G      .54     2.88     1.29     2.90
  250G     1.11     2.92     1.26     2.64
```

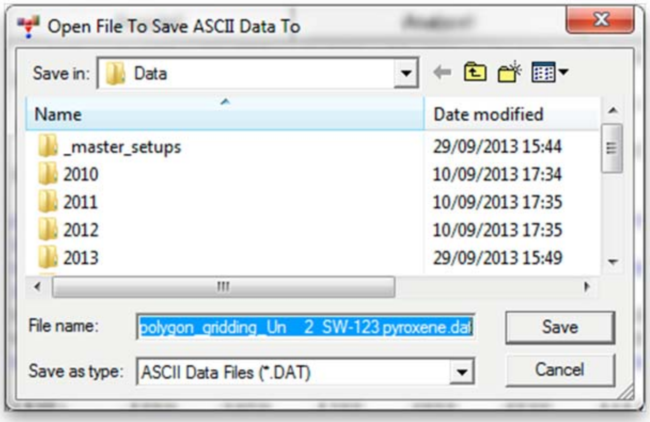
Select (highlight) the unknown digitized points in the Sample List field. Depending on how many points were digitised, the data might have more than one row. Click the *Minimum Total* check box to skip low points (analyses in holes, etc). Select the *3-D* check button under *Graph Type*.

Click the *Send Data to ASCII File* check button. This activates other the output check boxes. Click the *SURFER.BAS File* check box. Finally, select "*X Stage Coordinates*" for *X-Axis*, "*Y Stage Coordinates*" for *Y-Axis*, and for example all the *Oxide Percents* for the *Z-Axis (multi-select)*.



Click the **Output** button. Calculations happen for all samples.

The **Open File To Save ASCII Data To** window opens. Adjust the *Save in:* location if required. Enter a *File name:* in the text field provided.



Save in: Data

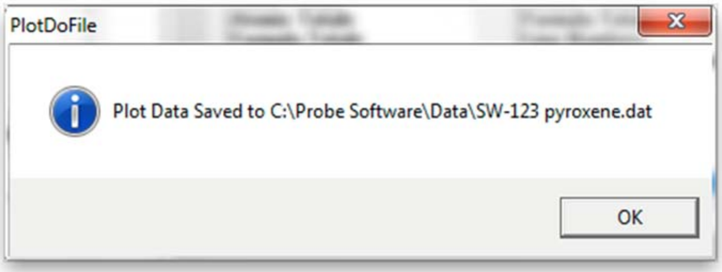
Name	Date modified
_master_setups	29/09/2013 15:44
2010	10/09/2013 17:34
2011	10/09/2013 17:35
2012	10/09/2013 17:35
2013	29/09/2013 15:49

File name: polygon_gridding_Un 2 SW-123 pyroxene.dat

Save as type: ASCII Data Files (*.DAT)

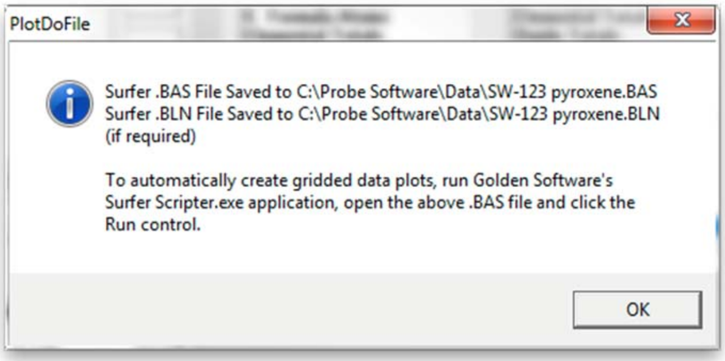
Click the **Save** button.

The **PlotDoFile** window opens, click the **OK** button.



Plot Data Saved to C:\Probe Software\Data\SW-123 pyroxene.dat

Another **PlotDoFile** window appears.

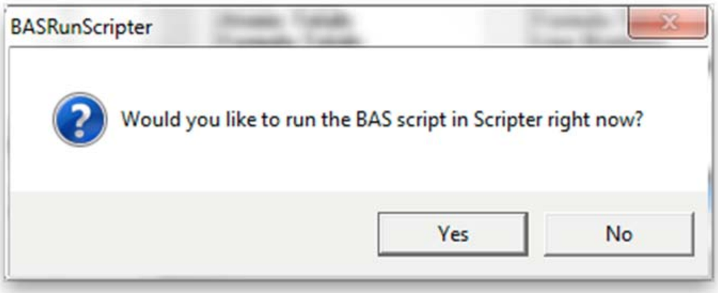


Surfer .BAS File Saved to C:\Probe Software\Data\SW-123 pyroxene.BAS
Surfer .BLN File Saved to C:\Probe Software\Data\SW-123 pyroxene.BLN
(if required)

To automatically create gridded data plots, run Golden Software's Surfer Scripter.exe application, open the above .BAS file and click the Run control.

Click the **OK** button to create these files. They contains OLE code for generating contour and surface plots of the digitized probe data.

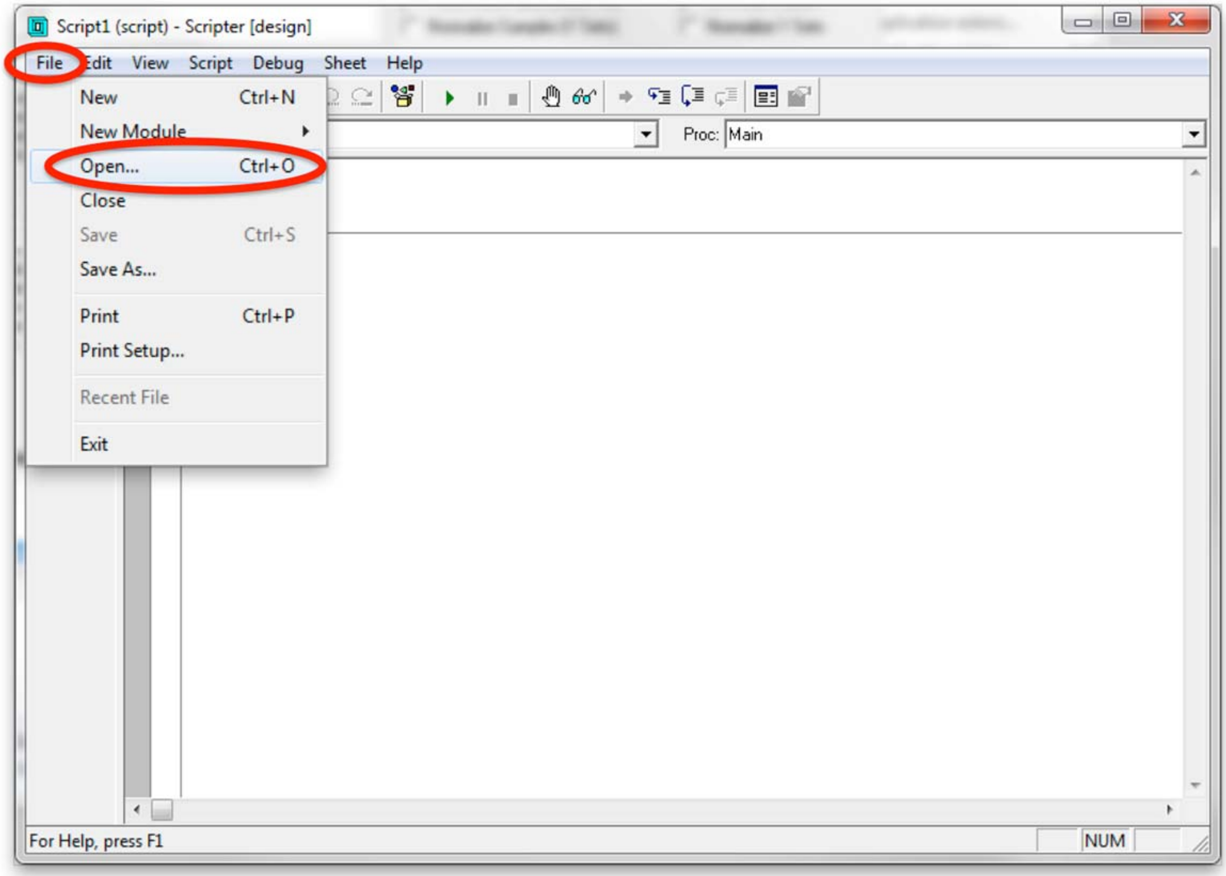
The **BASRunScripter** window opens.


BASRunScripter

Would you like to run the BAS script in Scripter right now?

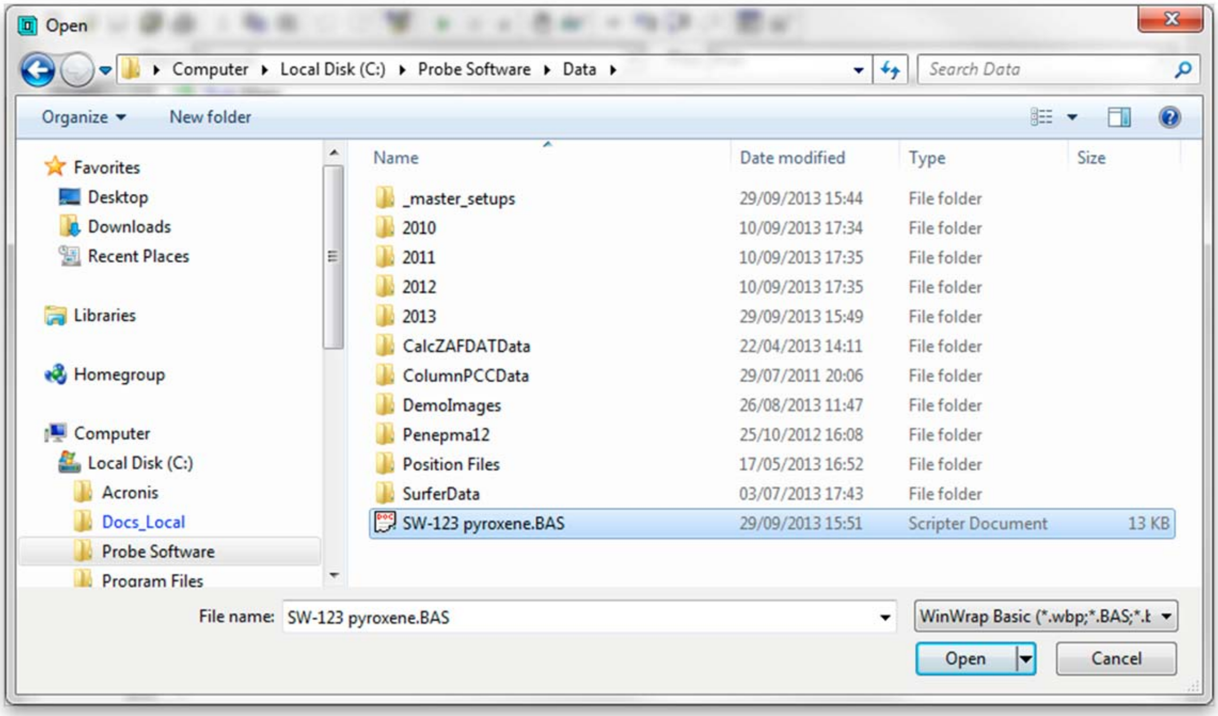
Click **Yes** to automatically open the created script file in Golden Software Scripter. This requires the correct location of the Golden Software applications to be specified in the [software] section of PROBEWIN.INI using the GrapherAppDirectory and SurferAppDirectory keywords. PROBE FOR EPMA will look for Scripter.exe in the Scripter subdirectories of the Grapher and Surfer folders.

Alternatively, click **No** to manually open the .BAS file. Launch Scripter.exe, for example from the Golden Software Surfer program group in the Start menu.



The **Open Document** window appears.

Locate the SW-123 pyroxene.BAS file.



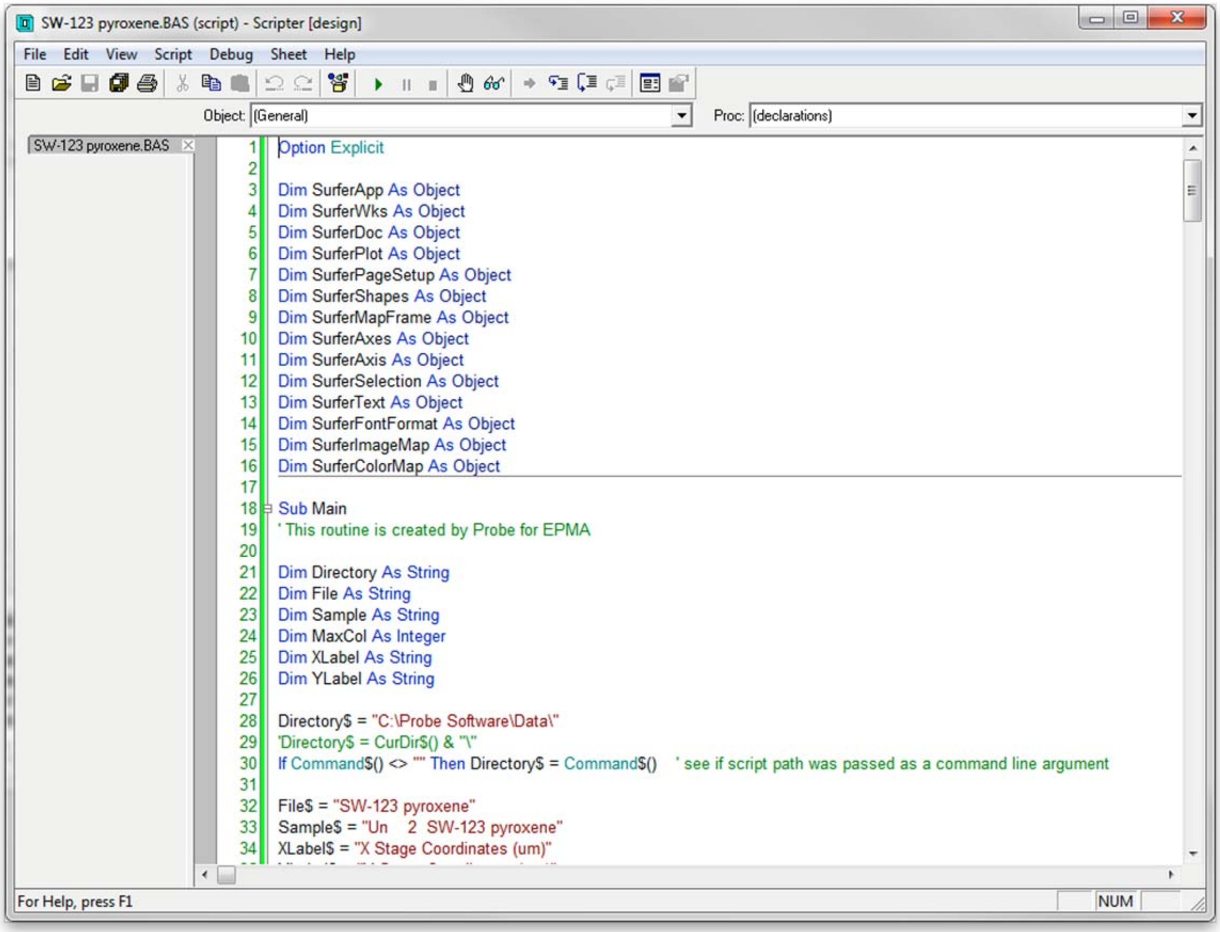
Name	Date modified	Type	Size
_master_setups	29/09/2013 15:44	File folder	
2010	10/09/2013 17:34	File folder	
2011	10/09/2013 17:35	File folder	
2012	10/09/2013 17:35	File folder	
2013	29/09/2013 15:49	File folder	
CalcZAFDATData	22/04/2013 14:11	File folder	
ColumnPCCData	29/07/2011 20:06	File folder	
DemoImages	26/08/2013 11:47	File folder	
Penepma12	25/10/2012 16:08	File folder	
Position Files	17/05/2013 16:52	File folder	
SurferData	03/07/2013 17:43	File folder	
SW-123 pyroxene.BAS	29/09/2013 15:51	Scripter Document	13 KB

File name: SW-123 pyroxene.BAS

WinWrap Basic (*.wbp;*.BAS;*.t

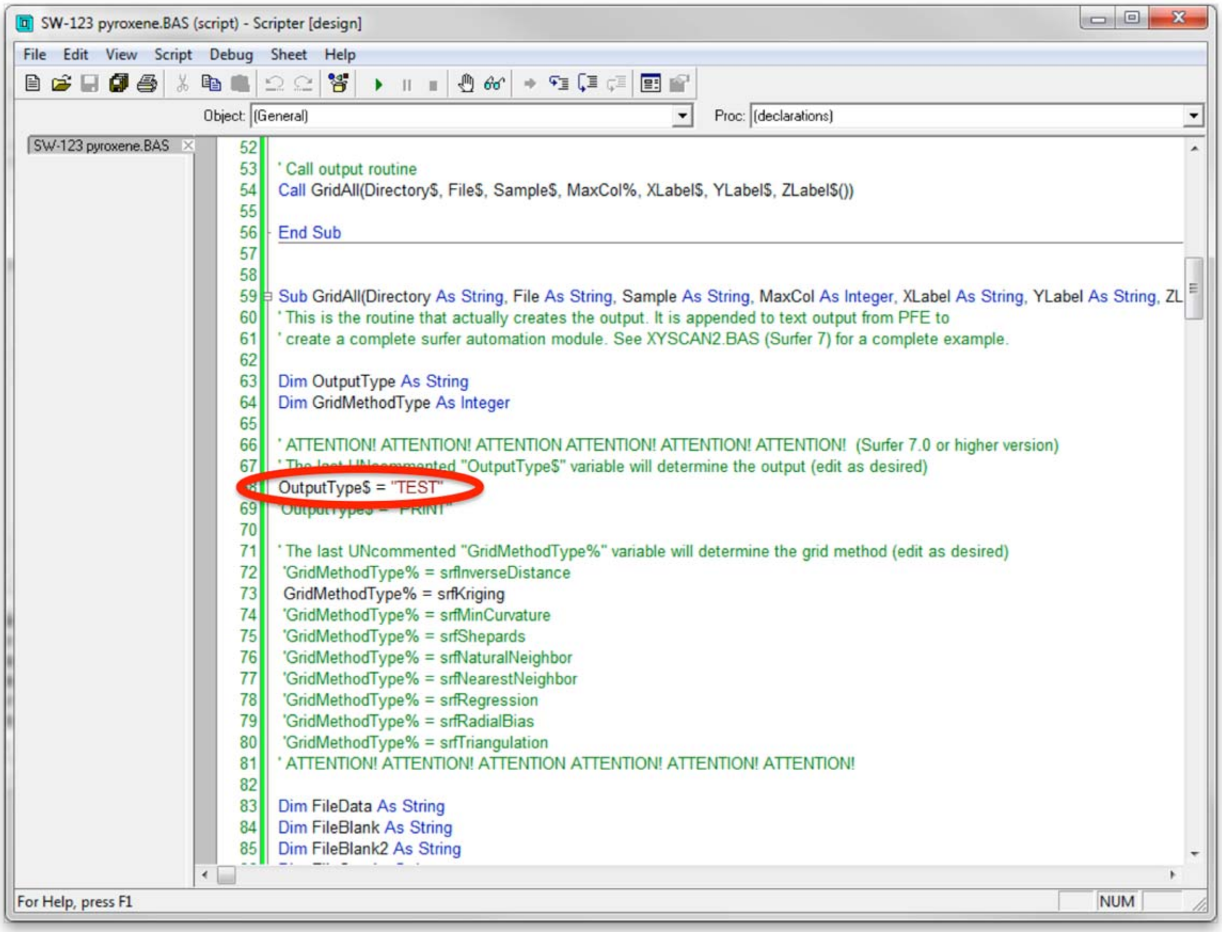
Click the **Open** button.

GS Scripter now details the open SW123.BAS file, of which a portion is illustrated below.



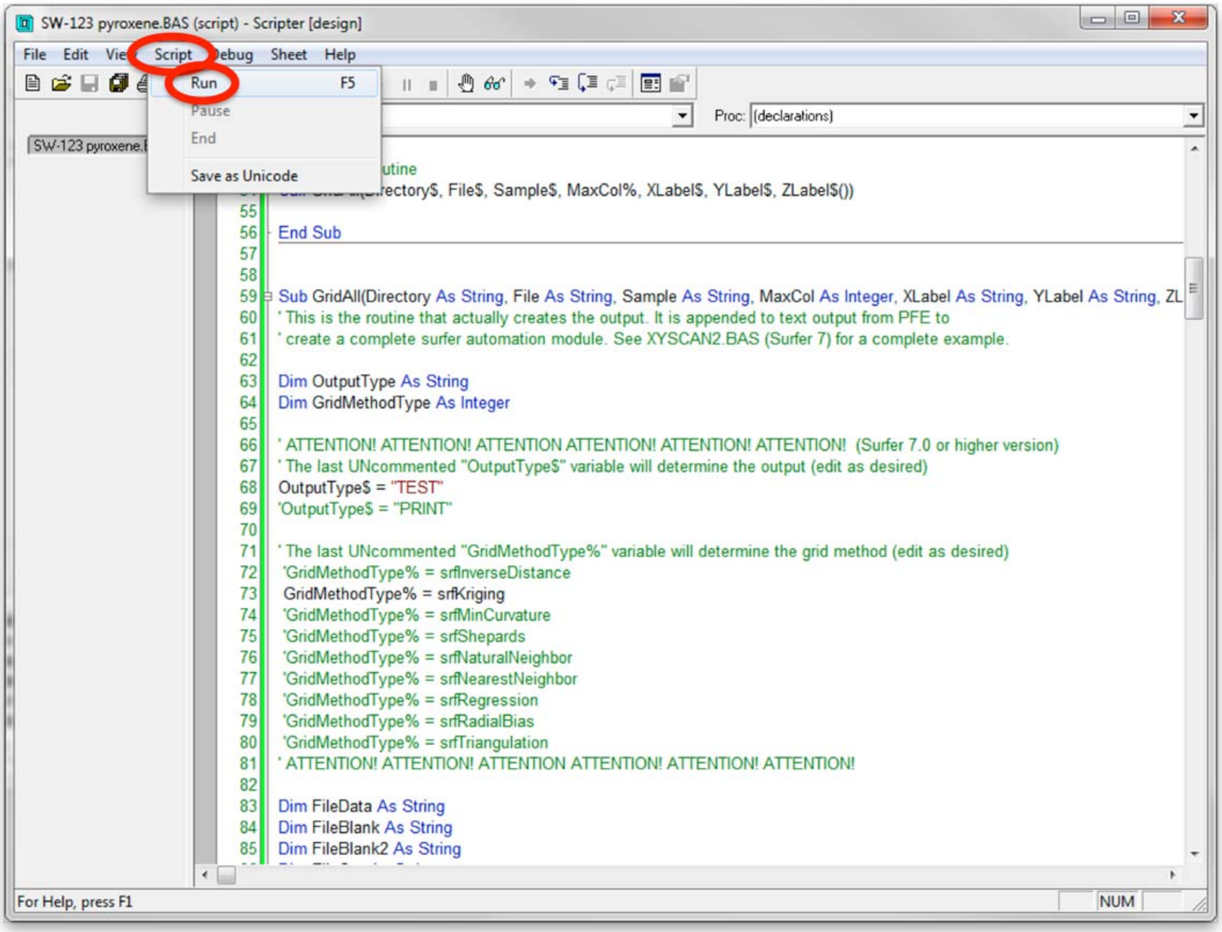
```
Option Explicit

Dim SurferApp As Object
Dim SurferWks As Object
Dim SurferDoc As Object
Dim SurferPlot As Object
Dim SurferPageSetup As Object
Dim SurferShapes As Object
Dim SurferMapFrame As Object
Dim SurferAxes As Object
Dim SurferAxis As Object
Dim SurferSelection As Object
Dim SurferText As Object
Dim SurferFontFormat As Object
Dim SurferImageMap As Object
Dim SurferColorMap As Object

Sub Main
' This routine is created by Probe for EPMA

Dim Directory As String
Dim File As String
Dim Sample As String
Dim MaxCol As Integer
Dim XLabel As String
Dim YLabel As String

Directory$ = "C:\Probe Software\Data\"
'Directory$ = CurDir$() & "\"
If Command$() <> "" Then Directory$ = Command$()    ' see if script path was passed as a command line argument

File$ = "SW-123 pyroxene"
Sample$ = "Un    2  SW-123 pyroxene"
XLabel$ = "X Stage Coordinates (um)"
```

The default output mode of the script file is "TEST", which will only output the plots to the screen. Scroll down to see more output options and edit as desired. Deactivate (comment out) lines by inserting a single quotation mark at the beginning of a line. Activate by removing the single quote.



```
' Call output routine
Call GridAll(Directory$, File$, Sample$, MaxCol%, XLabel$, YLabel$, ZLabel$())

End Sub


Sub GridAll(Directory As String, File As String, Sample As String, MaxCol As Integer, XLabel As String, YLabel As String, ZL
' This is the routine that actually creates the output. It is appended to text output from PFE to
' create a complete surfer automation module. See XYSCAN2.BAS (Surfer 7) for a complete example.

Dim OutputType As String
Dim GridMethodType As Integer

' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! ATTENTION!  (Surfer 7.0 or higher version)
' The last UNcommented "OutputType$" variable will determine the output (edit as desired)
OutputType$ = "TEST"
'OutputType$ = "PRINT"

' The last UNcommented "GridMethodType%" variable will determine the grid method (edit as desired)
 'GridMethodType% = srfInverseDistance
 GridMethodType% = srfKriging
 'GridMethodType% = srfMinCurvature
 'GridMethodType% = srfShepards
 'GridMethodType% = srfNaturalNeighbor
 'GridMethodType% = srfNearestNeighbor
 'GridMethodType% = srfRegression
 'GridMethodType% = srfRadialBias
 'GridMethodType% = srfTriangulation
' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! ATTENTION!

Dim FileData As String
Dim FileBlank As String
Dim FileBlank2 As String
```

Select the **Script | Run** menu item to begin the automated plotting.

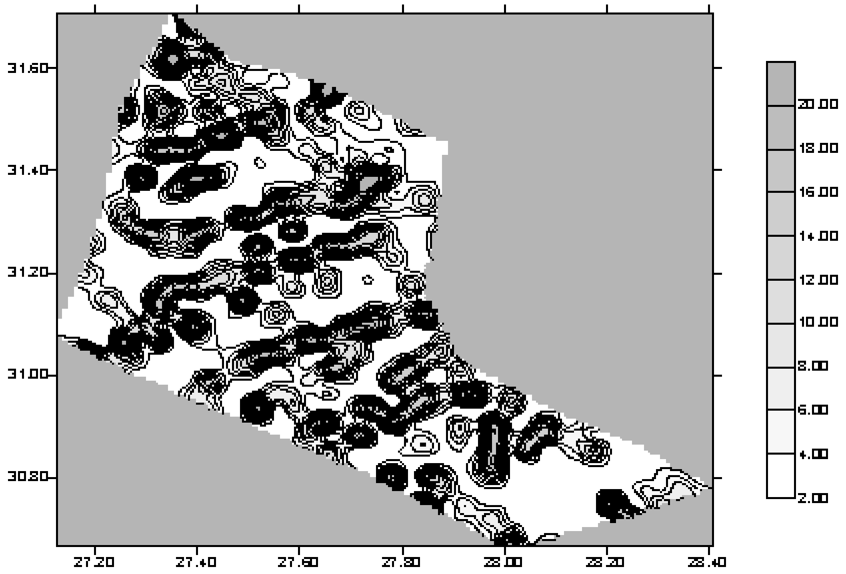


```
utine
rectory$, File$, Sample$, MaxCol%, XLabel$, YLabel$, ZLabel$())

End Sub


Sub GridAll(Directory As String, File As String, Sample As String, MaxCol As Integer, XLabel As String, YLabel As String, ZL
' This is the routine that actually creates the output. It is appended to text output from PFE to
' create a complete surfer automation module. See XYSCAN2.BAS (Surfer 7) for a complete example.

Dim OutputType As String
Dim GridMethodType As Integer

' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! ATTENTION!  (Surfer 7.0 or higher version)
' The last UNcommented "OutputType$" variable will determine the output (edit as desired)
OutputType$ = "TEST"
'OutputType$ = "PRINT"

' The last UNcommented "GridMethodType%" variable will determine the grid method (edit as desired)
 'GridMethodType% = srfInverseDistance
 GridMethodType% = srfKriging
 'GridMethodType% = srfMinCurvature
 'GridMethodType% = srfShepards
 'GridMethodType% = srfNaturalNeighbor
 'GridMethodType% = srfNearestNeighbor
 'GridMethodType% = srfRegression
 'GridMethodType% = srfRadialBias
 'GridMethodType% = srfTriangulation
' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! ATTENTION!

Dim FileData As String
Dim FileBlank As String
Dim FileBlank2 As String
```

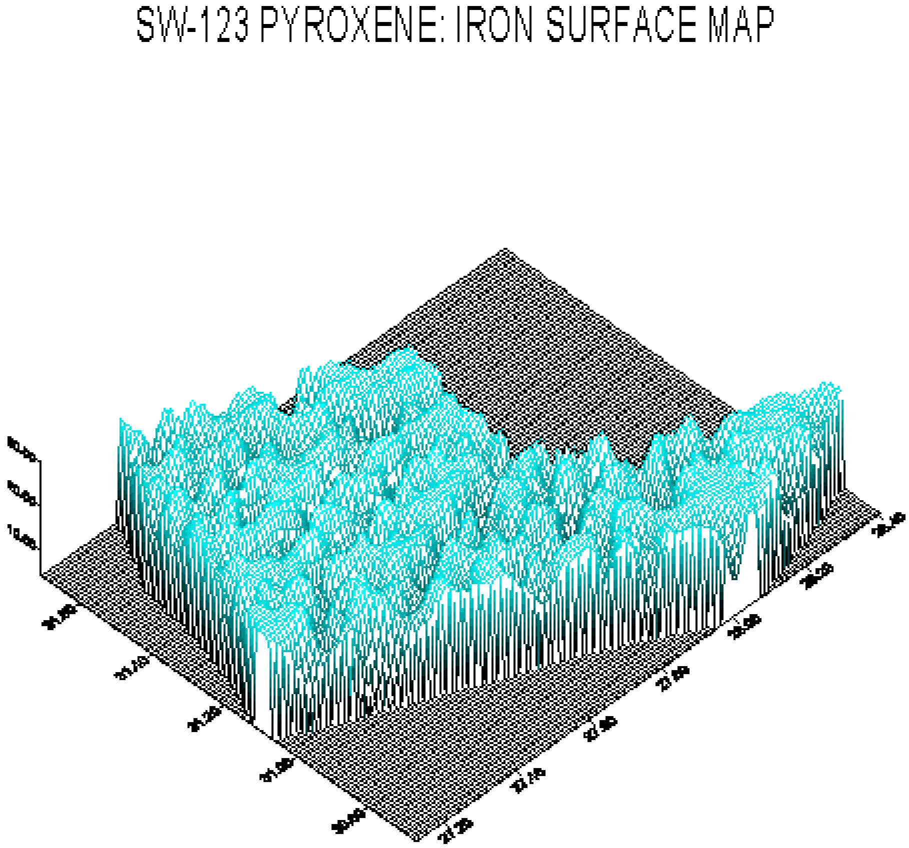
Basic contour and surface maps will be created. Raw data concentration (*.GRD) files will also be created; these may be opened in SURFER for further modification and output.

An example of a basic contour map for calcium is shown below. The perimeter of the pyroxene grain is visible. Regions of higher calcium concentrations appear dark in this view.

SW-123 PYROXENE: CALCIUM CONTOUR MAP



The next screen capture illustrates a 3-D surface map for iron in the pyroxene. Here, the image of iron concentration (vertical scale) has been rotated and tilted slightly.

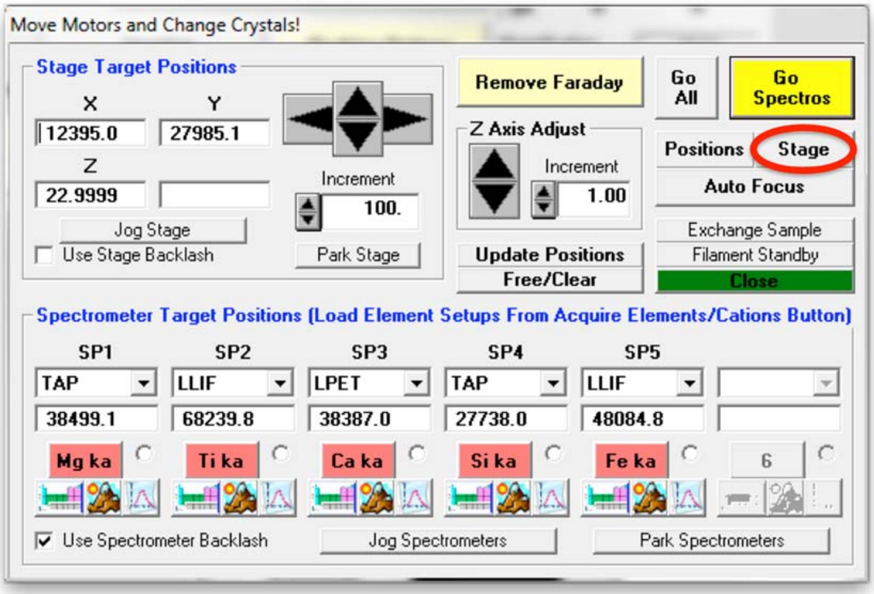


Stage Bit Maps and Picture Snap! Feature

Unknown or standard samples loaded into the electron microprobe can present some difficulty to the user in terms of rapid and precise positioning or the location of small phases or specific areas of interest to analyze upon a large sample. On most microprobes the user has several options for searching for analysis or standard locations. An optical image (reflected and/or transmitted light) and/or a video feed of the same image are usually available, but on some instruments only at relatively high magnification. Additionally, one can search for the area of interest utilizing the secondary or backscattered detectors at variable magnifications, but this can be time consuming. Still the entire sample may not be in one field of view upon observation in the chamber.

Another device employed to aid in feature location and rapid positioning is a gridding device that holds a sample mounted in a standard holder under a moveable grid system. The rough coordinates of a region on the sample may be read off to effectively narrow the search for the analysis position. Some facilities also use standalone digitized light microscopes to program points into ASCII text files which can be transferred to the microprobe and recoordinated using fiducials.

In PROBE FOR EPMA, navigation around and exact positioning can also be easily accomplished using the stage bit map and Picture Snap! features. The Stage Bit Map feature will be discussed first. The **Stage** button is located in many locations in PROBE FOR EPMA programs; such as in the **Acquire!** window or from any **Move Motors and Change Crystals** (**Move** button) window.


Move Motors and Change Crystals!

Stage Target Positions

X 12395.0
Y 27985.1
Z 22.9999
Increment 100.
☐ Use Stage Backlash

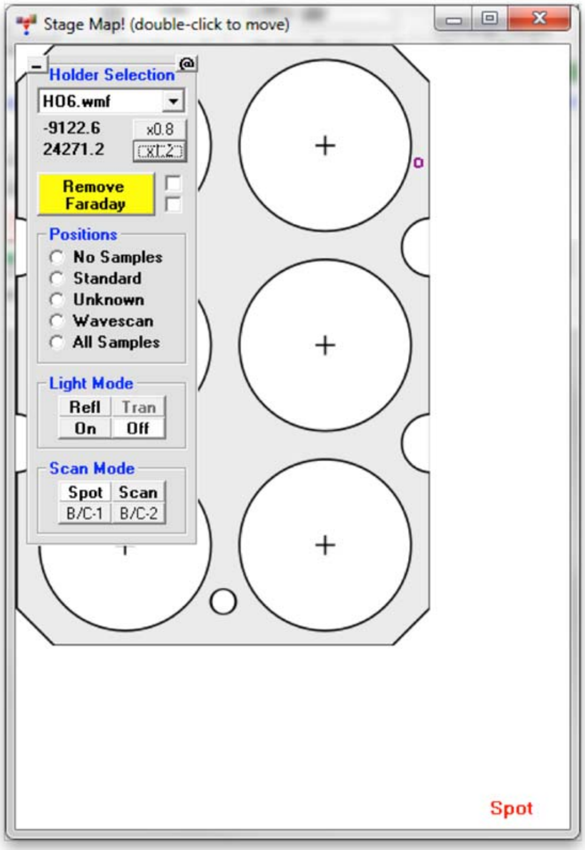
Z Axis Adjust
Increment 1.00

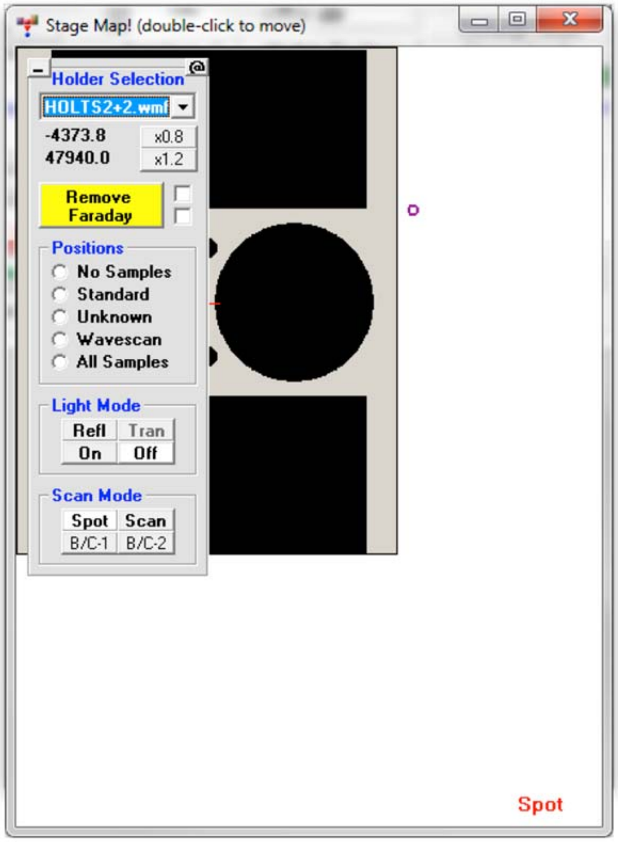
Spectrometer Target Positions (Load Element Setups From Acquire Elements/Cations Button)

SP1	SP2	SP3	SP4	SP5	
TAP	LLIF	LPET	TAP	LLIF	
38499.1	68239.8	38387.0	27738.0	48084.8	
Mg ka	Ti ka	Ca ka	Si ka	Fe ka	6

☑ Use Spectrometer Backlash

Clicking the **Stage** button opens the **Stage Map** window. Two different maps are displayed below.



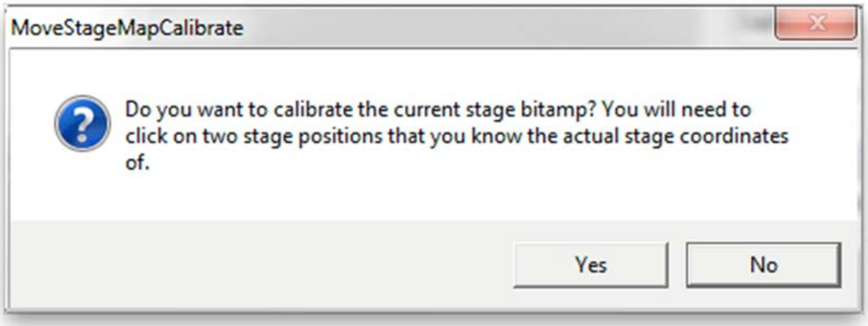


To select another *Holder Selection* image, simply select the file from the drop-down list box. Image files (windows metafiles (*.WMF)) and coordinate limits are specified in the Standards section of the PROBEWIN.INI file. The entire map maybe reduced or enlarged retaining scale using the **x0.8** or **x1.2** buttons or to re-size the Stage Bit Map window simply drag any corner of the window to the desired size and shape. The **minus** and **plus** button (upper left) minimizes the stage bitmap selection and cursor position display.

The current position is indicated as a small red-purple circle on the map. To move from one location to another, simply double-click on the spot you wish the stage to travel to. The current position (X and Y stage coordinates) is displayed above the **Remove Faraday/ Insert Faraday** button. Digitized positions of various samples can also be viewed by selecting the appropriate radio button.

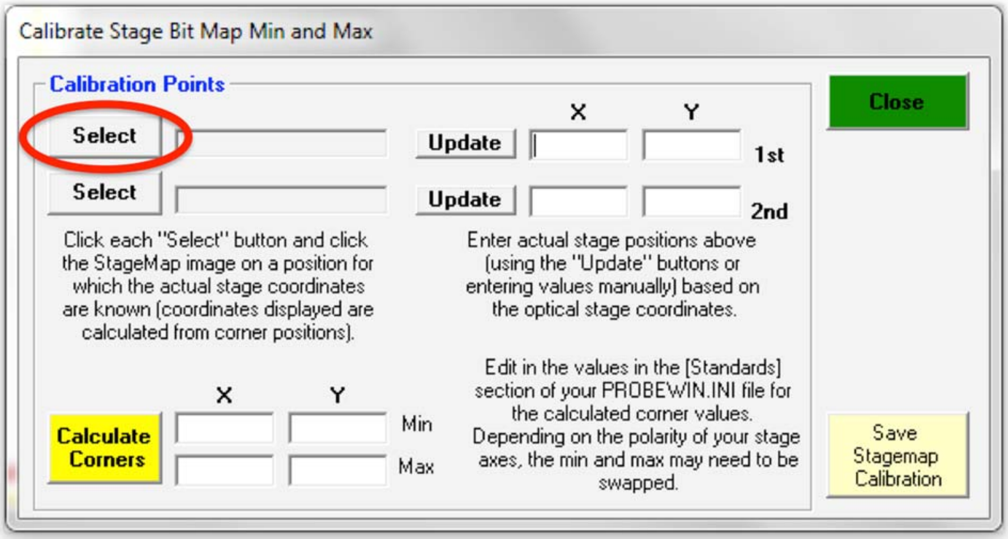
To create stage drawing maps of your standard holders, for instance, use a vector based drawing program and the exact dimensions of your holders to build dimensionally correct drawings. These can be exported as windows metafiles and directly loaded into the graphical stage move feature in PROBE FOR EPMA.

Each stage map must be calibrated in coordinate space for accurate movement to features on the map. Typically two diagonally located points near the edge of the map are chosen for calibration. Initiate the calibration routine by clicking the **@** button (upper right) in the **Stage Map** window. The **MoveStageMapCalibrate** window appears.


MoveStageMapCalibrate

Do you want to calibrate the current stage bitamp? You will need to click on two stage positions that you know the actual stage coordinates of.

Click the **Yes** button to open the **Calibrate Stage Bit Map Min and Max** window for calibration.


Calibrate Stage Bit Map Min and Max

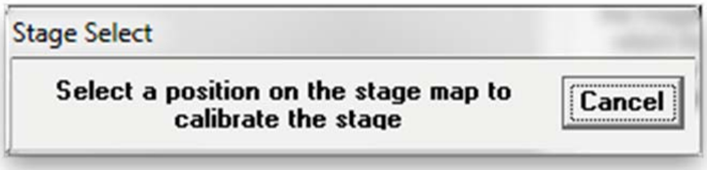
Calibration Points

Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions).

Enter actual stage positions above (using the "Update" buttons or entering values manually) based on the optical stage coordinates.

Edit in the values in the [Standards] section of your PROBEWIN.INI file for the calculated corner values. Depending on the polarity of your stage axes, the min and max may need to be swapped.

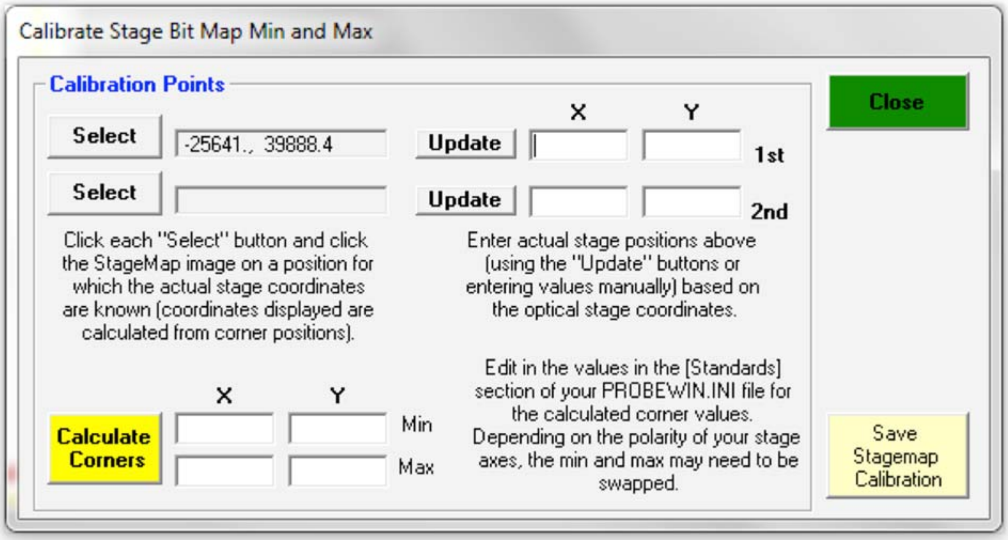
Click the top **Select** button, opening the **Stage Select** window.


Stage Select

Select a position on the stage map to calibrate the stage

Click on the unique position on the stage map to identify the stage coordinates.

These values appear next to the **Select** button chosen.



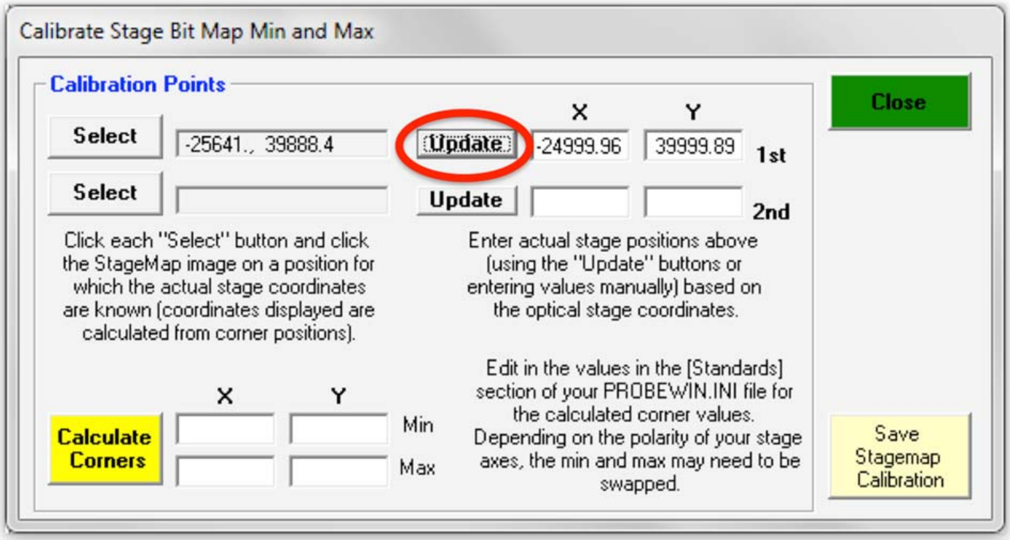
-25641., 39888.4

Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions).

Enter actual stage positions above (using the "Update" buttons or entering values manually) based on the optical stage coordinates.

Edit in the values in the [Standards] section of your PROBEWIN.INI file for the calculated corner values. Depending on the polarity of your stage axes, the min and max may need to be swapped.

Next, activate the microprobe imaging and zoom up in magnification to locate the exact spot you just selected. Either click the **Update** button or manually enter the stage coordinate information for the 1st calibration point.



-25641., 39888.4

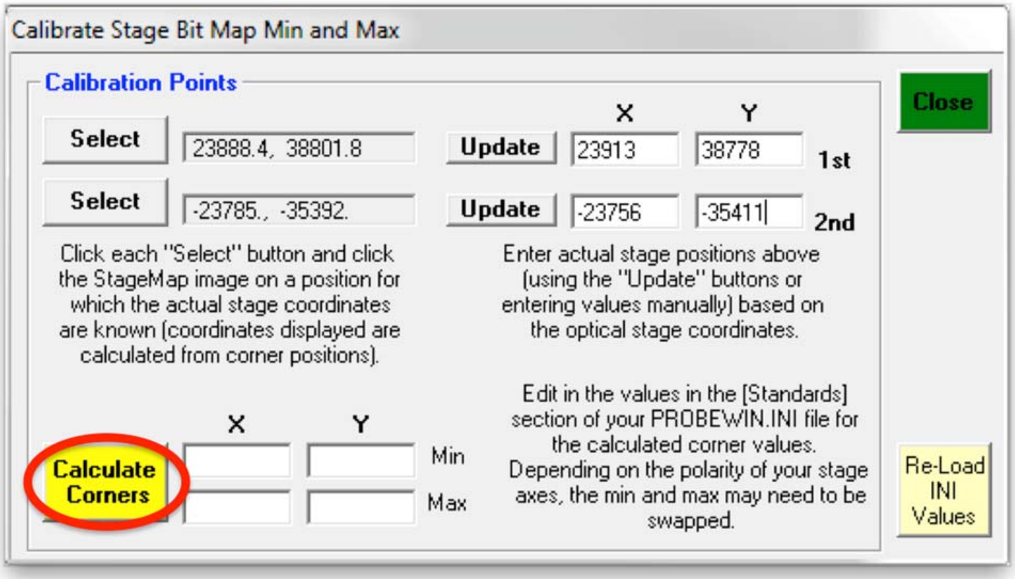
1st: X -24999.96, Y 39999.89

Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions).

Enter actual stage positions above (using the "Update" buttons or entering values manually) based on the optical stage coordinates.

Edit in the values in the [Standards] section of your PROBEWIN.INI file for the calculated corner values. Depending on the polarity of your stage axes, the min and max may need to be swapped.

Click the lower **Select** button and repeat the process. Click on the second position on the image. Activate the imaging and find this exact point and update the position. The **Calibrate Stage Bit Map Min and Max** window will appear as below.



	Selected	X	Y	
Select	23888.4, 38801.8	23913	38778	1st
Select	-23785., -35392.	-23756	-35411	2nd

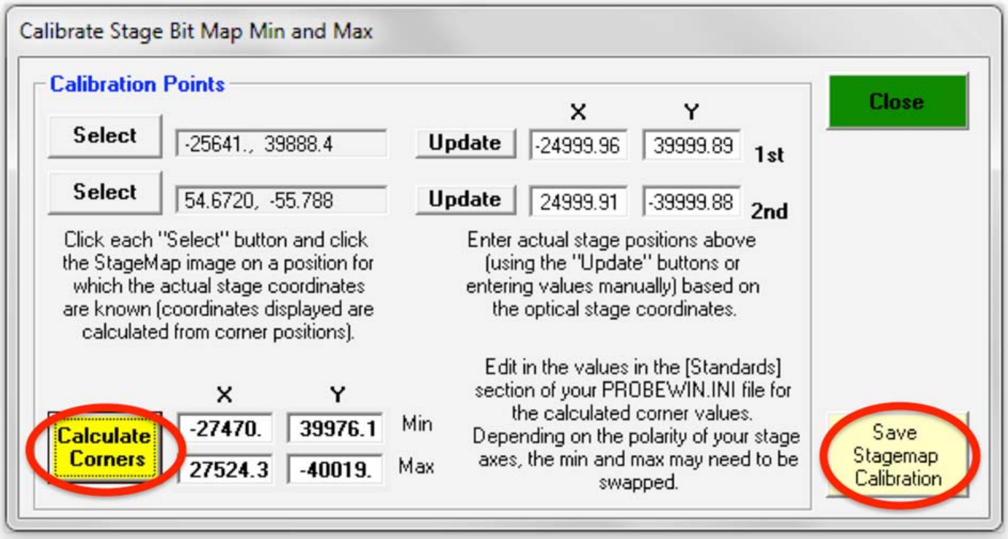
Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions).

Enter actual stage positions above (using the "Update" buttons or entering values manually) based on the optical stage coordinates.

Edit in the values in the [Standards] section of your PROBEWIN.INI file for the calculated corner values. Depending on the polarity of your stage axes, the min and max may need to be swapped.

	X	Y
Min		
Max		

Click the **Calculate Corners** button to obtain the correct corner values to calibrate your Stage Map. Click **Save Stagemap Calibration** to enter these min and max values are into the Standards section of the PROBEWIN.INI file.



	Selected	X	Y	
Select	-25641., 39888.4	-24999.96	39999.89	1st
Select	54.6720, -55.788	24999.91	-39999.88	2nd

Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions).

Enter actual stage positions above (using the "Update" buttons or entering values manually) based on the optical stage coordinates.

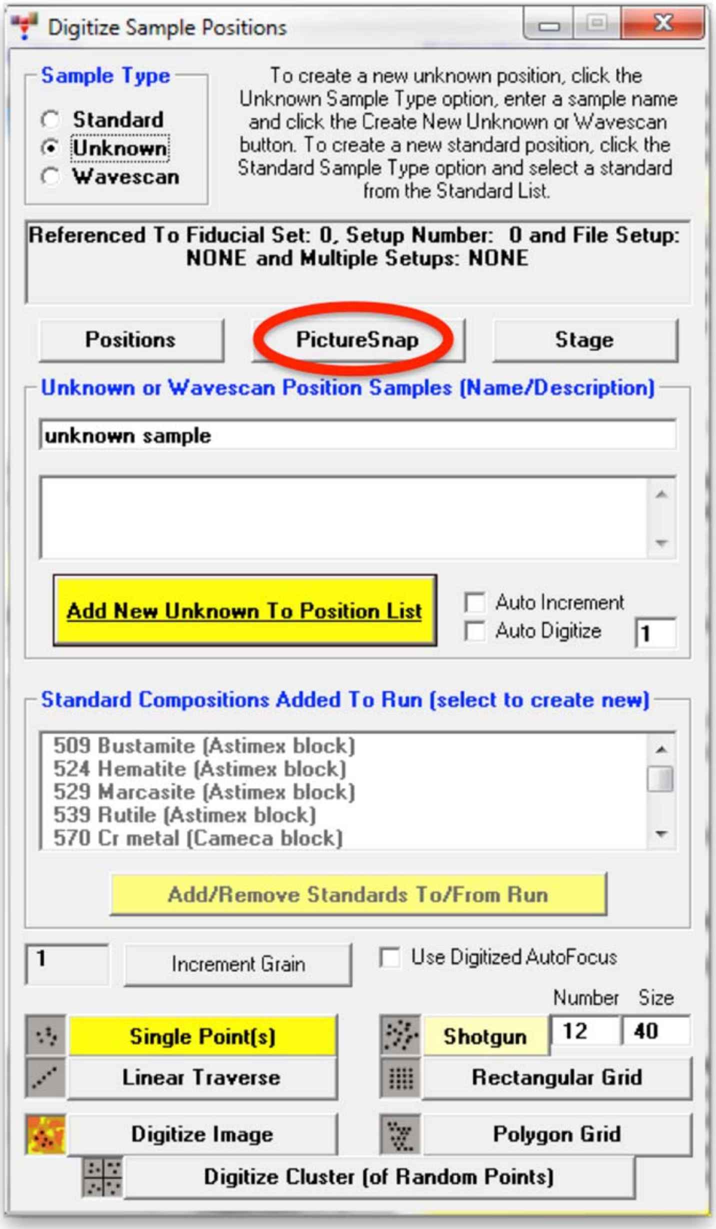
Edit in the values in the [Standards] section of your PROBEWIN.INI file for the calculated corner values. Depending on the polarity of your stage axes, the min and max may need to be swapped.

	X	Y
Min	-27470.	39976.1
Max	27524.3	-40019.

Now this image is calibrated, so the user can easily “drive around” on the image.

The **Picture Snap!** feature allows the user to incorporate images of your unknown thin section or polished mounts into PROBE FOR EPMA to aid in navigation and the digitizing of analysis locations. Images (BMP, JPEG, GRD) taken with a flatbed scanner or other camera system can be entered into **Picture Snap!**, then calibrated and used for analysis.

Picture Snap! dialog can be accessed from the **Automate | Digitize Sample Positions** window.



Digitize Sample Positions

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 or Wavescan Position Samples (Name/Description)

unknown sample

☐ Auto Increment
☐ Auto Digitize 1

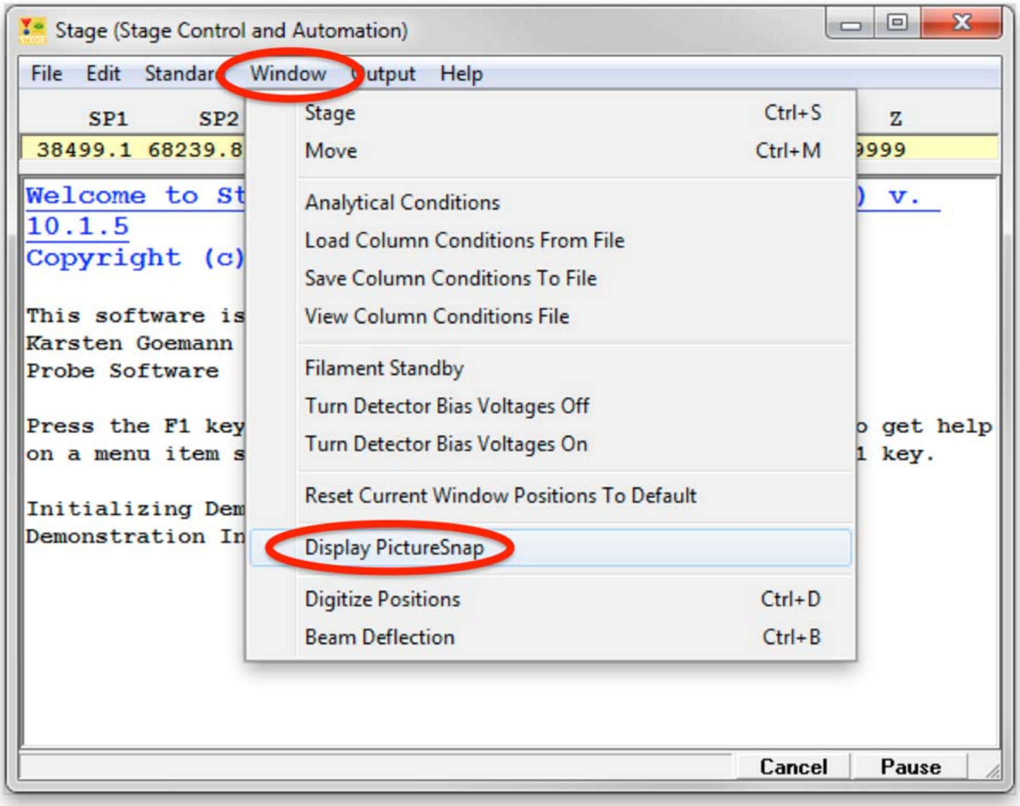
Standard Compositions Added To Run (select to create new)

509 Bustamite (Astimex block)
524 Hematite (Astimex block)
529 Marcasite (Astimex block)
539 Rutile (Astimex block)
570 Cr metal (Cameca block)

1 Increment Grain
☐ Use Digitized AutoFocus

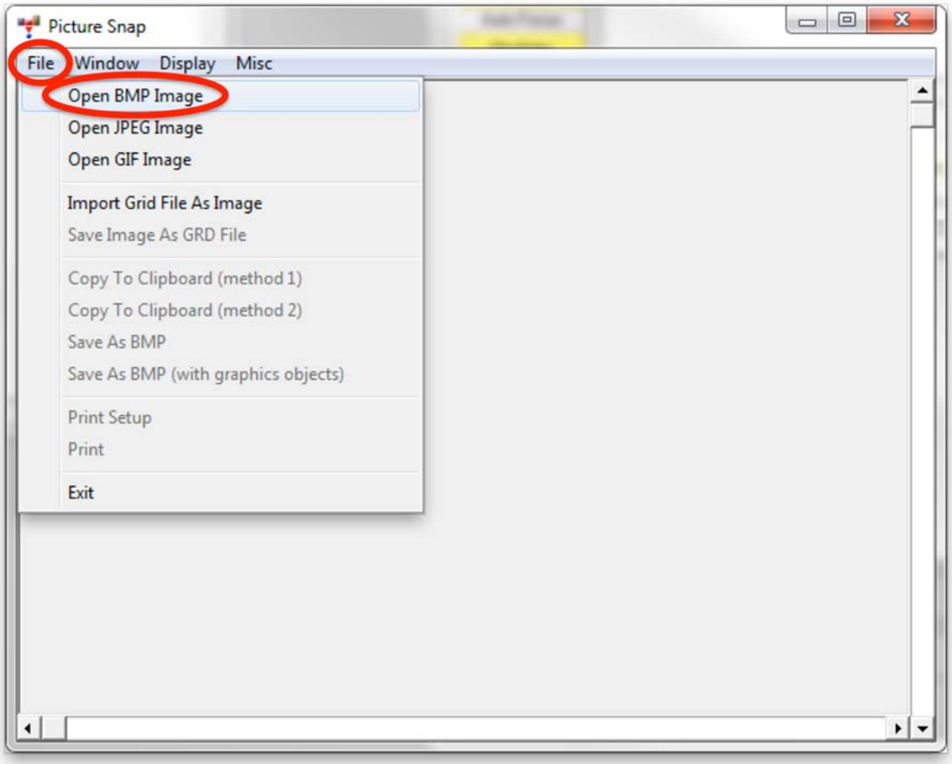
Number 12
Size 40

Picture Snap! can also be accessed from the STAGE program by selecting the **Window | Display Picture Snap!** menu item.

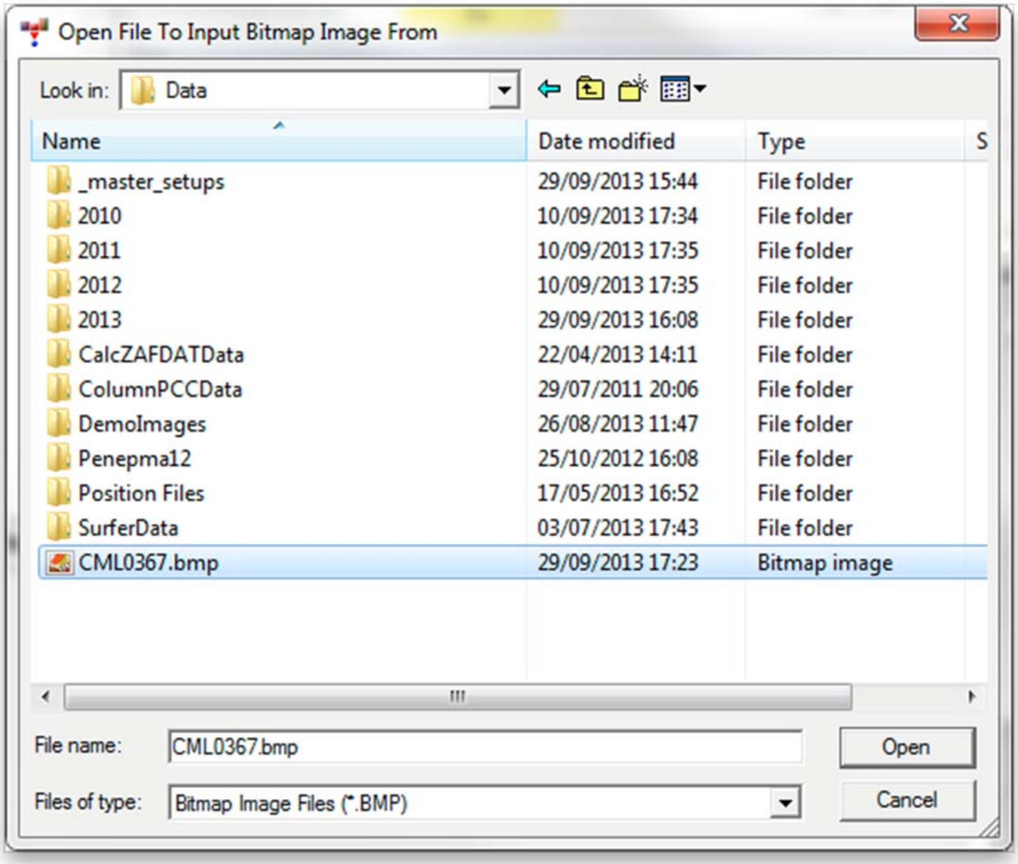


```
Welcome to St                                  ) v.
10.1.5
Copyright (c)

This software is
Karsten Goemann
Probe Software

Press the F1 key                               o get help
on a menu item s                               1 key.

Initializing Dem
Demonstration In
```

The main **Picture Snap!** window appears. Select the **File** menu and open the appropriate image file.



The **Open File To Input Bitmap Image From** window opens.



Look in: Data

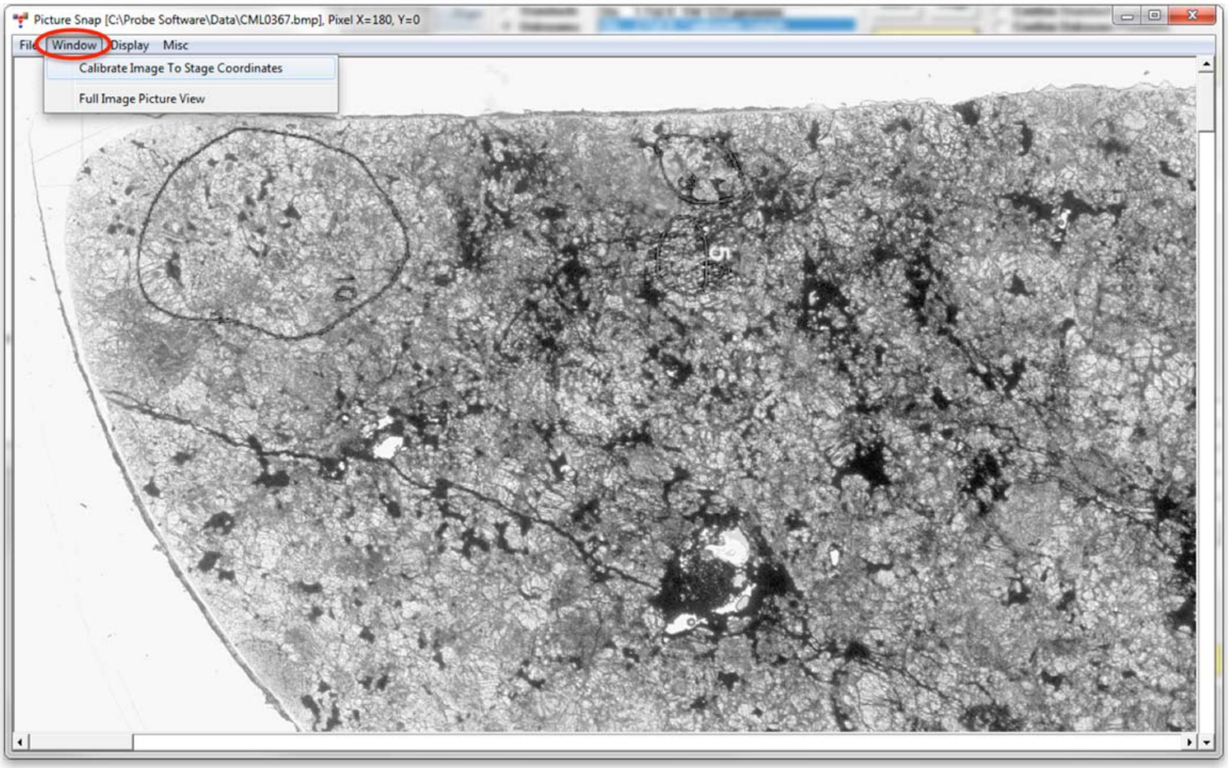
Name	Date modified	Type
_master_setups	29/09/2013 15:44	File folder
2010	10/09/2013 17:34	File folder
2011	10/09/2013 17:35	File folder
2012	10/09/2013 17:35	File folder
2013	29/09/2013 16:08	File folder
CalcZAFDATData	22/04/2013 14:11	File folder
ColumnPCCData	29/07/2011 20:06	File folder
DemoImages	26/08/2013 11:47	File folder
Penepma12	25/10/2012 16:08	File folder
Position Files	17/05/2013 16:52	File folder
SurferData	03/07/2013 17:43	File folder
CML0367.bmp	29/09/2013 17:23	Bitmap image

File name: CML0367.bmp

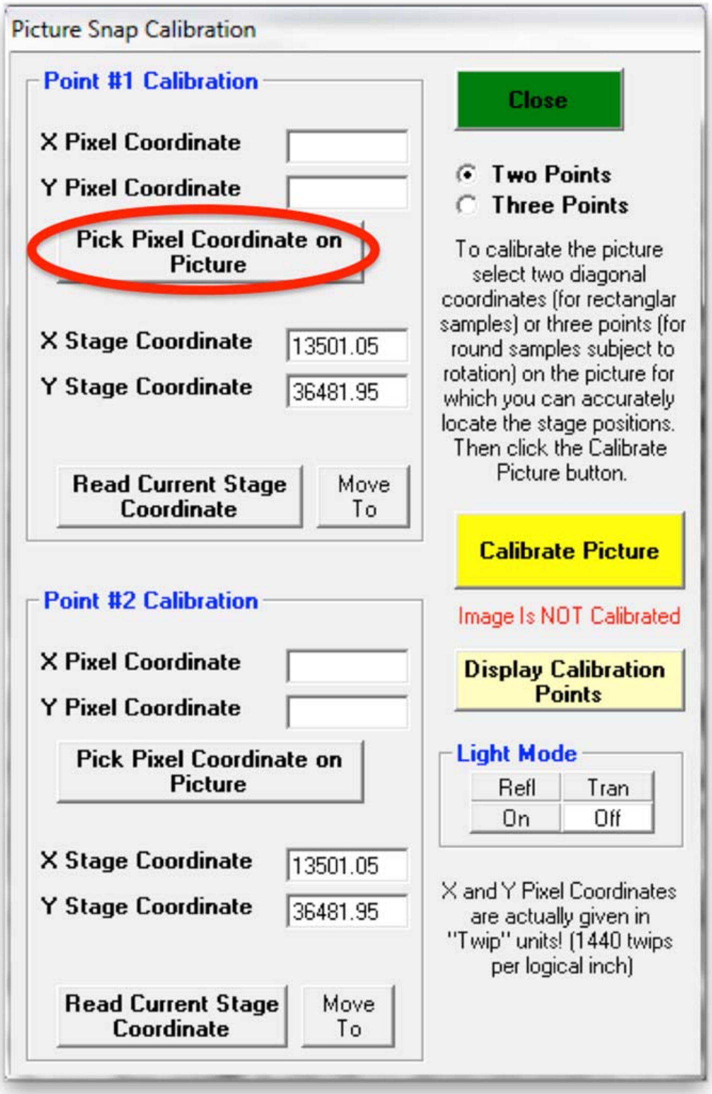
Files of type: Bitmap Image Files (*.BMP)

Select the appropriate directory and file to open and click the **Open** button.

The image is displayed in the **Picture Snap!** window. Select the **Window | Calibrate** menu.



The **Picture Snap Calibration** window appears.



Point #1 Calibration

X Pixel Coordinate
Y Pixel Coordinate
X Stage Coordinate 13501.05
Y Stage Coordinate 36481.95

Point #2 Calibration

X Pixel Coordinate
Y Pixel Coordinate
X Stage Coordinate 13501.05
Y Stage Coordinate 36481.95

● Two Points
○ Three Points

To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

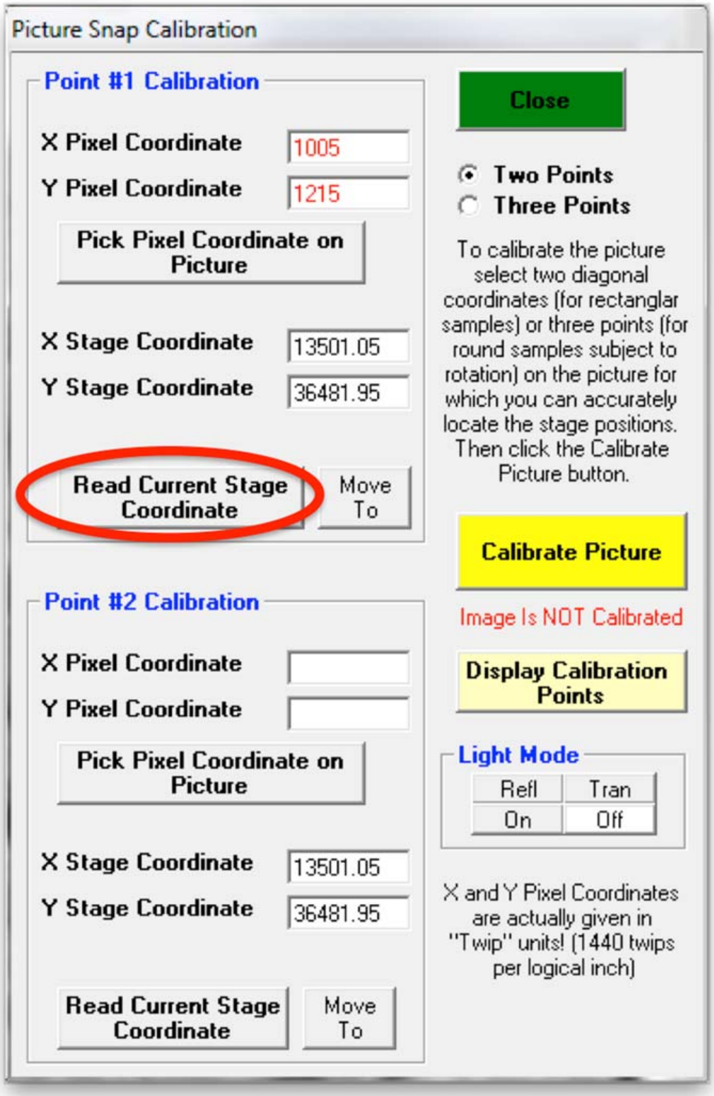
Image Is NOT Calibrated

X and Y Pixel Coordinates are actually given in "Twip" units! (1440 twips per logical inch)

Image calibration is accomplished using a two point method. Click the Point #1 Calibration **Pick Pixel Coordinate on Picture** button The **Picture Select Point** window appears, select the first unique point on the image.

Select a position on the image to calibrate the picture

The X,Y Pixel Coordinates are entered.



Picture Snap Calibration

Point #1 Calibration

X Pixel Coordinate	1005
Y Pixel Coordinate	1215
X Stage Coordinate	13501.05
Y Stage Coordinate	36481.95

Point #2 Calibration

X Pixel Coordinate	
Y Pixel Coordinate	
X Stage Coordinate	13501.05
Y Stage Coordinate	36481.95

● Two Points
○ Three Points

To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

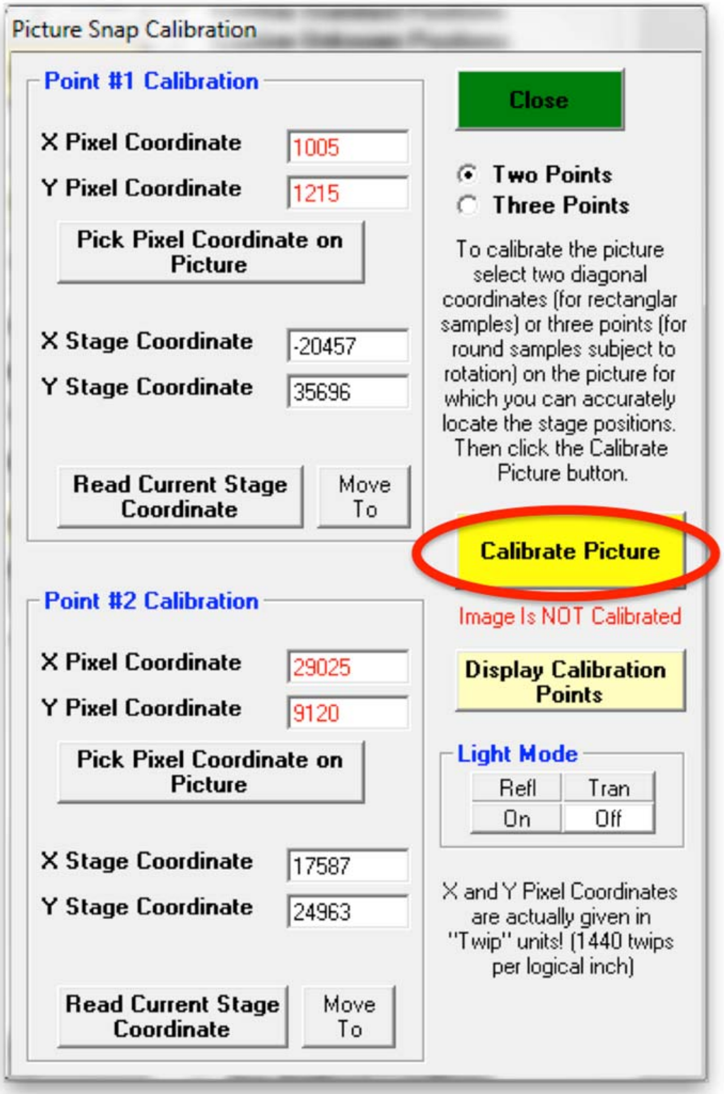
Image Is NOT Calibrated

Light Mode

X and Y Pixel Coordinates are actually given in "Twip" units! (1440 twips per logical inch)

The values shown in the *X, Y Stage Coordinates* text boxes are the current stage location. Drive the stage to the same unique location and click the **Read Current Stage Coordinate** button.

Repeat these steps for the second calibration point, resulting in the following window.



Picture Snap Calibration

Point #1 Calibration

X Pixel Coordinate: 1005
Y Pixel Coordinate: 1215
X Stage Coordinate: -20457
Y Stage Coordinate: 35696

Point #2 Calibration

X Pixel Coordinate: 29025
Y Pixel Coordinate: 9120
X Stage Coordinate: 17587
Y Stage Coordinate: 24963

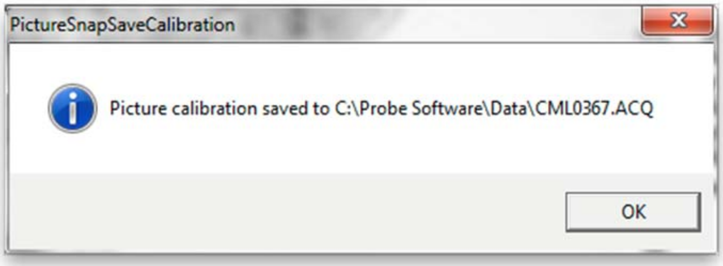
● Two Points
○ Three Points

To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

Image Is NOT Calibrated

X and Y Pixel Coordinates are actually given in "Twip" units! (1440 twips per logical inch)

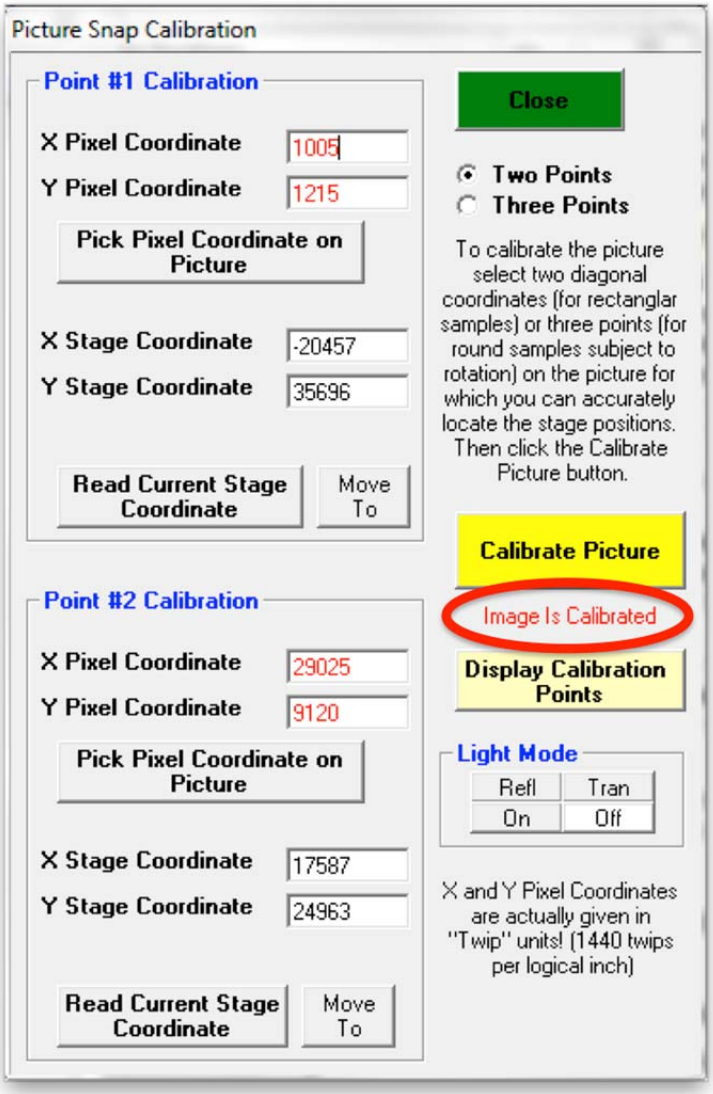
Click the **Calibrate Picture** button opening the **PictureSnapSaveCalibration** window.



Picture calibration saved to C:\Probe Software\Data\CML0367.ACQ

Click the **OK** button to save the picture calibration.

The **Picture Snap Calibration** window now indicates that the *Image Is Calibrated*.



Point #1 Calibration
X Pixel Coordinate 1005
Y Pixel Coordinate 1215
X Stage Coordinate -20457
Y Stage Coordinate 35696

Point #2 Calibration
X Pixel Coordinate 29025
Y Pixel Coordinate 9120
X Stage Coordinate 17587
Y Stage Coordinate 24963

● Two Points
○ Three Points

To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

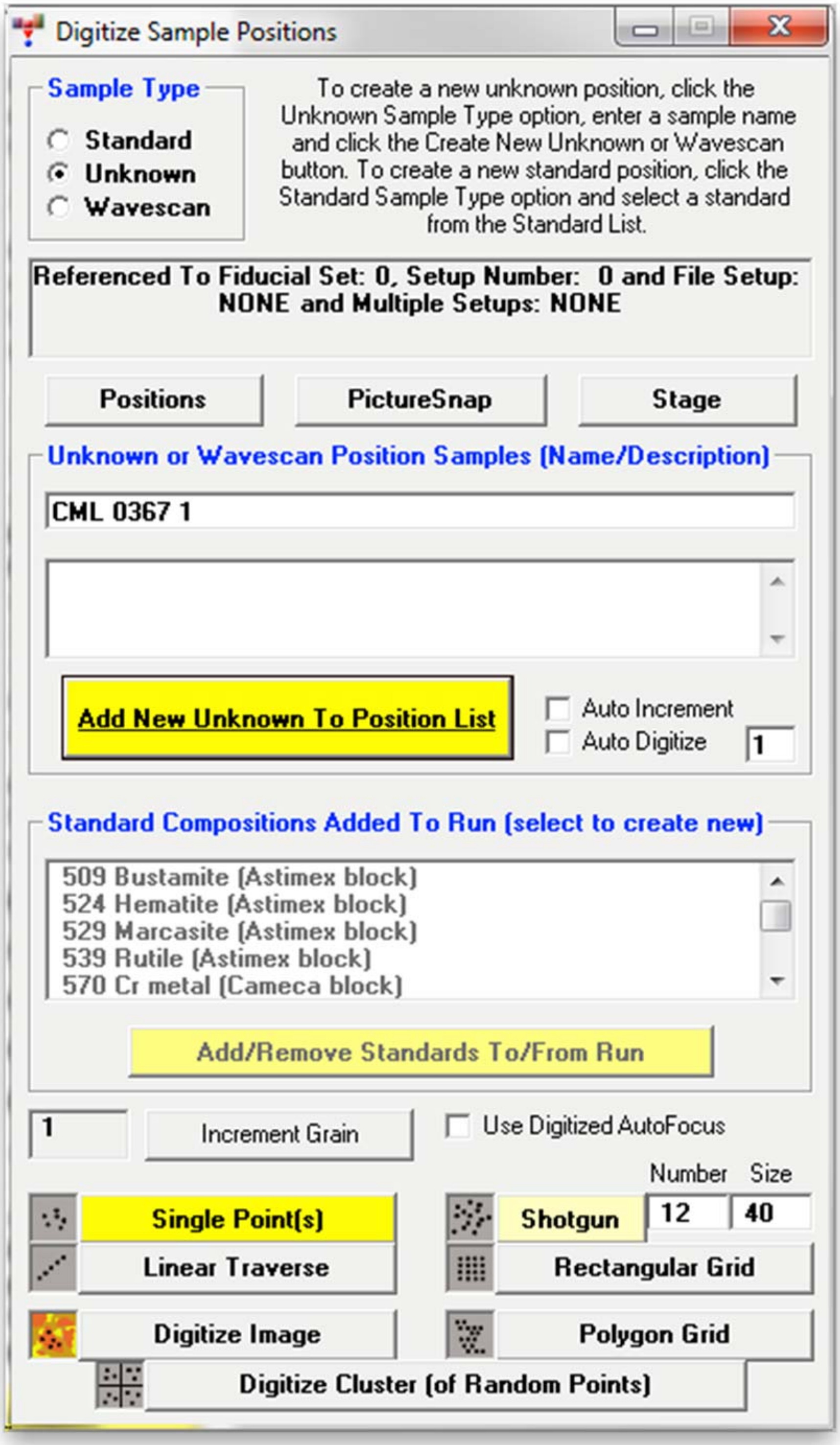
Image Is Calibrated

X and Y Pixel Coordinates are actually given in "Twip" units! (1440 twips per logical inch)

Close the **Picture Snap Calibration** window.

The operator can digitize analysis locations for later unattended work. Click the **Digitize** button.

This opens the familiar **Digitize Sample Positions** window.



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 or Wavescan Position Samples (Name/Description): CML 0367 1

Auto Digitize: 1

Standard Compositions Added To Run:

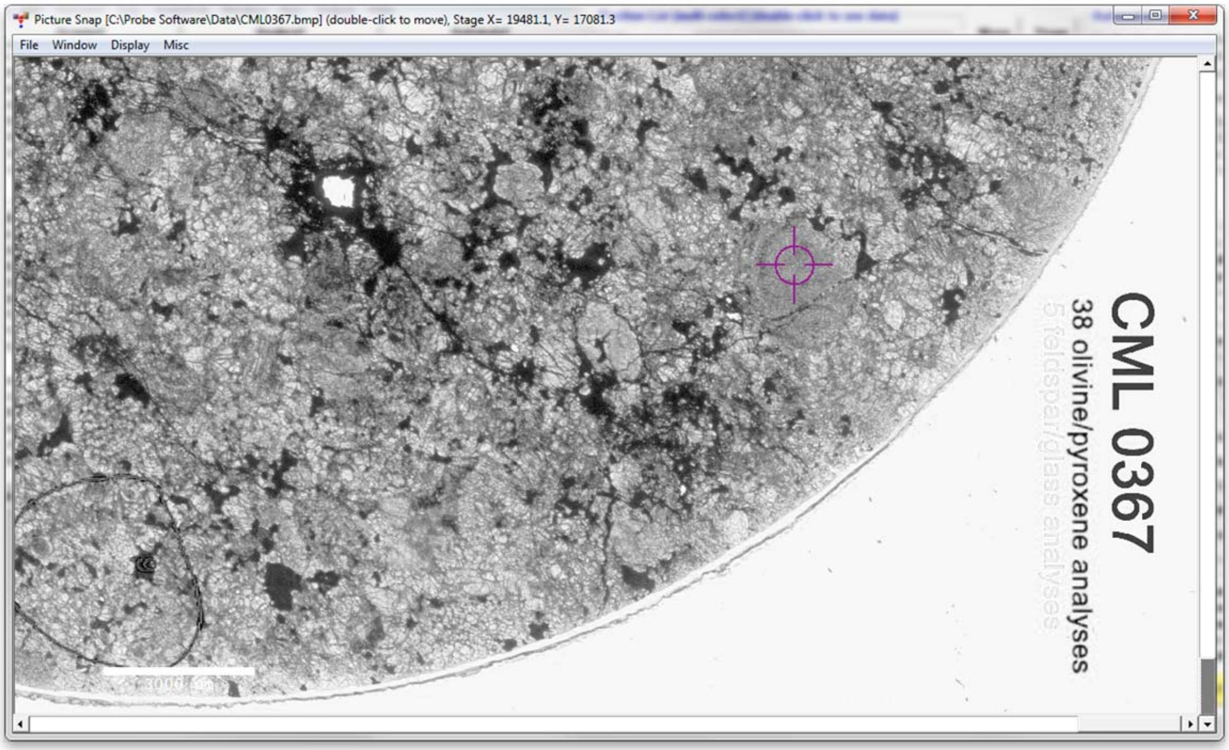
509 Bustamite (Astimex block)
524 Hematite (Astimex block)
529 Marcasite (Astimex block)
539 Rutile (Astimex block)
570 Cr metal (Cameca block)

Increment Grain: 1

Shotgun Number: 12, Size: 40

Create a new unknown.

In the **Picture Snap!** window, double click on the spot for the first analysis point on the just calibrated image to drive the stage to those coordinates. The location is displayed with a purple crosshair marker.



To now use the calibrated image for position programming, click for example **SinglePoint(s)** in the **Digitize Sample Positions** window to add a single point in this position.

All acquisition locations can be viewed in the **Picture Snap!** window by selecting the **Display | Digitized Unknown Position Samples** menu and acquired via the **Automate!** window.

Modal Analysis

Modal analysis is a statement of the composition of a sample expressed in terms of the relative amounts of phases or minerals present. These volumetric proportions can be estimated from quantitative measurements made on the specimen by point counting analysis. This quantitative modal analysis on unknown compositions is based on a defined set of modal phases, selected from a standard database. Any database of standard compositions may be used to define the phases.

There are three basic steps involved in the modal analysis routine. This procedure involves initially the acquisition of a large set of compositional data acquired using either multiple traverses or large area gridding. It is assumed that this data set is statistically representative of the sample. In the example illustrated below, a large representative area of a fine-grained sandstone thin section was gridded and some 324 quantitative analysis points were collected.

The second step involves the creation of an input file to load into STANDARD for the actual modal analysis calculation. The simplest method of generating this input file is to use the **Plot!** window in PROBE FOR EPMA to output a *.DAT file of the elemental or oxide weight percent compositions to disk.

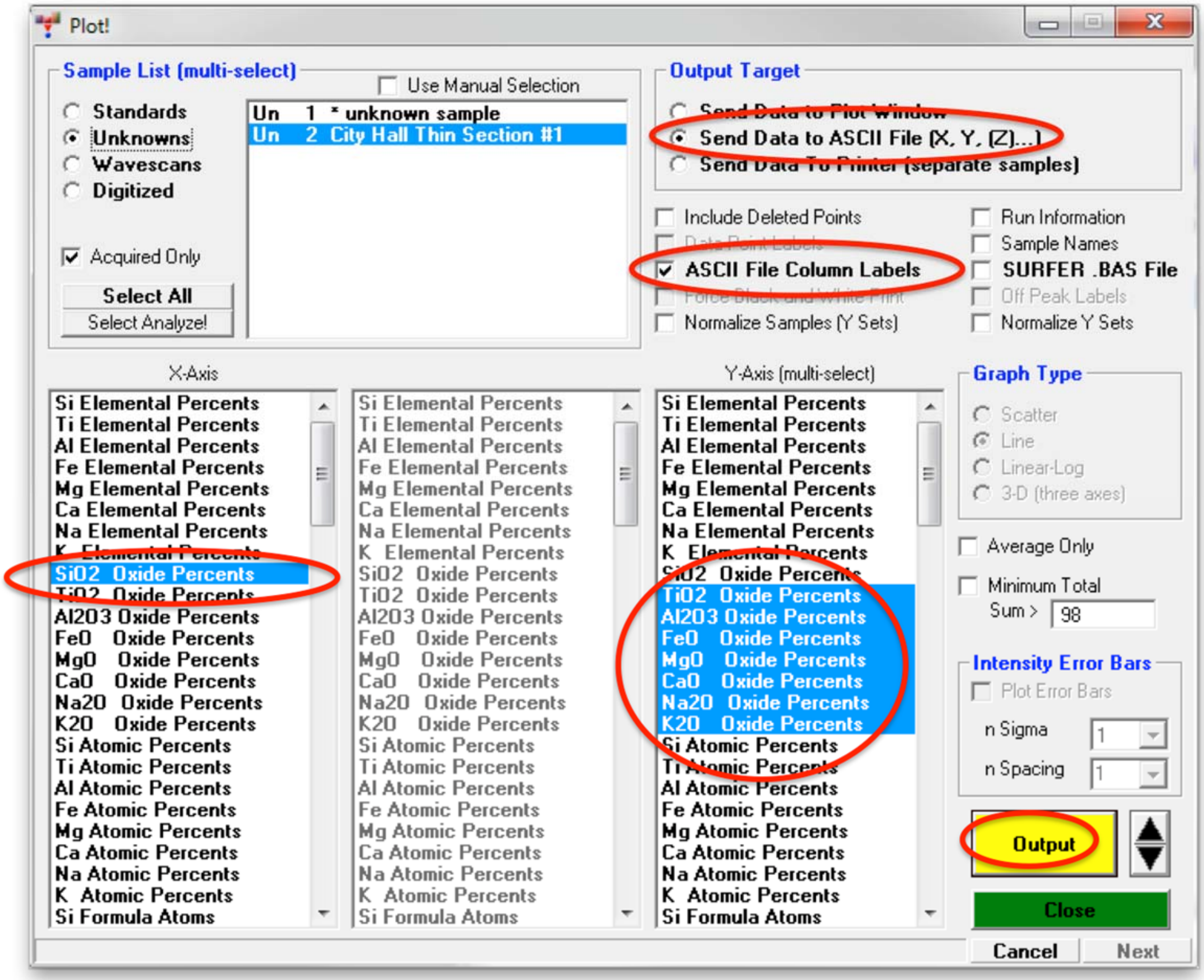
After data collection has been completed, select **Output Standard and Unknown Plots** in the **Output** menu.

Highlight the compositional dataset in the *Sample List*.

Select the first oxide for the *X-Axis* and the remainder in the *Y-Axis (multi-select)* range.

Activate the *Send Data to ASCII File (X, Y, (Z)…)* check button and the *ASCII File Column Labels* check box. The labels are required so that the modal analysis routine can identify the elements in the input file.

The input file can come from any source as long as the element or oxide symbols are in the first line, enclosed within double quotes, and the data is in weight percent. The weight percent data can be in any format. Do not include a totals column.



Plot!

Sample List (multi-select)

○ Standards
● Unknowns
○ Wavescans
○ Digitized

☐ Use Manual Selection

Un 1 * unknown sample
Un 2 City Hall Thin Section #1

☑ Acquired Only

Output Target

○ Send Data to Plot Window
● Send Data to ASCII File (X, Y, (Z)...)
○ Send Data To Printer (separate samples)

☐ Include Deleted Points
☐ Data Point Labels
☑ ASCII File Column Labels
☐ Force Black and White Print
☐ Normalize Samples (Y Sets)
☐ Run Information
☐ Sample Names
☐ SURFER .BAS File
☐ Off Peak Labels
☐ Normalize Y Sets

X-Axis

SiO2 Oxide Percents

Y-Axis (multi-select)

TiO2 Oxide Percents, Al2O3 Oxide Percents, FeO Oxide Percents, MgO Oxide Percents, CaO Oxide Percents, Na2O Oxide Percents, K2O Oxide Percents

Graph Type

○ Scatter
● Line
○ Linear-Log
○ 3-D (three axes)

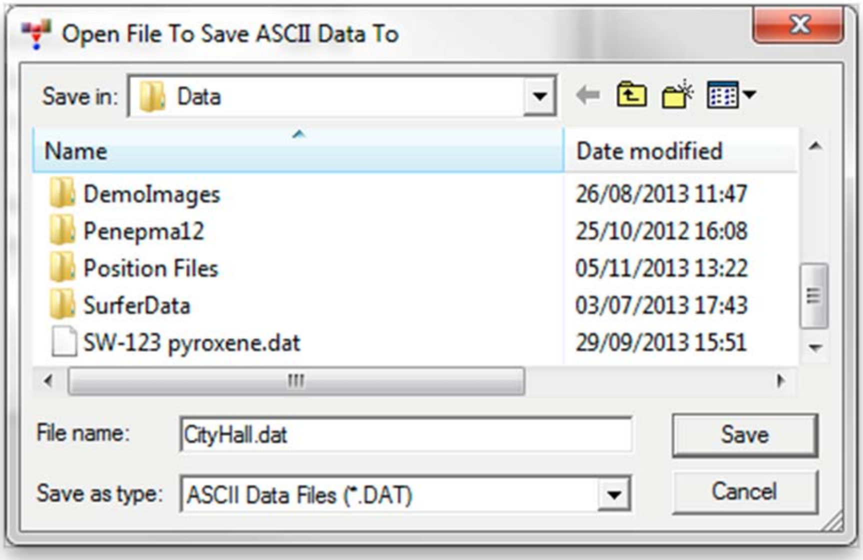
☐ Average Only
☐ Minimum Total Sum > 98

Intensity Error Bars

☐ Plot Error Bars
n Sigma 1
n Spacing 1

Click the **Output** button.

The **Open File To Save ASCII Data To** window appears. Locate the appropriate directory under *Save in:* and type in a *File name:* in the text field provided.

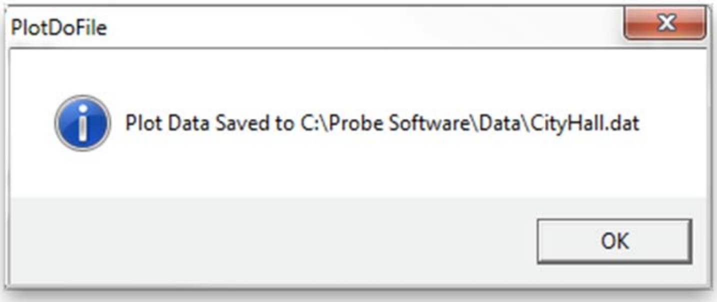


File name: CityHall.dat

Save as type: ASCII Data Files (*.DAT)

Click the **Save** button.

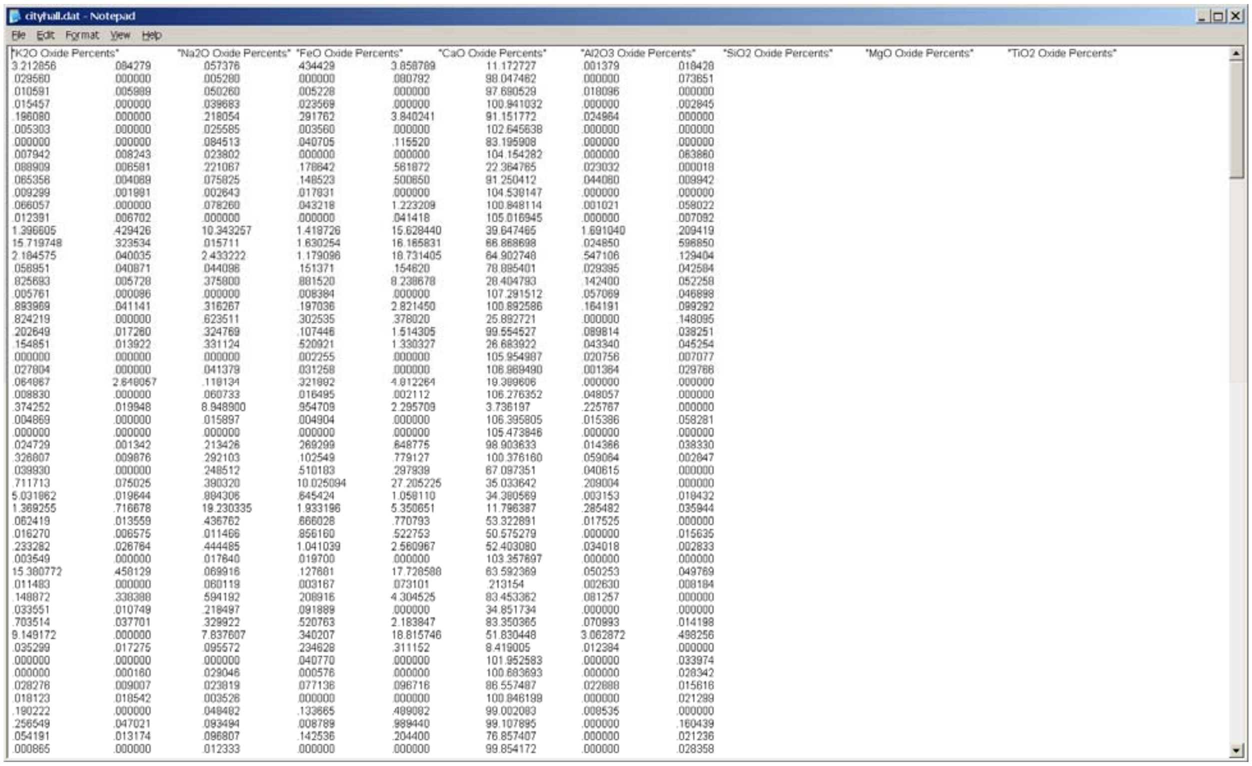
The **PlotDoFile** window appears, indicating that the data was saved.



Plot Data Saved to C:\Probe Software\Data\CityHall.dat

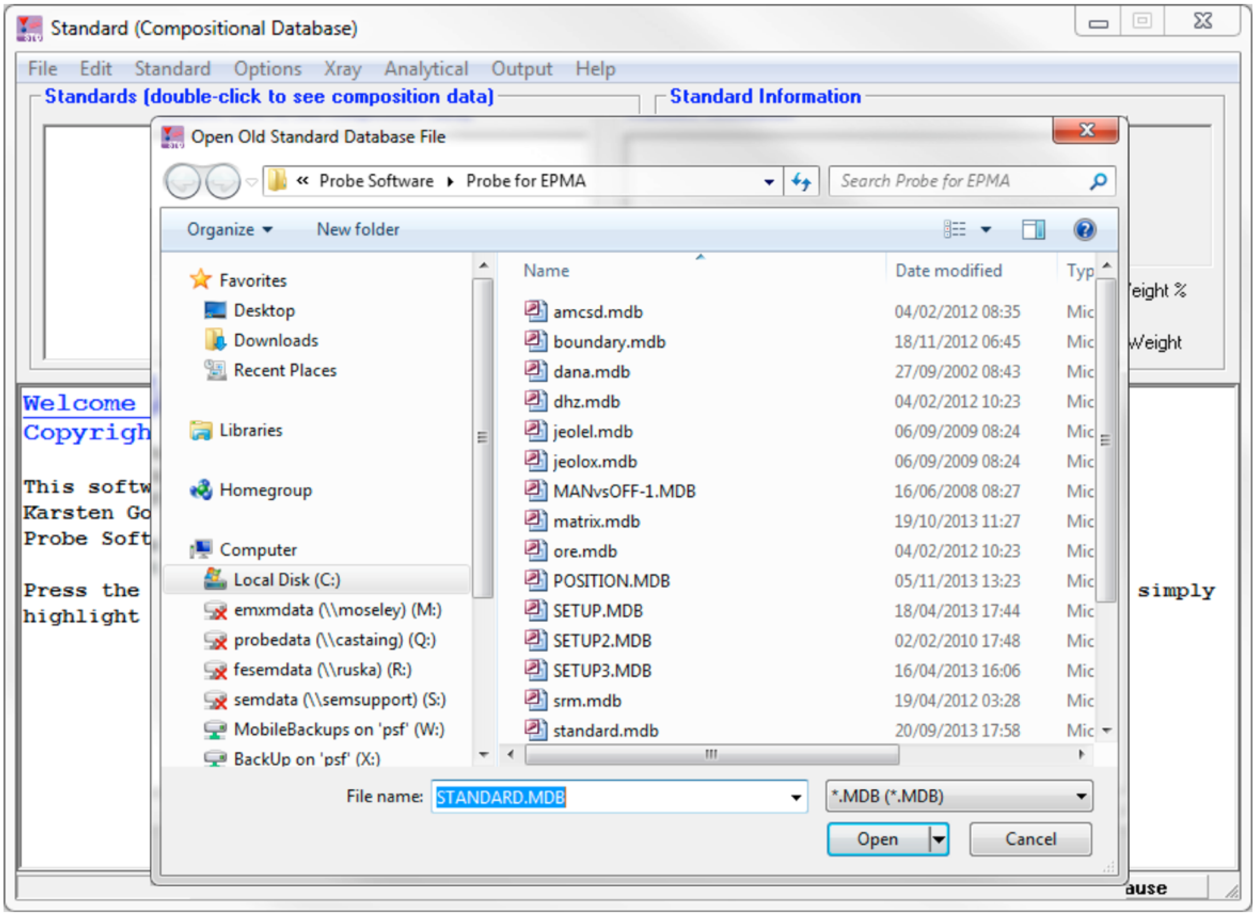
Click the **OK** button.

The data saved to the *.DAT file may be viewed using an editor such as Notepad. Here a portion of the CITYHALL.DAT file is displayed.



```
"K2O Oxide Percents"        "Na2O Oxide Percents" "FeO Oxide Percents"    "CaO Oxide Percents"    "Al2O3 Oxide Percents"    "SiO2 Oxide Percents"    "MgO Oxide Percents"    "TiO2 Oxide Percents"
3.212856        .084279     .057376     .434429     3.858789    11.172727   .001379     .018428
.029560         .000000     .005280     .000000     .080792     98.047462   .000000     .073651
.010591         .005989     .050260     .005228     .000000     97.690529   .018096     .000000
.015457         .000000     .039683     .023569     .000000     100.941032  .000000     .002845
.196080         .000000     .218054     .291762     3.840241    91.151772   .024964     .000000
.005303         .000000     .025585     .003560     .000000     102.645638  .000000     .000000
.000000         .000000     .084513     .040705     .115520     83.195908   .000000     .000000
.007942         .008243     .023802     .000000     .000000     104.154282  .000000     .063860
.088909         .006581     .221067     .178642     .561872     22.364765   .023032     .000018
.065356         .004089     .075825     .148523     .500650     91.250412   .044080     .009942
.009299         .001981     .002643     .017831     .000000     104.538147  .000000     .000000
.066057         .000000     .078260     .043218     1.223209    100.848114  .001021     .058022
.012391         .006702     .000000     .000000     .041418     105.016945  .000000     .007092
1.396605        .429426     10.343257   1.418726    15.628440   39.647465   1.691040    .209419
15.719748       .323534     .015711     1.630254    16.165831   66.868698   .024850     .596850
2.184575        .040035     2.433222    1.179098    18.731405   64.902748   .547106     .129404
.058951         .040871     .044096     .151371     .154620     78.895401   .029395     .042584
.825693         .005728     .375800     .881520     8.238678    28.404793   .142400     .052258
.005761         .000086     .000000     .008384     .000000     107.291512  .057069     .046898
.893969         .041141     .316267     .197036     2.821450    100.892586  .164191     .099292
.824219         .000000     .623511     .302535     .378020     25.892721   .000000     .148095
.202649         .017260     .324769     .107446     1.514305    99.554527   .089814     .038251
.154851         .013922     .331124     .520921     1.330327    26.683922   .043340     .045254
.000000         .000000     .000000     .002255     .000000     105.954987  .020756     .007077
.027804         .000000     .041379     .031258     .000000     106.969490  .001364     .029766
.064967         2.648057    .118134     .321892     4.812264    19.389606   .000000     .000000
.008830         .000000     .060733     .016495     .002112     106.276352  .048057     .000000
.374252         .019948     8.948900    .954709     2.295709    3.736197    .225767     .000000
.004869         .000000     .015897     .004904     .000000     106.395805  .015386     .058281
.000000         .000000     .000000     .000000     .000000     105.473846  .000000     .000000
.024729         .001342     .213426     .269299     .648775     98.903633   .014366     .038330
.326807         .009876     .292103     .102549     .779127     100.376160  .059064     .002847
.039930         .000000     .248512     .510183     .297939     67.097351   .040615     .000000
.711713         .075025     .390320     10.025094   27.205225   35.033642   .209004     .000000
5.031862        .019644     .884306     .645424     1.058110    34.380569   .003153     .018432
1.369255        .716678     19.230335   1.933196    5.350651    11.796387   .285482     .035944
.062419         .013559     .436762     .666028     .770793     53.322891   .017525     .000000
.016270         .006575     .011466     .856160     .522753     50.575279   .000000     .015635
.233282         .026764     .444485     1.041039    2.560967    52.403080   .034018     .002833
.003549         .000000     .017640     .019700     .000000     103.357697  .000000     .000000
15.380772       .458129     .069916     .127681     17.728588   63.592369   .050253     .049769
.011483         .000000     .060119     .003167     .073101     .213154     .002630     .008184
.148872         .338388     .594192     .208916     4.304525    83.453362   .081257     .000000
.033551         .010749     .218497     .091889     .000000     34.851734   .000000     .000000
.703514         .037701     .329922     .520763     2.183847    83.350365   .070993     .014198
9.149172        .000000     7.837607    .340207     18.815746   51.830448   3.062872    .498256
.035299         .017275     .095572     .234628     .311152     8.419005    .012384     .000000
.000000         .000000     .000000     .040770     .000000     101.952583  .000000     .033974
.000000         .000160     .029046     .000576     .000000     100.683693  .000000     .028342
.028276         .009007     .023819     .077136     .096716     86.557487   .022888     .015616
.018123         .018542     .003526     .000000     .000000     100.846199  .000000     .021299
.190222         .000000     .048482     .133665     .489082     99.002083   .008535     .000000
.256549         .047021     .093494     .008789     .989440     99.107895   .000000     .160439
.054191         .013174     .096807     .142536     .204400     76.857407   .000000     .021236
.000865         .000000     .012333     .000000     .000000     99.854172   .000000     .028358
```

The third and final step involves the setup and running of the modal analysis calculation. The modal analysis routine is located in STANDARD. Select the **Standard | Standard Database** menu to open the **Standard** application.



Name	Date modified	Typ
amcsd.mdb	04/02/2012 08:35	Mic
boundary.mdb	18/11/2012 06:45	Mic
dana.mdb	27/09/2002 08:43	Mic
dhz.mdb	04/02/2012 10:23	Mic
jeolel.mdb	06/09/2009 08:24	Mic
jeolox.mdb	06/09/2009 08:24	Mic
MANvsOFF-1.MDB	16/06/2008 08:27	Mic
matrix.mdb	19/10/2013 11:27	Mic
ore.mdb	04/02/2012 10:23	Mic
POSITION.MDB	05/11/2013 13:23	Mic
SETUP.MDB	18/04/2013 17:44	Mic
SETUP2.MDB	02/02/2010 17:48	Mic
SETUP3.MDB	16/04/2013 16:06	Mic
srm.mdb	19/04/2012 03:28	Mic
standard.mdb	20/09/2013 17:58	Mic

This softw
Karsten Go
Probe Soft

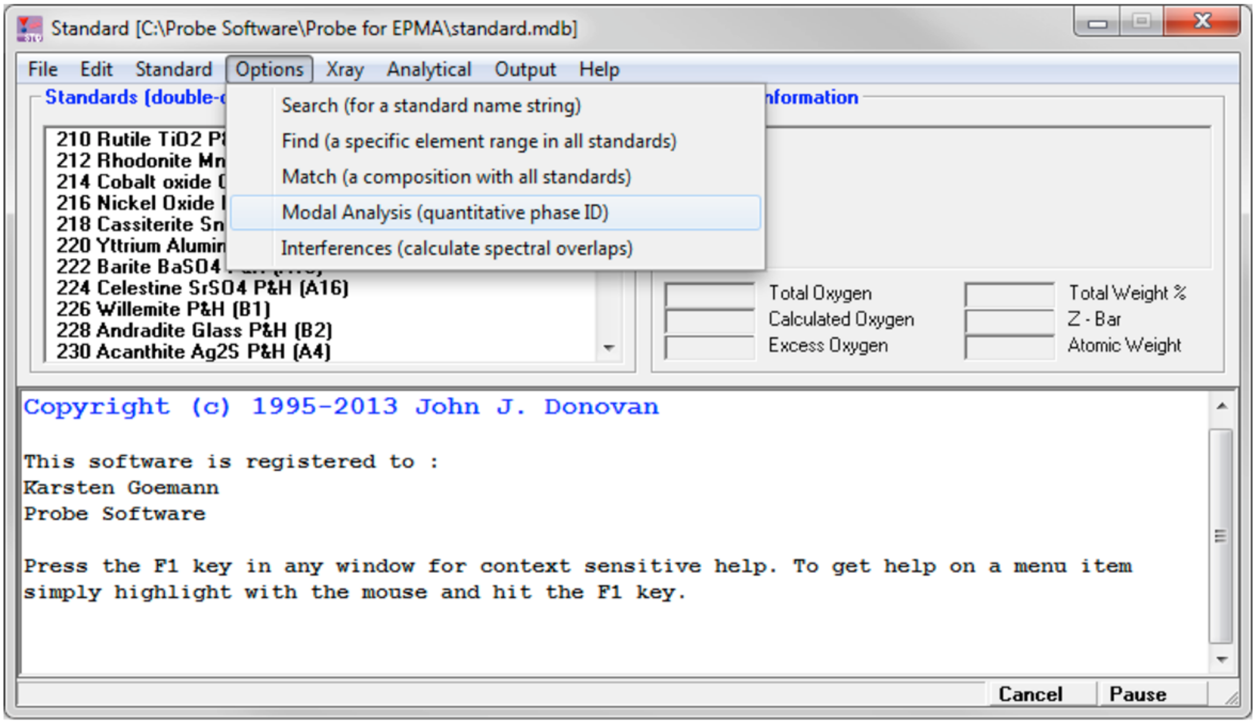
Press the
highlight

File name: STANDARD.MDB

.MDB (.MDB)

Select (highlight) a standard database that will be used to define the modal phases. Click the **Open** button to load this database.

Select **Options** | **Modal Analysis** from the menu.



```
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This software is registered to :
Karsten Goemann
Probe Software

Press the F1 key in any window for context sensitive help. To get help on a menu item
simply highlight with the mouse and hit the F1 key.
```
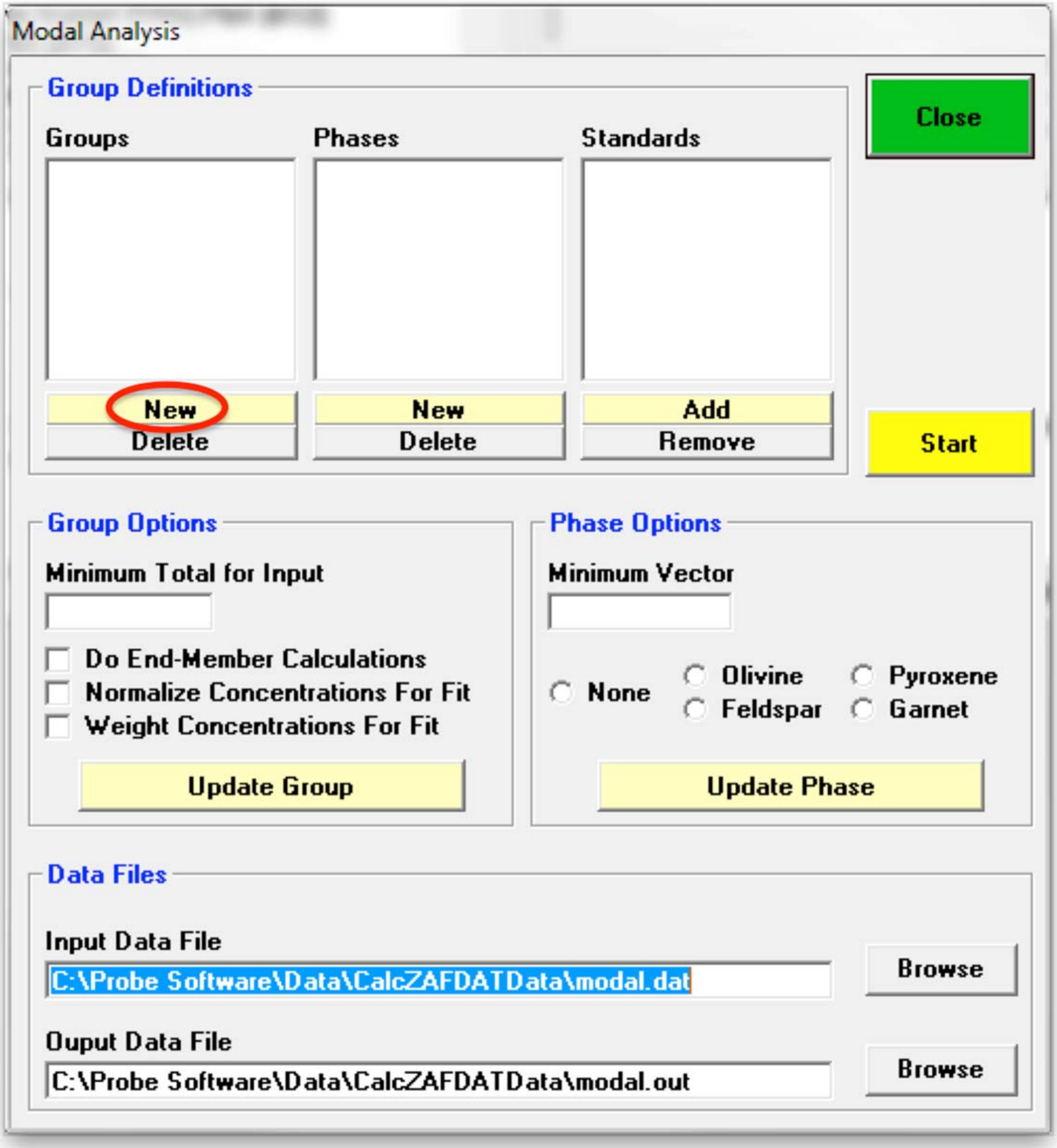
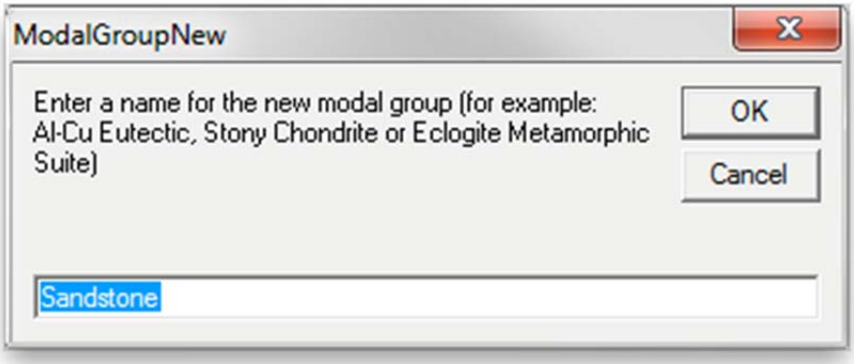

The **Modal Analysis** window opens. Start by defining an overall Group. Click the **New** button under *Groups*.



Input Data File
C:\Probe Software\Data\CalcZAFDATData\modal.dat

Ouput Data File
C:\Probe Software\Data\CalcZAFDATData\modal.out

The **ModalGroupNew** window opens. Enter a descriptive name for the group of phases.



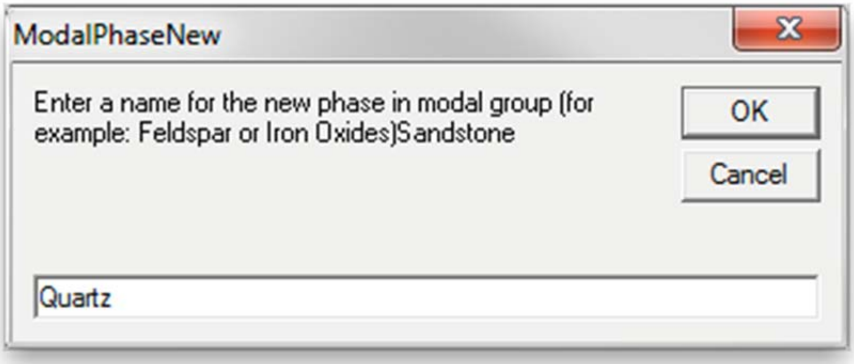
Enter a name for the new modal group (for example: Al-Cu Eutectic, Stony Chondrite or Eclogite Metamorphic Suite)

Sandstone

Click the **OK** button. Default *Group* and *Phase Options* are loaded; these will be discussed and modified shortly.

Click the **New** button under *Phases*.

The **ModalPhaseNew** window opens. Enter the first modal phase. In this example, the sandstone is composed of mostly quartz with two minor feldspars; an alkali (sodium-potassium) phase and a plagioclase phase along with iron oxides and other trace accessory minerals. The first modal phase is entered into the text field.

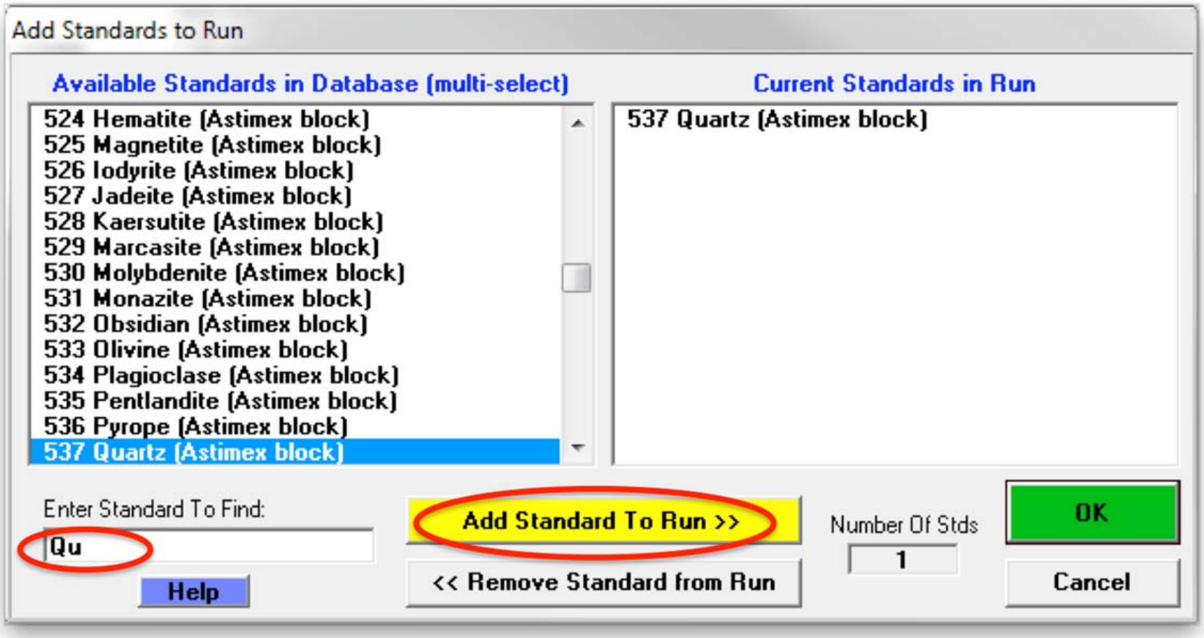


Enter a name for the new phase in modal group (for example: Feldspar or Iron Oxides)Sandstone

Quartz

Click the **OK** button.

Select the **Add** button under *Standards*, opening the **Add Standards to Run** window.



Available Standards in Database (multi-select):

524 Hematite (Astimex block)
525 Magnetite (Astimex block)
526 Iodyrite (Astimex block)
527 Jadeite (Astimex block)
528 Kaersutite (Astimex block)
529 Marcasite (Astimex block)
530 Molybdenite (Astimex block)
531 Monazite (Astimex block)
532 Obsidian (Astimex block)
533 Olivine (Astimex block)
534 Plagioclase (Astimex block)
535 Pentlandite (Astimex block)
536 Pyrope (Astimex block)
537 Quartz (Astimex block)

Current Standards in Run:

537 Quartz (Astimex block)

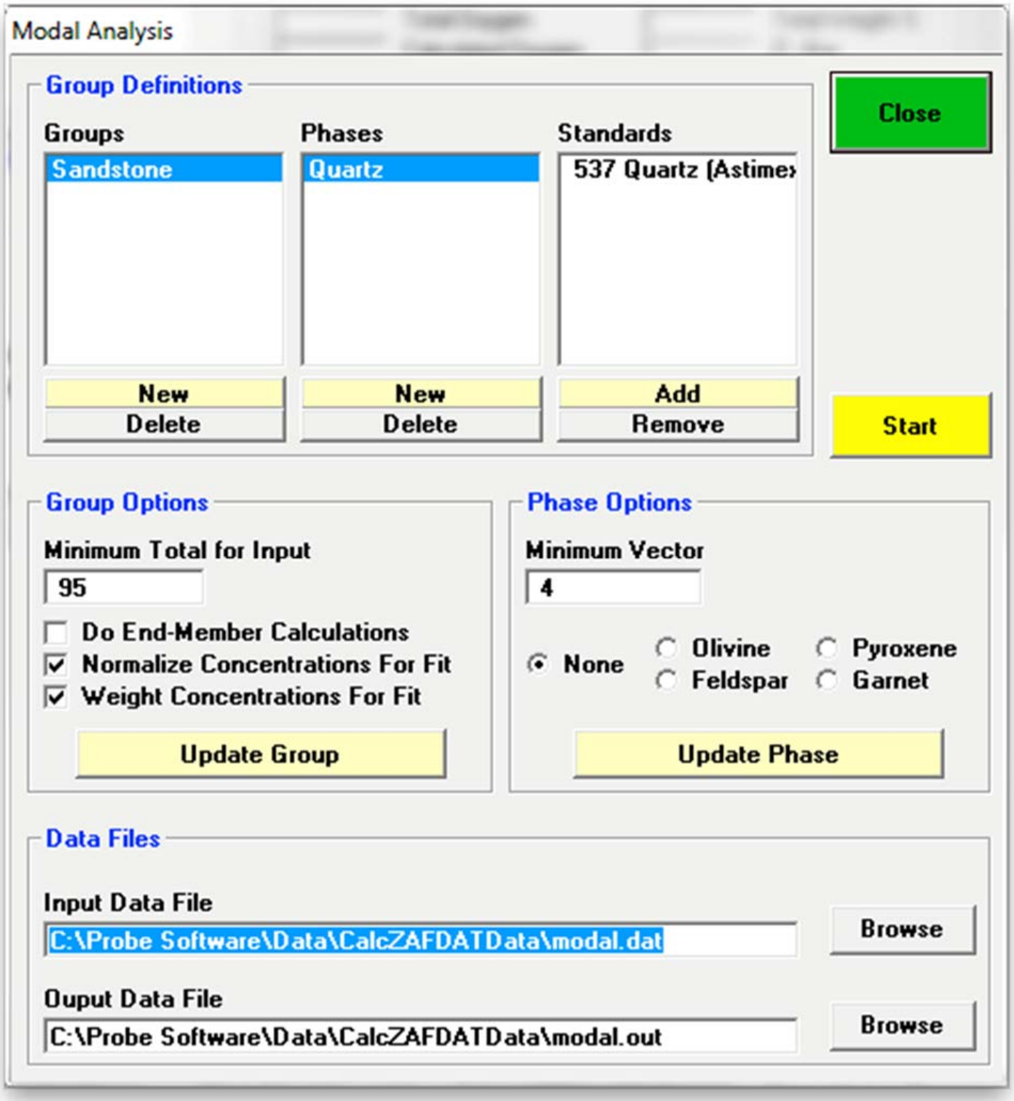
Enter Standard To Find: Qu

Number Of Stds: 1

Choose standards to define this modal phase. You can enter a search string into the **Enter Standard To Find** field and the software will highlight the first occurrence. **Click the Add Standard To Run** >> button to add the standard to this phase.

These are the phase compositions that the program will use to match against the unknown point analyses. Try to avoid over-determining the phase. For example, when defining a sodium-potassium feldspar, select the two end-members (albite and microcline).

The **Modal Analysis** window would now appear as below.



Groups: Sandstone

Phases: Quartz

Standards: 537 Quartz (Astime

Minimum Total for Input: 95

☐ Do End-Member Calculations

☑ Normalize Concentrations For Fit

☑ Weight Concentrations For Fit

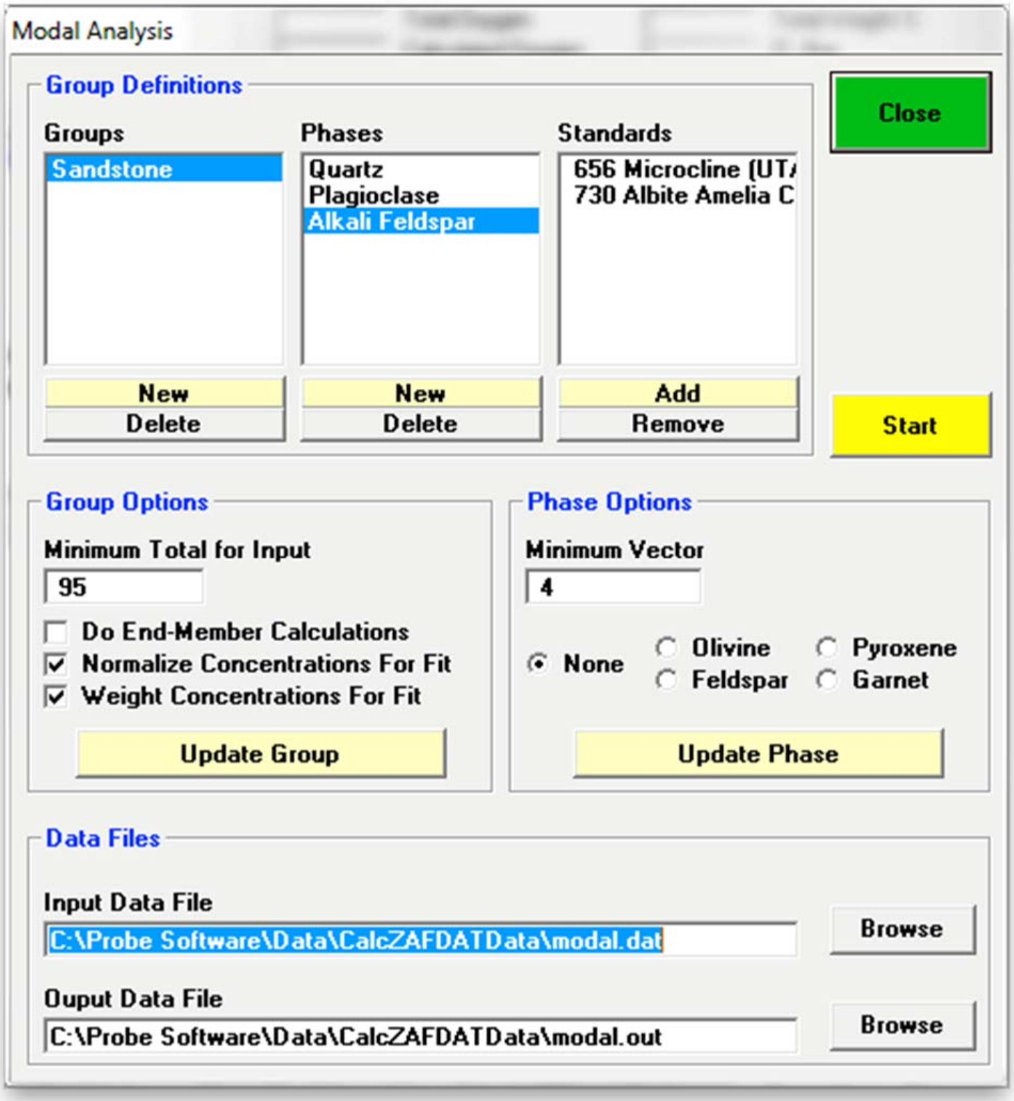
Minimum Vector: 4

● None ○ Olivine ○ Feldspar ○ Pyroxene ○ Garnet

Input Data File: C:\Probe Software\Data\CalcZAFDATData\modal.dat

Ouput Data File: C:\Probe Software\Data\CalcZAFDATData\modal.out

Continue and enter all phases, defining the phase compositions (standards) to match. The Alkali Feldspar entry is illustrated below.



Groups
Sandstone

Phases
Quartz
Plagioclase
Alkali Feldspar

Standards
656 Microcline (UT
730 Albite Amelia C

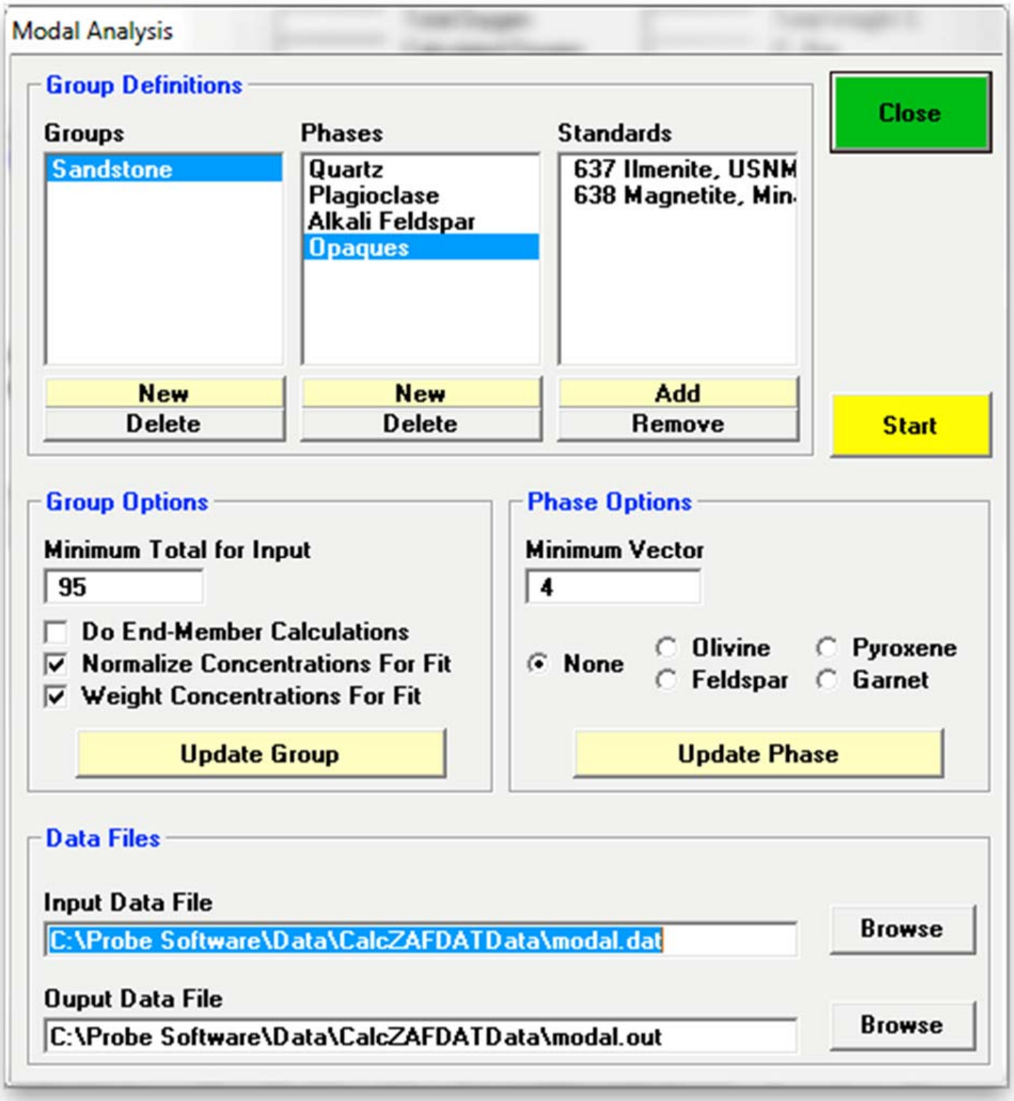
Minimum Total for Input: 95
☐ Do End-Member Calculations
☑ Normalize Concentrations For Fit
☑ Weight Concentrations For Fit

Minimum Vector: 4
● None ○ Olivine ○ Feldspar ○ Pyroxene ○ Garnet

Input Data File: C:\Probe Software\Data\CalcZAFDATData\modal.dat

Ouput Data File: C:\Probe Software\Data\CalcZAFDATData\modal.out

Once all of the phases have been identified and standards defined for matching, adjust the *Group* and *Phase Options*.



Groups: Sandstone

Phases: Quartz, Plagioclase, Alkali Feldspar, Opaques

Standards: 637 Ilmenite, USNM; 638 Magnetite, Min.

Minimum Total for Input: 95

☐ Do End-Member Calculations
☑ Normalize Concentrations For Fit
☑ Weight Concentrations For Fit

Minimum Vector: 4

● None ○ Olivine ○ Pyroxene ○ Feldspar ○ Garnet

Input Data File: C:\Probe Software\Data\CalcZAFDATData\modal.dat

Ouput Data File: C:\Probe Software\Data\CalcZAFDATData\modal.out

The *Minimum Total for Input* is the rejection sum for the unknown compositions, sums below this value will not be used in the modal analysis. Typically 90-95% are good cutoffs.

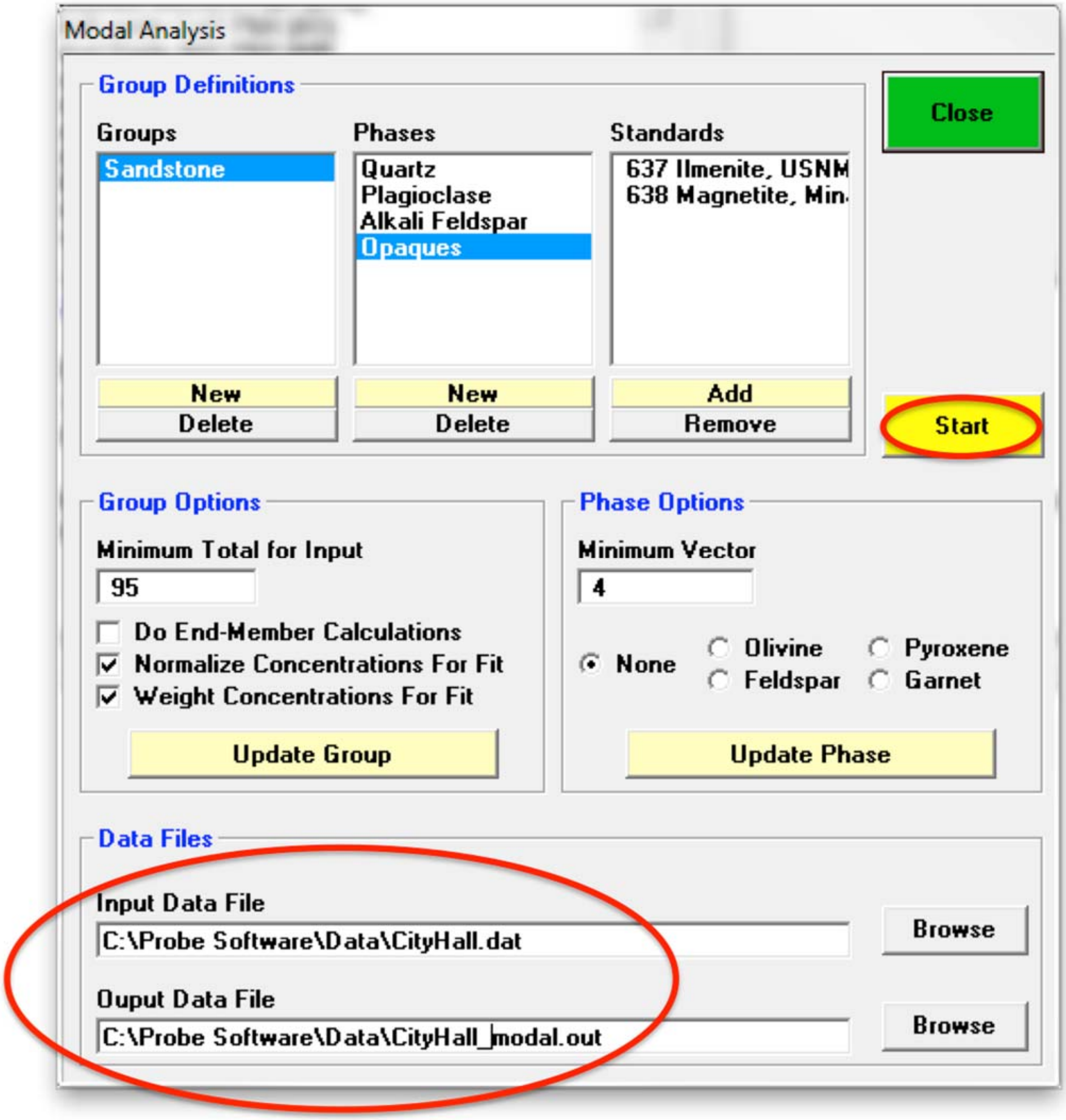
Select the *Do End-Member Calculations* option and check the appropriate mineral name under *Phase Options* to perform end-member calculations as listed.

The *Normalize Concentrations For Fit* option is used to specify whether the standard and unknown concentrations (above the just defined minimum input total) should be normalized to 100% before the vector fit is calculated.

The *Weight Concentrations For Fit* option is used to specify if the element concentrations for the standards should be weighted, based on the composition of the element in that phase. Select this option if the major elements in a phase should have greater influence in determining the vector fit. Leave unselected, if all concentrations, regardless of their abundance should have equal weight in the vector fit.

The *Minimum Vector* number (default is 4.0) is basically the tolerance for the match to a defined phase. If a closer match is desired for one or more phases in the group, decrease the vector value for that phase. See the User's Guide and Reference documentation for specific details on the calculation of this vector.

Finally, under *Data Files*, select the appropriate *Input* and *Output Data File* locations and click the **Start** button to initiate the modal analysis calculation on each data point.



Modal Analysis

Group Definitions

Groups: Sandstone

Phases:
- Quartz
- Plagioclase
- Alkali Feldspar
- Opaques

Standards:
- 637 Ilmenite, USNM
- 638 Magnetite, Min.

Group Options

Minimum Total for Input: 95

☐ Do End-Member Calculations
☑ Normalize Concentrations For Fit
☑ Weight Concentrations For Fit

Phase Options

Minimum Vector: 4

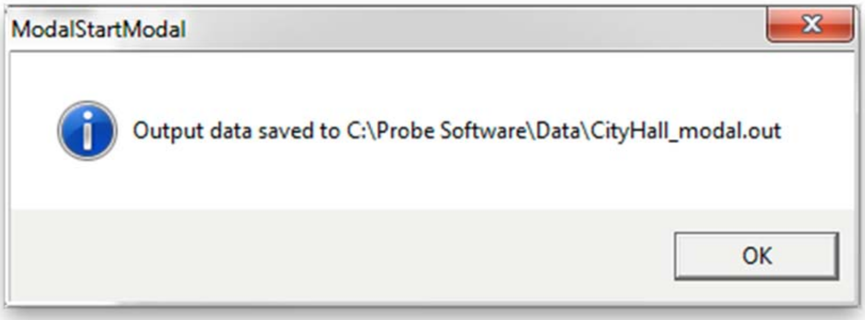
● None ○ Olivine ○ Pyroxene ○ Feldspar ○ Garnet

Data Files

Input Data File: C:\Probe Software\Data\CityHall.dat

Ouput Data File: C:\Probe Software\Data\CityHall_modal.out

After the calculation finishes the **ModalStartModal** window appears, stating that the output data has been saved to the specified *.OUT file.



Output data saved to C:\Probe Software\Data\CityHall_modal.out

Click this **OK** button.

The modal analysis data may now be viewed in the log window in STANDARD or simply open the newly created *.OUT file. The output file contains the vector fit, matched phase, end-member calculation (if checked), totals column and composition of each line in the input file. Lines that do not meet the minimum total requirement are excluded from the output, if those lines are desired either cut and paste the entire output from the main STANDARD log window or capture the entire output by EARLIER selecting the **Output | Save To Disk Log** menu.

The results of the modal analysis are also tabulated and summarized. The end summary lists the total number of analyses, the minimum total for a valid composition, number of valid points that sum above the minimum sum, the number of matched points and the percentage of points that were matched.

For each phase, the summary output then lists the phase name, the number of matches for that phase, the percent of matched points, valid points and total matched points for the matches in that phase. This is followed by the average end-member (if selected), weight percent sum and composition for that phase and the standard deviation for each element.

The last page of the just run output file is displayed below.

```
    Line  Vector   Phase     Sum     K2O    Na2O     FeO     CaO   Al2O3    SiO2     MgO    TiO2

………….268     .05  Quartz  100.30     .03     .02     .10     .10     .08   99.93     .00     .04
     269     .04  Quartz   99.50     .02     .01     .12     .00     .12   99.17     .00     .06
     270     .00  Quartz   99.66     .00     .00     .02     .00     .00   99.60     .00     .04
     271     .06  Quartz   99.97     .02     .01     .20     .00     .12   99.62     .00     .00
     272  ------  ------     .21     .04     .00     .00     .02     .03     .12     .01     .00
     273     .00  Quartz   99.10     .01     .00     .02     .01     .00   99.04     .00     .02
     274     .02  Quartz  100.07     .00     .00     .01     .00     .19   99.87     .00     .00
     275     .02 Alkali    99.50     .23   11.50     .32     .03   18.85   68.57     .00     .00
     276  ------  ------   36.50    5.25     .13    1.22    1.35    6.90   21.61     .04     .00
     277     .00  Quartz   99.68     .00     .00     .01     .00     .00   99.68     .00     .00
     278     .04  Quartz   98.30     .07     .00     .00     .03     .15   97.96     .03     .06
     279  ------  ------     .13     .00     .00     .05     .02     .01     .06     .00     .00
     280     .02  Quartz   99.17     .00     .00     .13     .03     .00   99.00     .01     .00
     281     .06 Alkali    98.43   15.22     .24     .07     .01   18.23   64.65     .01     .00
     282     .00  Quartz   99.79     .01     .00     .03     .00     .00   99.75     .00     .00
     283     .01 Plagioc   98.09     .13     .02     .03   18.91   35.54   43.35     .07     .03
     284     .00  Quartz   99.75     .00     .00     .04     .00     .00   99.68     .02     .01
     285     .00  Quartz   99.59     .01     .00     .04     .00     .00   99.53     .02     .00
     286     .67  Quartz   92.61     .07     .01     .29     .54     .16   91.46     .02     .06
     287     .00  Quartz   99.43     .00     .00     .00     .03     .03   99.32     .00     .05
     288     .02 Opaques   92.35     .03     .04   88.00     .01     .12     .42     .38    3.36
     289  ------  ------   31.13     .23     .01     .15    1.66    1.45   27.55     .08     .00
     290     .02  Quartz   99.65     .00     .00     .13     .00     .00   99.52     .00     .00
     291     .13 Plagioc   99.23     .87     .08     .03   18.34   36.21   43.59     .09     .01
     292  ------  ------   13.55     .04     .27     .07     .30     .19   12.55     .11     .03
     293     .03 Plagioc   99.23     .03     .30     .12   18.88   36.27   43.54     .02     .07
     294  ------  ------    9.42     .45     .00     .47     .56     .07    7.72     .00     .15
     295  ------  ------   35.75     .30     .01     .61     .72   11.33   22.68     .09     .00
     296  ------  ------     .86     .00     .00     .01     .01     .00     .85     .00     .00
     297     .00  Quartz   99.88     .01     .00     .04     .01     .03   99.78     .00     .01
     298     .21  Quartz   93.18     .13     .02     .20     .07     .20   92.48     .01     .07
     299     .10  Quartz   98.14     .05     .03     .14     .12     .12   97.63     .03     .02
     300     .00  Quartz  100.08     .00     .00     .04     .00     .00  100.05     .00     .00
     301     .01  Quartz   99.49     .01     .00     .04     .02     .00   99.34     .02     .06
     302     .02  Quartz  100.11     .00     .00     .08     .04     .00   99.91     .02     .07
     303     .00  Quartz  100.32     .00     .00     .02     .02     .00  100.28     .00     .01
     304     .00  Quartz   99.95     .00     .00     .00     .00     .00   99.95     .00     .00
     305     .00  Quartz   99.97     .00     .00     .00     .00     .00   99.92     .00     .05
     306     .02  Quartz  100.39     .01     .00     .09     .01     .00  100.21     .00     .06
     307  ------  ------    7.62     .79     .00     .12     .33    1.09    5.27     .01     .00
     308  ------  ------   15.00     .14     .01     .22     .22     .72   13.64     .04     .01
     309  ------  ------    2.08     .06     .01     .14     .23     .36    1.26     .02     .00
     310     .01 Plagioc   98.90     .14     .15     .01   19.20   35.63   43.65     .06     .06
     311     .00  Quartz  101.36     .02     .00     .00     .02     .00  101.32     .00     .01
     312     .02 Plagioc   99.02     .27     .01     .00   19.01   35.78   43.84     .11     .00
     313  ------  ------   19.98     .32     .02    1.38    1.25    4.13   12.56     .30     .01
     314  ------  ------   44.17     .04     .00     .15     .26   17.47   26.15     .01     .08
     315  ------  ------    6.51     .00     .01     .05     .00     .10    6.34     .00     .00
     316     .01  Quartz  100.85     .01     .00     .07     .00     .00  100.76     .00     .00
     317  ------  ------     .40     .00     .00     .02     .02     .02     .32     .01     .01
     318     .01  Quartz  100.95     .03     .00     .05     .02     .00  100.81     .04     .01
     319     .00  Quartz  101.53     .00     .00     .03     .01     .00  101.46     .00     .03
     320     .56  Quartz   98.51     .06     .00     .01     .33     .71   97.31     .07     .01
     321     .01  Quartz  101.04     .02     .00     .07     .00     .00  100.92     .03     .00
     322     .01  Quartz  101.03     .02     .00     .05     .02     .01  100.88     .00     .06
     323     .00  Quartz  100.46     .00     .00     .00     .00     .00  100.45     .00     .01
     324  ------  ------     .13     .00     .01     .02     .00     .00     .08     .00     .02
```

```
Results of Modal Analysis

InputFile    : C:\UserData\Probe Projects FY11\cityhall.dat
OutputFile   : C:\UserData\Probe Projects FY11\modal.out
Date and Time: 1/24/2011 7:46:51 PM


Group Name   : Sandstone
Total Number of Points in File :  324
Valid Number of Points in File :  240
Match Number of Points in File :  237

Minimum Total for Valid Points :    90.00
Percentage of Valid Points :     74.1
Percentage of Match Points :     73.1

   Phase  #Match  %Total  %Valid  %Match  AvgVec
  Quartz     190    58.6    79.2    80.2     .09
             Sum     K2O    Na2O     FeO     CaO   Al2O3    SiO2     MgO    TiO2
Average:   99.27     .03     .01     .06     .04     .10   98.99     .01     .03
Std Dev:    2.00     .08     .03     .08     .08     .21    2.12     .03     .03
Minimum:   90.60     .00     .00     .00     .00     .00   89.53     .00     .00
Maximum:  102.77     .89     .34     .50     .54    1.52  101.46     .32     .20

Phase  #Match  %Total  %Valid  %Match  AvgVec
Plagiocl      20     6.2     8.3     8.4     .05
             Sum     K2O    Na2O     FeO     CaO   Al2O3    SiO2     MgO    TiO2
Average:   99.15     .31     .05     .08   18.73   36.01   43.90     .05     .02
Std Dev:     .78     .34     .07     .10     .47     .28     .40     .03     .02
Minimum:   97.58     .02     .00     .00   17.95   35.54   43.32     .00     .00
Maximum:  100.25    1.31     .30     .39   19.42   36.48   44.88     .11     .07

   Phase  #Match  %Total  %Valid  %Match  AvgVec
Alkali F      21     6.5     8.8     8.9     .06
             Sum     K2O    Na2O     FeO     CaO   Al2O3    SiO2     MgO    TiO2
Average:   99.11   13.19    1.83     .07     .22   18.40   65.33     .02     .03
Std Dev:     .61    5.39    4.01     .07     .19     .28    1.50     .03     .04
Minimum:   97.60     .11     .02     .00     .01   18.02   63.91     .00     .00
Maximum:  100.05   15.86   11.65     .32     .71   18.85   69.24     .08     .13

   Phase  #Match  %Total  %Valid  %Match  AvgVec
 Opaques       6     1.9     2.5     2.5     .16
             Sum     K2O    Na2O     FeO     CaO   Al2O3    SiO2     MgO    TiO2
Average:   91.69     .09     .05   88.86     .18     .39     .94     .43     .75
Std Dev:    1.10     .07     .04     .64     .22     .46     .43     .33    1.31
Minimum:   90.33     .01     .02   88.00     .00     .12     .42     .22     .03
Maximum:   93.13     .18     .11   89.56     .59    1.29    1.38    1.09    3.36
```

Click the **Close** button on the **Modal Analysis** window.

Finish by exiting STANDARD.

Deadtime Calculations

This section describes how to calibrate the deadtime constants for each spectrometer and where to enter them so that PROBE FOR EPMA will utilize these factors.

Deadtime (τ) is defined as the time interval (after arrival of a pulse) when the counting system does not respond to additional incoming pulses (Reed, 1993). The equation normally used to correct for deadtime losses is given as:

$$n = \frac{n'}{(1 - \tau n')} \quad (1)$$

Where: n is the deadtime corrected count rate in counts per second
n' is the measured count rate in counts per second
τ is the deadtime constant in seconds

The time interval when the counting system is dead to additional pulses is defined as $\tau n'$. The live time then, is $(1-\tau n')$. The true count rate (n) is proportional to the beam current (i) by a constant factor, designated k. Thus, equation (1) may be rewritten as:

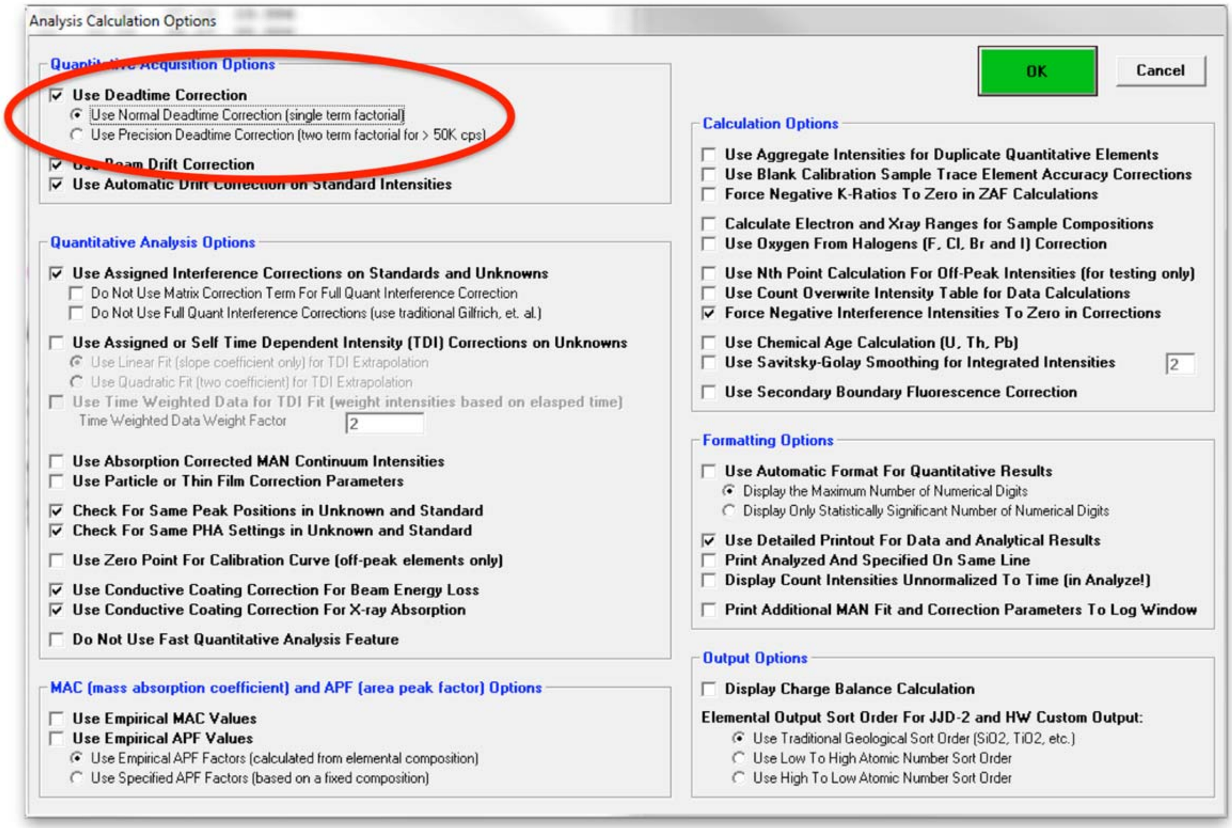
$$\frac{n'}{i} = k(1 - \tau n') \quad (2)$$

A plot of n'/i (cps/nA) versus n' (cps) will yield a straight line with slope of ($-k\tau$). The intercept on the n'/i axis will be the constant, k, and thus the deadtime factor (τ) may be determined.

A second deadtime correction option is also available in PROBE FOR EPMA. This is a high precision expression for use with very high count rates (Willis, 1993). This expression differs from the normal equation **only** when very high count rates (>50K cps) are achieved. The precision deadtime expression is:

$$n = \frac{n'}{1 - \left(\tau n' + n'^2 \left(\frac{\tau^2}{2} \right) \right)} \quad (3)$$

The deadtime correction option and type is selected from the **Analysis Calculation Options** window. Click **Analytical | Analysis Options** menu from the main PROBE FOR EPMA log window. Click the **OK** button to confirm the selections.



Quantitative Acquisition Options

- ☑ Use Deadtime Correction
  - ● Use Normal Deadtime Correction (single term factorial)
  - ○ Use Precision Deadtime Correction (two term factorial for > 50K cps)
- ☑ Use Beam Drift Correction
- ☑ Use Automatic Drift Correction on Standard Intensities

Quantitative Analysis Options

- ☑ Use Assigned Interference Corrections on Standards and Unknowns
  - ☐ Do Not Use Matrix Correction Term For Full Quant Interference Correction
  - ☐ Do Not Use Full Quant Interference Corrections (use traditional Gilfrich, et. al.)
- ☐ Use Assigned or Self Time Dependent Intensity (TDI) Corrections on Unknowns
  - ● Use Linear Fit (slope coefficient only) for TDI Extrapolation
  - ○ Use Quadratic Fit (two coefficient) for TDI Extrapolation
- ☐ Use Time Weighted Data for TDI Fit (weight intensities based on elasped time)
  - Time Weighted Data Weight Factor: 2
- ☐ Use Absorption Corrected MAN Continuum Intensities
- ☐ Use Particle or Thin Film Correction Parameters
- ☑ Check For Same Peak Positions in Unknown and Standard
- ☑ Check For Same PHA Settings in Unknown and Standard
- ☐ Use Zero Point For Calibration Curve (off-peak elements only)
- ☑ Use Conductive Coating Correction For Beam Energy Loss
- ☑ Use Conductive Coating Correction For X-ray Absorption
- ☐ Do Not Use Fast Quantitative Analysis Feature

MAC (mass absorption coefficient) and APF (area peak factor) Options

- ☐ Use Empirical MAC Values
- ☐ Use Empirical APF Values
  - ● Use Empirical APF Factors (calculated from elemental composition)
  - ○ Use Specified APF Factors (based on a fixed composition)

Calculation Options

- ☐ Use Aggregate Intensities for Duplicate Quantitative Elements
- ☐ Use Blank Calibration Sample Trace Element Accuracy Corrections
- ☐ Force Negative K-Ratios To Zero in ZAF Calculations
- ☐ Calculate Electron and Xray Ranges for Sample Compositions
- ☐ Use Oxygen From Halogens (F, Cl, Br and I) Correction
- ☐ Use Nth Point Calculation For Off-Peak Intensities (for testing only)
- ☐ Use Count Overwrite Intensity Table for Data Calculations
- ☑ Force Negative Interference Intensities To Zero in Corrections
- ☐ Use Chemical Age Calculation (U, Th, Pb)
- ☐ Use Savitsky-Golay Smoothing for Integrated Intensities: 2
- ☐ Use Secondary Boundary Fluorescence Correction

Formatting Options

- ☐ Use Automatic Format For Quantitative Results
  - ● Display the Maximum Number of Numerical Digits
  - ○ Display Only Statistically Significant Number of Numerical Digits
- ☑ Use Detailed Printout For Data and Analytical Results
- ☐ Print Analyzed And Specified On Same Line
- ☐ Display Count Intensities Unnormalized To Time (in Analyze!)
- ☐ Print Additional MAN Fit and Correction Parameters To Log Window

Output Options

- ☐ Display Charge Balance Calculation

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

- ● Use Traditional Geological Sort Order (SiO2, TiO2, etc.)
- ○ Use Low To High Atomic Number Sort Order
- ○ Use High To Low Atomic Number Sort Order

STARTWIN can be used to obtain the x-ray intensities required for the deadtime calculation. The procedure involves collecting precise beam current and count rate data over a wide range of beam currents. This data set can then be loaded into the supplied Excel template to automatically calculate the deadtime factor for your spectrometers. Paul Carpenter has put together an excellent but slightly more elaborate Excel template, contact Probe Software, Inc. for further details on obtaining his spreadsheet and related documentation.

To calibrate the deadtime factors for your WDS system use high purity, homogeneous metal standards. Depending on the microprobe configuration one standard may be employed to collect data on all spectrometers. Here, a silicon metal standard will be used.

Open the **Count Times** window and disable both the *Use Beam Drift Correction* and the *Normalize To Counts Per Second* options to allow raw intensity data to be collected. Set an *On Peak Count Time* that will give a precise measurement of intensities.

Peak each spectrometer to the x-ray line that will be used (Si Kα on the PET and TAP crystals). Upon completion of the peak center routine, park the spectrometers on the new peak positions.

Prior to collecting data, run PHA scans on each spectrometer for Si Kα, check the pulse height distribution at low and very high beam currents (ideally duplicating the range of beam currents for the deadtime measurements). At very high count rates (large beam currents), significant pulse pileup and gain shifts do occur. Fully open your pulse height windows, optimize your gain settings to see all the signal over the range of beam currents employed.

Data collection and analysis is straightforward. Select **Output | Open Link To Excel** menu from the main STARTWIN log window. Collect three replicate intensity measurements and beam current data. Each time count rate data is acquired, it will automatically be sent to an Excel spreadsheet along with column labels. Measure the replicate count intensities at ten different beam currents; ranging from a few nanoamps to several hundred nanoamps.

Create a count time column, prior to the beam current column in the Excel raw data spreadsheet and enter the relevant count times (in this example 10 seconds was used). The resulting spreadsheet may look similar to the one printed below except you may have data from more than three spectrometers.

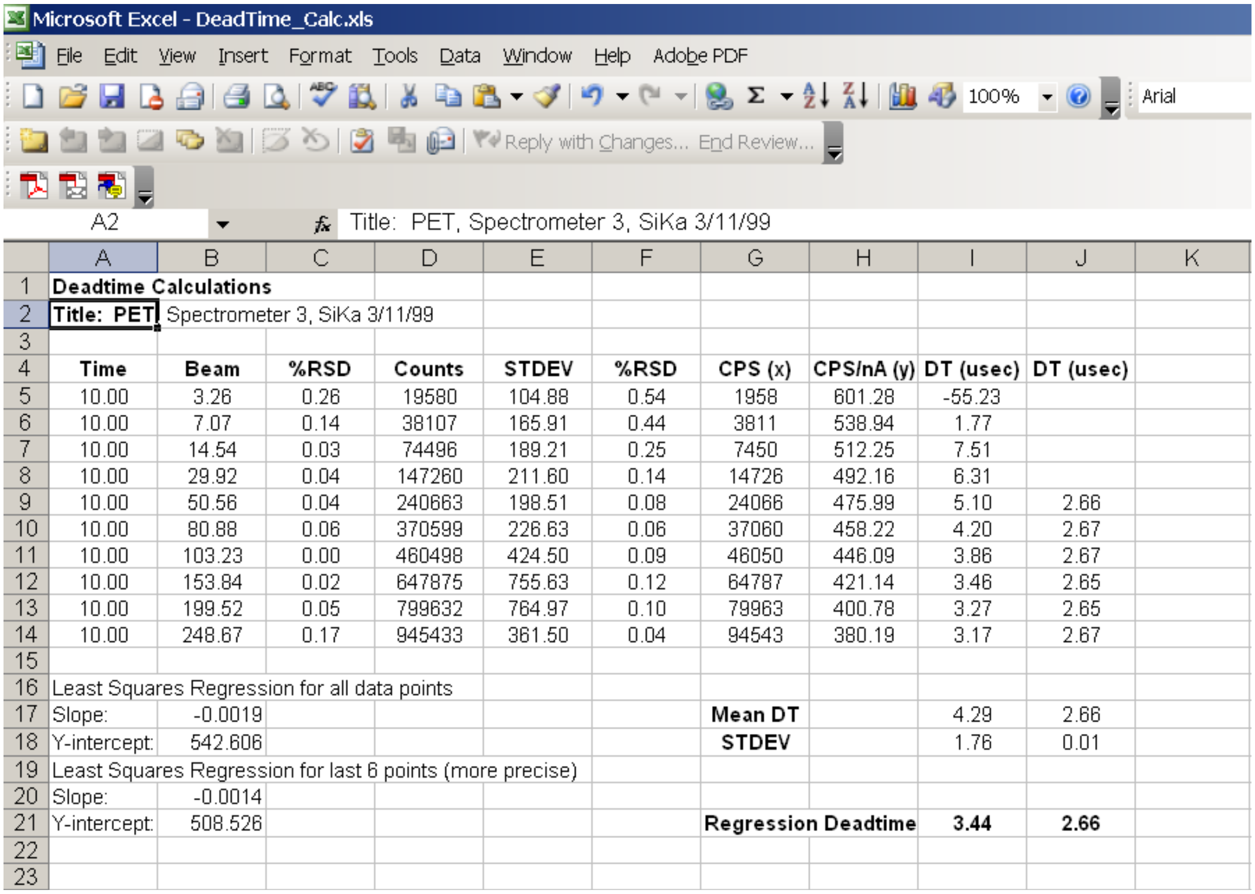
Time	Beam	1	2	3
10	3.259	22083	79765	19470
10	3.263	22069	79995	19590
10	3.247	21755	80091	19679
10	7.08	42503	154130	37952
10	7.06	42642	154665	38087
10	7.072	42168	154182	38282
10	14.547	83163	293002	74572
10	14.539	83315	292602	74281
10	14.543	82998	293326	74636
10	29.911	162904	547744	147492
10	29.917	164053	549493	147209
10	29.935	163684	548386	147078
10	50.539	266841	838976	240665
10	50.562	266672	837625	240860
10	50.58	267751	837948	240463
10	80.844	409290	1169741	370608
10	80.856	410142	1169175	370821
10	80.933	409098	1168965	370368
10	103.225	507351	1352944	460976
10	103.229	507971	1354039	460353
10	103.235	508408	1352991	460165
10	153.811	709360	1640458	647802
10	153.828	711086	1640015	647158
10	153.871	710654	1641034	648664
10	199.604	873187	1790253	800511
10	199.545	871582	1788206	799268
10	199.402	873093	1788780	799117
10	248.192	1027320	1878180	945455
10	248.884	1027517	1878519	945061
10	248.947	1026681	1878716	945783

Open the DEADTIME_CALC.XLS file from the floppy disk supplied. Copy and paste count times, beam current information and counts for the first spectrometer into the raw data template starting in cell **A26**.

By placing data into this template, the program will automatically calculate the following items: the average of three replicate time counts, the average of three replicate beam current measurements, the %RSD on the average beam current, the average of three replicate raw intensity measurements and the %RSD on the average raw intensity measurement.

Next, the counts per second (x-axis) and the counts per second per nanoamp (y-axis) are determined. A least squares method is then used to calculate a straight line that best fits your data. The slope and Y-intercept are reported for a straight line fit to all 10 data pairs and also for the last 6. The latter being a more precise determination of deadtime.

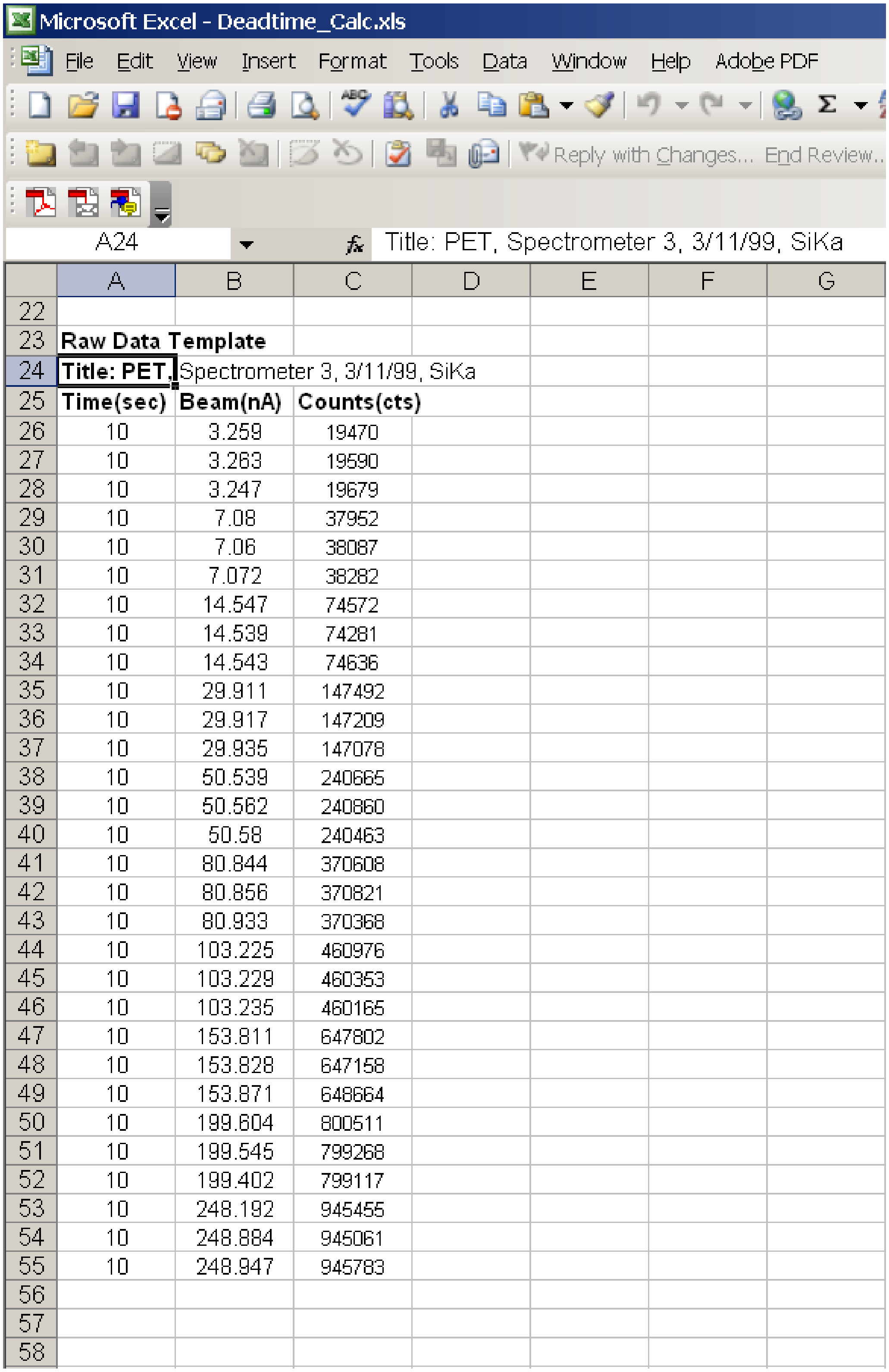
Below is the calculation portion of the Excel template.



A2 Title: PET, Spectrometer 3, SiKa 3/11/99

	A	B	C	D	E	F	G	H	I	J	K
1	**Deadtime Calculations**										
2	**Title: PET**	Spectrometer 3, SiKa 3/11/99									
3											
4	**Time**	**Beam**	**%RSD**	**Counts**	**STDEV**	**%RSD**	**CPS (x)**	**CPS/nA (y)**	**DT (usec)**	**DT (usec)**	
5	10.00	3.26	0.26	19580	104.88	0.54	1958	601.28	-55.23		
6	10.00	7.07	0.14	38107	165.91	0.44	3811	538.94	1.77		
7	10.00	14.54	0.03	74496	189.21	0.25	7450	512.25	7.51		
8	10.00	29.92	0.04	147260	211.60	0.14	14726	492.16	6.31		
9	10.00	50.56	0.04	240663	198.51	0.08	24066	475.99	5.10	2.66	
10	10.00	80.88	0.06	370599	226.63	0.06	37060	458.22	4.20	2.67	
11	10.00	103.23	0.00	460498	424.50	0.09	46050	446.09	3.86	2.67	
12	10.00	153.84	0.02	647875	755.63	0.12	64787	421.14	3.46	2.65	
13	10.00	199.52	0.05	799632	764.97	0.10	79963	400.78	3.27	2.65	
14	10.00	248.67	0.17	945433	361.50	0.04	94543	380.19	3.17	2.67	
15											
16	Least Squares Regression for all data points										
17	Slope:	-0.0019					**Mean DT**		4.29	2.66	
18	Y-intercept:	542.606					**STDEV**		1.76	0.01	
19	Least Squares Regression for last 6 points (more precise)										
20	Slope:	-0.0014									
21	Y-intercept:	508.526					**Regression Deadtime**		**3.44**	**2.66**	
22											
23											

The following screen capture illustrates the raw data template.



Raw Data Template

Title: PET, Spectrometer 3, 3/11/99, SiKa

Time(sec)	Beam(nA)	Counts(cts)
10	3.259	19470
10	3.263	19590
10	3.247	19679
10	7.08	37952
10	7.06	38087
10	7.072	38282
10	14.547	74572
10	14.539	74281
10	14.543	74636
10	29.911	147492
10	29.917	147209
10	29.935	147078
10	50.539	240665
10	50.562	240860
10	50.58	240463
10	80.844	370608
10	80.856	370821
10	80.933	370368
10	103.225	460976
10	103.229	460353
10	103.235	460165
10	153.811	647802
10	153.828	647158
10	153.871	648664
10	199.604	800511
10	199.545	799268
10	199.402	799117
10	248.192	945455
10	248.884	945061
10	248.947	945783

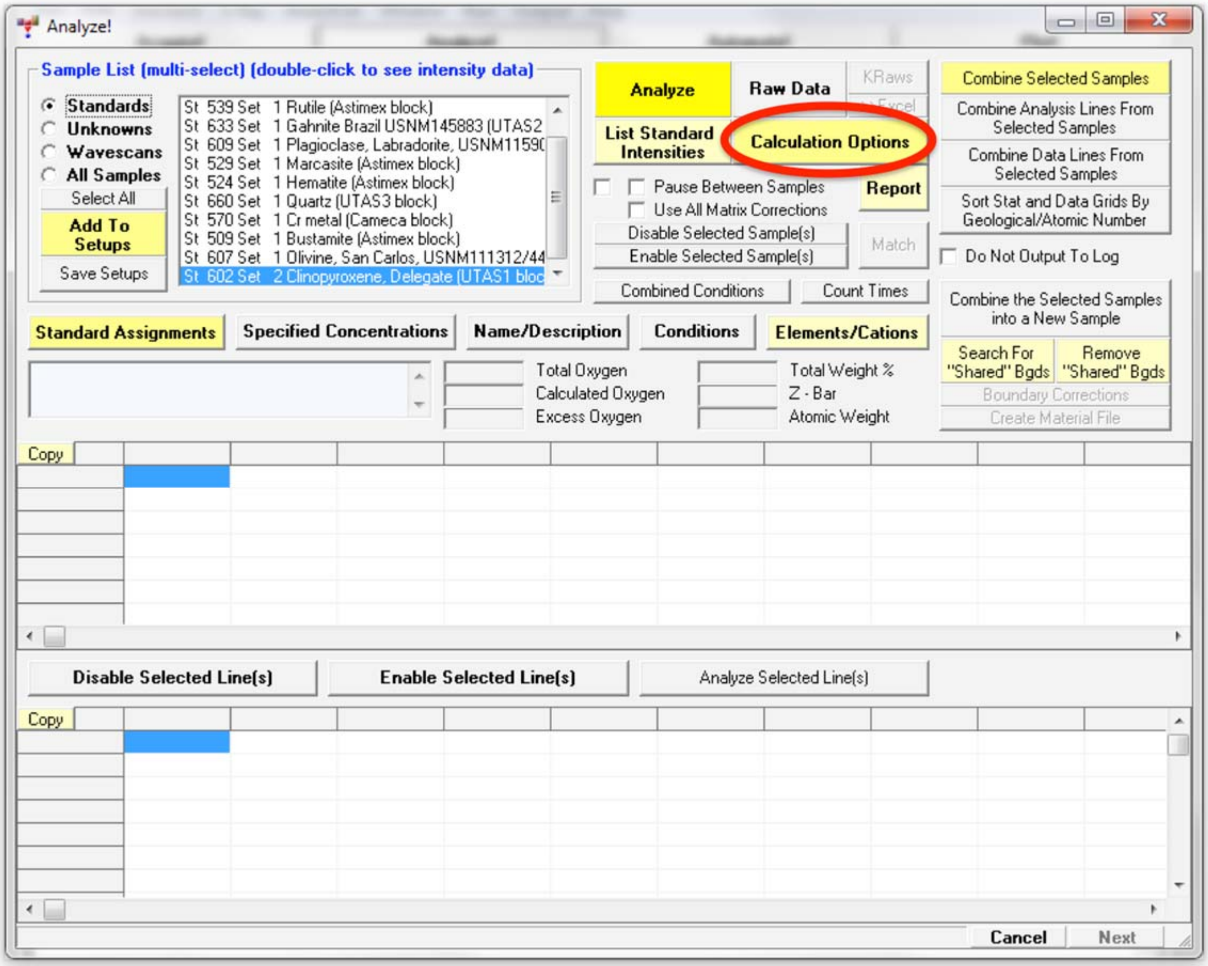
Calculate the deadtime factor for each spectrometer in turn, by overwriting the last column of count data in the raw data template portion of the Excel spreadsheet. Simply highlight the data in the Excel linked spreadsheet (from STARTWIN), use the copy function and paste it into the appropriate column. Edit cells **A2** and **A24** to update the title of the spreadsheet, for documentation and printout purposes. Calculations on the new data set will be automatically updated and output.

The deadtime constants are placed into the SCALERS.DAT file (line 13). Enter a value for each spectrometer (units of microseconds, as output from the Excel spreadsheet).

Deadtime may not be a constant and probably varies with the line energy of the x-ray being measured. One way to get around this is to place a pulse stretching circuit before the counter timer board to ensure that a forced deadtime is used to mask the actual deadtime range of the spectrometer. A pulse width (from the pulse stretcher) greater than the worse case deadtime found for the spectrometer is produced. Using this value will lead to a more accurate deadtime correction at all energies.

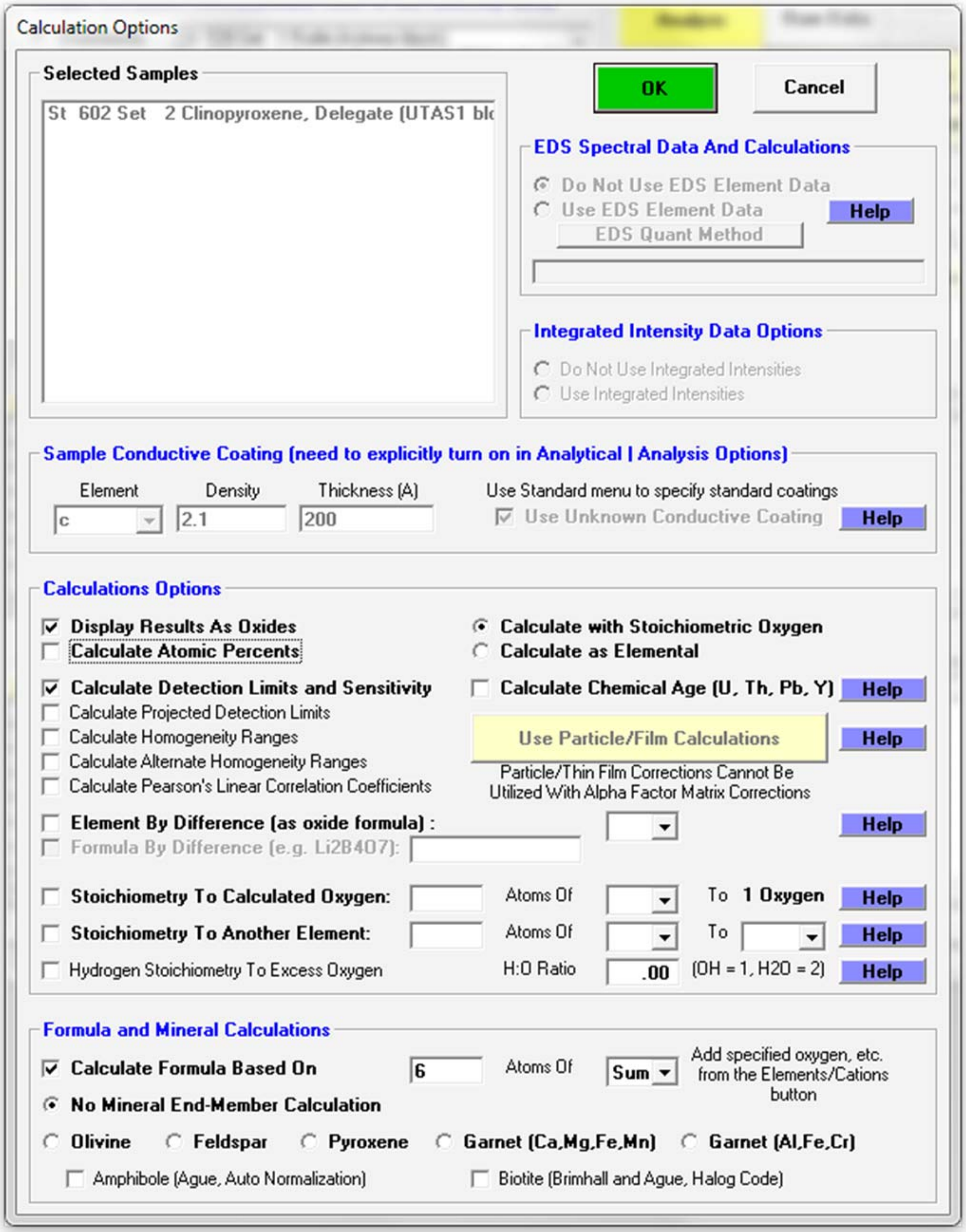
Calculation Options

Prior to analyzing collected x-ray data, the user may wish to specify various output calculation options. These choices may be found by clicking the **Calculation Options** button in the **Analyze!** window.



St 539 Set 1 Rutile (Astimex block)
St 633 Set 1 Gahnite Brazil USNM145883 (UTAS2
St 609 Set 1 Plagioclase, Labradorite, USNM1159(
St 529 Set 1 Marcasite (Astimex block)
St 524 Set 1 Hematite (Astimex block)
St 660 Set 1 Quartz (UTAS3 block)
St 570 Set 1 Cr metal (Cameca block)
St 509 Set 1 Bustamite (Astimex block)
St 607 Set 1 Olivine, San Carlos, USNM111312/44
St 602 Set 2 Clinopyroxene, Delegate (UTAS1 bloc

The **Calculation Options** window opens.



Calculation Options

Selected Samples

St 602 Set 2 Clinopyroxene, Delegate (UTAS1 bl

EDS Spectral Data And Calculations

● Do Not Use EDS Element Data
○ Use EDS Element Data

Integrated Intensity Data Options

○ Do Not Use Integrated Intensities
○ Use Integrated Intensities

Sample Conductive Coating (need to explicitly turn on in Analytical | Analysis Options)

Element	Density	Thickness (A)
c	2.1	200

Use Standard menu to specify standard coatings

☑ Use Unknown Conductive Coating

Calculations Options

☑ Display Results As Oxides
☐ Calculate Atomic Percents
● Calculate with Stoichiometric Oxygen
○ Calculate as Elemental
☑ Calculate Detection Limits and Sensitivity
☐ Calculate Projected Detection Limits
☐ Calculate Homogeneity Ranges
☐ Calculate Alternate Homogeneity Ranges
☐ Calculate Pearson's Linear Correlation Coefficients
☐ Calculate Chemical Age (U, Th, Pb, Y)

Particle/Thin Film Corrections Cannot Be Utilized With Alpha Factor Matrix Corrections

☐ Element By Difference (as oxide formula) :
☐ Formula By Difference (e.g. Li2B4O7):
☐ Stoichiometry To Calculated Oxygen: Atoms Of To 1 Oxygen
☐ Stoichiometry To Another Element: Atoms Of To
☐ Hydrogen Stoichiometry To Excess Oxygen H:O Ratio .00 (OH = 1, H2O = 2)

Formula and Mineral Calculations

☑ Calculate Formula Based On 6 Atoms Of Sum

Add specified oxygen, etc. from the Elements/Cations button

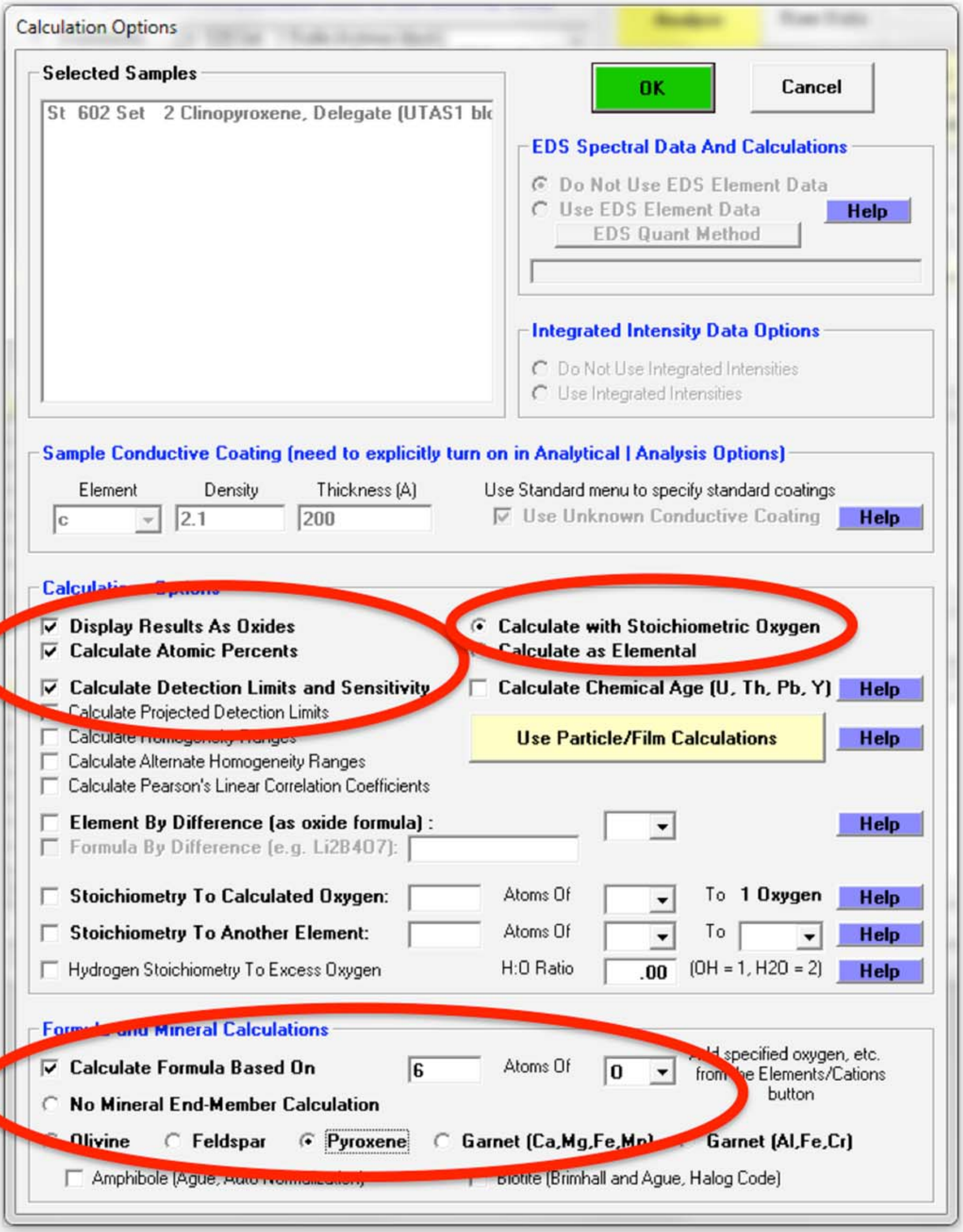
● No Mineral End-Member Calculation
○ Olivine ○ Feldspar ○ Pyroxene ○ Garnet (Ca,Mg,Fe,Mn) ○ Garnet (Al,Fe,Cr)
☐ Amphibole (Ague, Auto Normalization) ☐ Biotite (Brimhall and Ague, Halog Code)

Each of the selected options in the above window will be briefly discussed in conjunction with the data output for a clinopyroxene analysis.

```
St  602 Set   2 Clinopyroxene, Delegate (UTAS1 block)
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 20.0  Beam Size =    2
(Magnification (analytical) =   2533),        Beam Mode = Analog  Spot
(Magnification (default) =     2533, Magnification (imaging) =   2533)
Image Shift (X,Y):                                        -2.00,  3.00

Number of Data Lines:   4            Number of 'Good' Data Lines:   4
WARNING- Using Slope-Hi Off-Peak correction for Mn ka
WARNING- Forcing negative interference intensities to zero

Average Total Oxygen:       44.136     Average Total Weight%:  101.203
Average Calculated Oxygen:  44.131     Average Atomic Number:   12.558
Average Excess Oxygen:        .005     Average Atomic Weight:   21.937
Average ZAF Iteration:        3.00     Average Quant Iterate:     4.00

Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction

St  602 Set   2 Clinopyroxene, Delegate (UTAS1 block), Results in Elemental Weight Percents

SPEC:        O
TYPE:     CALC

AVER:   44.136
SDEV:     .169

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K
BGDS:      MAN     MAN     MAN     MAN     MAN     MAN     MAN     MAN     MAN     MAN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00   10.00   10.00   10.00   10.00
BEAM:    20.00   20.00   20.00   20.00   20.00   20.00   20.00   20.00   20.00   20.00

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K   SUM
    34  23.947    .324   2.976    .530   3.601    .069   9.929  15.066    .675    .068 101.433
    35  23.972    .384   2.963    .542   3.783    .071   9.781  15.077    .661    .043 101.536
    36  23.779    .327   2.945    .501   3.626    .070   9.875  14.864    .655    .035 100.574
    37  23.827    .360   3.029    .560   3.715    .081   9.791  15.140    .607    .023 101.271

AVER:   23.881    .349   2.978    .533   3.681    .073   9.844  15.037    .650    .042 101.203
SDEV:     .093    .029    .036    .025    .084    .005    .071    .120    .030    .019    .434
SERR:     .047    .014    .018    .013    .042    .003    .035    .060    .015    .009
%RSD:      .39    8.24    1.21    4.71    2.28    7.26     .72     .80    4.55   44.67

PUBL:   23.840    .310   2.910    .470   3.120    .060   9.700  15.050    .620    n.a.  99.780
%VAR:    (.17)   12.58    2.35   13.44   17.98   21.13    1.48  (-.09)    4.77     ---
DIFF:    (.04)    .039    .068    .063    .561    .013    .144  (-.01)    .030     ---
STDS:      602     539     609     631     524     509     607     602     730     656

STKF:    .1884   .5474   .1277   .3856   .6539   .1612   .2085   .1386   .0488   .1104
STCT:    93.83  275.50   63.97  194.00  333.06   80.83  104.47   69.64   24.16   55.15

UNKF:    .1884   .0029   .0208   .0045   .0309   .0006   .0661   .1387   .0033   .0004
UNCT:    93.82    1.47   10.43    2.27   15.74     .30   33.11   69.66    1.65     .19
UNBG:      .99    1.32     .75    1.27   -1.49    1.13     .56    1.71     .55    1.65

ZCOR:   1.2678  1.1975  1.4301  1.1817  1.1910  1.2119  1.4898  1.0844  1.9514  1.0859
KRAW:    .9999   .0053   .1631   .0117   .0473   .0037   .3169  1.0002   .0683   .0035
PKBG:    95.58    2.12   14.97    2.78     .00    1.27   60.57   41.74    4.01    1.12
INT%:     ----    ----    ----    ----    ----    ----    ----    ----    ----    ----
```

```
St  602 Set   2 Clinopyroxene, Delegate (UTAS1 block), Results in Oxide Weight Percents

SPEC:        O
TYPE:     CALC

AVER:     .005
SDEV:     .000

ELEM:     SiO2    TiO2   Al2O3   Cr2O3     FeO     MnO     MgO     CaO    Na2O     K2O   SUM
    34  51.232    .540   5.624    .774   4.632    .090  16.465  21.080    .910    .082 101.433
    35  51.284    .641   5.598    .792   4.867    .091  16.219  21.096    .891    .052 101.536
    36  50.871    .546   5.565    .732   4.664    .091  16.377  20.798    .883    .043 100.574
    37  50.974    .601   5.723    .819   4.779    .104  16.236  21.184    .818    .028 101.271

AVER:   51.090    .582   5.627    .779   4.736    .094  16.324  21.039    .876    .051 101.203
SDEV:     .199    .048    .068    .037    .108    .007    .117    .168    .040    .023    .434
SERR:     .099    .024    .034    .018    .054    .003    .059    .084    .020    .011
%RSD:      .39    8.24    1.21    4.71    2.28    7.26     .72     .80    4.55   44.67

PUBL:   51.002    .517   5.498    .687   4.014    .077  16.086  21.058    .836    n.a.  99.780
%VAR:    (.17)   12.58    2.35   13.44   17.98   21.13    1.48  (-.09)    4.77     ---
DIFF:    (.09)    .065    .129    .092    .722    .016    .239  (-.02)    .040     ---
STDS:      602     539     609     631     524     509     607     602     730     656

St  602 Set   2 Clinopyroxene, Delegate (UTAS1 block), Results in Atomic Percents

SPEC:        O
TYPE:     CALC

AVER:   59.792
SDEV:     .014

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K   SUM
    34  18.429    .146   2.384    .220   1.394    .027   8.829   8.124    .635    .037 100.000
    35  18.452    .173   2.374    .225   1.465    .028   8.700   8.133    .622    .024 100.000
    36  18.451    .149   2.379    .210   1.415    .028   8.855   8.082    .621    .020 100.000
    37  18.390    .163   2.433    .234   1.442    .032   8.732   8.189    .572    .013 100.000

AVER:   18.431    .158   2.393    .222   1.429    .029   8.779   8.132    .612    .023 100.000
SDEV:     .029    .013    .027    .010    .031    .002    .075    .044    .027    .010    .000
SERR:     .015    .006    .014    .005    .016    .001    .037    .022    .014    .005
%RSD:      .16    8.08    1.15    4.49    2.17    7.29     .85     .54    4.47   44.43

St  602 Set   2 Clinopyroxene, Delegate (UTAS1 block), Results Based on 6 Atoms of O

SPEC:        O
TYPE:     CALC

AVER:    6.000
SDEV:     .000

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K   SUM
    34   1.850    .015    .239    .022    .140    .003    .886    .816    .064    .004  10.038
    35   1.851    .017    .238    .023    .147    .003    .873    .816    .062    .002  10.033
    36   1.852    .015    .239    .021    .142    .003    .889    .811    .062    .002  10.035
    37   1.845    .016    .244    .023    .145    .003    .876    .822    .057    .001  10.033

AVER:    1.849    .016    .240    .022    .143    .003    .881    .816    .061    .002  10.035
SDEV:     .003    .001    .003    .001    .003    .000    .008    .004    .003    .001    .002
SERR:     .001    .001    .001    .000    .002    .000    .004    .002    .001    .001
%RSD:      .16    8.06    1.14    4.48    2.15    7.28     .87     .53    4.49   44.46
```

```
Pyroxene Mineral End-Member Calculations

            Wo      En      Fs
    34    44.3    48.1     7.6
    35    44.4    47.5     8.0
    36    44.0    48.3     7.7
    37    44.6    47.6     7.9

AVER:     44.3    47.9     7.8
SDEV:       .2      .4      .2

Detection limit at 99 % Confidence in Elemental Weight Percent (Single Line):

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K
    34    .054    .058    .052    .056    .000    .055    .047    .060    .062    .059
    35    .054    .058    .052    .056    .000    .055    .047    .060    .062    .059
    36    .054    .058    .052    .056    .000    .055    .047    .060    .062    .059
    37    .054    .058    .052    .056    .000    .055    .047    .060    .062    .059

AVER:     .054    .058    .052    .056    .000    .055    .047    .060    .062    .059
SDEV:     .000    .000    .000    .000    .000    .000    .000    .000    .000    .000
SERR:     .000    .000    .000    .000    .000    .000    .000    .000    .000    .000

Percent Analytical Relative Error (One Sigma, Single Line):

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K
    34      .7    10.4     2.3     6.9      .0    39.4     1.2      .9     6.9    43.1
    35      .7     9.0     2.3     6.8      .0    38.7     1.3      .9     7.0    66.8
    36      .7    10.3     2.4     7.2      .0    38.8     1.2      .9     7.1    81.1
    37      .7     9.5     2.3     6.6      .0    34.2     1.3      .9     7.5   123.0

AVER:       .7     9.8     2.3     6.8      .0    37.8     1.2      .9     7.1    78.5
SDEV:       .0      .7      .0      .3      .0     2.4      .0      .0      .2    33.5
SERR:       .0      .3      .0      .1      .0     1.2      .0      .0      .1    16.8

Detection Limit (t-test) in Elemental Weight Percent (Average of Sample):

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K
  60ci     ---    .018     ---    .016     ---    .003     ---     ---    .019    .014
  80ci     ---    .030     ---    .026     ---    .006     ---     ---    .031    .023
  90ci     ---    .043     ---    .037     ---    .008     ---     ---    .045    .033
  95ci     ---    .058     ---    .051     ---    .011     ---     ---    .061    .045
  99ci     ---    .106     ---    .093     ---    .020     ---     ---    .112    .083

Analytical Sensitivity (t-test) in Elemental Weight Percent (Average of Sample):

ELEM:       Si      Ti      Al      Cr      Fe      Mn      Mg      Ca      Na       K
  60ci    .068    .010    .023    .011    .061    .001    .054    .083    .016    .001
  80ci    .114    .017    .039    .018    .101    .001    .090    .139    .026    .002
  90ci    .164    .025    .056    .026    .146    .002    .130    .199    .038    .003
  95ci    .222    .034    .076    .036    .197    .002    .175    .270    .051    .005
  99ci    .408    .062    .140    .065    .362    .004    .322    .495    .094    .008
```



Calculation Options

Selected Samples

St 602 Set 2 Clinopyroxene, Delegate (UTAS1 blc

EDS Spectral Data And Calculations

● Do Not Use EDS Element Data
○ Use EDS Element Data

Integrated Intensity Data Options

○ Do Not Use Integrated Intensities
○ Use Integrated Intensities

Sample Conductive Coating (need to explicitly turn on in Analytical | Analysis Options)

Element: c
Density: 2.1
Thickness (A): 200
Use Standard menu to specify standard coatings
☑ Use Unknown Conductive Coating

Calculation Options

☑ Display Results As Oxides
☑ Calculate Atomic Percents
☑ Calculate Detection Limits and Sensitivity
☐ Calculate Projected Detection Limits
☐ Calculate Homogeneity Ranges
☐ Calculate Alternate Homogeneity Ranges
☐ Calculate Pearson's Linear Correlation Coefficients

● Calculate with Stoichiometric Oxygen
○ Calculate as Elemental
☐ Calculate Chemical Age (U, Th, Pb, Y)

☐ Element By Difference (as oxide formula) :
☐ Formula By Difference (e.g. Li2B4O7):

☐ Stoichiometry To Calculated Oxygen: Atoms Of To 1 Oxygen
☐ Stoichiometry To Another Element: Atoms Of To
☐ Hydrogen Stoichiometry To Excess Oxygen H:O Ratio .00 (OH = 1, H2O = 2)

Formula and Mineral Calculations

☑ Calculate Formula Based On 6 Atoms Of O
Add specified oxygen, etc. from the Elements/Cations button
○ No Mineral End-Member Calculation
○ Olivine ○ Feldspar ● Pyroxene ○ Garnet (Ca,Mg,Fe,Mn) ○ Garnet (Al,Fe,Cr)
☐ Amphibole (Ague, Auto Normalization) ☐ Biotite (Brimhall and Ague, Halog Code)

Selecting the *Display Results As Oxides* check box permits the user to display the results of an analysis in oxide weight percents based on the cation ratios defined for each element in the **Element/Cations** dialog window. Results are also, always reported in elemental weight percents.

Analyses can also be output as atomic percents if the *Calculate Atomic Percents* check box is marked. This calculation is based on the fraction of the atomic weight of each element and is normalized to a 100% total.

The *Calculate with Stoichiometric Oxygen* button allows the user to calculate oxygen by stoichiometry if oxygen is not an analyzed element in the routine. If oxygen is either measured or calculated by stoichiometry and the *Display Results As Oxides* check box is selected, then the program will automatically calculate and report the actual excess or deficit oxygen in the analysis. This information can be very useful in determining if the selected cation ratios are correct (iron bearing oxides, for example).

All elements to be calculated by stoichiometry, difference or formula basis must be listed in the sample setup. Add these elements using the **Elements/Cations** button in the **Analyze!** window. Each must be added as a “not analyzed” element; To do this, click any empty row in the element list, type in the element symbol and leave the x-ray line blank.

The *Formula and Mineral Calculation* fields at the bottom of the **Calculation Options** window allow the user to compute formulas based on any number of oxygens for oxide runs or any analyzed or specified element in elemental runs. Further, olivine, feldspar, pyroxene, and two garnet end-member calculations are written into the software. These formula calculations are based only on atomic weight and do not consider charge balance and site occupancy. See the appendix sections in *An introduction to The Rock-Forming Minerals* by Deer, Howie, and Zussman (1992) for details on calculating formulas for hydrous phases.

The user may also select the *Calculate Detection Limits and Homogeneity* check box. The calculation of the sample detection limits is based on the standard counts, the unknown background counts, and includes the magnitude of the ZAF correction factor. The calculation is adapted from Scott et al., (1995). This detection limit calculation is useful in that it can be used even on inhomogenous samples and can be quoted as the detection limit in weight percent for a single analysis line with a confidence of 99% (assuming 3 standard deviations).

$$C_{\mathrm{MDL}} = (\mathrm{ZAF})\frac{3\sqrt{\mathrm{I}_{\mathrm{B}}/t}}{\mathrm{I}_{\mathrm{S}}}\cdot 100$$

Where:	ZAF	is the ZAF correction factor for the sample matrix
	I_S	is the count rate on the analytical (pure element) standard
	I_B	is the background count rate on the unknown sample
	t	is the counting time on the unknown sample

After this, a rigorous calculation of the analytical error also for single analysis lines, is performed based on the peak and background count rates (Scott et al., 1995). 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. The analytical error calculation is as follows:

$$\varepsilon_{P-B} = \sqrt{\frac{N_p}{t_P^2} + \frac{N_B}{t_B^2}} \Bigg/ \left(\frac{N_P}{t_P} - \frac{N_B}{t_B} \right)$$

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 will also be performed. These statistics are based on equations adapted from *Scanning Electron Microscopy and X-Ray Microanalysis*, *Second Edition* by Goldstein, et al., (1992). 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 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:

The range of homogeneity in plus or minus weight percent.

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

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

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

The trace elementdetection limit in weight percent.

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

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

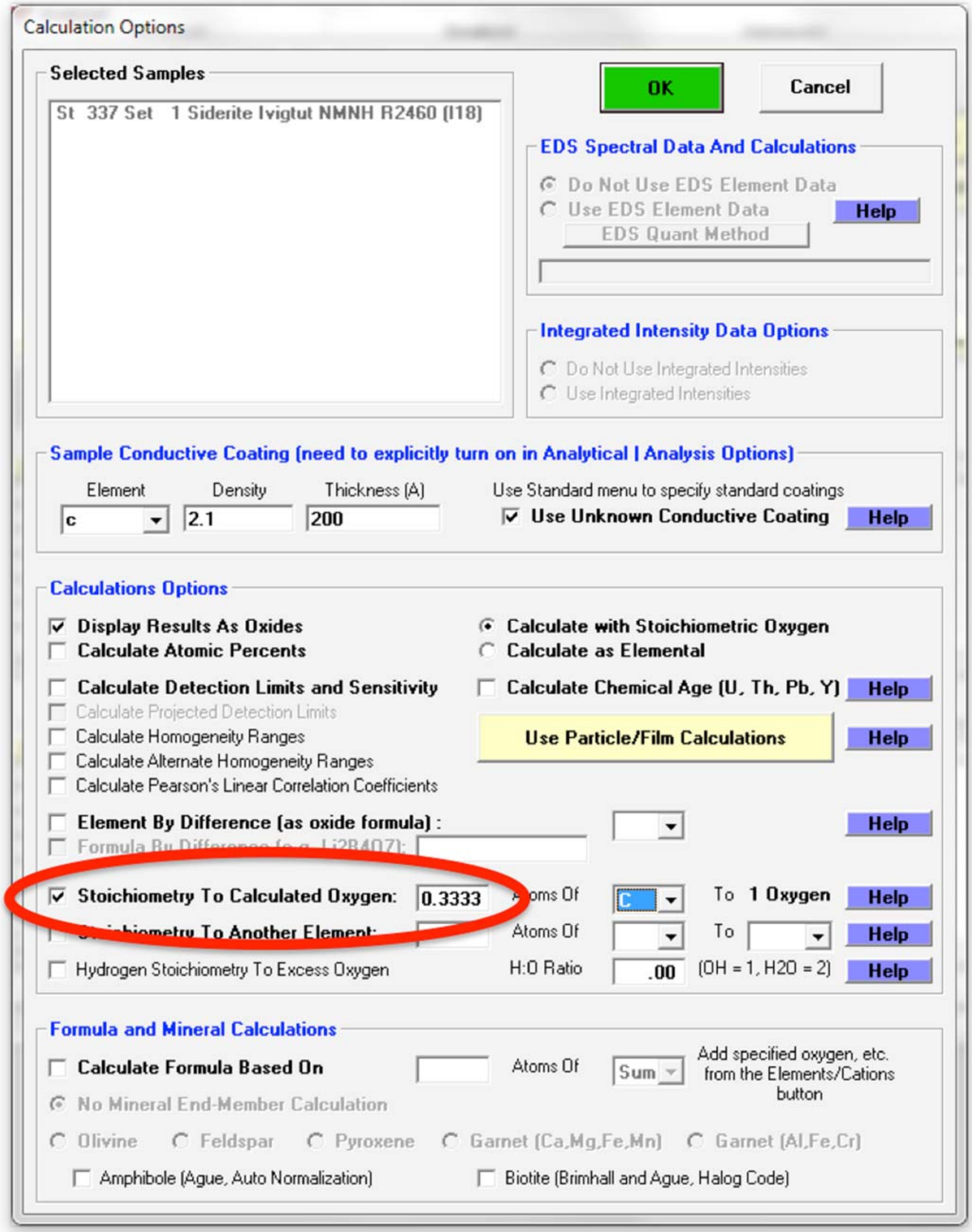
The homogeneity test compares the 99% confidence range of homogeneity value with 1% of the sample concentration for each element. If the range of homogeneity is less than 1% of the sample concentration then the sample may be considered to be homogenous within 1%. The detection limit calculation here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

Three other calculation options are available to the user: *Element By Difference, Stoichiometry To Calculated Oxygen,* and *Stoichiometry To Another Element*.

When the *Element By Difference* check box is selected, the user can include an element in the analysis which is assumed to make up the difference to 100% total to account for their effect on the other x-ray intensities. This element must be specified in the sample setup. Note this method causes the calculation to result in a 100% total.

The *Stoichiometry To Calculated Oxygen* option is often used in the analysis of carbonate or borate samples in an oxide run or for hydrogen (water, hydroxyl) bearing silicate minerals. This feature permits the user to analyze just the cations in the sample and have oxygen calculated by stoichiometry and another specified element (usually C in carbonates and B in borates) calculated relative to oxygen. In the carbonate scenario ($CaCO_3$), carbon is always in the ratio of 1 to 3 to oxygen. If the user specifies carbon by stoichiometry relative to the stoichiometric element oxygen at 0.333 (1 divided by 3) the correct amount of both carbon and oxygen will be incorporated into the ZAF matrix correction and totals without analyzing for either element. This method should only be used with phases where the ratio to oxygen is both fixed and known.



Selected Samples

St 337 Set 1 Siderite Ivigtut NMNH R2460 (I18)

EDS Spectral Data And Calculations

● Do Not Use EDS Element Data
○ Use EDS Element Data
EDS Quant Method

Integrated Intensity Data Options

○ Do Not Use Integrated Intensities
○ Use Integrated Intensities

Sample Conductive Coating (need to explicitly turn on in Analytical | Analysis Options)

Element: c
Density: 2.1
Thickness (A): 200
Use Standard menu to specify standard coatings
☑ Use Unknown Conductive Coating

Calculations Options

☑ Display Results As Oxides
☐ Calculate Atomic Percents
● Calculate with Stoichiometric Oxygen
○ Calculate as Elemental
☐ Calculate Detection Limits and Sensitivity
☐ Calculate Chemical Age (U, Th, Pb, Y)
☐ Calculate Projected Detection Limits
☐ Calculate Homogeneity Ranges
☐ Calculate Alternate Homogeneity Ranges
☐ Calculate Pearson's Linear Correlation Coefficients
Use Particle/Film Calculations
☐ Element By Difference (as oxide formula) :
☐ Formula By Difference (e.g. Li2B4O7):
☑ Stoichiometry To Calculated Oxygen: 0.3333 Atoms Of C To 1 Oxygen
☐ Stoichiometry To Another Element: Atoms Of To
☐ Hydrogen Stoichiometry To Excess Oxygen H:O Ratio .00 (OH = 1, H2O = 2)

Formula and Mineral Calculations

☐ Calculate Formula Based On Atoms Of Sum
Add specified oxygen, etc. from the Elements/Cations button
● No Mineral End-Member Calculation
○ Olivine ○ Feldspar ○ Pyroxene ○ Garnet (Ca,Mg,Fe,Mn) ○ Garnet (Al,Fe,Cr)
☐ Amphibole (Ague, Auto Normalization) ☐ Biotite (Brimhall and Ague, Halog Code)

The following iron carbonate mineral (siderite) output illustrates oxygen calculated by cation stoichiometry with the element carbon is calculated at 0.333 atoms relative to 1.0 atom of oxygen.

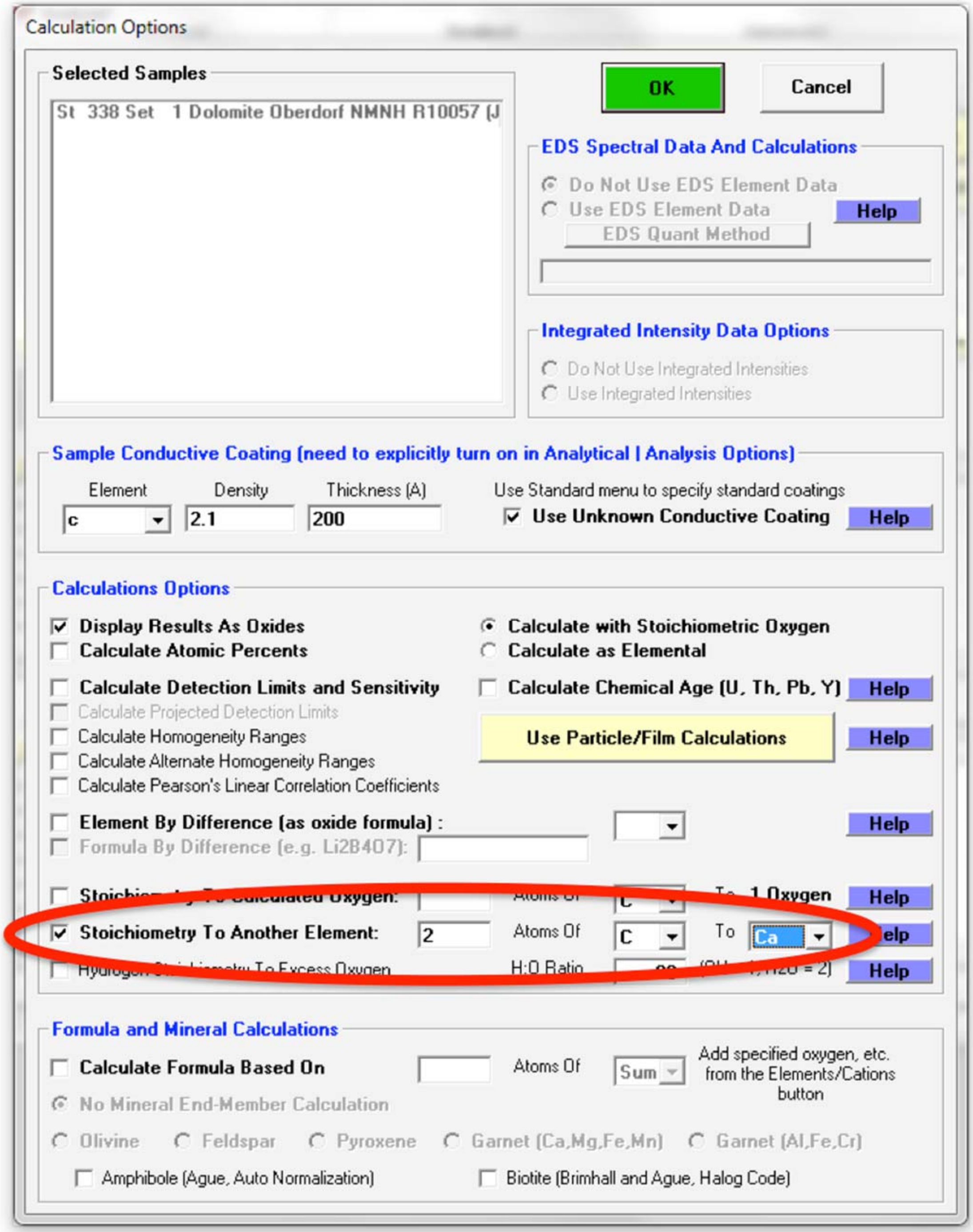
```
St  337 Siderite Ivigtut NMNH R2460 (I18)
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 15.0  Beam Size =   10
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   3             Number of 'Good' Data Lines:   3
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:       41.449     Average Total Weight%:  100.042
Average Calculated Oxygen:  41.449     Average Atomic Number:   16.438
Average Excess Oxygen:        .000     Average Atomic Weight:   23.164
Average ZAF Iteration:        8.00     Average Quant Iterate:     2.00

Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction
Element C is Calculated  .333 Atoms Relative To 1.0 Atom of Oxygen

St  337 Siderite Ivigtut NMNH R2460 (I18), Results in Elemental Weight Percents

SPEC:        C       O
TYPE:     STOI    CALC

AVER:   10.356  41.449
SDEV:     .017    .013

ELEM:       Ca      Mg      Mn      Fe
BGDS:      LIN     LIN     LIN     LIN
TIME:    20.00   30.00   40.00   40.00
BEAM:    10.34   10.34   10.34   10.34

ELEM:       Ca      Mg      Mn      Fe   SUM
    19    .000    .067   2.235  45.825  99.929
    20    .014    .072   2.375  46.005 100.264
    21    .013    .077   2.323  45.708  99.933

AVER:     .009    .072   2.311  45.846 100.042
SDEV:     .008    .005    .071    .150    .192
SERR:     .004    .003    .041    .086
%RSD:    86.77    6.95    3.06     .33
STDS:      130     131     132     132

STKF:    .3826   .0853   .0202   .4131
STCT:   3040.8  1502.9    43.1   955.3

UNKF:    .0001   .0003   .0205   .4124
UNCT:       .2     6.1    43.6   953.6
UNBG:     11.0    11.0     3.0     5.6

ZCOR:    .9873  2.0734  1.1296  1.1117
KRAW:    .0001   .0041  1.0111   .9982
PKBG:     1.03    1.55   16.50  172.56

St  337 Siderite Ivigtut NMNH R2460 (I18), Results in Oxide Weight Percents

SPEC:      CO2       O
TYPE:     STOI    CALC

AVER:   37.946    .000
SDEV:     .062    .000

ELEM:      CaO     MgO     MnO     FeO   SUM
    19    .000    .111   2.886  58.954  99.929
    20    .019    .119   3.066  59.185 100.264
    21    .018    .128   3.000  58.803  99.933

AVER:     .012    .119   2.984  58.981 100.042
SDEV:     .011    .008    .091    .192    .192
SERR:     .006    .005    .053    .111
%RSD:    86.77    6.95    3.06     .33
```

Another interesting example demonstrating this feature is nicely documented in the User's Guide and Reference manual (see Stoichiometry to Oxygen section). There, several trace metals are analyzed for in a stoichiometric Al_2O_3 matrix without measuring aluminum or oxygen, BUT the correct amount of Al_2O_3 is added to the matrix correction!

The *Stoichiometry To Another Element* option gives the user another recalculation method similar to the *Stoichiometry To Calculated Oxygen* option just discussed. Here, the user may select any other analyzed or specified element as the stoichiometric basis element.

The example below calculates CO_2 on the basis of moles of CaO, rather than by stoichiometry to oxygen.

The setup is shown in the **Calculation Options** window below.



St 338 Set 1 Dolomite Oberdorf NMNH R10057 (J

● Do Not Use EDS Element Data
○ Use EDS Element Data

○ Do Not Use Integrated Intensities
○ Use Integrated Intensities

Element: c
Density: 2.1
Thickness (A): 200
Use Standard menu to specify standard coatings
☑ Use Unknown Conductive Coating

☑ Display Results As Oxides
☐ Calculate Atomic Percents
● Calculate with Stoichiometric Oxygen
○ Calculate as Elemental
☐ Calculate Detection Limits and Sensitivity
☐ Calculate Projected Detection Limits
☐ Calculate Homogeneity Ranges
☐ Calculate Alternate Homogeneity Ranges
☐ Calculate Pearson's Linear Correlation Coefficients
☐ Calculate Chemical Age (U, Th, Pb, Y)
☐ Element By Difference (as oxide formula) :
☐ Formula By Difference (e.g. Li2B4O7):
☐ Stoichiometry To Calculated Oxygen: Atoms Of C To 1 Oxygen
☑ Stoichiometry To Another Element: 2 Atoms Of C To Ca
☐ Hydrogen Stoichiometry To Excess Oxygen H:O Ratio .00 (OH = 1, H2O = 2)

☐ Calculate Formula Based On Atoms Of Sum
● No Mineral End-Member Calculation
○ Olivine ○ Feldspar ○ Pyroxene ○ Garnet (Ca,Mg,Fe,Mn) ○ Garnet (Al,Fe,Cr)
☐ Amphibole (Ague, Auto Normalization)
☐ Biotite (Brimhall and Ague, Halog Code)

The resulting carbonate output is seen next.

```
St  338 Dolomite Oberdorf NMNH R10057 (J2)
TakeOff = 40.0  KiloVolt = 15.0  Beam Current = 15.0  Beam Size =   10
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                        -2,      3
Number of Data Lines:   3             Number of 'Good' Data Lines:   3
WARNING- Forcing negative k-ratios to zero
```

```
Average Total Oxygen:       52.237     Average Total Weight%:  100.376
Average Calculated Oxygen:  52.237     Average Atomic Number:   10.882
Average Excess Oxygen:        .000     Average Atomic Weight:   18.446
Average ZAF Iteration:        3.00     Average Quant Iterate:     2.00

Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction
Element C is Calculated  2 Atoms Relative To 1.0 Atom of Ca

St  338 Dolomite Oberdorf NMNH R10057 (J2), Results in Elemental Weight Percents

SPEC:        C       O
TYPE:     RELA    CALC

AVER:   13.070  52.237
SDEV:     .042    .111

ELEM:       Ca      Mg      Mn      Fe
BGDS:      LIN     LIN     LIN     LIN
TIME:    20.00   30.00   40.00   40.00
BEAM:    10.34   10.34   10.34   10.34

ELEM:       Ca      Mg      Mn      Fe   SUM
    16  21.744  13.226    .044    .033 100.210
    17  21.881  13.159    .023    .030 100.560
    18  21.793  13.246    .000    .028 100.356

AVER:   21.806  13.210    .022    .030 100.376
SDEV:     .069    .045    .022    .003    .176
SERR:     .040    .026    .013    .002
%RSD:      .32     .34   98.33    8.66
STDS:      130     131     132     132

STKF:    .3826   .0853   .0202   .4131
STCT:   3040.8  1502.9    43.1   955.3

UNKF:    .2045   .0847   .0002   .0003
UNCT:   1625.7  1492.4      .3      .6
UNBG:      8.6     9.0     2.1     3.4

ZCOR:   1.0661  1.5597  1.2224  1.2016
KRAW:    .5346   .9930   .0070   .0006
PKBG:   189.50  167.57    1.19    1.18

St  338 Dolomite Oberdorf NMNH R10057 (J2), Results in Oxide Weight Percents

SPEC:      CO2       O
TYPE:     RELA    CALC

AVER:   47.890    .000
SDEV:     .152    .000

ELEM:      CaO     MgO     MnO     FeO   SUM
    16  30.425  21.932    .056    .043 100.210
    17  30.616  21.822    .030    .038 100.560
    18  30.493  21.966    .000    .036 100.356

AVER:   30.511  21.907    .029    .039 100.376
SDEV:     .097    .075    .028    .003    .176
SERR:     .056    .043    .016    .002
%RSD:      .32     .34   98.33    8.66
```

Linear Calibration - Curve Method

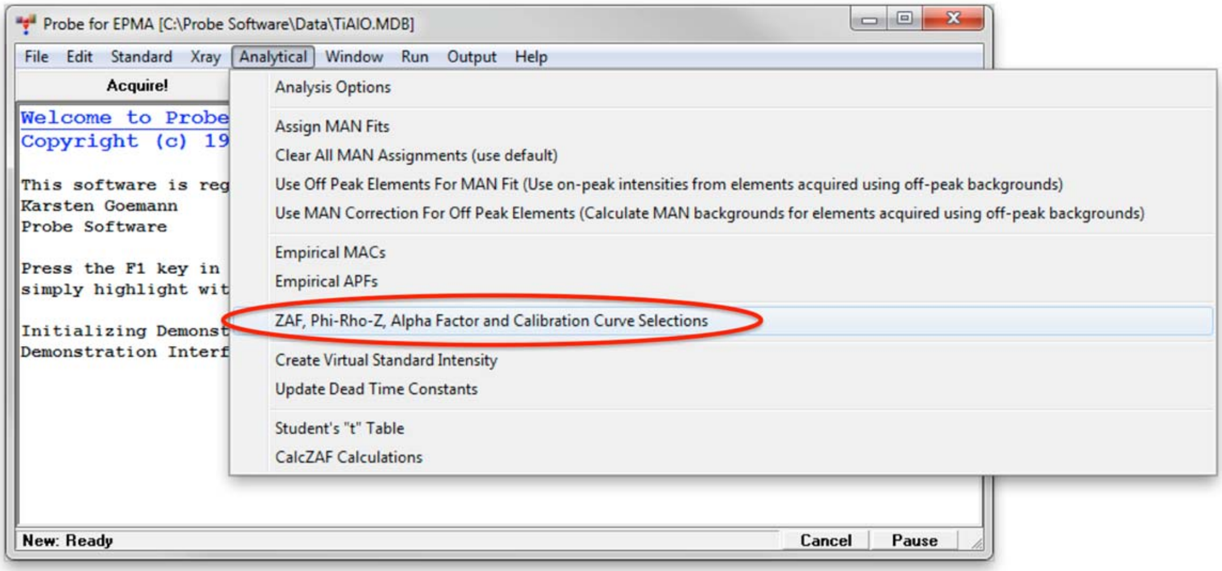
PROBE FOR EPMA offers a sophisticated calibration curve (multi-standard) method for correcting x-ray data. It is based on a second order polynomial fit to multiple standard intensity data. This option has been utilized in special situations such as the analysis of trace carbon in steels and when a suitable set of well characterized standards are available.

The example outlined below will document this calibration curve method for the specific analysis of Al, Ti and O in titanium aluminides doped with oxygen. This data and mdb file was generously supplied from research conducted by Jim Smith at the NASA Glenn Research Center. These low density, high strength alloys are part of an ongoing study of the transport kinetics of oxygen in these metals in conjunction with the development of superior alloys for aircraft engine gas turbine turn blades.

A series of nine titanium-aluminides (varying Ti/Al ratio) were carefully prepared, each doped with a specific concentration of oxygen, ranging from 0 to 3.21%, thereby bracketing the expected unknowns range of oxygen concentration. Each standard alloy was analyzed by other techniques to verify the nominal compositions. The nine standard compositions were then entered into the STANDARD.MDB database and the positions of each standard digitized in PROBE FOR EPMA.

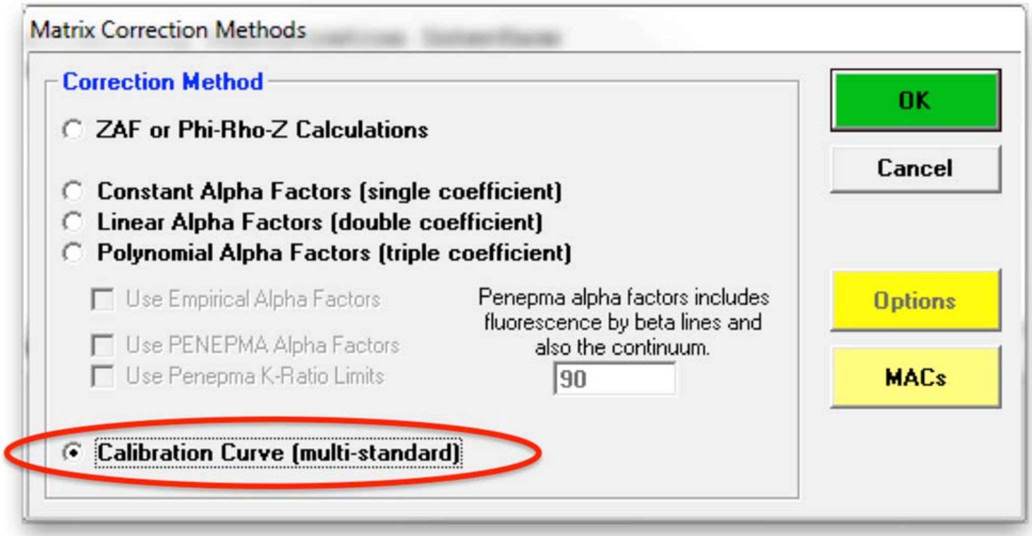
Aluminum, titanium and oxygen were peaked on the appropriate standards and count rate data (five spots each) were acquired on each of the nine standards. The count rate data was then examined in the **Analyze!** window to ascertain the precision of the five data points on each standard, deleting any selected lines as deemed appropriate.

After standard collection, the user must select the calibration curve approach as the matrix correction method. From the main PROBE FOR EPMA log window, select **Analytical | ZAF, Phi-Rho-Z, Alpha Factor and Calibration Curve Selections** from the menu.



```
Welcome to Probe
Copyright (c) 19

This software is reg
Karsten Goemann
Probe Software

Press the F1 key in
simply highlight wit

Initializing Demonst
Demonstration Interf
```

The **Matrix Correction Methods** window opens. Select the *Calibration Curve (multi-standard)* button for the *Correction Method*.



○ ZAF or Phi-Rho-Z Calculations

○ Constant Alpha Factors (single coefficient)
○ Linear Alpha Factors (double coefficient)
○ Polynomial Alpha Factors (triple coefficient)

☐ Use Empirical Alpha Factors
☐ Use PENEPMA Alpha Factors
☐ Use Penepma K-Ratio Limits

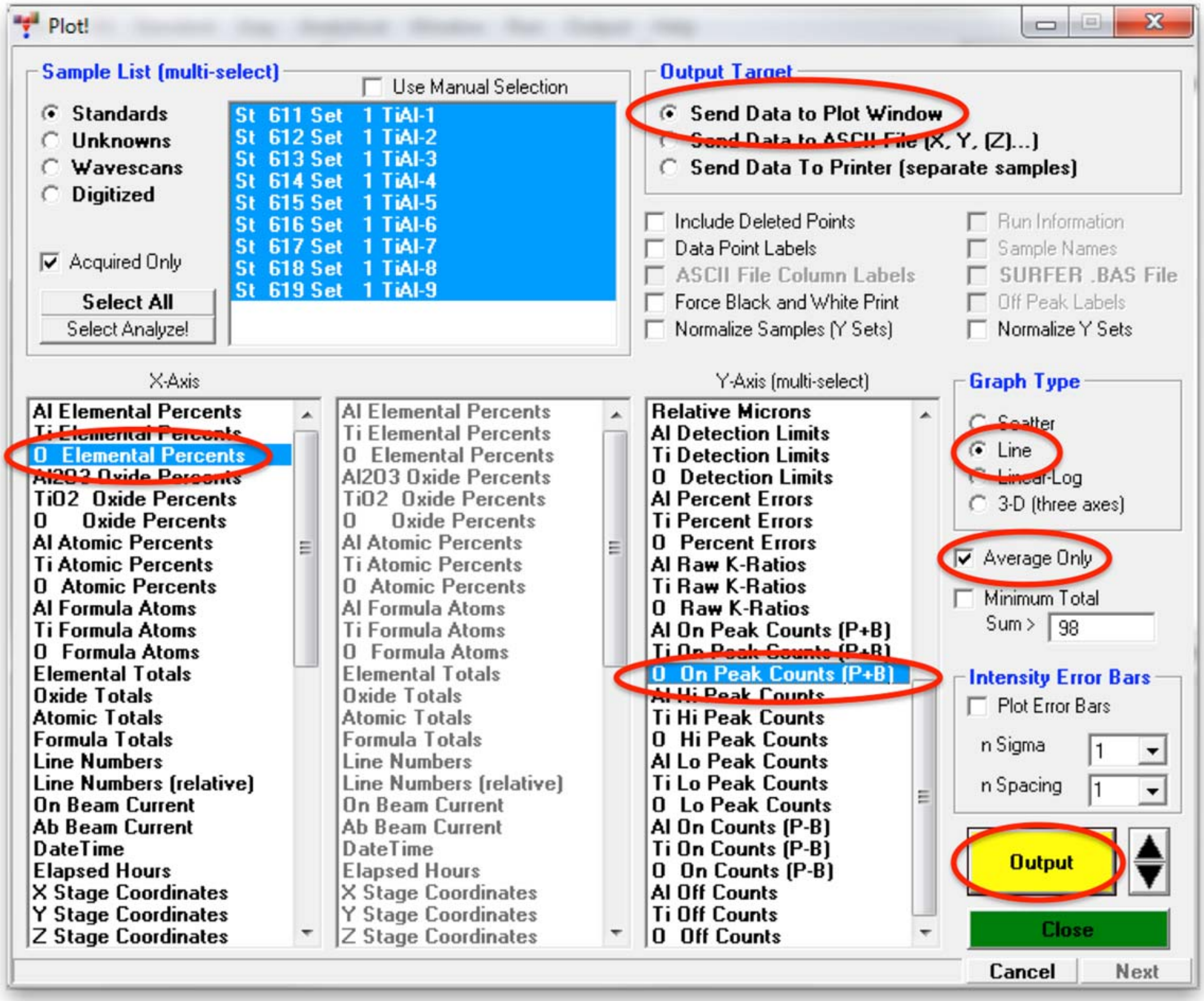
Penepma alpha factors includes fluorescence by beta lines and also the continuum. 90

● Calibration Curve (multi-standard)

Click the **OK** button, returning to the main PROBE FOR EPMA log window.

Next, the user will evaluate each of the three calibration curves. Select **Output Standard and Unknow Plots** in the **Output** menu of the main **Probe For EPMA** window. Shift-click to select all nine titanium-aluminide alloy standards to plot. Select *Send Data to Plot Window* under *Output Target* and select a *Graph Type*. Check the *Average Only* check box to use the average value of each standard sample.

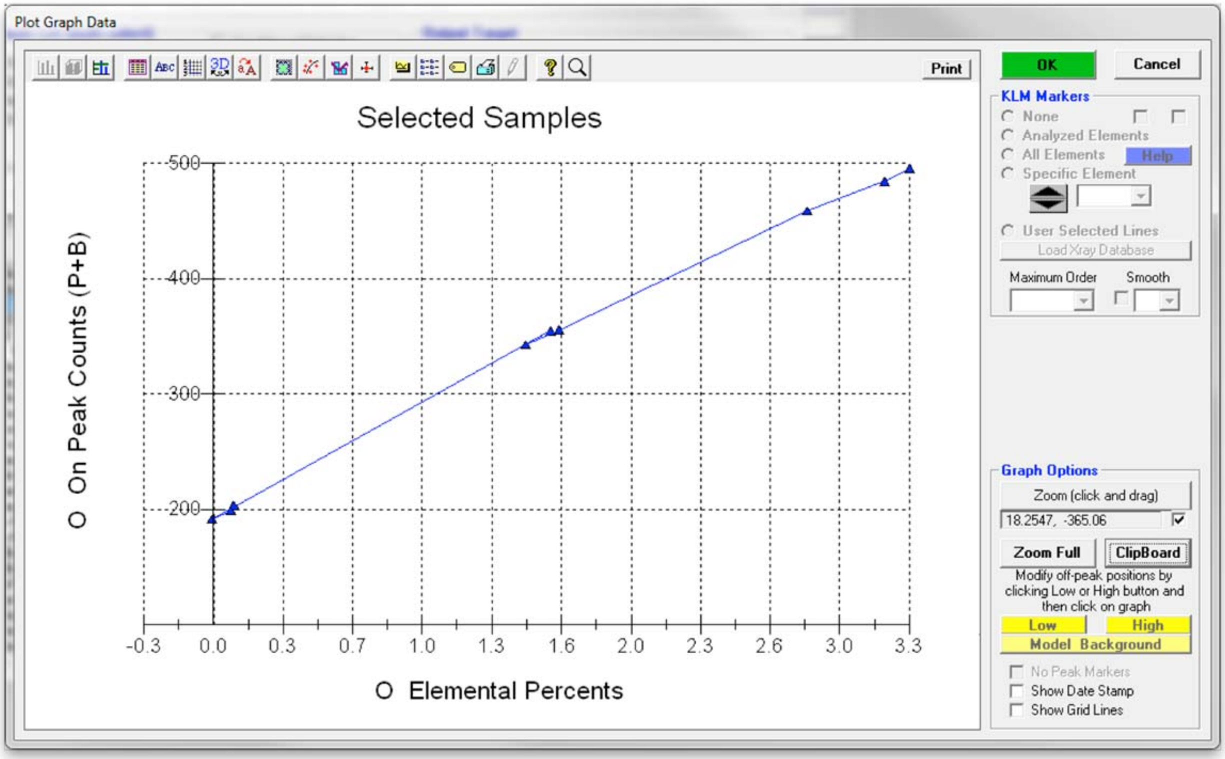
Finally, plot *O Elemental Percents* on the X axis versus *O On Peak Counts (P+B)* on the Y axis.



Click the **Output** button.

All of the selected standards are analyzed and reported in the main PROBE FOR EPMA log window.

The **Plot Graph Data** window appears.



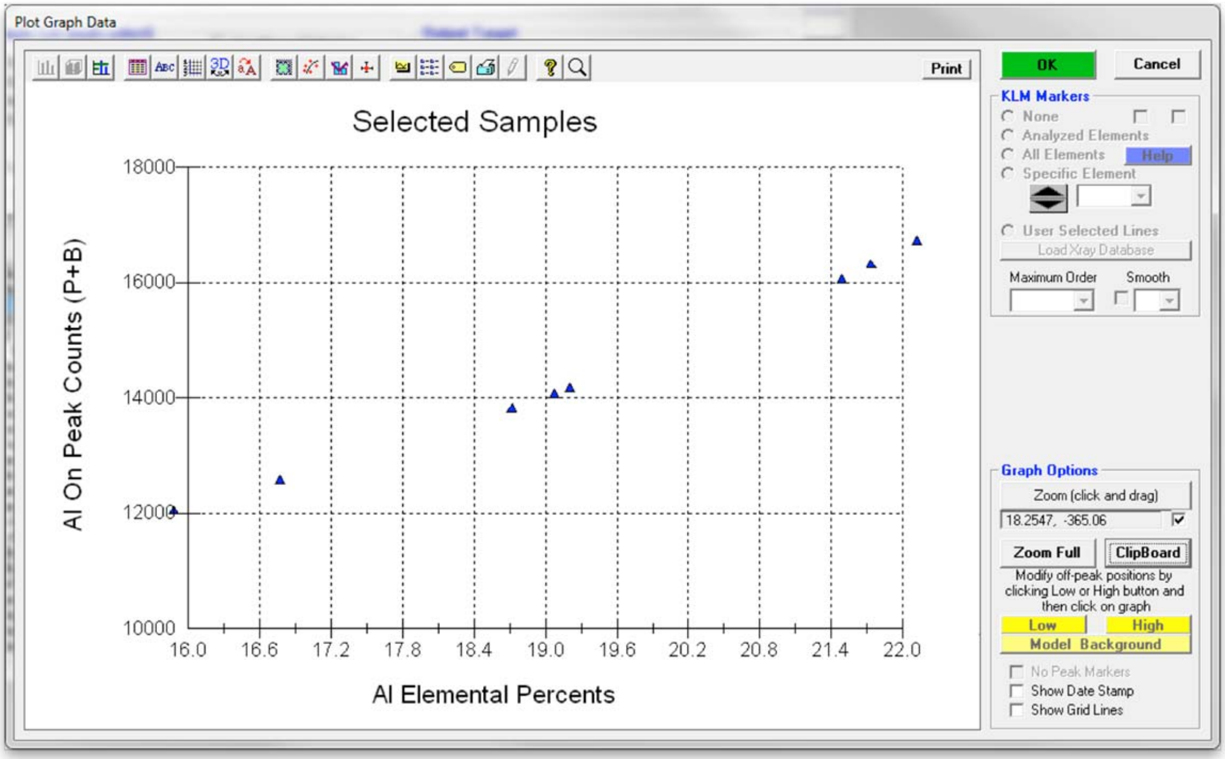
Modify off-peak positions by clicking Low or High button and then click on graph

The *Show Grid Lines* check box has been marked to facilitate reading the percent and count values.

The user may evaluate the data using the **Zoom Full** capabilities (click and drag mouse over region of interest on graph) to expand the scaling. Here, in the center group, two data points clearly overlap. Placing the mouse cursor over any selected point on the graph returns the x and y values of that position (read above the **Zoom Full** button).

When finished, click the **OK** button to return to the **Plot!** window to next review the other calibration curves.

The output for aluminum is plotted similarly. Select the *Al Elemental Percents* versus *Al On Peak Counts (P+B),* (the counts per second determined on peak) and click the **Output** button in the **Plot!** window. This curve is viewed below.

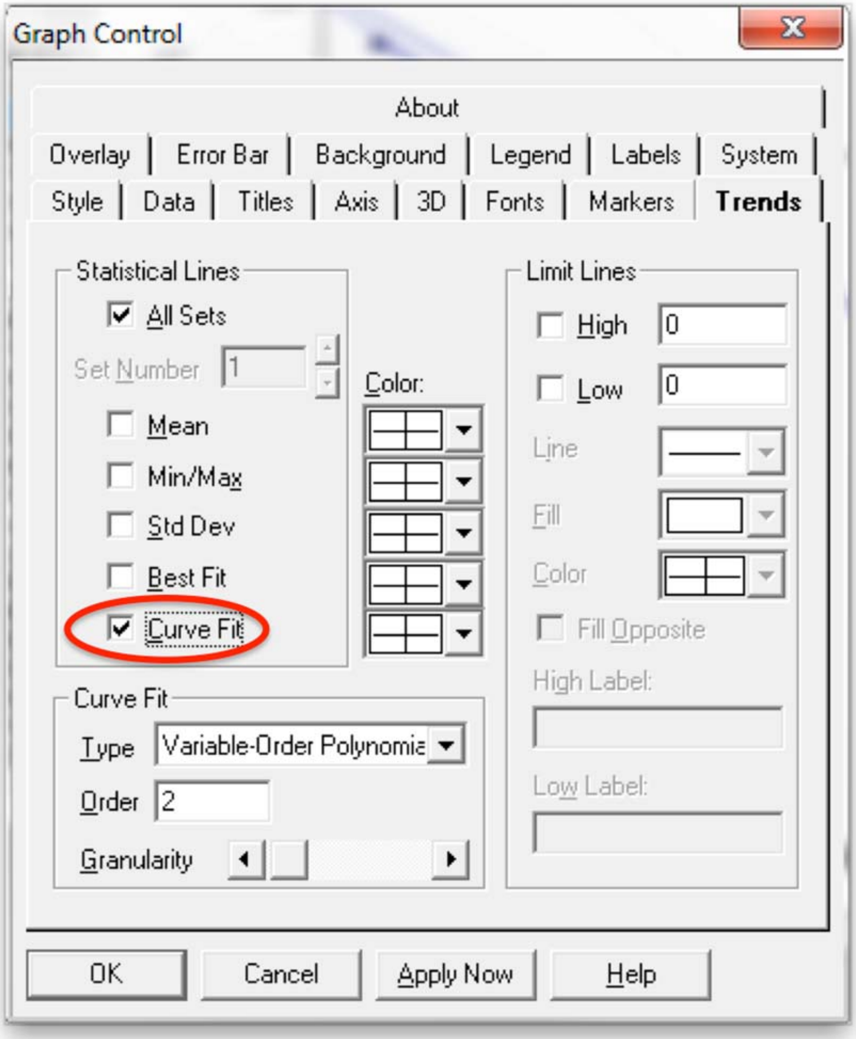


18.2547, -365.06

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

The graph may be modified by selecting any of the buttons across the top to enter the **Graph Control** module.

Graph Control (see tabs in display below) can be used to edit numerous graph parameters. Under the **Trends** tab, for instance, are the curve fitting options. Select *Curve Fit* under *Statistical Lines* and edit the *Curve Fit Type* and *Order* options below as required.



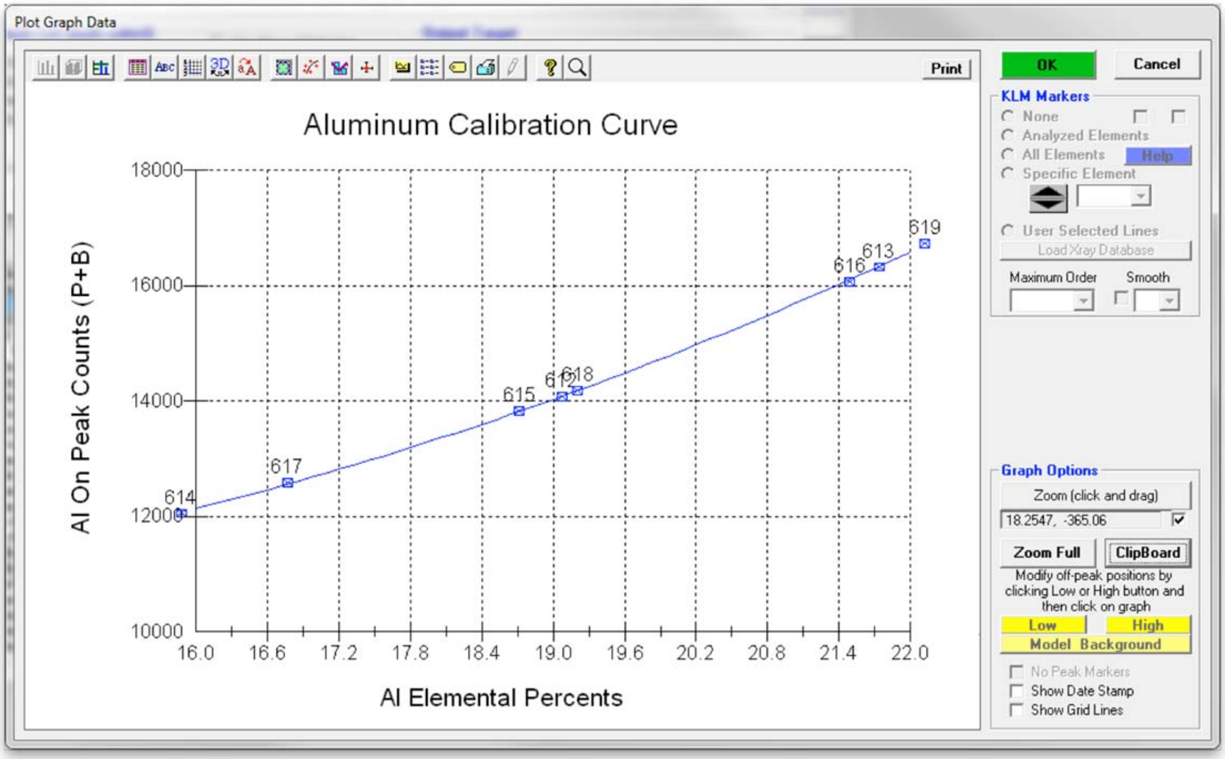
☑ All Sets
Set Number 1
☐ Mean
☐ Min/Max
☐ Std Dev
☐ Best Fit
☑ Curve Fit

☐ High 0
☐ Low 0
☐ Fill Opposite

Type Variable-Order Polynomia
Order 2

Click the **Apply Now** or **OK** button to see the changes in the **Graph Data** window.

The modified **Plot Graph Data** window returns. Here, a title, different, larger symbols, standard numbers and the second order polynomial curve have been added to the graph below.



Upon creating the previous plots, the selected standards were analyzed, each of the nine standards were reported in the main PROBE FOR EPMA log window along with the second order polynomial fit parameters.

The following output displays the log window output for one of these: St 617 Set   5 TiAl-7 standard.

```
St  617 Set   5 TiAl-7
TakeOff = 52.5  KiloVolt = 15.0  Beam Current = 30.0  Beam Size =    1
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3

Titanium aluminide 3.03 Oxygen
Number of Data Lines:   5             Number of 'Good' Data Lines:   5
WARNING- Using Calibration Curve Matrix Corrections
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  100.651
Average Calculated Oxygen:    .000     Average Atomic Number:   20.177
Average Excess Oxygen:        .000     Average Atomic Weight:   40.571

St  617 Set   5 TiAl-7, Results in Elemental Weight Percents

ELEM:       Al      Ti       O
BGDS:      LIN     LIN     LIN
TIME:    10.00   10.00   10.00
BEAM:   300.00  300.00  300.00

ELEM:       Al      Ti       O   SUM
   978  15.452  81.618   2.986 100.056
   979  15.680  81.966   3.114 100.761
   980  15.864  81.880   3.053 100.796
   981  15.788  81.957   3.000 100.744
   982  15.747  82.245   2.908 100.900

AVER:   15.706  81.933   3.012 100.651
SDEV:      .157    .224    .077    .338
SERR:      .070    .100    .035
%RSD:     1.00     .27    2.56

PUBL:   15.730  81.240   3.030 100.000
%VAR:     -.15     .85    -.59
DIFF:    -.024    .693   -.018

UNCT:  13020.8 11807.2   329.4
UNBG:    215.5    29.2   116.0
KRAW:   1.0000  1.0000  1.0000
PKBG:    61.44  406.68    3.84

FIT1:    .4671-363.4302  -.5152
FIT2:    .0013   .0712   .0098
FIT3:  .000000-.000003 .000003
DEV:       2.2      .9     7.1
```

The coefficients for the second order polynomial are listed last (Fit 1, Fit 2, Fit 3 and Dev). The three Fit terms represent the intercept, the slope and the second order curvature factor, respectively. The DEV term represents the total deviation (sum of the residuals) between the calculated curve and the original data. The smaller the number, the better here. The software prints a warning line if this correction method is active.

The analysis of unknown samples is straightforward. Create a new sample and collect the x-ray intensity data on the unknown. Select the **Analyze!** window and click **Analyze**.

An example is printed next.

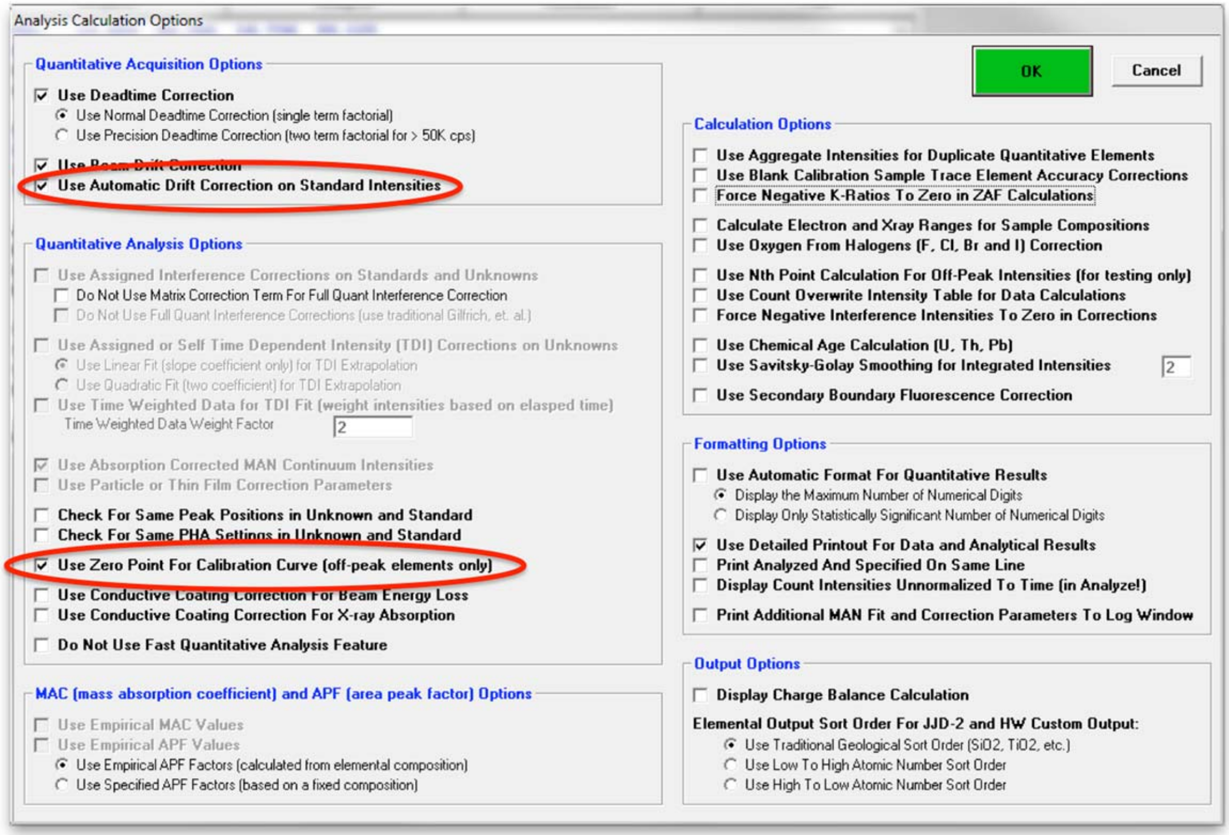
```
Un   25 Sample 3-9 LowOx 0-30u 2u increments
TakeOff = 52.5  KiloVolt = 15.0  Beam Current = 30.0  Beam Size =    1
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =       0, Magnification (imaging) =     40)
Image Shift (X,Y):                                         -2,     3
Number of Data Lines:  16             Number of 'Good' Data Lines:  16
WARNING- Using Calibration Curve Matrix Corrections
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:   99.869
Average Calculated Oxygen:    .000     Average Atomic Number:   19.838
Average Excess Oxygen:        .000     Average Atomic Weight:   39.903

Un   25 Sample 3-9 LowOx 0-30u 2u increments, Results in Elemental Weight Percents

ELEM:       Al      Ti       O
BGDS:      LIN     LIN     LIN
TIME:    10.00   10.00   10.00
BEAM:   300.24  300.24  300.24

ELEM:       Al      Ti       O   SUM
   851  21.260  76.350   1.956  99.566
   852  21.236  76.469   2.003  99.708
   853  21.193  76.689   1.957  99.839
   854  21.128  76.174   1.941  99.244
   855  21.222  76.599   1.842  99.663
   856  21.120  76.425   1.755  99.300
   857  21.126  76.494   1.838  99.459
   858  21.125  77.135   1.767 100.027
   859  21.142  76.686   1.791  99.619
   860  21.153  76.835   1.796  99.784
   861  21.139  77.248   1.703 100.089
   862  21.256  77.439   1.685 100.379
   863  21.190  77.360   1.833 100.383
   864  21.216  77.503   1.779 100.499
   865  21.286  77.127   1.643 100.055
   866  21.264  77.541   1.482 100.287

AVER:   21.191  76.880   1.798  99.869
SDEV:     .058    .454    .133    .393
SERR:     .015    .113    .033
%RSD:      .28     .59    7.42

UNCT:  18339.0 11021.6   222.4
UNBG:    218.2    26.6   113.8
KRAW:   1.0000  1.0000  1.0000
PKBG:    85.05  417.09    2.96

FIT1:    .4718-363.4019  -.5152
FIT2:    .0013   .0712   .0098
FIT3:  .000000-.000003 .000003
DEV:       2.2      .9     7.1
```

The second order polynomial coefficients are always listed last (just above). Elements calculated by difference or stoichiometry can be calculated along with calibration curve corrected elements. And if both off-peak and MAN acquired data are present, PROBE FOR EPMA will construct separate sets of calibration curves and fit a second order polynomial expression that is used in the iteration procedure to determine the concentration of the element.

The user may elect to run standards after completing unknown sample acquisition and then correct for any standard intensity drift. From the main PROBE FOR EPMA log window select **Analytical** and then choose **Analysis Options** from the drop-down menu.

The **Analysis Calculation Options** window appears, remember to check that the *Use Automatic Drift Correction on Standard Intensities* check box is marked.

In some instances, it may be useful to add to the acquired data set a zero point (off-peak elements only) to improve the polynomial fit. To include a zero point, check the box (prior to analyzing the standards) labeled *Use Zero Point For Calibration Curve (Off-Peak Elements Only)*. This choice is also found in the **Analysis Calculation Options** window.



Quantitative Acquisition Options

- ☑ Use Deadtime Correction
  - ● Use Normal Deadtime Correction (single term factorial)
  - ○ Use Precision Deadtime Correction (two term factorial for > 50K cps)
- ☑ Use Beam Drift Correction
- ☑ Use Automatic Drift Correction on Standard Intensities

Quantitative Analysis Options

- ☐ Use Assigned Interference Corrections on Standards and Unknowns
  - ☐ Do Not Use Matrix Correction Term For Full Quant Interference Correction
  - ☐ Do Not Use Full Quant Interference Corrections (use traditional Gilfrich, et. al.)
- ☐ Use Assigned or Self Time Dependent Intensity (TDI) Corrections on Unknowns
  - ● Use Linear Fit (slope coefficient only) for TDI Extrapolation
  - ○ Use Quadratic Fit (two coefficient) for TDI Extrapolation
- ☐ Use Time Weighted Data for TDI Fit (weight intensities based on elasped time)
  - Time Weighted Data Weight Factor 2
- ☑ Use Absorption Corrected MAN Continuum Intensities
- ☐ Use Particle or Thin Film Correction Parameters
- ☐ Check For Same Peak Positions in Unknown and Standard
- ☐ Check For Same PHA Settings in Unknown and Standard
- ☑ Use Zero Point For Calibration Curve (off-peak elements only)
- ☐ Use Conductive Coating Correction For Beam Energy Loss
- ☐ Use Conductive Coating Correction For X-ray Absorption
- ☐ Do Not Use Fast Quantitative Analysis Feature

MAC (mass absorption coefficient) and APF (area peak factor) Options

- ☐ Use Empirical MAC Values
- ☐ Use Empirical APF Values
  - ● Use Empirical APF Factors (calculated from elemental composition)
  - ○ Use Specified APF Factors (based on a fixed composition)

Calculation Options

- ☐ Use Aggregate Intensities for Duplicate Quantitative Elements
- ☐ Use Blank Calibration Sample Trace Element Accuracy Corrections
- ☐ Force Negative K-Ratios To Zero in ZAF Calculations
- ☐ Calculate Electron and Xray Ranges for Sample Compositions
- ☐ Use Oxygen From Halogens (F, Cl, Br and I) Correction
- ☐ Use Nth Point Calculation For Off-Peak Intensities (for testing only)
- ☐ Use Count Overwrite Intensity Table for Data Calculations
- ☐ Force Negative Interference Intensities To Zero in Corrections
- ☐ Use Chemical Age Calculation (U, Th, Pb)
- ☐ Use Savitsky-Golay Smoothing for Integrated Intensities 2
- ☐ Use Secondary Boundary Fluorescence Correction

Formatting Options

- ☐ Use Automatic Format For Quantitative Results
  - ● Display the Maximum Number of Numerical Digits
  - ○ Display Only Statistically Significant Number of Numerical Digits
- ☑ Use Detailed Printout For Data and Analytical Results
- ☐ Print Analyzed And Specified On Same Line
- ☐ Display Count Intensities Unnormalized To Time (in Analyze!)
- ☐ Print Additional MAN Fit and Correction Parameters To Log Window

Output Options

- ☐ Display Charge Balance Calculation

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

- ● Use Traditional Geological Sort Order (SiO2, TiO2, etc.)
- ○ Use Low To High Atomic Number Sort Order
- ○ Use High To Low Atomic Number Sort Order

Time Dependent Intensity (TDI) Corrections

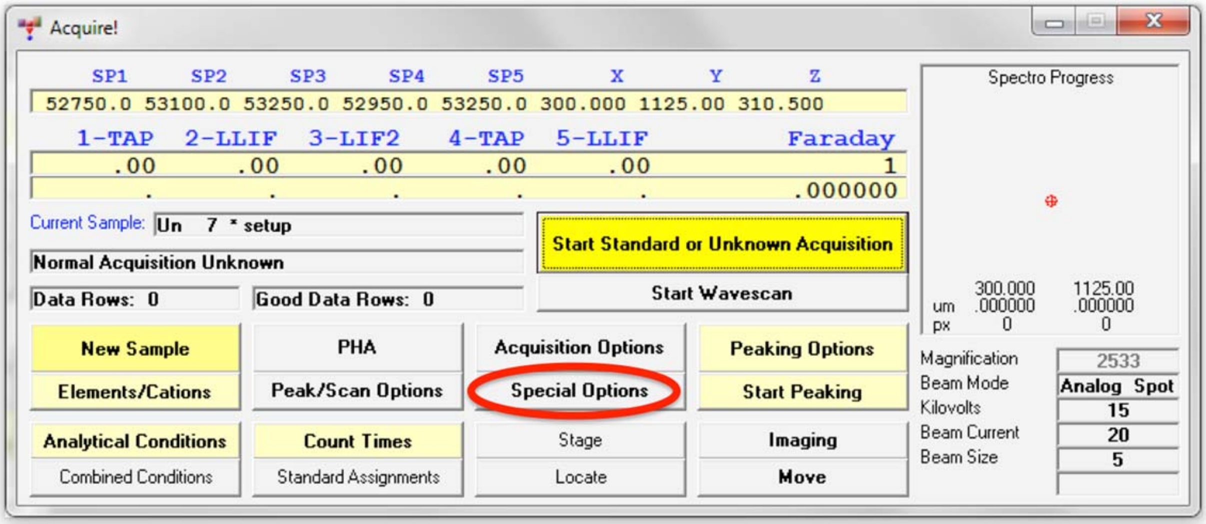
PROBE FOR EPMA gives the user two powerful methods for the correction of time dependent intensity element effects unknown samples. Each correction option provides a means to automatically correct data for the time dependent loss of x-ray intensity due to continuous electron bombardment (heating damage/charge buildup) or carbon contamination that occurs during normal electron microprobe work. The time dependent intensity element extrapolation may be applied to any degradation (or enhancement) of the x-ray intensity over time. Elements most susceptible include sodium, potassium, fluorine, perhaps sulfur and bound water. This correction is most useful for samples that are too small to utilize a defocused beam and also allows the operator to run higher than normal sample currents to improve analytical sensitivity.

Two different methods are available for volatile element corrections; the *Self Calibration Time Dependent Intensity (TDI) Acquisition* and the *Assigned Calibration Time Dependent Intensity (TDI) Acquisition.* Each will be documented.

In the *Self Calibration Time Dependent Intensity (TDI) Acquisition* method, the program acquires the on-peak count data for the volatile element **during** the normal sample acquisition process for the unknown sample. This method works well when samples to be analyzed have widely differing compositions as the calibration is determined with every sample acquisition.

Open PROBE FOR EPMA, and proceed through the normal calibration and standardization routine. Check suitable standards for accuracy, these should not be volatile or beam sensitive.

Move to your first unknown sample. Open the **New Sample** window from the **Acquire!** window and create a new unknown sample. Click the **Special Options** button.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 7 * setup

Normal Acquisition Unknown

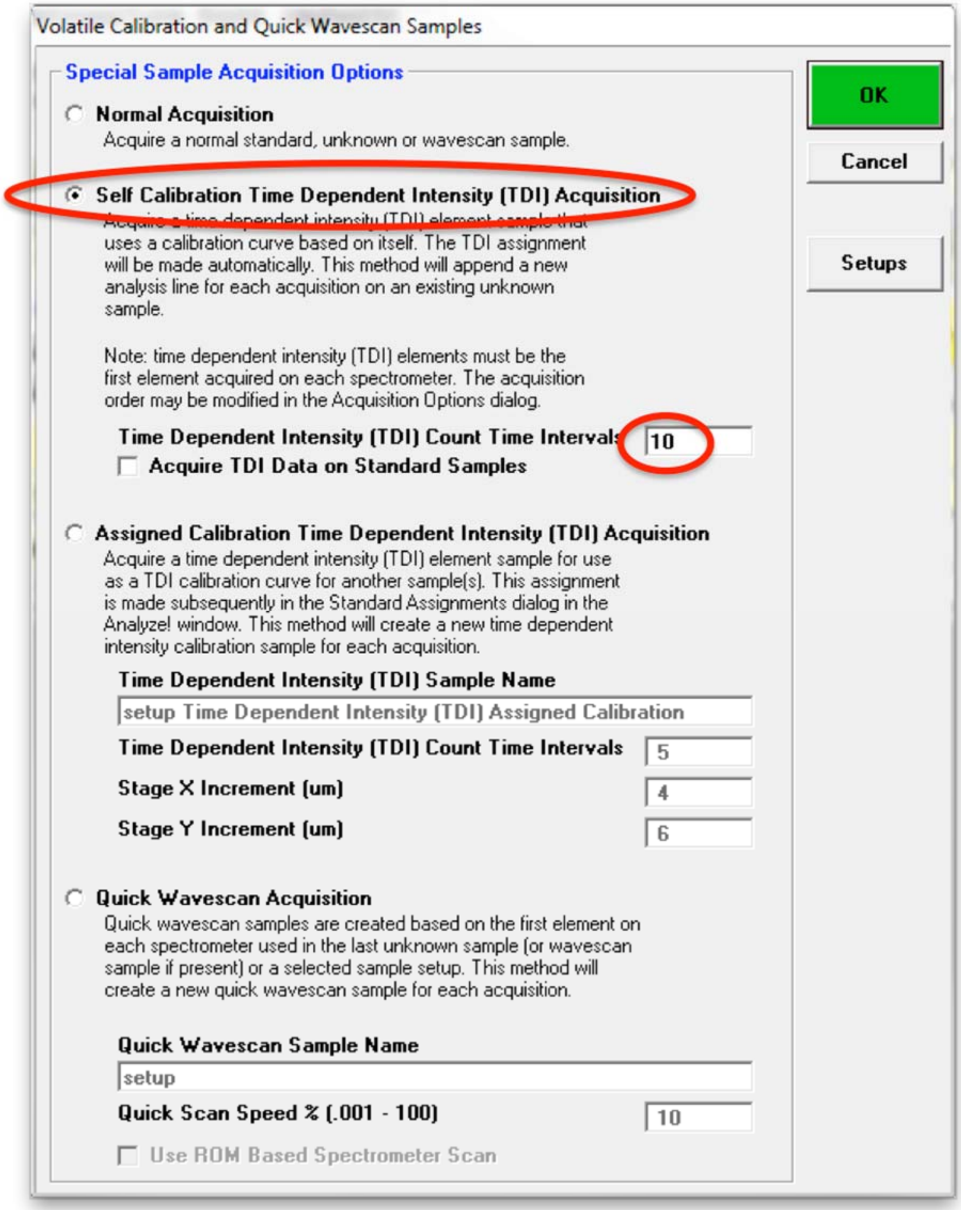
Data Rows: 0

Good Data Rows: 0

	X	Y
	300.000	1125.00
um	.000000	.000000
px	0	0

Magnification	2533
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	20
Beam Size	5

The **Volatile Calibration and Quick Wavescan Samples** window opens. Select the *Self Calibration Time Dependent Intensity (TDI) Acquisition* option. The time dependent intensity element correction is only applied to the first element analyzed for on each spectrometer. Enter a number into the *Volatile Count Time Intervals* text field (up to 50 intervals may be used). The program will use this interval number and the on-peak count time to create a calibration curve. In this example, Na is counted for 40 seconds on peak and with an interval of 10 entered, the program will automatically count ten 4 second intervals. Each element listed first on each spectrometer is treated in this way. The off peak counts are not affected.



Volatile Calibration and Quick Wavescan Samples

Special Sample Acquisition Options

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

● **Self Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample that uses a calibration curve based on itself. The TDI assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing unknown sample.

Note: time dependent intensity (TDI) elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Time Dependent Intensity (TDI) Count Time Intervals: 10
☐ Acquire TDI Data on Standard Samples

○ **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI 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 time dependent intensity calibration sample for each acquisition.

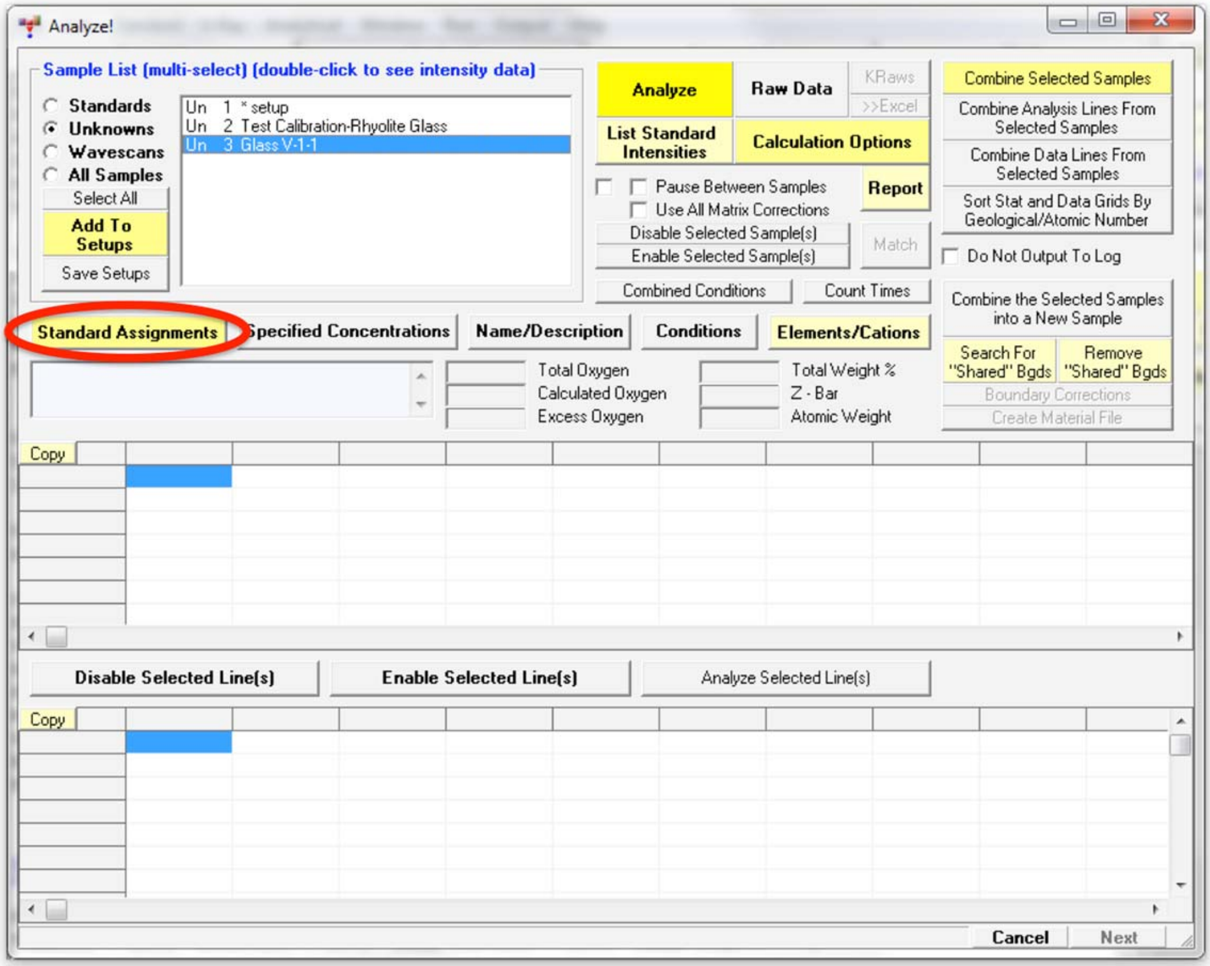
Time Dependent Intensity (TDI) Sample Name: setup Time Dependent Intensity (TDI) Assigned Calibration
Time Dependent Intensity (TDI) Count Time Intervals: 5
Stage X Increment (um): 4
Stage Y Increment (um): 6

○ **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: setup
Quick Scan Speed % (.001 - 100): 10
☐ Use ROM Based Spectrometer Scan

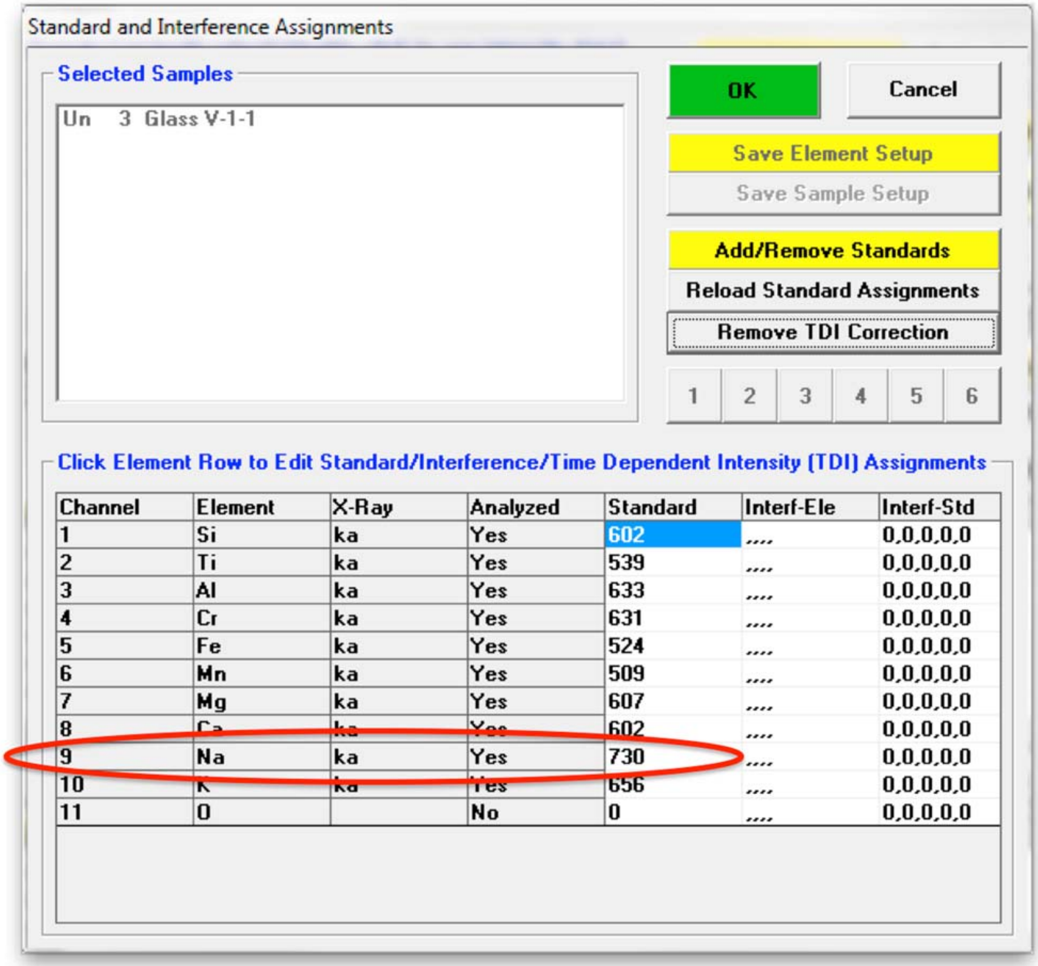
Click the **OK** button to return to the **Acquire!** window.

After collecting an unknown sample the user may display the volatile correction from the **Analyze!** window. Select a sample and click the **Standard Assignments** button.



Un 1 * setup
Un 2 Test Calibration-Rhyolite Glass
Un 3 Glass V-1-1

The **Standard and Interference Assignments** window opens.

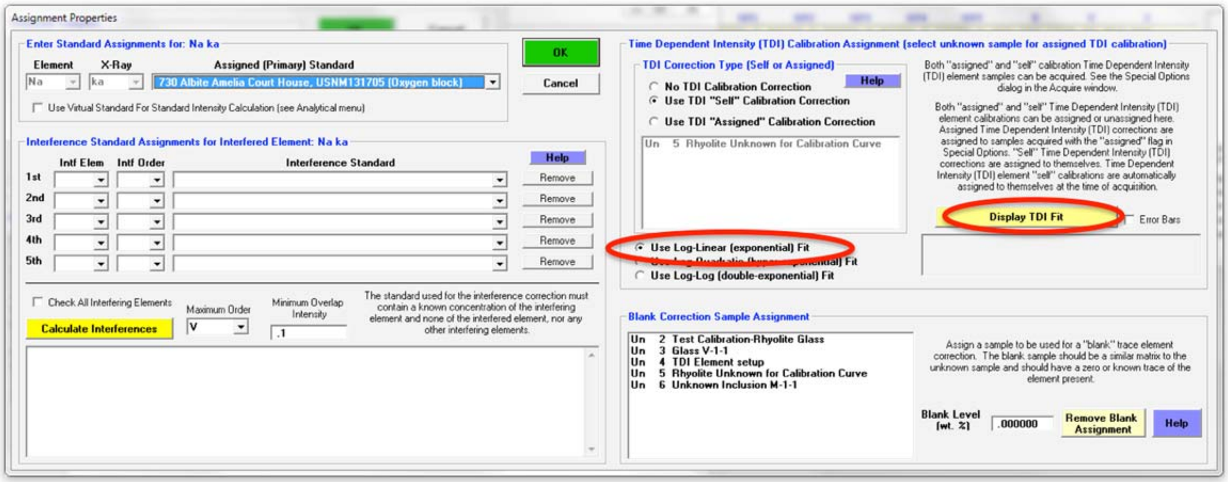


Un 3 Glass V-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	Si	ka	Yes	602	,,,,	0,0,0,0,0
2	Ti	ka	Yes	539	,,,,	0,0,0,0,0
3	Al	ka	Yes	633	,,,,	0,0,0,0,0
4	Cr	ka	Yes	631	,,,,	0,0,0,0,0
5	Fe	ka	Yes	524	,,,,	0,0,0,0,0
6	Mn	ka	Yes	509	,,,,	0,0,0,0,0
7	Mg	ka	Yes	607	,,,,	0,0,0,0,0
8	Ca	ka	Yes	602	,,,,	0,0,0,0,0
9	Na	ka	Yes	730	,,,,	0,0,0,0,0
10	K	ka	Yes	656	,,,,	0,0,0,0,0
11	O		No	0	,,,,	0,0,0,0,0

Select the element row (sodium in this example) to view the TDI calibration data.

The **Assignment Properties** window opens and lists all possible TDI element calibration samples. Three types of fit are possible; Log-Linear, Log -Quadratic, or Log-Log. Click the **Display TDI Fit** button:


Assignment Properties

Enter Standard Assignments for: Na ka

Element: Na

X-Ray: ka

Assigned (Primary) Standard: 730 Albite Amelia Court House, USNM131705 (Oxygen block)

☐ Use Virtual Standard For Standard Intensity Calculation (see Analytical menu)

Interference Standard Assignments for Interfered Element: Na ka

☐ Check All Interfering Elements

Maximum Order: V

Minimum Overlap Intensity: .1

The standard used for the interference correction must contain a known concentration of the interfering element and none of the interfered element, nor any other interfering elements.

Time Dependent Intensity (TDI) Calibration Assignment (select unknown sample for assigned TDI calibration)

TDI Correction Type (Self or Assigned)

○ No TDI Calibration Correction

● Use TDI "Self" Calibration Correction

○ Use TDI "Assigned" Calibration Correction

Un 5 Rhyolite Unknown for Calibration Curve

Both "assigned" and "self" calibration Time Dependent Intensity (TDI) element samples can be acquired. See the Special Options dialog in the Acquire window.

Both "assigned" and "self" Time Dependent Intensity (TDI) element calibrations can be assigned or unassigned here. Assigned Time Dependent Intensity (TDI) corrections are assigned to samples acquired with the "assigned" flag in Special Options. "Self" Time Dependent Intensity (TDI) corrections are assigned to themselves. Time Dependent Intensity (TDI) element "self" calibrations are automatically assigned to themselves at the time of acquisition.

● Use Log-Linear (exponential) Fit

○ Use Log-Quadratic (hyper-exponential) Fit

○ Use Log-Log (double-exponential) Fit

☐ Error Bars

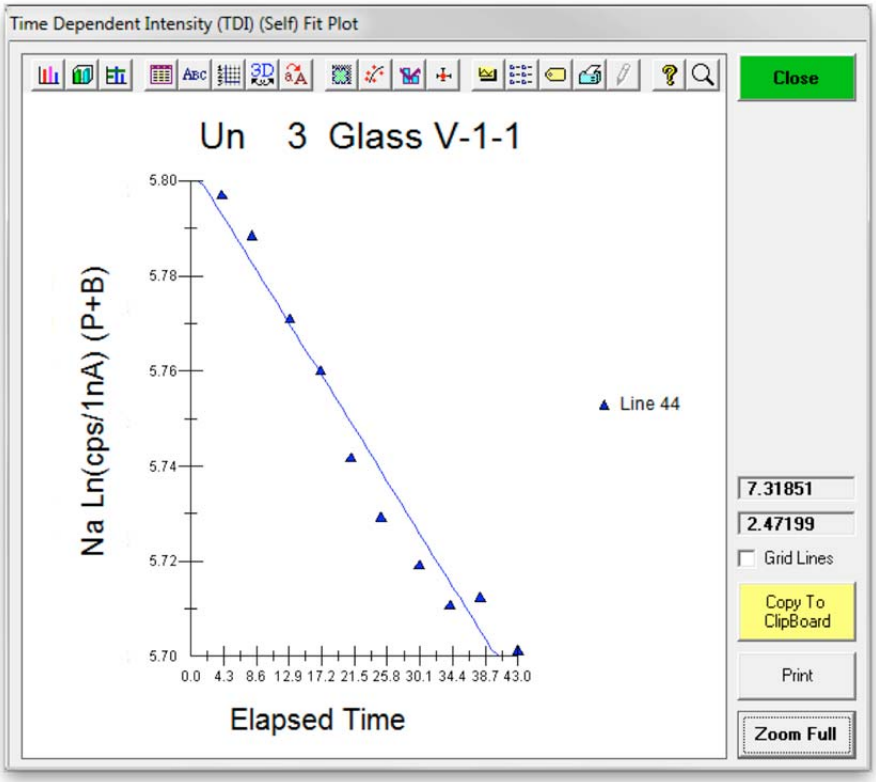
Blank Correction Sample Assignment

Un 2 Test Calibration-Rhyolite Glass
Un 3 Glass V-1-1
Un 4 TDI Element setup
Un 5 Rhyolite Unknown for Calibration Curve
Un 6 Unknown Inclusion M-1-1

Assign a sample to be used for a "blank" trace element correction. The blank sample should be a similar matrix to the unknown sample and should have a zero or known trace of the element present.

Blank Level (wt. %): .000000

The **Time Dependent Intensity (Self) Fit Plot** window opens.


Time Dependent Intensity (TDI) (Self) Fit Plot

The drop in sodium count intensity with time appears to fit an exponential function (Nielson and Sigurdsson, 1981). A plot of the natural log of the intensity data versus time should yield a straight line relationship as seen above.

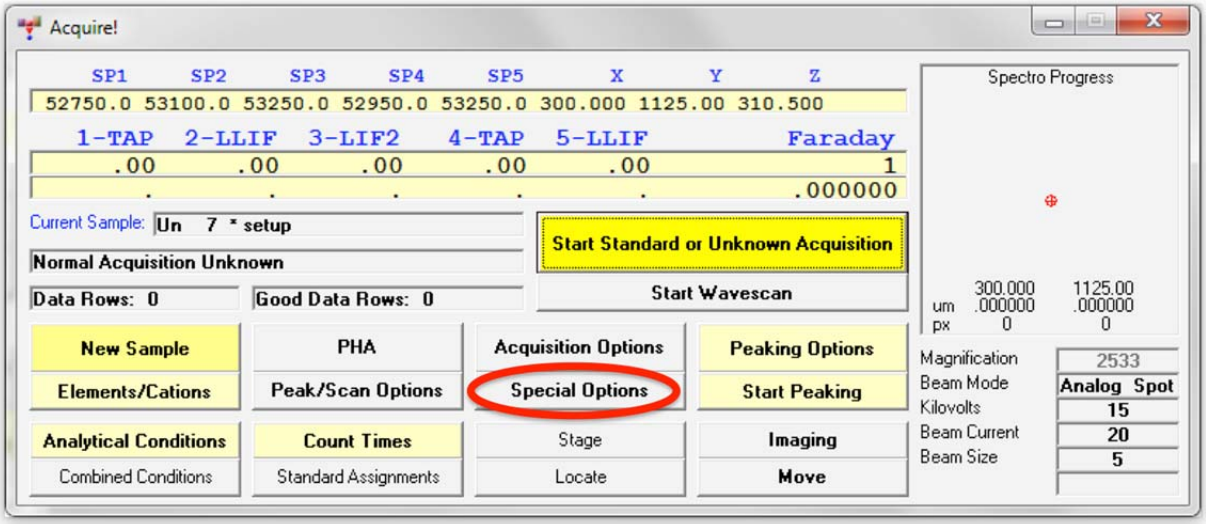
The extrapolation correction is quantitative in that the correction is based on a self calibration curve acquired during the run. The correction uses the actual elapsed time for all calculations. It is applied during the ZAF or Phi-Rho-Z iteration phase of the analysis to correct for changes in the matrix correction due to the extrapolation correction.

The next example will illustrate the *Assigned Calibration Time Dependent Intensity Acquisition* method. Here, small rhyolitic glass inclusions of similar composition will be analyzed.

Start PROBE FOR EPMA in the normal manner. Go through the calibration and standardization process, then check standards. Save the analysis routine as a sample setup. Next, create a separate sample setup with a subset of elements to which the TDI correction will be assigned, in this example silicon and sodium. Note TDI element calibration corrections can only be applied to elements that are the first element collected by each spectrometer.

Locate the sample to obtain the TDI element correction acquisition upon. This should be either the unknown sample or a material similar to the unknowns.

Again click the **Special Options** button in the **Acquire!** window.



SP1	SP2	SP3	SP4	SP5	X	Y	Z
52750.0	53100.0	53250.0	52950.0	53250.0	300.000	1125.00	310.500

1-TAP	2-LLIF	3-LIF2	4-TAP	5-LLIF	Faraday
.00	.00	.00	.00	.00	1
.	.	.	.	.	.000000

Current Sample: Un 7 * setup

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

Magnification 2533

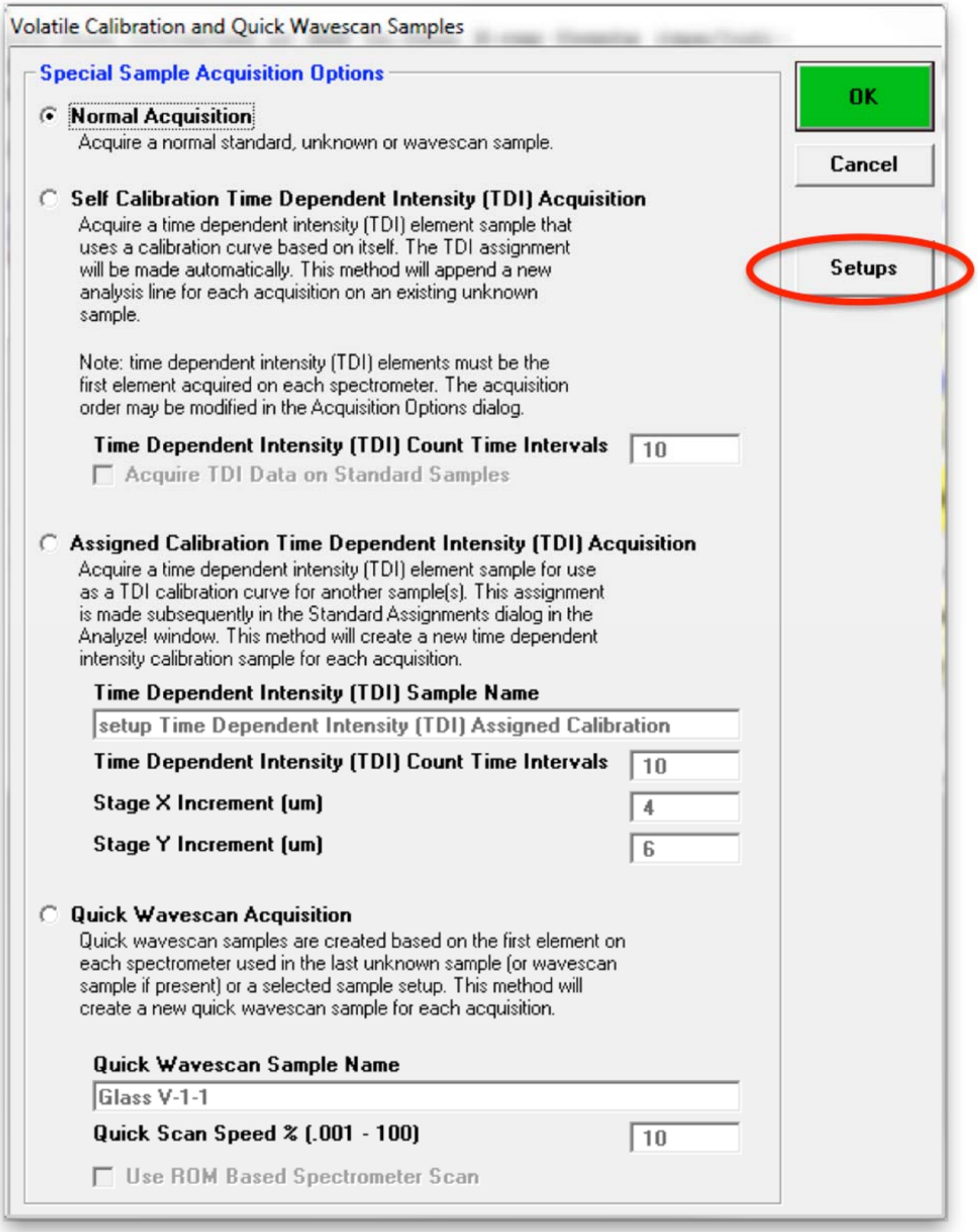
Beam Mode Analog Spot

Kilovolts 15

Beam Current 20

Beam Size 5

The **Volatile Calibration and Quick Wavescan Samples** window opens. The default acquisition choice is *Normal Acquisition*. Click the **Setups** button in the **Volatile Calibration and Quick Wavescan Samples** window.



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

○ **Self Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample that uses a calibration curve based on itself. The TDI assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing unknown sample.

Note: time dependent intensity (TDI) elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Time Dependent Intensity (TDI) Count Time Intervals 10
☐ Acquire TDI Data on Standard Samples

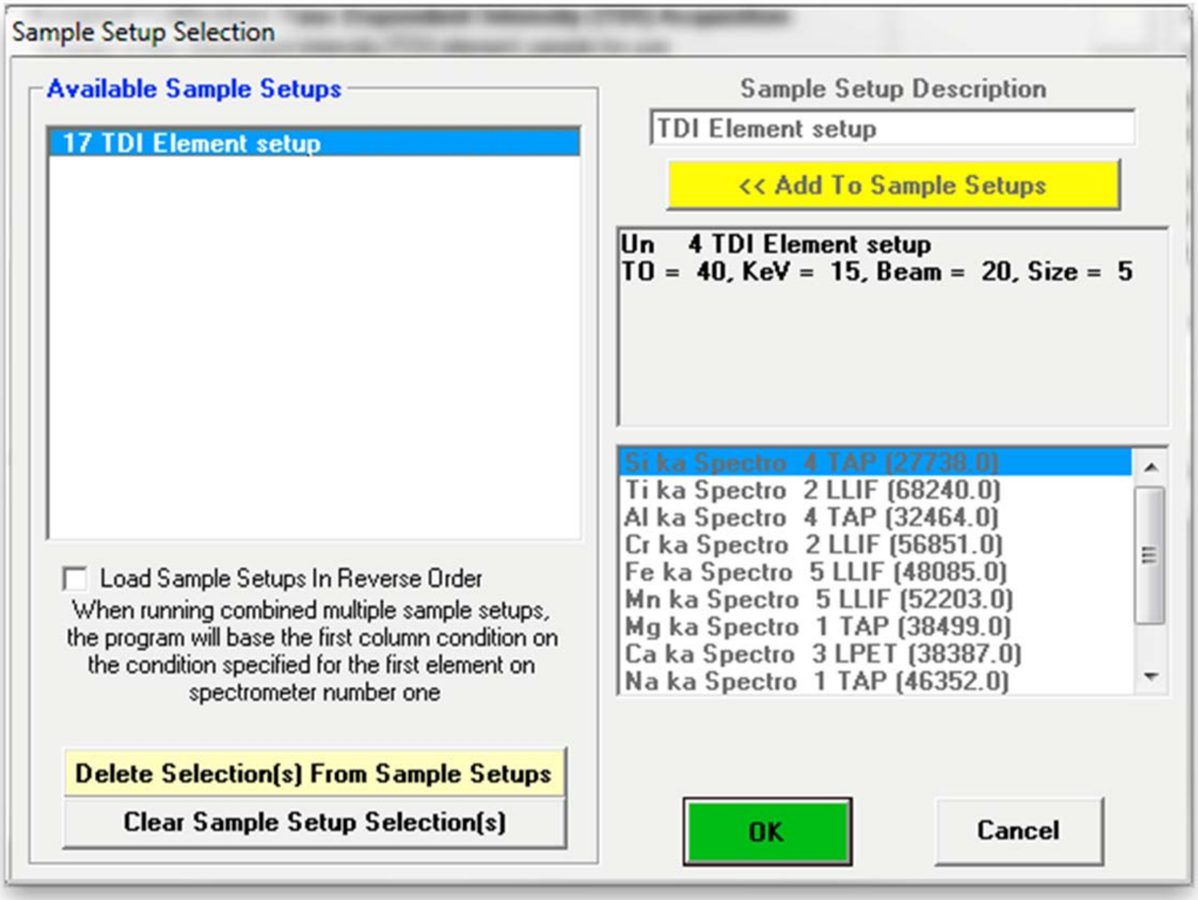
○ **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI calibration curve for another sample(s). This assignment is made subsequently in the Standard Assignments dialog in the Analyze! window. This method will create a new time dependent intensity calibration sample for each acquisition.

Time Dependent Intensity (TDI) Sample Name
setup Time Dependent Intensity (TDI) Assigned Calibration
Time Dependent Intensity (TDI) Count Time Intervals 10
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
Glass V-1-1
Quick Scan Speed % (.001 - 100) 10
☐ Use ROM Based Spectrometer Scan

The **Sample Setup Selection** dialog box opens. Check that the appropriate volatile setup is active.



17 TDI Element setup

TDI Element setup

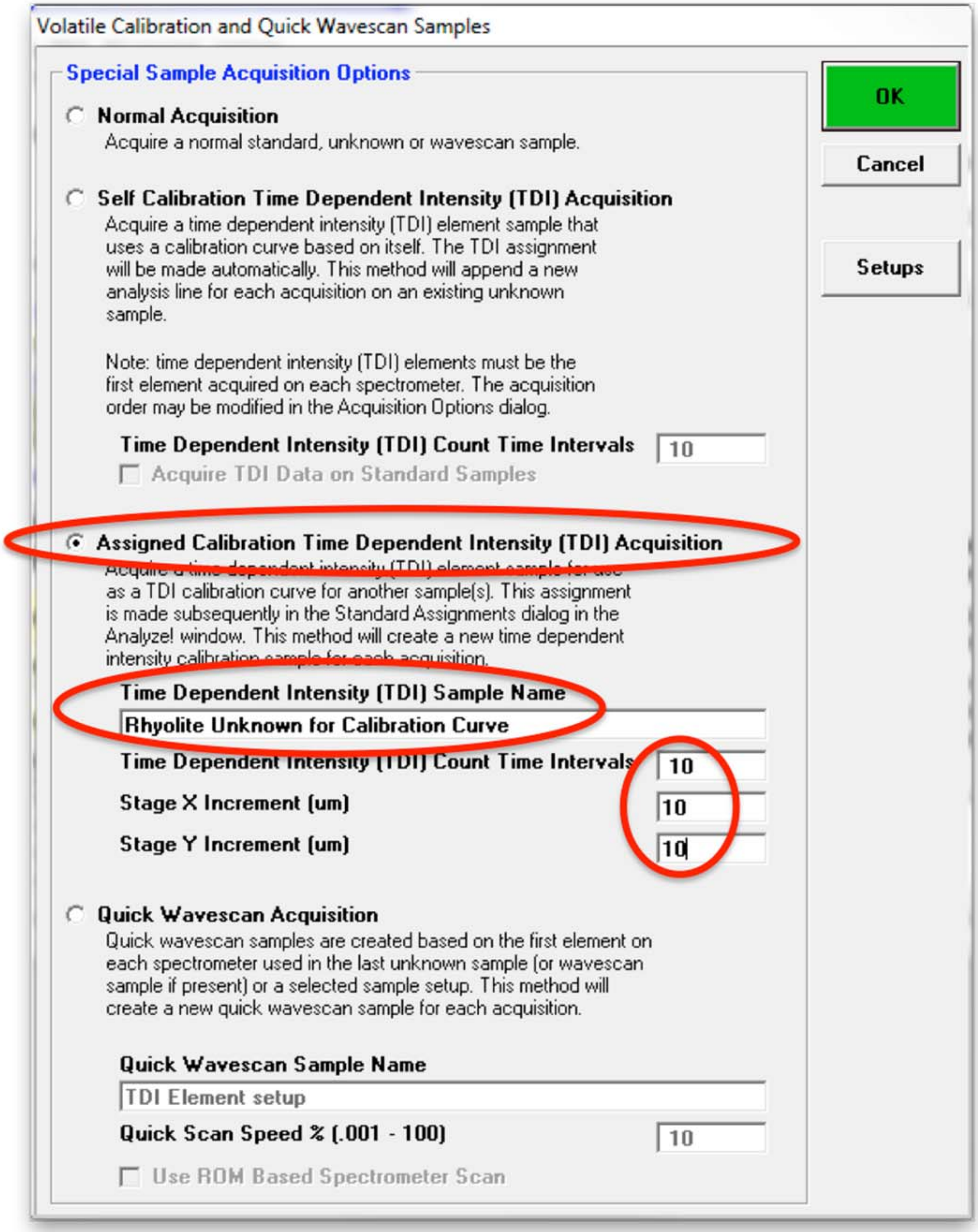
```
Un    4 TDI Element setup
TO =  40, KeV =  15, Beam =  20, Size =  5
```

```
Si ka Spectro  4 TAP (27738.0)
Ti ka Spectro  2 LLIF (68240.0)
Al ka Spectro  4 TAP (32464.0)
Cr ka Spectro  2 LLIF (56851.0)
Fe ka Spectro  5 LLIF (48085.0)
Mn ka Spectro  5 LLIF (52203.0)
Mg ka Spectro  1 TAP (38499.0)
Ca ka Spectro  3 LPET (38387.0)
Na ka Spectro  1 TAP (46352.0)
```

☐ Load Sample Setups In Reverse Order
When running combined multiple sample setups, the program will base the first column condition on the condition specified for the first element on spectrometer number one

Click the **OK** button.

Select the *Assigned Calibration Time Dependent Intensity Acquisition* method. Enter text into the *Time Dependent Intensity Sample Name* field. Edit the *TDI Count Time Intervals* (number of steps in the calibration line) and adjust the *Stage X and Y Increment (um)* values if required, resulting in the following window.



Volatile Calibration and Quick Wavescan Samples

Special Sample Acquisition Options

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

○ **Self Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample that uses a calibration curve based on itself. The TDI assignment will be made automatically. This method will append a new analysis line for each acquisition on an existing unknown sample.

Note: time dependent intensity (TDI) elements must be the first element acquired on each spectrometer. The acquisition order may be modified in the Acquisition Options dialog.

Time Dependent Intensity (TDI) Count Time Intervals 10
☐ Acquire TDI Data on Standard Samples

● **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI 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 time dependent intensity calibration sample for each acquisition.

Time Dependent Intensity (TDI) Sample Name
Rhyolite Unknown for Calibration Curve
Time Dependent Intensity (TDI) Count Time Intervals 10
Stage X Increment (um) 10
Stage Y Increment (um) 10

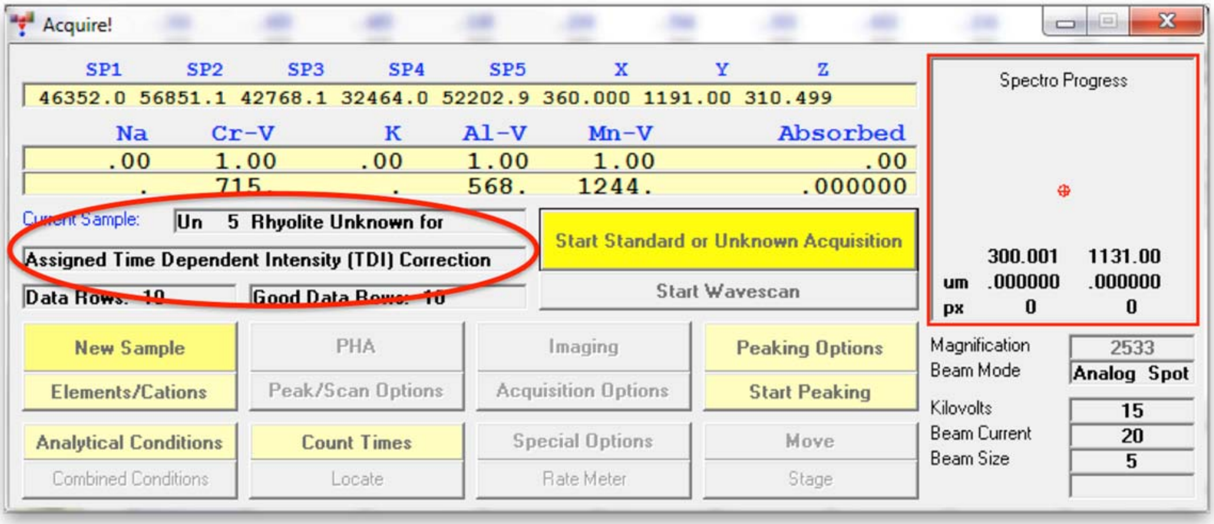
○ **Quick Wavescan Acquisition**
Quick wavescan samples are created based on the first element on each spectrometer used in the last unknown sample (or wavescan sample if present) or a selected sample setup. This method will create a new quick wavescan sample for each acquisition.

Quick Wavescan Sample Name
TDI Element setup
Quick Scan Speed % (.001 - 100) 10
☐ Use ROM Based Spectrometer Scan

The TDI element effect will be calibrated precisely on the first unknown sample. One important assumption is that the TDI element behavior on the calibration sample is similar to all the unknowns to be analyzed. Therefore, because a consistent TDI correction is used, variation in composition represents real differences in composition (or volatilization) not precision of the analyses. Each element in the method (sample setup) will be acquired one element at a time. In this example, 10 time intervals are specified and the default on-peak count times for silicon and sodium are 20 and 40 respectively. Thus the calibration curve for each will be composed of 10 spots of 2 and 4 seconds each. The program will acquire each element in the sample (at a fresh spot) at a new stage position based on the X and Y increments specified to allow the volatile element effect to be calibrated precisely.

Click the **OK** button to return to the **Acquire!** window.

The TDI sample acquisition will start automatically upon clicking the **Start Standard or Unknown Acquisition** button, using the sample name entered in *the TDI Sample Name* field.



```
    SP1       SP2       SP3       SP4       SP5        X         Y         Z
 46352.0 56851.1 42768.1 32464.0 52202.9 360.000 1191.00 310.499

       Na      Cr-V         K      Al-V      Mn-V              Absorbed
      .00      1.00       .00      1.00      1.00                   .00
        .      715.         .      568.     1244.               .000000
```

Current Sample: Un 5 Rhyolite Unknown for Assigned Time Dependent Intensity (TDI) Correction

Data Rows: 10

Good Data Rows: 10

```
       300.001    1131.00
um     .000000    .000000
px           0          0
```

Magnification 2533

Beam Mode Analog Spot

Kilovolts 15

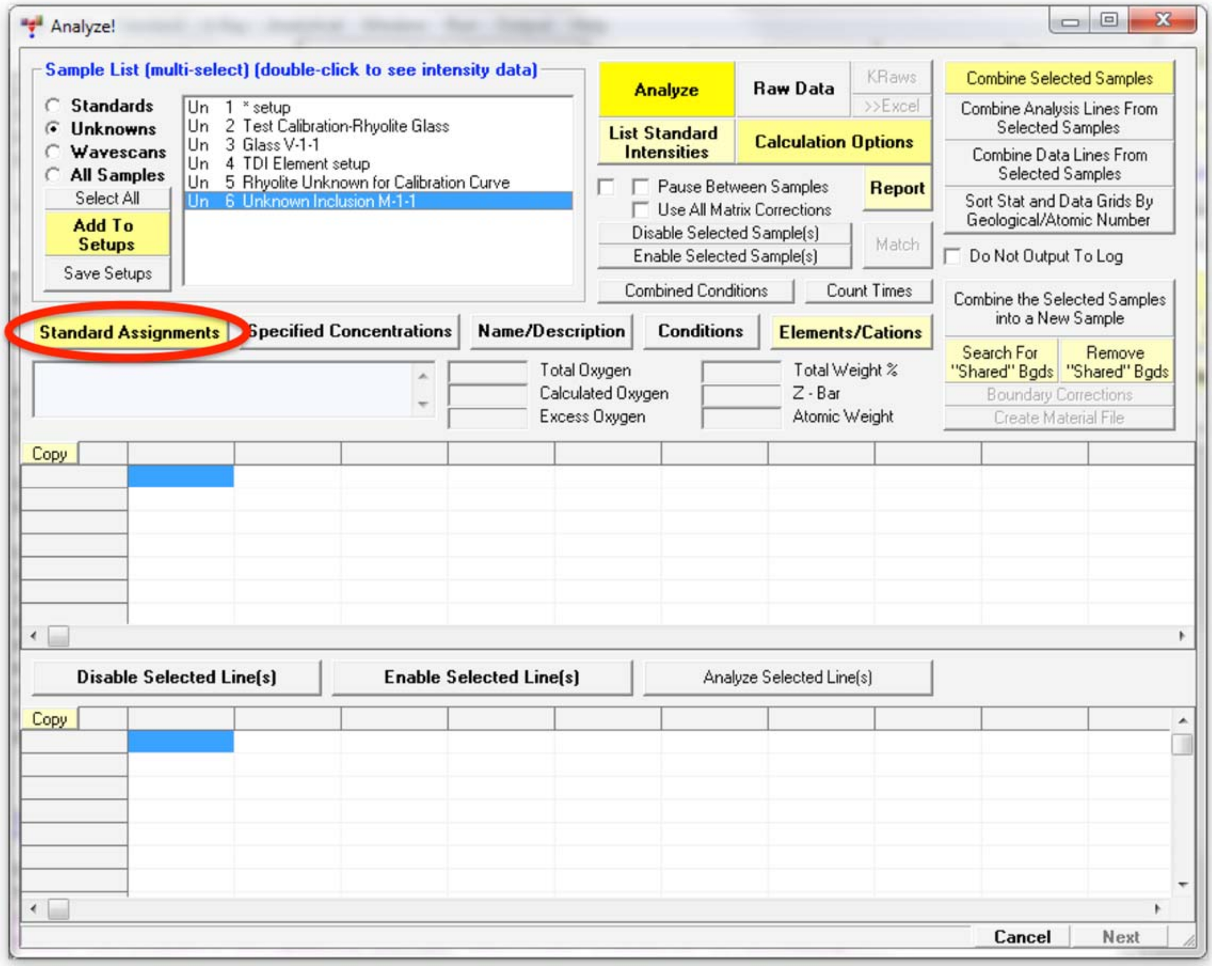
Beam Current 20

Beam Size 5

The user may now collect unknown data points. **REMEMBER** to load in the appropriate sample setup **AND** under the **Special Options** button of the **Acquire!** window, click the *Normal Acquisition* button.

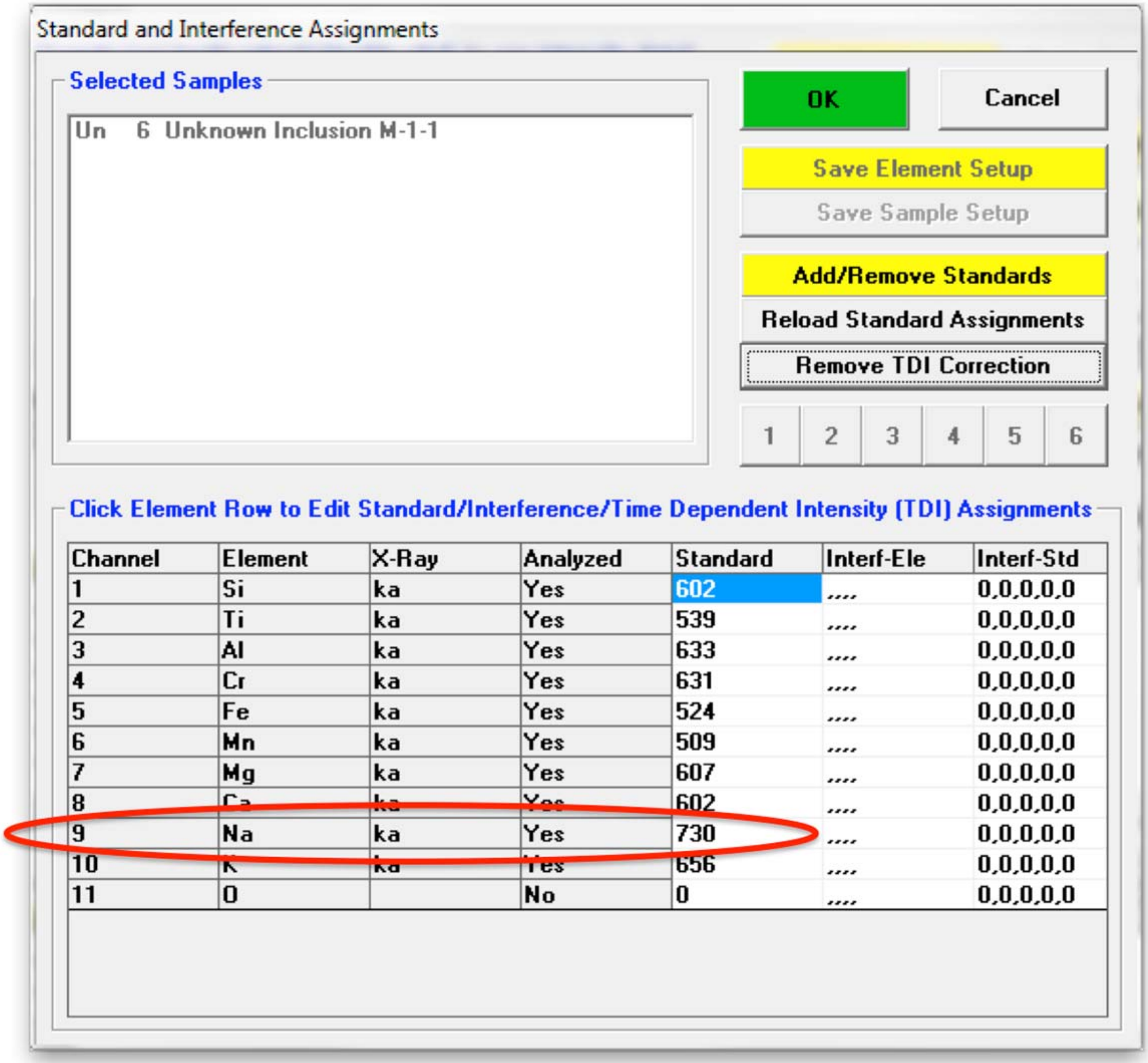
After collecting an unknown sample the user may assign the volatile correction from the **Analyze!** window. The volatile element calibration can be assigned to any element in a sample provided that it was acquired as the **FIRST** element on that spectrometer.

Click the **Standard Assignments** button.



Un 1 * setup
Un 2 Test Calibration-Rhyolite Glass
Un 3 Glass V-1-1
Un 4 TDI Element setup
Un 5 Rhyolite Unknown for Calibration Curve
Un 6 Unknown Inclusion M-1-1

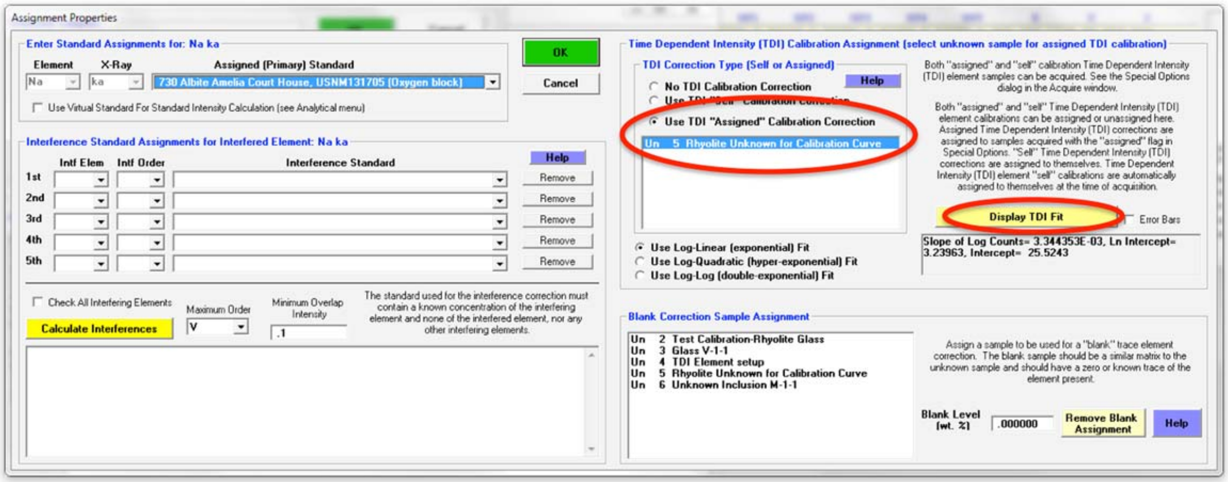
The **Standard and Interference Assignments** window opens. To evaluate the correction effect on Na, click the respective row to view and edit the TDI assignment.



Un 6 Unknown Inclusion M-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	Si	ka	Yes	602	....	0,0,0,0,0
2	Ti	ka	Yes	539	....	0,0,0,0,0
3	Al	ka	Yes	633	....	0,0,0,0,0
4	Cr	ka	Yes	631	....	0,0,0,0,0
5	Fe	ka	Yes	524	....	0,0,0,0,0
6	Mn	ka	Yes	509	....	0,0,0,0,0
7	Mg	ka	Yes	607	....	0,0,0,0,0
8	Ca	ka	Yes	602	....	0,0,0,0,0
9	Na	ka	Yes	730	....	0,0,0,0,0
10	K	ka	Yes	656	....	0,0,0,0,0
11	O		No	0	....	0,0,0,0,0

The **Assignment Properties** window opens and lists all possible volatile element calibration samples. Select *Use TDI "Assigned" Calibration Correction* as *TDI Correction Type*, highlight the appropriate sample and click the **Display TDI Fit** button.



Enter Standard Assignments for: Na ka

Element	X-Ray	Assigned (Primary) Standard
Na	ka	730 Albite Amelia Court House, USNM131705 (Oxygen block)

☐ Use Virtual Standard For Standard Intensity Calculation (see Analytical menu)

Interference Standard Assignments for Interfered Element: Na ka

	Intf Elem	Intf Order	Interference Standard
1st			
2nd			
3rd			
4th			
5th			

☐ Check All Interfering Elements

Maximum Order: V

Minimum Overlap Intensity: .1

The standard used for the interference correction must contain a known concentration of the interfering element and none of the interfered element, nor any other interfering elements.

Time Dependent Intensity (TDI) Calibration Assignment (select unknown sample for assigned TDI calibration)

TDI Correction Type (Self or Assigned)

○ No TDI Calibration Correction
○ Use TDI "Self" Calibration Correction
● Use TDI "Assigned" Calibration Correction

Un 5 Rhyolite Unknown for Calibration Curve

Both "assigned" and "self" calibration Time Dependent Intensity (TDI) element samples can be acquired. See the Special Options dialog in the Acquire window.

Both "assigned" and "self" Time Dependent Intensity (TDI) element calibrations can be assigned or unassigned here. Assigned Time Dependent Intensity (TDI) corrections are assigned to samples acquired with the "assigned" flag in Special Options. "Self" Time Dependent Intensity (TDI) corrections are assigned to themselves. Time Dependent Intensity (TDI) element "self" calibrations are automatically assigned to themselves at the time of acquisition.

● Use Log-Linear (exponential) Fit
○ Use Log-Quadratic (hyper-exponential) Fit
○ Use Log-Log (double-exponential) Fit

Slope of Log Counts= 3.344353E-03, Ln Intercept= 3.23963, Intercept= 25.5243

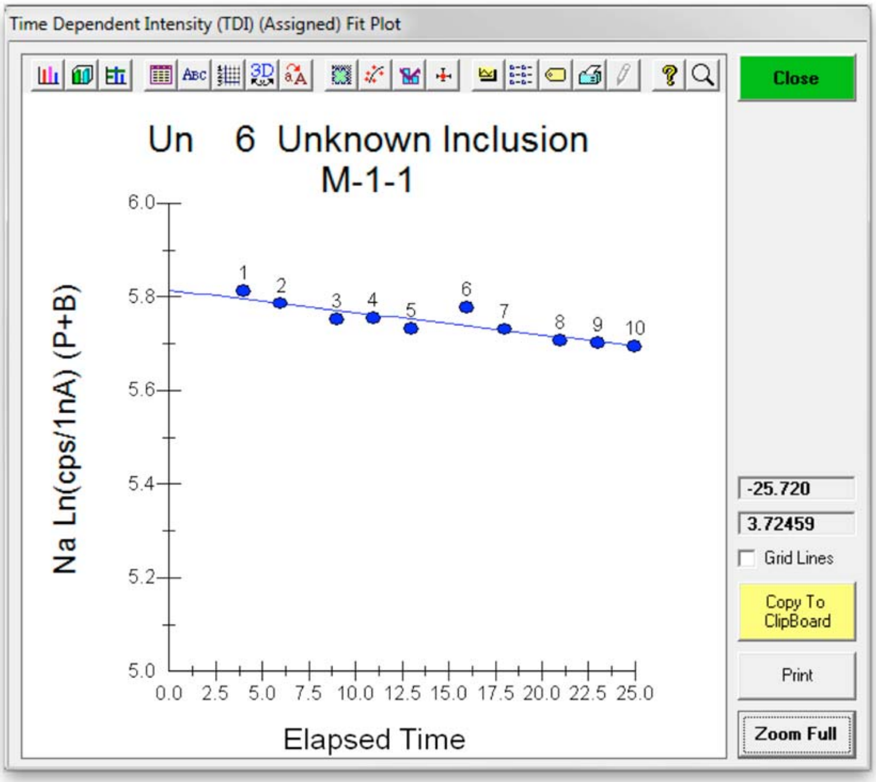
Blank Correction Sample Assignment

Un 2 Test Calibration-Rhyolite Glass
Un 3 Glass V-1-1
Un 4 TDI Element setup
Un 5 Rhyolite Unknown for Calibration Curve
Un 6 Unknown Inclusion M-1-1

Assign a sample to be used for a "blank" trace element correction. The blank sample should be a similar matrix to the unknown sample and should have a zero or known trace of the element present.

Blank Level (wt. %): .000000

The **Time Dependent Intensity (Assigned) Fit Plot** window opens.



-25.720

3.72459

☐ Grid Lines

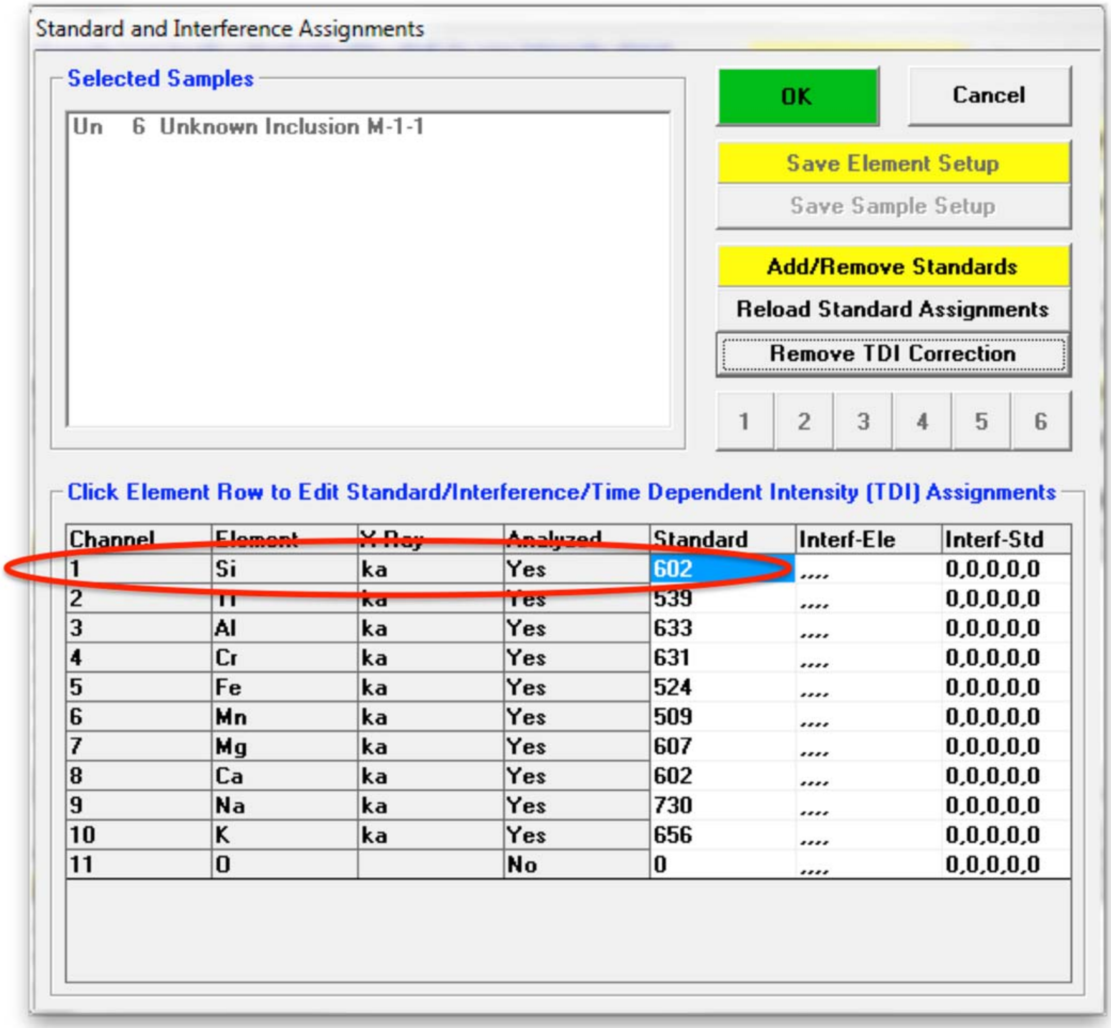
The drop in sodium count intensity with time appears to fit an exponential function (Nielson and Sigurdsson, 1981). A plot of the natural log of the intensity data versus time should yield a straight line relationship as seen above.

The extrapolation correction is quantitative in that the correction is based on a calibration curve acquired during the run. The correction uses the actual elapsed time for all calculations. It 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.

Along with alkali loss, the operator may notice an increase in count intensity from the non-mobile elements (such as silicon and aluminum) in the sample. The possible enhancement with time may be corrected for as well.

Close the **Time Dependent Intensity (Assigned) Fit Plot** window, returning to the **Assignment Properties** window. Click the **OK** button.

To evaluate the possible enhancement of intensity with time on silicon in the rhyolitic glass, click on the element row for silicon in the **Standard and Interference Assignments** window.

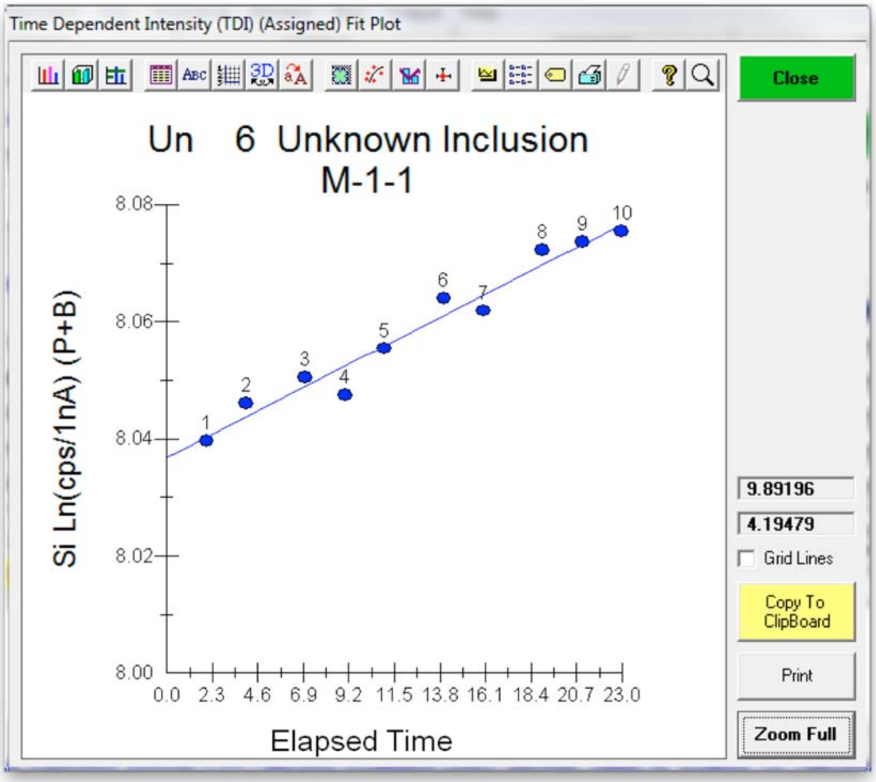


Un 6 Unknown Inclusion M-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	Si	ka	Yes	602	....	0,0,0,0,0
2	Ti	ka	Yes	539	....	0,0,0,0,0
3	Al	ka	Yes	633	....	0,0,0,0,0
4	Cr	ka	Yes	631	....	0,0,0,0,0
5	Fe	ka	Yes	524	....	0,0,0,0,0
6	Mn	ka	Yes	509	....	0,0,0,0,0
7	Mg	ka	Yes	607	....	0,0,0,0,0
8	Ca	ka	Yes	602	....	0,0,0,0,0
9	Na	ka	Yes	730	....	0,0,0,0,0
10	K	ka	Yes	656	....	0,0,0,0,0
11	O		No	0	....	0,0,0,0,0

The **Assignment Properties** window opens. Again, highlight the appropriate *TDI Calibration Sample Assignment* sample and click the **Display TDI Fit** button.

The **Time Dependent Intensity (Assigned) Fit Plot** window opens displaying the natural log of silicon x-ray intensity versus time. The enhancement is evident and maybe corrected for quantitatively.



Return to the **Analyze!** window by clicking the **Close** button above.

Click the **OK** button of the **Assignment Properties** and the **Standard and Interference Assignments** windows, respectively.

Advanced Interference Corrections

PROBE FOR EPMA permits the user to select a fully quantitative correction for spectral interferences (Donovan et al., 1993). The user can correct for up to four interfering elements per channel. The program requires that both the interfered and interfering elements be analyzed for. Further, an interference calibration standard must be acquired that contains a major concentration of the interfering element and none of the interfered element nor any other elements that interfere with the interfered element.

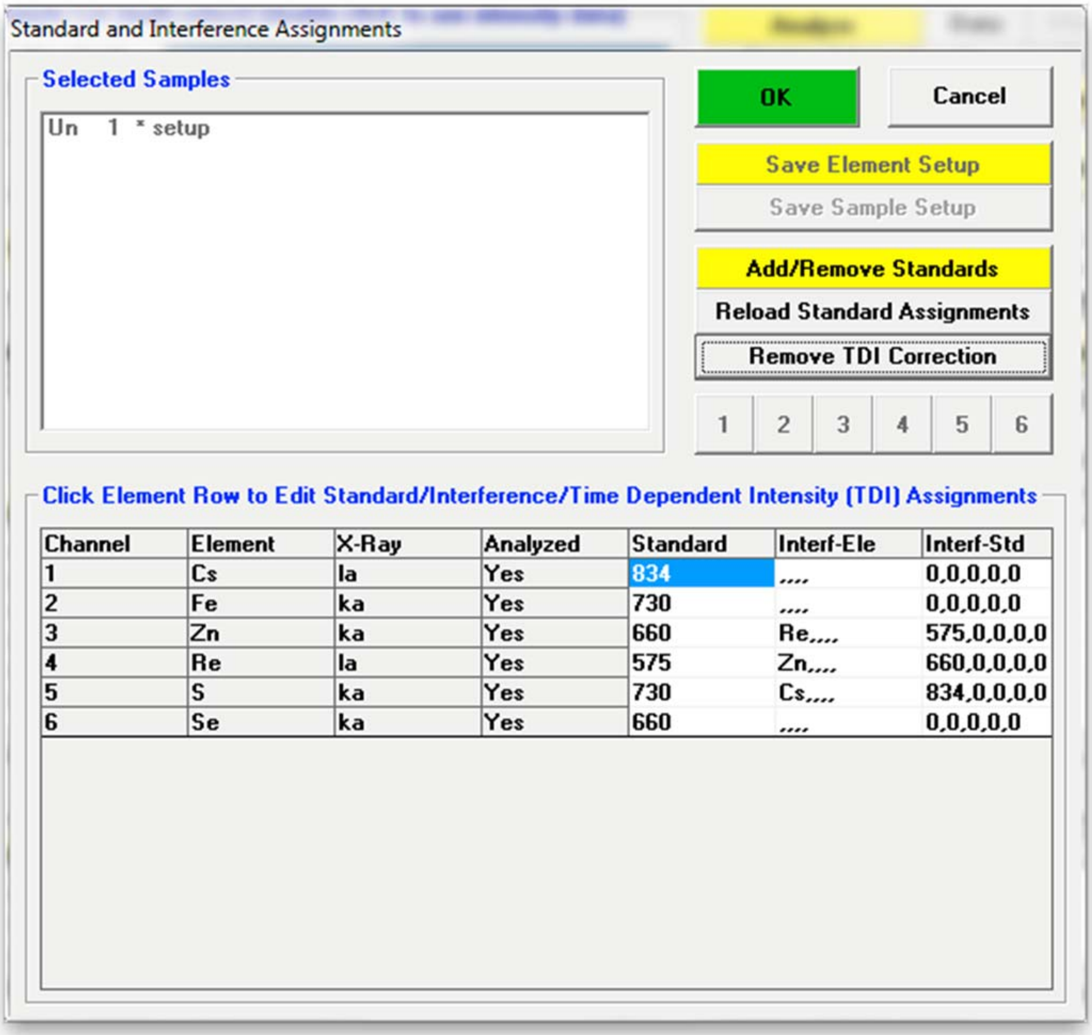
Most interferences between a pair of elements work in one direction. Consider a phase with high concentrations of manganese in the presence of the iron. Here the Mn Kβ line interferes with the Fe Kα analytical line. The reverse situation does not cause a problem, iron does not interfere with manganese. However, there are some cases where both elements interfere with each other! These dual interfering elements are extremely difficult to correctly quantify. Fortunately, PROBE FOR EPMA can handle this situation because it's quantitative interference correction is an iterated solution (see Donovan et al., 1993 for details).

The following example (analyzed at U.C. Berkeley by John Donovan) involves the dual interference of zinc and rhenium in a natural organo-metallic phase. Both lines interfere with each other (Zn Kα and Re Lα) and both lines are used for quantitative analysis. Other elements analyzed for are cesium, iron, sulfur, and selenium. Oxygen, nitrogen, carbon and hydrogen are also in the samples. Each is listed in the **Element/Cations** window for use in the matrix correction routine but are not analyzed.

Solving these interferences requires the analyses of both rhenium and zinc and two interference standards. To correct for the interference on zinc, a standard that contains rhenium but no zinc is required. Likewise, to handle the interference on rhenium, a standard will be needed that contains zinc but no rhenium.

The procedure to specify interferences and the correction thereof was documented in the silicate chapter in the Users Guide to Getting Started manual, cogent details will briefly mentioned here.

To view the various interference assignments, click the **Standard Assignment** button in the **Analyze!** window. The **Standard and Interference Assignments** window opens.



Un 1 * setup

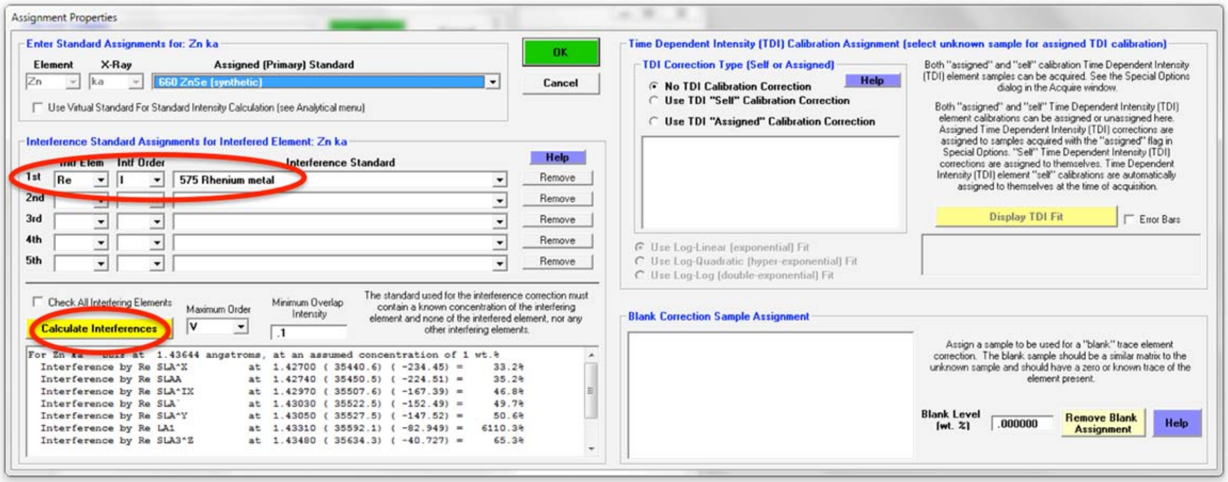
Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	Cs	la	Yes	834	,,,,	0,0,0,0,0
2	Fe	ka	Yes	730	,,,,	0,0,0,0,0
3	Zn	ka	Yes	660	Re,,,,	575,0,0,0,0
4	Re	la	Yes	575	Zn,,,,	660,0,0,0,0
5	S	ka	Yes	730	Cs,,,,	834,0,0,0,0
6	Se	ka	Yes	660	,,,,	0,0,0,0,0

In John’s routine, Cs Lα is measured on the standard CsBr, likewise Fe Kα is done on a pyrite (FeS_2) standard and the Se Kα line is measured on the ZnSe standard.

Zinc, rhenium and sulfur require additional discussion.

Highlighting the zinc element row opens the **Assignment Properties** window for that element. The user has the option to display all possible interferences based on the current set of analyzed and interfered elements. Clicking the **Calculate Interference** button displays these. The program calculates the interference based on a gaussian peak shape assuming a worst case scenario of 0.1% of the analyzed element and 100% of each of the other analyzed and possibly interfering elements.

As mentioned earlier and seen below, Re Lα interferes with the Zn Kα on the LIF crystal. To correct for this overlap, a standard with no zinc present (rhenium metal) is employed for the calculation. Click the *Calculate Interferences* button to list known interferences.



Enter Standard Assignments for: Zn ka

Element	X-Ray	Assigned (Primary) Standard
Zn	ka	660 ZnSe (synthetic)

☐ Use Virtual Standard For Standard Intensity Calculation (see Analytical menu)

Interference Standard Assignments for Interfered Element: Zn ka

	Intf Elem	Intf Order	Interference Standard
1st	Re	I	575 Rhenium metal
2nd			
3rd			
4th			
5th			

☐ Check All Interfering Elements

Calculate Interferences

Maximum Order: V

Minimum Overlap Intensity: .1

The standard used for the interference correction must contain a known concentration of the interfering element and none of the interfered element, nor any other interfering elements.

```
For Zn ka   LLIF at  1.43644 angstroms, at an assumed concentration of 1 wt.%
  Interference by Re SLA^X          at  1.42700 ( 35440.6) ( -234.45) =     33.2%
  Interference by Re SLAA           at  1.42740 ( 35450.5) ( -224.51) =     35.2%
  Interference by Re SLA^IX         at  1.42970 ( 35507.6) ( -167.39) =     46.8%
  Interference by Re SLA`           at  1.43030 ( 35522.5) ( -152.49) =     49.7%
  Interference by Re SLA^Y          at  1.43050 ( 35527.5) ( -147.52) =     50.6%
  Interference by Re LA1            at  1.43310 ( 35592.1) ( -82.949) =   6110.3%
  Interference by Re SLA3^Z         at  1.43480 ( 35634.3) ( -40.727) =     65.3%
```

Time Dependent Intensity (TDI) Calibration Assignment (select unknown sample for assigned TDI calibration)

TDI Correction Type (Self or Assigned)

● No TDI Calibration Correction
○ Use TDI "Self" Calibration Correction
○ Use TDI "Assigned" Calibration Correction

Both "assigned" and "self" calibration Time Dependent Intensity (TDI) element samples can be acquired. See the Special Options dialog in the Acquire window.

Both "assigned" and "self" Time Dependent Intensity (TDI) element calibrations can be assigned or unassigned here. Assigned Time Dependent Intensity (TDI) corrections are assigned to samples acquired with the "assigned" flag in Special Options. "Self" Time Dependent Intensity (TDI) corrections are assigned to themselves. Time Dependent Intensity (TDI) element "self" calibrations are automatically assigned to themselves at the time of acquisition.

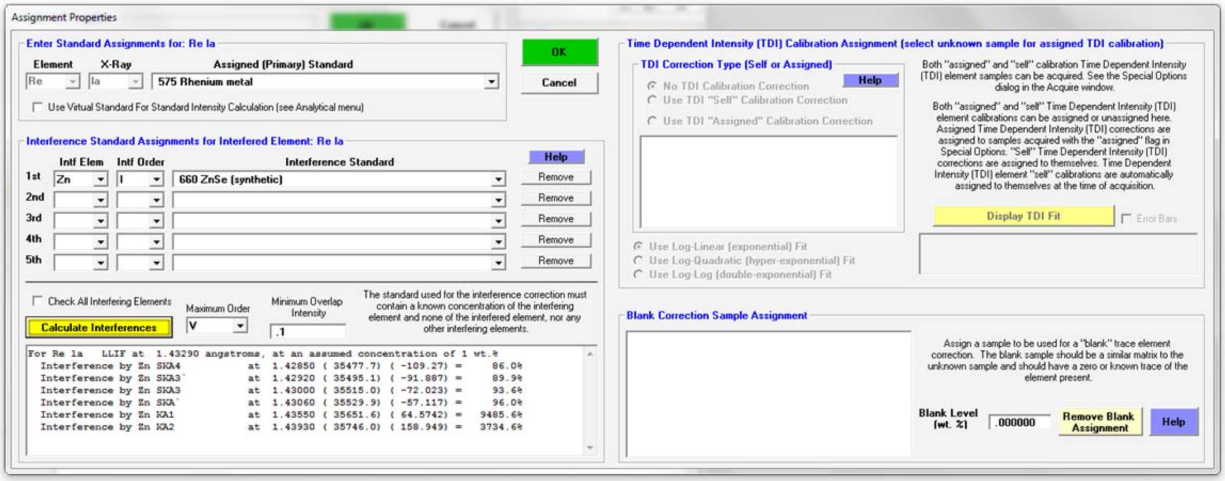
● Use Log-Linear (exponential) Fit
○ Use Log-Quadratic (hyper-exponential) Fit
○ Use Log-Log (double-exponential) Fit

Blank Correction Sample Assignment

Assign a sample to be used for a "blank" trace element correction. The blank sample should be a similar matrix to the unknown sample and should have a zero or known trace of the element present.

Blank Level (wt. %): .000000

The **Assignment Properties** window for Re Lα is shown next. Here, Zn Kα interferes with the Re Lα x-ray position. To make the quantitative correction the standard ZnSe (with no rhenium) is used.



Enter Standard Assignments for: Re la

Element	X-Ray	Assigned (Primary) Standard
Re	la	575 Rhenium metal

☐ Use Virtual Standard For Standard Intensity Calculation (see Analytical menu)

Interference Standard Assignments for Interfered Element: Re la

	Intf Elem	Intf Order	Interference Standard
1st	Zn	I	660 ZnSe (synthetic)
2nd			
3rd			
4th			
5th			

☐ Check All Interfering Elements

Calculate Interferences

Maximum Order: V

Minimum Overlap Intensity: .1

The standard used for the interference correction must contain a known concentration of the interfering element and none of the interfered element, nor any other interfering elements.

```
For Re la   LLIF at  1.43290 angstroms, at an assumed concentration of 1 wt.%
  Interference by Zn SKA4           at  1.42850 ( 35477.7) ( -109.27) =     86.0%
  Interference by Zn SKA3`          at  1.42920 ( 35495.1) ( -91.887) =     89.9%
  Interference by Zn SKA3           at  1.43000 ( 35515.0) ( -72.023) =     93.6%
  Interference by Zn SKA`           at  1.43060 ( 35529.9) ( -57.117) =     96.0%
  Interference by Zn KA1            at  1.43550 ( 35651.6) ( 64.5742) =   9485.6%
  Interference by Zn KA2            at  1.43930 ( 35746.0) ( 158.949) =   3734.6%
```

Time Dependent Intensity (TDI) Calibration Assignment (select unknown sample for assigned TDI calibration)

TDI Correction Type (Self or Assigned)

● No TDI Calibration Correction
○ Use TDI "Self" Calibration Correction
○ Use TDI "Assigned" Calibration Correction

Both "assigned" and "self" calibration Time Dependent Intensity (TDI) element samples can be acquired. See the Special Options dialog in the Acquire window.

Both "assigned" and "self" Time Dependent Intensity (TDI) element calibrations can be assigned or unassigned here. Assigned Time Dependent Intensity (TDI) corrections are assigned to samples acquired with the "assigned" flag in Special Options. "Self" Time Dependent Intensity (TDI) corrections are assigned to themselves. Time Dependent Intensity (TDI) element "self" calibrations are automatically assigned to themselves at the time of acquisition.

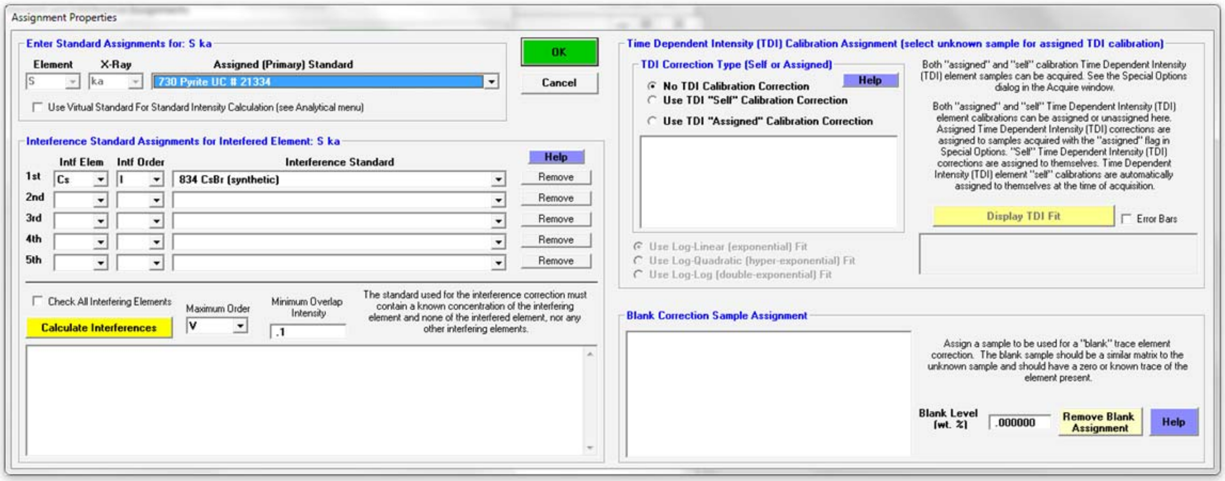
● Use Log-Linear (exponential) Fit
○ Use Log-Quadratic (hyper-exponential) Fit
○ Use Log-Log (double-exponential) Fit

Blank Correction Sample Assignment

Assign a sample to be used for a "blank" trace element correction. The blank sample should be a similar matrix to the unknown sample and should have a zero or known trace of the element present.

Blank Level (wt. %): .000000

Finally, the **Assignment Properties** window for S Kα is displayed. In this unique mineral, Cs Lβ overlaps with S Kα. Therefore, a cesium standard without sulfur (CsBr) is also required to complete the spectral interference deconvolution!



Enter Standard Assignments for: S ka

Element	X-Ray	Assigned (Primary) Standard
S	ka	730 Pyrite UC # 21334

☐ Use Virtual Standard For Standard Intensity Calculation (see Analytical menu)

Interference Standard Assignments for Interfered Element: S ka

	Intf Elem	Intf Order	Interference Standard
1st	Cs	I	834 CsBr (synthetic)
2nd			
3rd			
4th			
5th			

☐ Check All Interfering Elements

Maximum Order: V

Minimum Overlap Intensity: .1

The standard used for the interference correction must contain a known concentration of the interfering element and none of the interfered element, nor any other interfering elements.

Time Dependent Intensity (TDI) Calibration Assignment (select unknown sample for assigned TDI calibration)

TDI Correction Type (Self or Assigned)

● No TDI Calibration Correction
○ Use TDI "Self" Calibration Correction
○ Use TDI "Assigned" Calibration Correction

● Use Log-Linear (exponential) Fit
○ Use Log-Quadratic (hyper-exponential) Fit
○ Use Log-Log (double-exponential) Fit

Both "assigned" and "self" calibration Time Dependent Intensity (TDI) element samples can be acquired. See the Special Options dialog in the Acquire window.

Both "assigned" and "self" Time Dependent Intensity (TDI) element calibrations can be assigned or unassigned here. Assigned Time Dependent Intensity (TDI) corrections are assigned to samples acquired with the "assigned" flag in Special Options. "Self" Time Dependent Intensity (TDI) corrections are assigned to themselves. Time Dependent Intensity (TDI) element "self" calibrations are automatically assigned to themselves at the time of acquisition.

☐ Error Bars

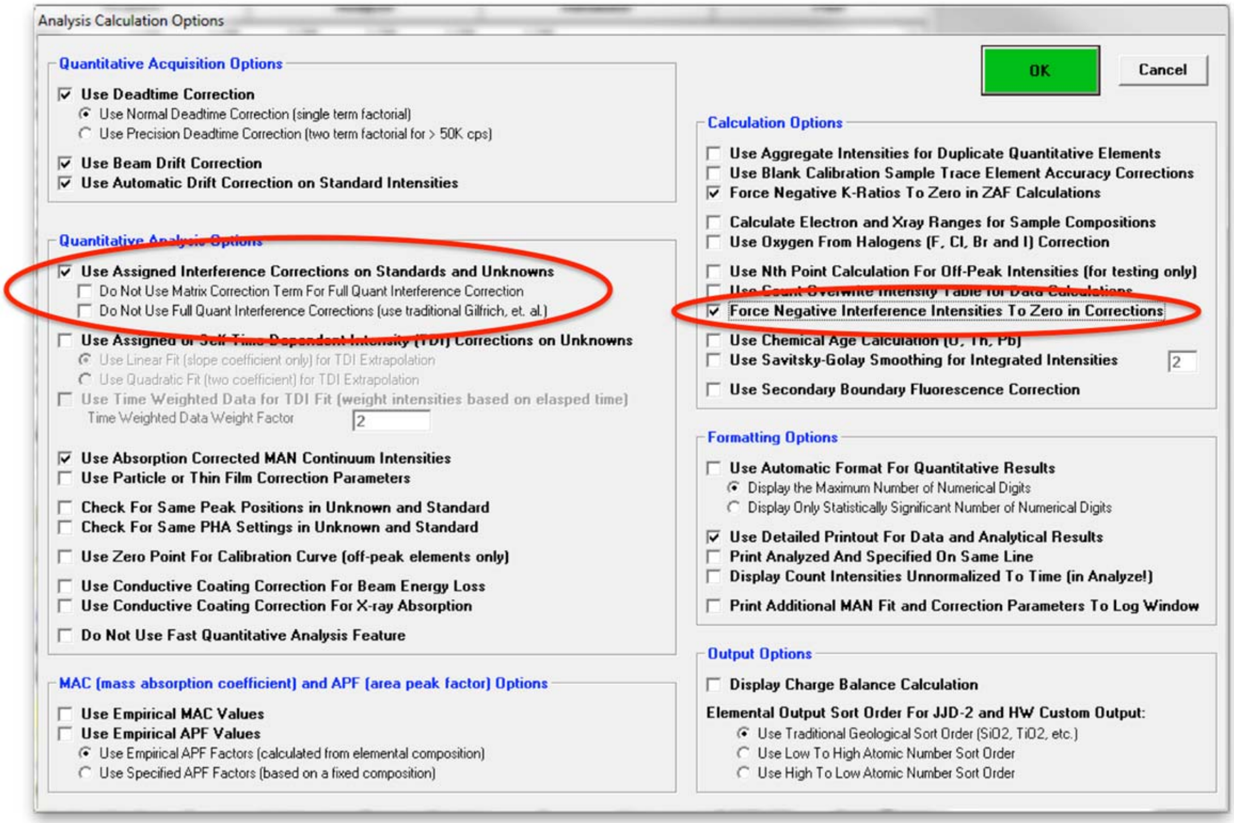
Blank Correction Sample Assignment

Assign a sample to be used for a "blank" trace element correction. The blank sample should be a similar matrix to the unknown sample and should have a zero or known trace of the element present.

Blank Level (wt. %): .000000

After setting up the parameters for the analysis session, calibration and standardization was accomplished, then several tiny and complex organometallic phases were probed for their chemistry.

The **Analysis Calculation Options** window allows the user to enable or disable the interference correction routine to view its effect on quantitative analysis results. This window is activated from the **Analytical | Analysis Options** menu in the main PROBE FOR EPMA log window. If required, another tick box is available to *Force Negative Interference Intensities To Zero in Corrections*:



Quantitative Acquisition Options
- ☑ Use Deadtime Correction
  - ● Use Normal Deadtime Correction (single term factorial)
  - ○ Use Precision Deadtime Correction (two term factorial for > 50K cps)
- ☑ Use Beam Drift Correction
- ☑ Use Automatic Drift Correction on Standard Intensities

Quantitative Analysis Options
- ☑ Use Assigned Interference Corrections on Standards and Unknowns
  - ☐ Do Not Use Matrix Correction Term For Full Quant Interference Correction
  - ☐ Do Not Use Full Quant Interference Corrections (use traditional Gilfrich, et. al.)
- ☐ Use Assigned or Self Time Dependent Intensity (TDI) Corrections on Unknowns
  - ● Use Linear Fit (slope coefficient only) for TDI Extrapolation
  - ○ Use Quadratic Fit (two coefficient) for TDI Extrapolation
- ☐ Use Time Weighted Data for TDI Fit (weight intensities based on elasped time)
  - Time Weighted Data Weight Factor: 2
- ☑ Use Absorption Corrected MAN Continuum Intensities
- ☐ Use Particle or Thin Film Correction Parameters
- ☐ Check For Same Peak Positions in Unknown and Standard
- ☐ Check For Same PHA Settings in Unknown and Standard
- ☐ Use Zero Point For Calibration Curve (off-peak elements only)
- ☐ Use Conductive Coating Correction For Beam Energy Loss
- ☐ Use Conductive Coating Correction For X-ray Absorption
- ☐ Do Not Use Fast Quantitative Analysis Feature

MAC (mass absorption coefficient) and APF (area peak factor) Options
- ☐ Use Empirical MAC Values
- ☐ Use Empirical APF Values
  - ● Use Empirical APF Factors (calculated from elemental composition)
  - ○ Use Specified APF Factors (based on a fixed composition)

Calculation Options
- ☐ Use Aggregate Intensities for Duplicate Quantitative Elements
- ☐ Use Blank Calibration Sample Trace Element Accuracy Corrections
- ☑ Force Negative K-Ratios To Zero in ZAF Calculations
- ☐ Calculate Electron and Xray Ranges for Sample Compositions
- ☐ Use Oxygen From Halogens (F, Cl, Br and I) Correction
- ☐ Use Nth Point Calculation For Off-Peak Intensities (for testing only)
- ☐ Use Count Overwrite Intensity Table for Data Calculations
- ☑ Force Negative Interference Intensities To Zero in Corrections
- ☐ Use Chemical Age Calculation (U, Th, Pb)
- ☐ Use Savitsky-Golay Smoothing for Integrated Intensities: 2
- ☐ Use Secondary Boundary Fluorescence Correction

Formatting Options
- ☐ Use Automatic Format For Quantitative Results
  - ● Display the Maximum Number of Numerical Digits
  - ○ Display Only Statistically Significant Number of Numerical Digits
- ☑ Use Detailed Printout For Data and Analytical Results
- ☐ Print Analyzed And Specified On Same Line
- ☐ Display Count Intensities Unnormalized To Time (in Analyze!)
- ☐ Print Additional MAN Fit and Correction Parameters To Log Window

Output Options
- ☐ Display Charge Balance Calculation
- Elemental Output Sort Order For JJD-2 and HW Custom Output:
  - ● Use Traditional Geological Sort Order (SiO2, TiO2, etc.)
  - ○ Use Low To High Atomic Number Sort Order
  - ○ Use High To Low Atomic Number Sort Order

Data illustrating the power of the PROBE FOR EPMA interference correction routine is shown below. The results are for a real unknown sample that has some variability and was rather small to analyze. The following unknown analysis is without any interference corrections.

```
Un   10 Zn-ReSCN gr2
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                        -2,      3
Number of Data Lines:   5             Number of 'Good' Data Lines:   3
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:          .000     Average Total Weight%:  122.912
Average Calculated Oxygen:     .000     Average Atomic Number:   53.080
Average Excess Oxygen:         .000     Average Atomic Weight:   54.153
Average ZAF Iteration:         4.00     Average Quant Iterate:     2.00


Un   10 Zn-ReSCN gr2, Results in Elemental Weight Percents

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC
```

```
AVER:    1.900   5.000   4.200    .200
SDEV:     .000    .000    .000    .000

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000  19.553  73.669  17.465    .000 121.988
    55    .000    .007  20.556  74.517  16.507    .000 122.886
    56    .000    .019  19.668  74.715  18.159    .000 123.862

AVER:     .000    .009  19.926  74.301  17.377    .000 122.912
SDEV:     .000    .010    .549    .556    .830    .000    .937
SERR:     .000    .006    .317    .321    .479    .000
%RSD:      .10  113.30    2.75     .75    4.77     .13
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   627.07 3670.93 3712.94 3672.80 4423.12 1315.94

UNKF:    .0000   .0001   .2100   .6516   .0943   .0000
UNCT:    -2.69     .33 1559.22 2393.02  884.28   -3.16
UNBG:    11.62   28.03   67.30   61.54    6.57   64.00

ZCOR:   1.2016   .9276   .9487  1.1404  1.8421  1.0254
KRAW:   -.0043   .0001   .4199   .6516   .1999  -.0024
PKBG:      .77    1.01   24.18   40.00  135.89     .95

Un   10 Zn-ReSCN gr2, Results Based on 6 Atoms of re

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.786   5.368   5.258   2.983
SDEV:     .013    .040    .039    .022

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   4.536   6.000   8.260    .000  34.323
    55    .000    .002   4.714   6.000   7.718    .000  33.784
    56    .000    .005   4.499   6.000   8.468    .000  34.281

AVER:     .000    .002   4.583   6.000   8.149    .000  34.129
SDEV:     .000    .003    .115    .000    .387    .000    .300
SERR:     .000    .002    .067    .000    .224    .000
%RSD:      .77  113.20    2.51     .00    4.75     .79

%RSD:       .8   113.2     2.5      .0     4.8      .8
```

The user immediately realizes that there is a problem since the unknown sums to a total of 123%.

The following is the same unknown but with the iterated interference software applied.

```
Un   10 Zn-ReSCN gr2
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   5             Number of 'Good' Data Lines:   3
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  101.367
Average Calculated Oxygen:    .000     Average Atomic Number:   54.332
Average Excess Oxygen:        .000     Average Atomic Weight:   50.124
Average ZAF Iteration:        4.00     Average Quant Iterate:    13.00

Un   10 Zn-ReSCN gr2, Results in Elemental Weight Percents

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.900   5.000   4.200    .200
SDEV:     .000    .000    .000    .000

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   6.237  65.850  17.508    .000 100.895
    55    .000    .007   7.365  65.342  16.513    .000 100.527
    56    .000    .020   6.100  67.048  18.210    .000 102.678

AVER:     .000    .009   6.568  66.080  17.410    .000 101.367
SDEV:     .000    .010    .694    .876    .853    .000   1.150
SERR:     .000    .006    .401    .506    .492    .000
%RSD:      .13  113.29   10.57    1.33    4.90     .03
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   627.07 3670.93 3712.94 3672.80 4423.12 1315.94

UNKF:    .0000   .0001   .0691   .5781   .0943   .0000
UNCT:    -2.69     .33  512.67 2123.23  884.28   -3.16
UNBG:    11.62   28.03   67.30   61.54    6.57   64.00

ZCOR:   1.2162   .9395   .9511  1.1431  1.8455  1.0235
KRAW:   -.0043   .0001   .1381   .5781   .1999  -.0024
PKBG:      .77    1.01    8.61   35.59  135.89     .95
INT%:     ----    ----  -67.17  -11.27    ----    ----

Un   10 Zn-ReSCN gr2, Results Based on 6 Atoms of re

SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    2.008   6.036   5.913   3.355
SDEV:     .026    .080    .078    .044

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   1.619   6.000   9.264    .000  34.252
    55    .000    .002   1.926   6.000   8.805    .000  34.239
    56    .000    .006   1.555   6.000   9.463    .000  34.083

AVER:     .000    .003   1.700   6.000   9.177    .000  34.191
SDEV:     .000    .003    .199    .000    .337    .000    .094
SERR:     .000    .002    .115    .000    .195    .000
%RSD:     1.21  112.34   11.69     .00    3.68    1.30
```

The total now is acceptable, slightly over 100%.

Finally to demonstrate with standard samples (of known composition), both rhenium metal and the ZnSe standard will be reproduced without the benefit of the interference correction.

```
St  575 Set   1 rhenium metal
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   5             Number of 'Good' Data Lines:   5
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  124.489
Average Calculated Oxygen:    .000     Average Atomic Number:   67.420
Average Excess Oxygen:        .000     Average Atomic Weight:  142.028
Average ZAF Iteration:        3.00     Average Quant Iterate:     2.00

St  575 Set   1 rhenium metal, Results in Elemental Weight Percents

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
     1    .000    .000  21.083 103.240    .022    .000 124.344
     2    .161    .005  20.061 102.988    .008    .000 123.223
     3    .000    .000  21.644 103.274    .000    .176 125.093
     4    .000    .023  21.565 103.834    .000    .156 125.578
     5    .000    .000  19.873 104.122    .000    .213 124.207

AVER:     .032    .006  20.845 103.492    .006    .109 124.489
SDEV:     .072    .010    .833    .469    .009    .102    .902
SERR:     .032    .004    .372    .210    .004    .045
%RSD:   223.61  177.20    3.99     .45  159.05   93.18

PUBL:    n.a.    n.a.    n.a.  100.000   n.a.    n.a.  100.000
%VAR:      .00     .00     .00    3.49     .00     .00
DIFF:     .000    .000    .000   3.492    .000    .000
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   628.01 3665.44 3726.73 3679.31 4367.49 1316.18

UNKF:    .0003   .0001   .2405  1.0000   .0000   .0012
UNCT:     -.02   -1.11 1792.16 3679.35    -.42    1.76
UNBG:    11.57   41.92   95.49   93.54    8.43   93.41

ZCOR:   1.2008   .8713   .8667  1.0349  2.1623   .9212
KRAW:    .0000  -.0003   .4809  1.0000  -.0001   .0013
PKBG:     1.00     .97   19.77   40.37     .95    1.02
```

```
St  660 Set   1 ZnSe (synthetic)
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =       0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   5            Number of 'Good' Data Lines:   5
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  151.911
Average Calculated Oxygen:    .000     Average Atomic Number:   47.924
Average Excess Oxygen:        .000     Average Atomic Weight:   92.977
Average ZAF Iteration:        3.00     Average Quant Iterate:     2.00

St  660 Set   1 ZnSe (synthetic), Results in Elemental Weight Percents

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
     6    .000    .000  44.441  55.414    .019  51.417 151.290
     7    .000    .014  44.022  56.029    .036  51.668 151.768
     8    .000    .000  44.551  56.249    .035  51.099 151.934
     9    .000    .015  44.701  56.069    .037  50.975 151.796
    10    .000    .000  45.281  56.025    .052  51.409 152.767

AVER:     .000    .006  44.599  55.957    .036  51.314 151.911
SDEV:     .000    .008    .457    .317    .012    .277    .537
SERR:     .000    .003    .204    .142    .005    .124
%RSD:      .02  137.06    1.02     .57   33.50     .54

PUBL:    n.a.    n.a.   45.290   n.a.    n.a.   54.710 100.000
%VAR:      .00     .00   -1.53     .00     .00   -6.21
DIFF:     .000    .000   -.691    .000    .000  -3.396
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   628.01 3665.44 3726.64 3678.98 4367.49 1316.18

UNKF:    .0000   .0001   .5002   .5193   .0002   .5162
UNCT:   -23.07   -1.38 3726.73 1910.63    1.72 1316.18
UNBG:    29.32   22.96   48.34   47.66    5.61   47.46

ZCOR:   1.1332   .8826   .8917  1.0775  1.9149   .9940
KRAW:   -.0367  -.0004  1.0000   .5193   .0004  1.0000
PKBG:      .21     .95   78.18   41.17    1.31   28.85
```

The rhenium standard displays an apparent rhenium concentration of 103% and a zinc total of an additional 20%. The ZnSe is even more interesting in that the total is approaching 152% with 44% zinc, 56% rhenium and 51% selenium. The true composition is 45% zinc, and 55% selenium with no rhenium! The normal matrix correction comes close with respect to both zinc and selenium abundances but also reports a whopping 56% rhenium concentration.

Below, both standards are rerun with the interference corrections applied.

```
St  575 Set   1 rhenium metal
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =        0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   5             Number of 'Good' Data Lines:   5
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  100.138
Average Calculated Oxygen:    .000     Average Atomic Number:   74.736
Average Excess Oxygen:        .000     Average Atomic Weight:  184.273
Average ZAF Iteration:        2.00     Average Quant Iterate:    13.80

St  575 Set   1 rhenium metal, Results in Elemental Weight Percents

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
     1    .000    .000    .375  99.332    .023    .000  99.730
     2    .164    .005    .000  99.625    .007    .000  99.801
     3    .000    .000   1.096  98.532    .000    .168  99.796
     4    .000    .023    .847  99.364    .000    .149 100.383
     5    .000    .000    .000 100.776    .000    .203 100.979

AVER:     .033    .006    .463  99.526    .006    .104 100.138
SDEV:     .074    .010    .496    .810    .010    .097    .539
SERR:     .033    .004    .222    .362    .004    .043
%RSD:   223.61  177.20  107.02     .81  164.63   93.19

PUBL:    n.a.    n.a.    n.a.  100.000   n.a.    n.a.  100.000
%VAR:      .00     .00     .00    -.47     .00     .00
DIFF:     .000    .000    .000   -.474    .000    .000
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   628.01 3665.44 3726.73 3679.31 4367.49 1316.18

UNKF:    .0003   .0001   .0055   .9942   .0000   .0012
UNCT:     -.02   -1.11   10.26 3657.79    -.43    1.76
UNBG:    11.57   41.92   95.49   93.54    8.43   93.41

ZCOR:   1.2302   .8692   .8409  1.0011  2.3003   .8800
KRAW:    .0000  -.0003   .0028   .9942  -.0001   .0013
PKBG:     1.00     .97    1.11   40.14     .95    1.02
INT%:     ----    ----  -99.57    -.59   -2.86    ----
```

```
St  660 Set   1 ZnSe (synthetic)
TakeOff = 40.0  KiloVolt = 20.0  Beam Current = 20.0  Beam Size =    0
(Magnification (analytical) =   2000),        Beam Mode = Analog  Spot
(Magnification (default) =       0, Magnification (imaging) =     40)
Image Shift (X,Y):                                          -2,     3
Number of Data Lines:   5             Number of 'Good' Data Lines:   5
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:         .000     Average Total Weight%:  100.261
Average Calculated Oxygen:    .000     Average Atomic Number:   32.316
Average Excess Oxygen:        .000     Average Atomic Weight:   72.276
Average ZAF Iteration:        3.00     Average Quant Iterate:    15.00

St  660 Set   1 ZnSe (synthetic), Results in Elemental Weight Percents

ELEM:       Cs      Fe      Zn      Re       S      Se
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN
TIME:    10.00   10.00   10.00   10.00   10.00   10.00
BEAM:      .20     .20     .20     .20     .20     .20

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
     6    .000    .000  45.121    .000    .017  54.799  99.937
     7    .000    .014  44.451   1.080    .032  54.981 100.558
     8    .000    .000  45.153    .477    .032  54.459 100.120
     9    .000    .015  45.415    .000    .033  54.368  99.831
    10    .000    .000  46.003    .000    .047  54.807 100.857

AVER:     .000    .006  45.229    .311    .032  54.683 100.261
SDEV:     .000    .008    .560    .477    .011    .258    .434
SERR:     .000    .003    .251    .213    .005    .116
%RSD:      .05  137.06    1.24  153.10   33.46     .47

PUBL:    n.a.    n.a.   45.290   n.a.    n.a.   54.710 100.000
%VAR:      .00     .00    -.14     .00     .00    -.05
DIFF:     .000    .000   -.061    .000    .000   -.027
STDS:      834     730     660     575     730     660

STKF:    .5978   .4297   .5001  1.0000   .4719   .5162
STCT:   628.01 3665.44 3726.64 3678.98 4367.49 1316.18

UNKF:    .0000   .0001   .4995   .0028   .0002   .5162
UNCT:   -23.07   -1.38 3721.55    2.34    1.72 1316.18
UNBG:    29.32   22.96   48.34   47.66    5.61   47.46

ZCOR:   1.0893   .8842   .9055  1.1054  1.7229  1.0593
KRAW:   -.0367  -.0004   .9986   .0006   .0004  1.0000
PKBG:      .21     .95   78.08    1.05    1.31   28.85
INT%:     ----    ----    -.14  -99.88    ----    ----
```

Now, the apparent zinc in the rhenium metal standard is gone and the average total sums correctly near 100%. The ZnSe standard is perfect, matching the published standard composition for both zinc and selenium, and effectively removing all of the apparent 56% rhenium.

Light Element Analysis - Empirical APFs

Quantitative analysis of light elements (beryllium to fluorine) is difficult to do correctly with the electron microprobe. Numerous issues impede the analysis of light elements (see Appendix B in the User's Guide and Reference documentation as well as Goldstein et al., 1992 for further discussion). A few brief comments will be made here, as an introduction to this section.

Typically, for x-ray analysis in this energy range (0.1 to 0.7 keV), a large absorption correction is necessary. This large correction in conjunction with the fact that the mass absorption coefficients for the low energy x-rays are very large and not very well known (see Appendix C of the User's Guide and Reference documentation) and place a severe demand on the established ZAF and Phi-Rho-Z models for light element matrix corrections. Some reduction in this large x-ray absorption factor is possible by analyzing at higher take-off angles and at lower acceleration voltages. The former aids by shortening the path length for absorption in the sample while the latter involves a decrease in the electron beam penetration so that x-rays are generated closer to the surface and can escape to be detected.

Low count rates for these light elements are often found. This is due to the low fluorescent yields from the Kα x-ray lines and the inefficient nature of WDS counting systems. Count rates can be increased by increasing the beam current substantially but this may then lead to deadtime problems for metal lines that interfere with the light element lines of interest. The use of new layered dispersive element (LDE) synthetic multi-layer crystals with large d-spacings can also improve light element peak count rates.

There is also a strong possibility of interferences from higher order metal lines such as titanium, chromium, manganese, iron, nickel, zirconium, niobium, and molybdenum with the light element lines. These interferences are often severe for minor and trace level measurements. It is critical to eliminate peak overlaps and understand the background intensity around the light element peak position in both the sample and standard. The new LDE multi-layer crystals also help here by strongly suppressing these higher order reflections.

Finally, chemical bonding effects can result in wavelength shifts, increases or decreases in the relative intensities of various lines and alteration of the shape of the analytical line. These effects are most significant for the lightest (lowest energy) elements. Polarization phenomena and crystallographic orientation may also cause variations in peak shape and intensity especially for boron. Therefore, to measure the intensity of the light elements, one measures the integral intensity (area) under the characteristic peak rather than just the peak intensity.

Bastin and Heijligers (1984, 1991) pioneered the area-peak factor (APF) analysis method. The APF is defined as the ratio between the integral intensity (area) k-ratio from the sample and the standard and the peak intensity k-ratio from the same sample and the standard. This factor is only valid for a given compound with respect to a given standard and a specific spectrometer setup. These integral measurements can be made by scanning the spectrometer in small steps across the characteristic peak with the wavescan feature in PROBE FOR EPMA. After acquiring the peak shape profiles for a primary standard and a number of secondary standards and correcting for the background and removal of interfering peaks, the APF can be calculated as:

$$\mathrm{APF} = \frac{I_U^I \cdot I_S^P}{I_U^P \cdot I_S^I}$$

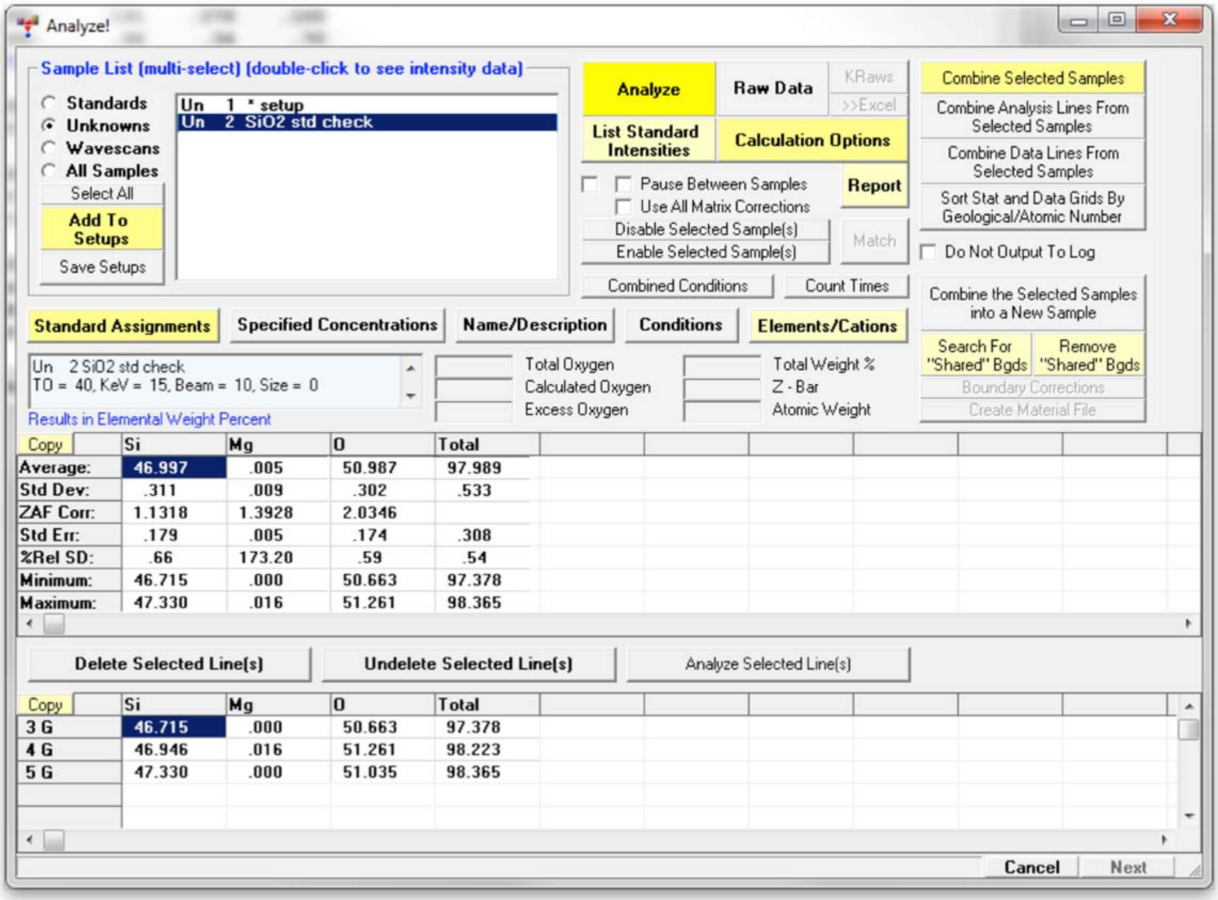
Where : I_U^I is the integrated intensity of the secondary standard
I_S^P is the peak intensity of the primary standard
I_U^P is the peak intensity of the secondary standard
I_S^I is the integrated intensity of the primary standard

After an APF has been determined, future measurements of that compound can be accomplished by measuring only the peak intensity in the sample and standard. Then, multiplication of the peak k-ratio with the appropriate APF will yield the correct integral k-ratio.

PROBE FOR EPMA allows the user to select an APF correction for use in correcting x-ray intensities for peak shift and shape changes between the standard and the multi-element unknown. This is critical when the user is analyzing the Kα lines of the light elements (boron, carbon, nitrogen and oxygen). This correction may also be of use for other elements such as S Kα that also exhibits peak shift and shape changes when comparing sulfate and sulfide peaks.

The power of this correction will be documented in the analysis of oxygen using several simple oxide standards. Open a new PROBE FOR EPMA run. Here oxygen Kα will be analyzed using MgO as the calibration standard. The spectrometer is equipped with a standard P-10 gas flow counter and a LDE (59.8Å) W/Si reflecting crystal. The other two elements to be determined are magnesium on MgO and silicon on SiO_2 . Peak the three elements and acquire standard samples for each.

Create a new unknown sample and collect data on the SiO_2 standard. Analyze the sample from the **Analyze!** window.



Un 1 * setup
Un 2 SiO2 std check

Un 2 SiO2 std check
TO = 40, KeV = 15, Beam = 10, Size = 0

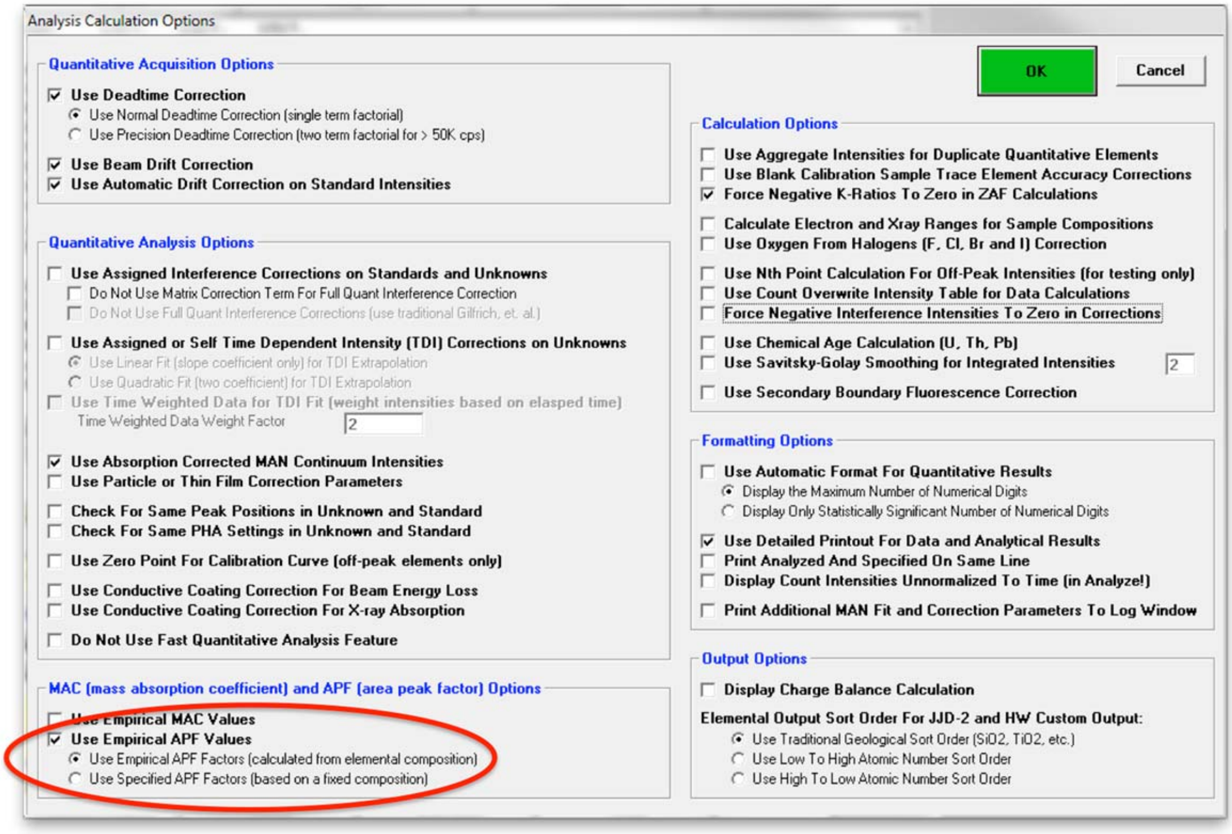
Results in Elemental Weight Percent

Copy	Si	Mg	O	Total
Average:	46.997	.005	50.987	97.989
Std Dev:	.311	.009	.302	.533
ZAF Corr:	1.1318	1.3928	2.0346	
Std Err:	.179	.005	.174	.308
%Rel SD:	.66	173.20	.59	.54
Minimum:	46.715	.000	50.663	97.378
Maximum:	47.330	.016	51.261	98.365

Copy	Si	Mg	O	Total
3 G	46.715	.000	50.663	97.378
4 G	46.946	.016	51.261	98.223
5 G	47.330	.000	51.035	98.365

A low total for the analysis is found. The nominal composition for the SiO_2 standard is silicon: 46.74 and oxygen: 53.26. Here, the discrepancy in the total rests primarily with the oxygen concentration. The low oxygen concentration is independent of the matrix correction (and mass absorption coefficient) and can only be corrected for by using the appropriate APFs.

Select **Analytical | Analysis Options** from the main PROBE FOR EPMA log window to open the **Analysis Calculation Options** window. Click the *Use Empirical APF Values* check box to activate this option.



Quantitative Acquisition Options

- ☑ Use Deadtime Correction
  - ● Use Normal Deadtime Correction (single term factorial)
  - ○ Use Precision Deadtime Correction (two term factorial for > 50K cps)
- ☑ Use Beam Drift Correction
- ☑ Use Automatic Drift Correction on Standard Intensities

Quantitative Analysis Options

- ☐ Use Assigned Interference Corrections on Standards and Unknowns
  - ☐ Do Not Use Matrix Correction Term For Full Quant Interference Correction
  - ☐ Do Not Use Full Quant Interference Corrections (use traditional Gilfrich, et. al.)
- ☐ Use Assigned or Self Time Dependent Intensity (TDI) Corrections on Unknowns
  - ● Use Linear Fit (slope coefficient only) for TDI Extrapolation
  - ○ Use Quadratic Fit (two coefficient) for TDI Extrapolation
- ☐ Use Time Weighted Data for TDI Fit (weight intensities based on elasped time)
  - Time Weighted Data Weight Factor: 2
- ☑ Use Absorption Corrected MAN Continuum Intensities
- ☐ Use Particle or Thin Film Correction Parameters
- ☐ Check For Same Peak Positions in Unknown and Standard
- ☐ Check For Same PHA Settings in Unknown and Standard
- ☐ Use Zero Point For Calibration Curve (off-peak elements only)
- ☐ Use Conductive Coating Correction For Beam Energy Loss
- ☐ Use Conductive Coating Correction For X-ray Absorption
- ☐ Do Not Use Fast Quantitative Analysis Feature

MAC (mass absorption coefficient) and APF (area peak factor) Options

- ☐ Use Empirical MAC Values
- ☑ Use Empirical APF Values
  - ● Use Empirical APF Factors (calculated from elemental composition)
  - ○ Use Specified APF Factors (based on a fixed composition)

Calculation Options

- ☐ Use Aggregate Intensities for Duplicate Quantitative Elements
- ☐ Use Blank Calibration Sample Trace Element Accuracy Corrections
- ☑ Force Negative K-Ratios To Zero in ZAF Calculations
- ☐ Calculate Electron and Xray Ranges for Sample Compositions
- ☐ Use Oxygen From Halogens (F, Cl, Br and I) Correction
- ☐ Use Nth Point Calculation For Off-Peak Intensities (for testing only)
- ☐ Use Count Overwrite Intensity Table for Data Calculations
- ☐ Force Negative Interference Intensities To Zero in Corrections
- ☐ Use Chemical Age Calculation (U, Th, Pb)
- ☐ Use Savitsky-Golay Smoothing for Integrated Intensities: 2
- ☐ Use Secondary Boundary Fluorescence Correction

Formatting Options

- ☐ Use Automatic Format For Quantitative Results
  - ● Display the Maximum Number of Numerical Digits
  - ○ Display Only Statistically Significant Number of Numerical Digits
- ☑ Use Detailed Printout For Data and Analytical Results
- ☐ Print Analyzed And Specified On Same Line
- ☐ Display Count Intensities Unnormalized To Time (in Analyze!)
- ☐ Print Additional MAN Fit and Correction Parameters To Log Window

Output Options

- ☐ Display Charge Balance Calculation

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

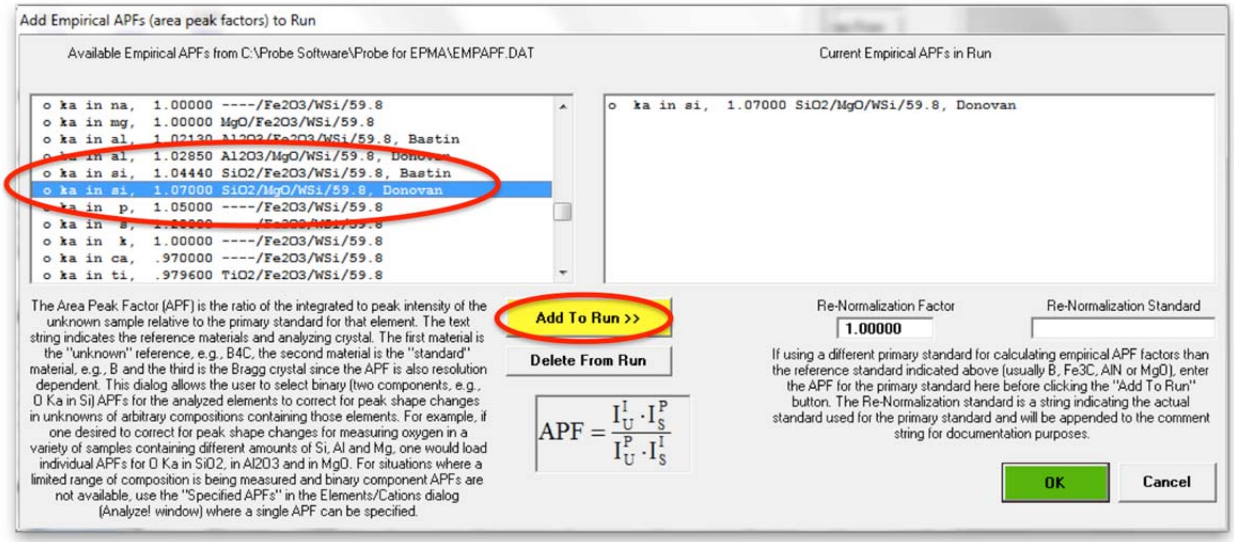
- ● Use Traditional Geological Sort Order (SiO2, TiO2, etc.)
- ○ Use Low To High Atomic Number Sort Order
- ○ Use High To Low Atomic Number Sort Order

Click the **OK** button.

Next, select **Analytical | Empirical APFs** from the main PROBE FOR EPMA log window to open the **Add Empirical APFs (area peak factors) to Run** window.

Find the appropriate correction. Two choices are given for oxygen in the presence of SiO_2, Bastin's value of 1.04440 using Fe_2O_3 as the calibration standard and Donovan's correction factor of 1.070 when using MgO as the calibration standard. Although the values seen in the text field below are relative to Fe_2O_3, the APF for MgO relative to Fe_2O_3 is also 1.000, which means that these correction factors apply equally well relative to MgO. Hence, the use of MgO as the calibration standard.

Click the **Add To Run** >> button to place the selected empirical APF into the run.



```
o ka in na,  1.00000 ----/Fe2O3/WSi/59.8
o ka in mg,  1.00000 MgO/Fe2O3/WSi/59.8
o ka in al,  1.02130 Al2O3/Fe2O3/WSi/59.8, Bastin
o ka in al,  1.02850 Al2O3/MgO/WSi/59.8, Donovan
o ka in si,  1.04440 SiO2/Fe2O3/WSi/59.8, Bastin
o ka in si,  1.07000 SiO2/MgO/WSi/59.8, Donovan
o ka in  p,  1.05000 ----/Fe2O3/WSi/59.8
o ka in  s,  [illegible]/Fe2O3/WSi/59.8
o ka in  k,  1.00000 ----/Fe2O3/WSi/59.8
o ka in ca,  .970000 ----/Fe2O3/WSi/59.8
o ka in ti,  .979600 TiO2/Fe2O3/WSi/59.8
```

```
o  ka in si,  1.07000 SiO2/MgO/WSi/59.8, Donovan
```

The Area Peak Factor (APF) is the ratio of the integrated to peak intensity of the unknown sample relative to the primary standard for that element. The text string indicates the reference materials and analyzing crystal. The first material is the "unknown" reference, e.g., B4C, the second material is the "standard" material, e.g., B and the third is the Bragg crystal since the APF is also resolution dependent. This dialog allows the user to select binary (two components, e.g., O Ka in Si) APFs for the analyzed elements to correct for peak shape changes in unknowns of arbitrary compositions containing those elements. For example, if one desired to correct for peak shape changes for measuring oxygen in a variety of samples containing different amounts of Si, Al and Mg, one would load individual APFs for O Ka in SiO2, in Al2O3 and in MgO. For situations where a limited range of composition is being measured and binary component APFs are not available, use the "Specified APFs" in the Elements/Cations dialog (Analyze! window) where a single APF can be specified.

$$\mathrm{APF} = \frac{I_U^I \cdot I_S^P}{I_U^P \cdot I_S^I}$$

Re-Normalization Factor: 1.00000

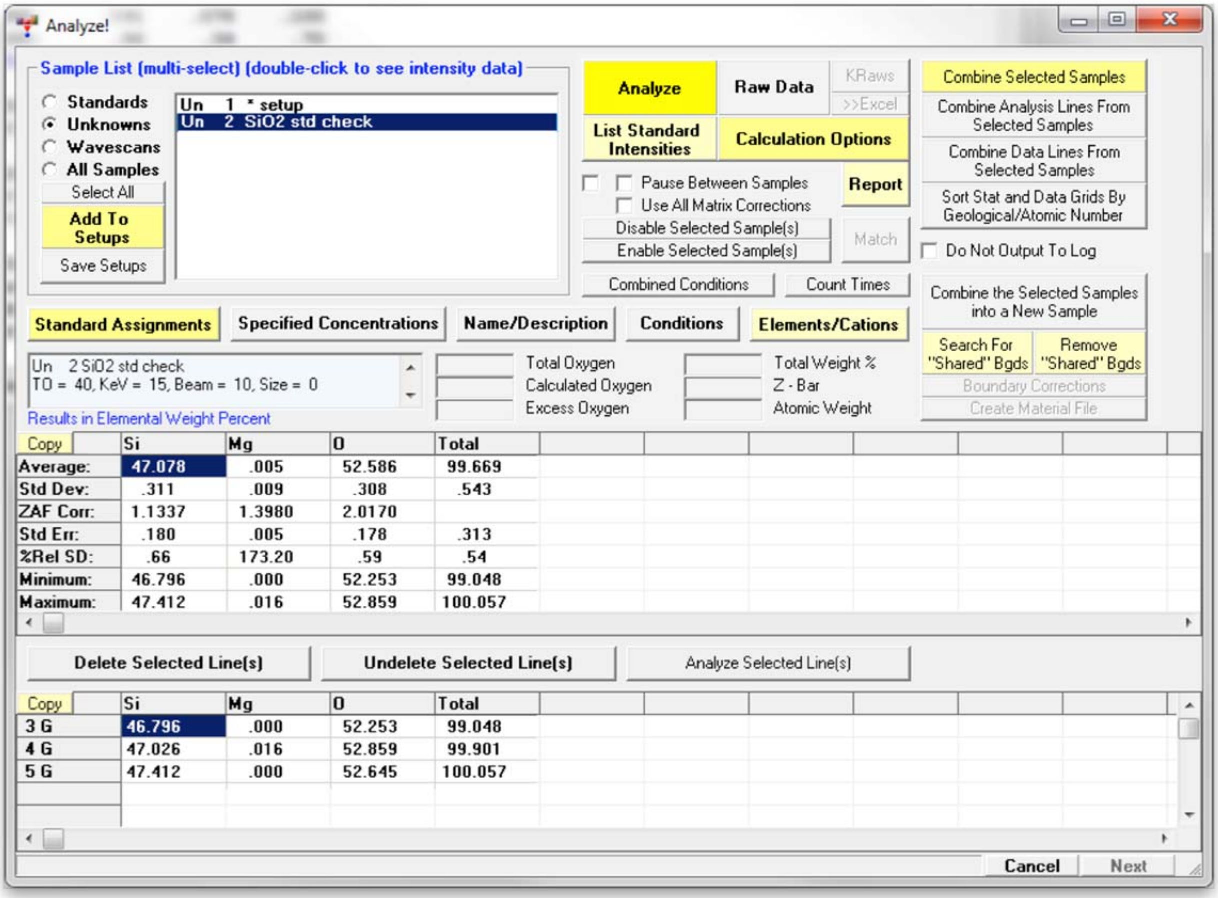
Re-Normalization Standard:

If using a different primary standard for calculating empirical APF factors than the reference standard indicated above (usually B, Fe3C, AlN or MgO), enter the APF for the primary standard here before clicking the "Add To Run" button. The Re-Normalization standard is a string indicating the actual standard used for the primary standard and will be appended to the comment string for documentation purposes.

The APF correction values are defined in the EMPAPF.DAT file in the PROBE FOR EPMA directory. The file contains some 80 values that may or may not be applicable, depending on the analyzing crystals and standards available. It is strongly recommended that the user measure the integral intensities and peak intensities and calculate the APFs for your particular spectrometer setup. And if necessary, edit the EMPAPR.DAT file using any ASCII text editor such as NotePad to insert their own measurements. See the User's Guide and Reference documentation for editing format and details.

Click the **OK** button.

Re-analyze the unknown SiO_2 sample. The total is now closer to 100% and a more reasonable oxygen concentration is calculated.



Un 1 * setup
Un 2 SiO2 std check

☐ ☐ Pause Between Samples
☐ Use All Matrix Corrections
☐ Do Not Output To Log

Un 2 SiO2 std check
TO = 40, KeV = 15, Beam = 10, Size = 0

Results in Elemental Weight Percent

	Si	Mg	O	Total
Average:	47.078	.005	52.586	99.669
Std Dev:	.311	.009	.308	.543
ZAF Corr:	1.1337	1.3980	2.0170	
Std Err:	.180	.005	.178	.313
%Rel SD:	.66	173.20	.59	.54
Minimum:	46.796	.000	52.253	99.048
Maximum:	47.412	.016	52.859	100.057

	Si	Mg	O	Total
3 G	46.796	.000	52.253	99.048
4 G	47.026	.016	52.859	99.901
5 G	47.412	.000	52.645	100.057

The APF values selected or entered are always measured relative to some standard sample. For example, if measuring oxygen Kα and using either MgO or Fe_2O_3 as the primary standard for oxygen, then any oxygen Kα APF values used must be those measured relative to either MgO or Fe_2O_3. For the same reason, if using APF values for a particular light element and the user decides to re-assign the standard for that element, the APF values for that element must also be re-normalized to reflect the standard re-assignment.

Thus, it is most efficient to 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 Fe_2O_3
- Nitrogen : AlN
- Carbon : Fe_3C
- Boron : B metal

The APF correction in PROBE FOR EPMA will allow the user to enter one or more empirical APF factors for each emitting element in each run, although they are generally applied to soft x-ray lines. 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.

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