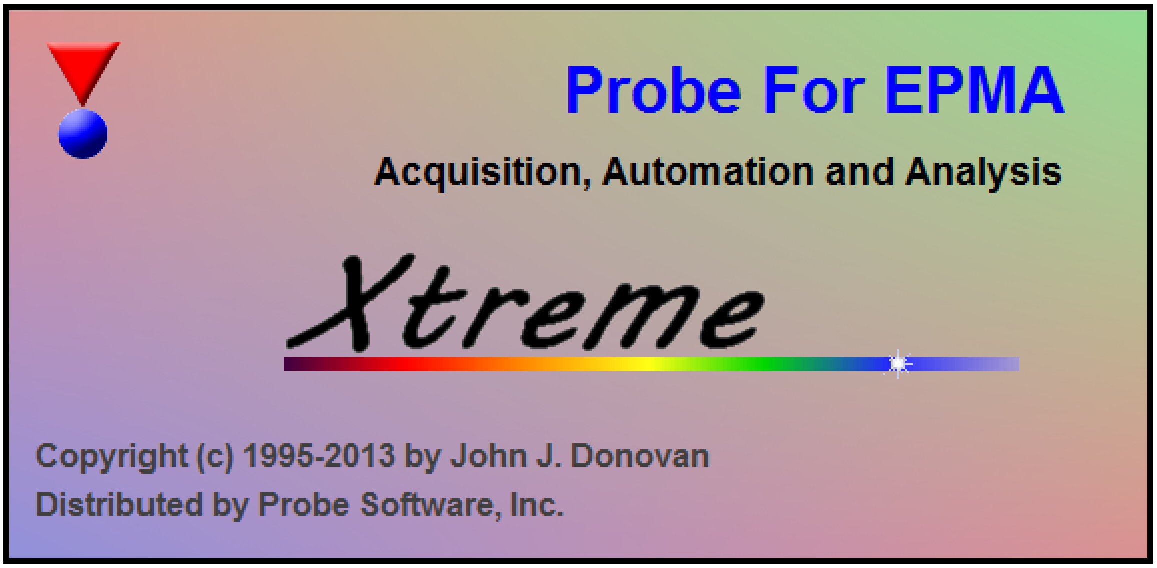
Probe for EPMA v. 9.4.3

Advanced Topics

Extreme Edition



Probe For EPMA

Acquisition, Automation and Analysis

Xtreme

Distributed by Probe Software, Inc.

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for Probe Software, Inc.

Contents

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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

Introduction

PROBE FOR EPMA is a very versatile and powerful 32-bit acquisition, automation and analysis package for WDS and EDS electron microprobe analysis running under Microsoft Windows operating system.

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 modified using PROBE FOR EPMA in demo mode.

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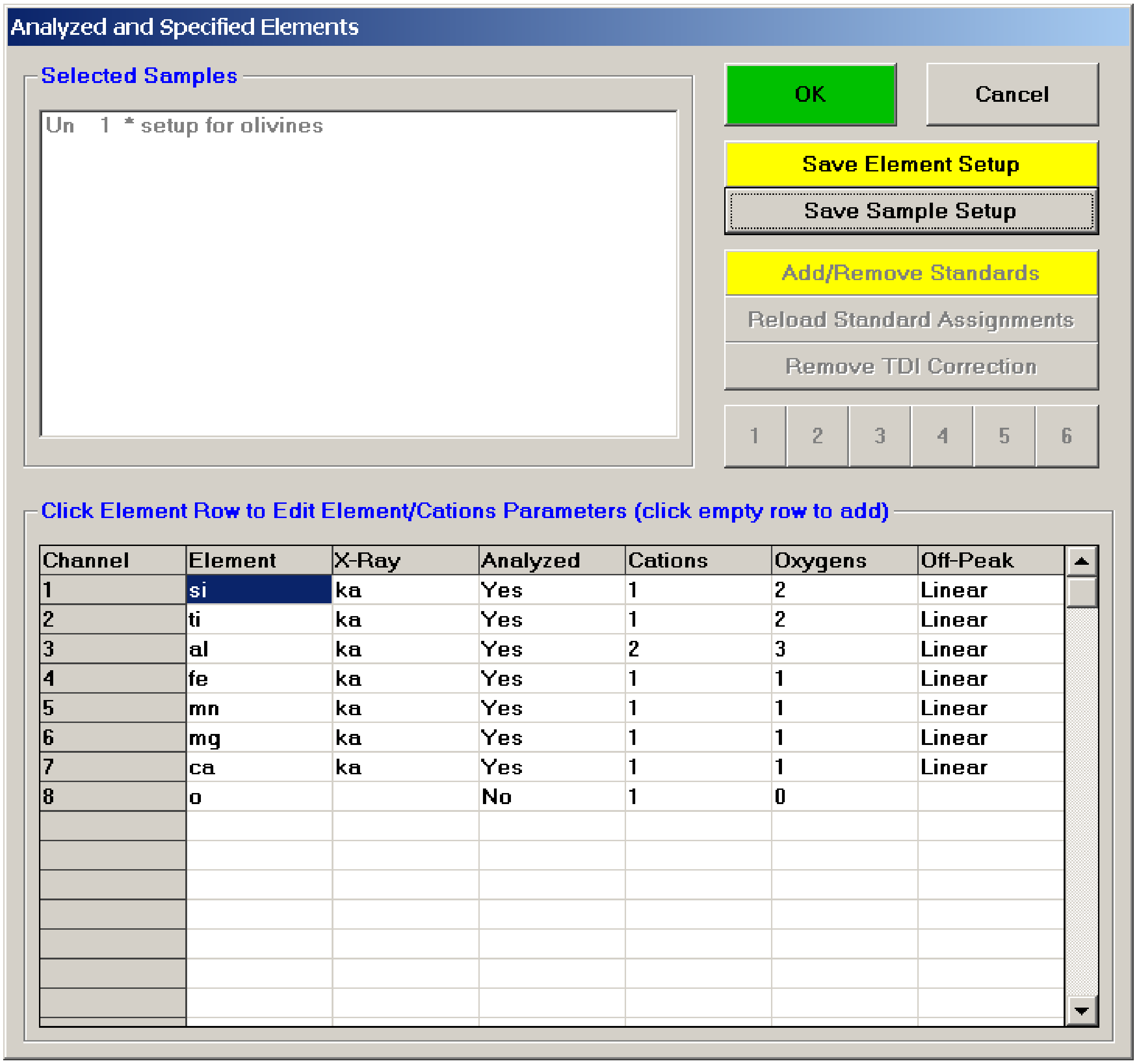
Element Setups

Individual element analytical configurations for a specific element, x-ray, spectrometer, and reflecting 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 **Analyzed and Specified Elements** window in the usual manner. Below is the completed **Analyzed and Specified Elements** window after the entry of all seven elements plus oxygen.

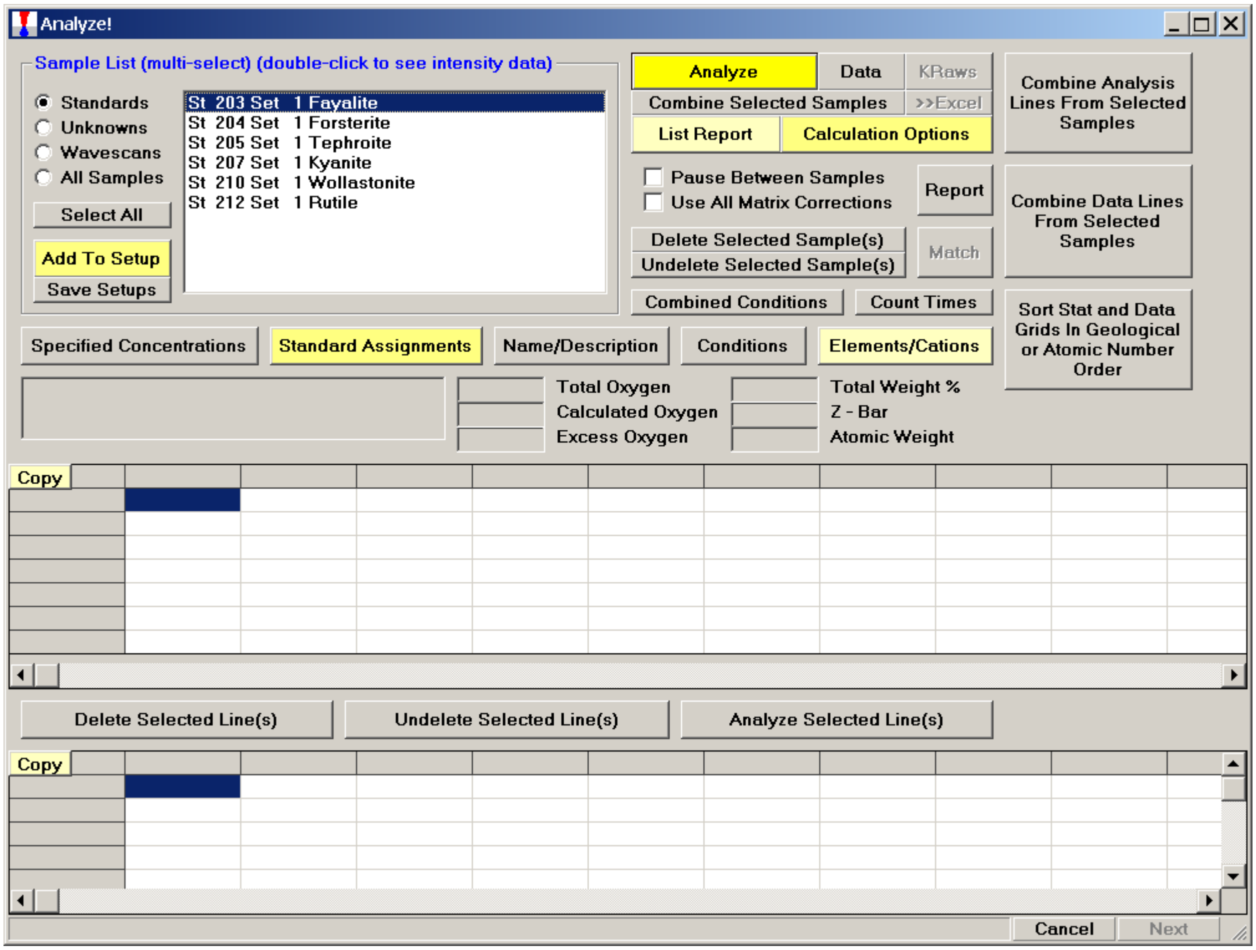


Un   1 * setup for olivines

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	

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 (iron in fayalite, in this example).



Sample List (multi-select) (double-click to see intensity data)

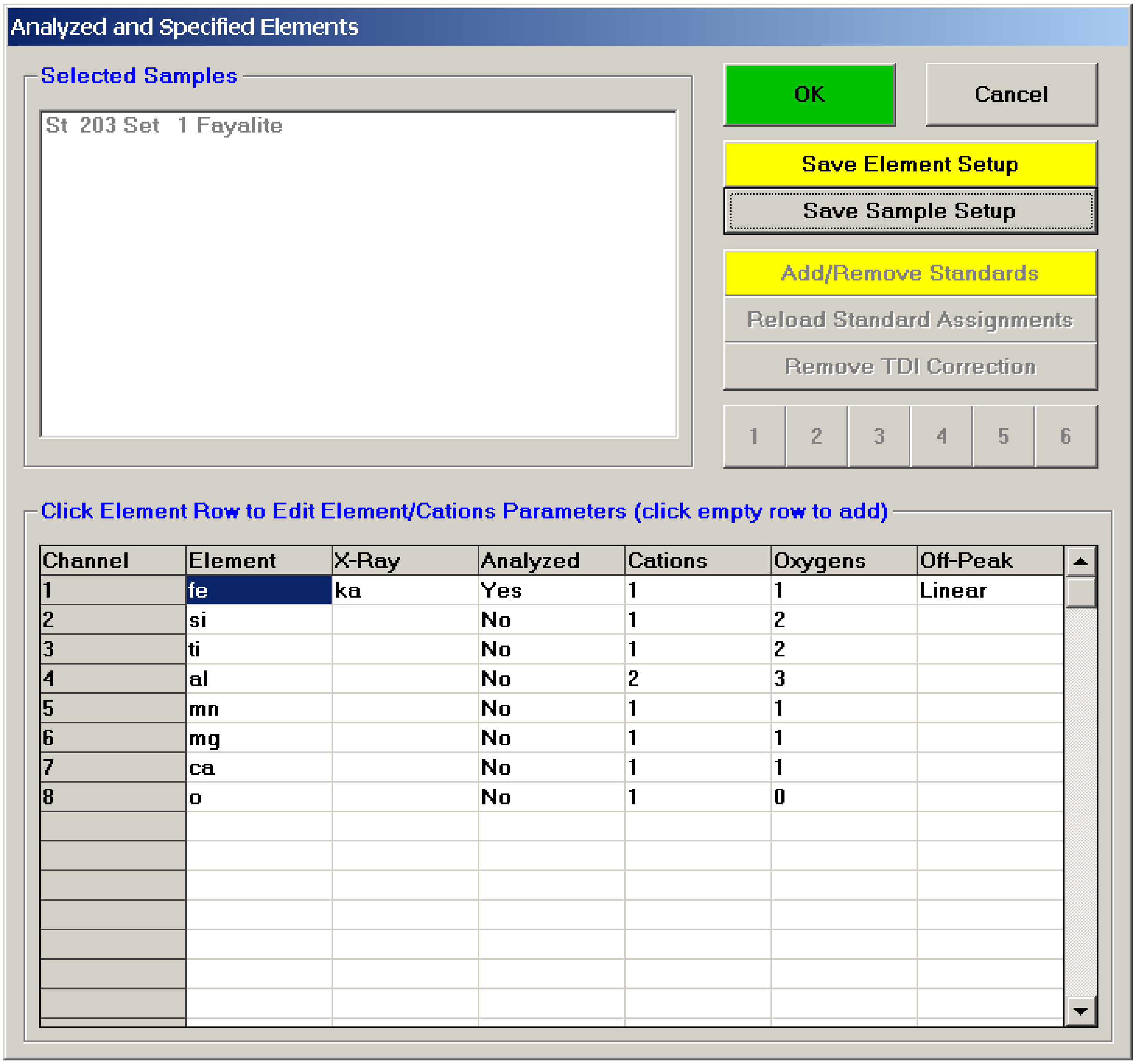
● Standards
○ Unknowns
○ Wavescans
○ All Samples

St 203 Set 1 Fayalite
St 204 Set 1 Forsterite
St 205 Set 1 Tephroite
St 207 Set 1 Kyanite
St 210 Set 1 Wollastonite
St 212 Set 1 Rutile

☐ Pause Between Samples
☐ Use All Matrix Corrections

Click the **Elements/Cations** button.

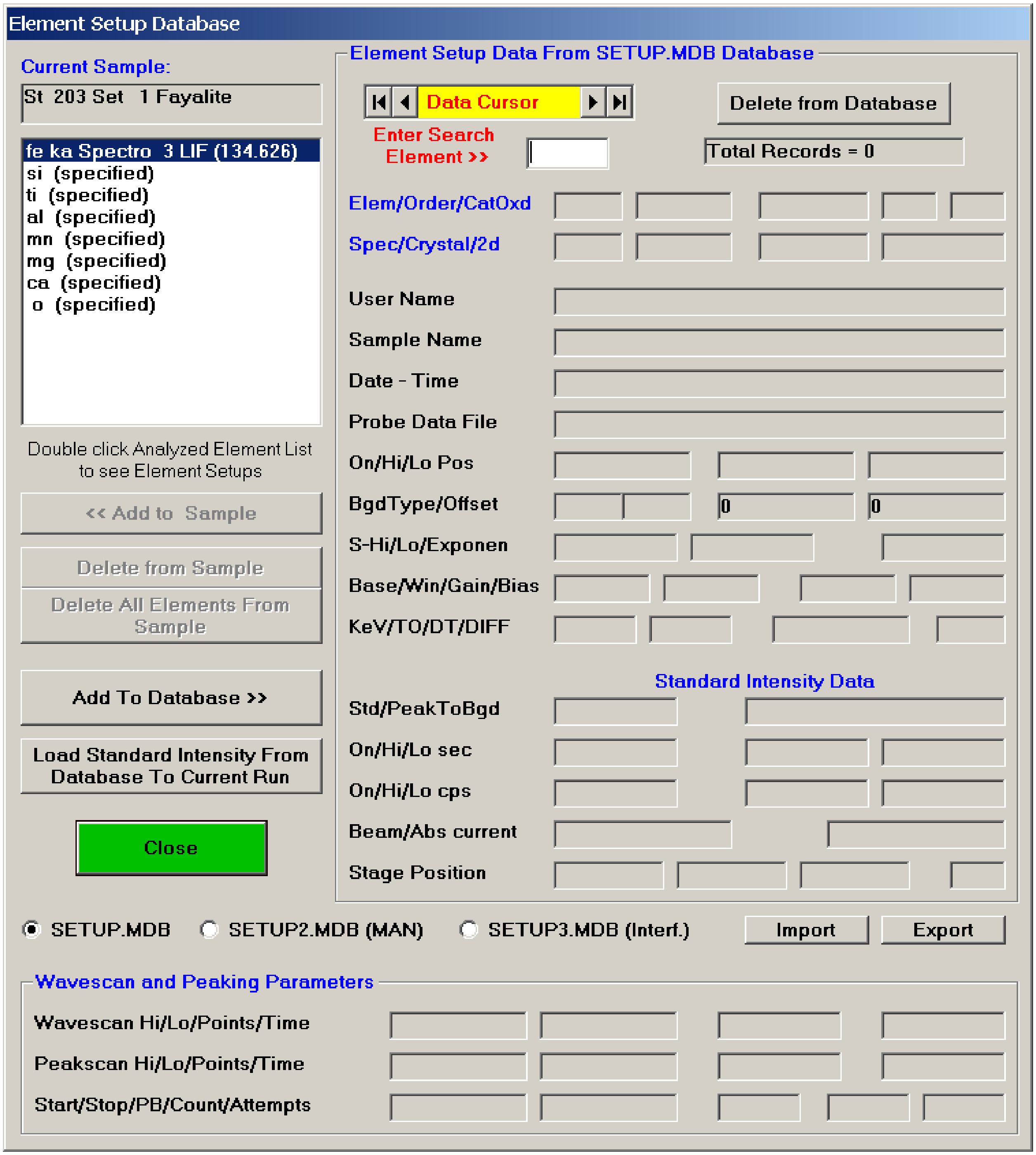
This opens the **Analyzed and Specified Elements** window.



Channel	Element	X-Ray	Analyzed	Cations	Oxygens	Off-Peak
1	fe	ka	Yes	1	1	Linear
2	si		No	1	2	
3	ti		No	1	2	
4	al		No	2	3	
5	mn		No	1	1	
6	mg		No	1	1	
7	ca		No	1	1	
8	o		No	1	0	

Click the **Save Element Setup** button.

The **Element Setup Database** opens.



Current Sample: St 203 Set 1 Fayalite

fe ka Spectro 3 LIF (134.626)
si (specified)
ti (specified)
al (specified)
mn (specified)
mg (specified)
ca (specified)
o (specified)

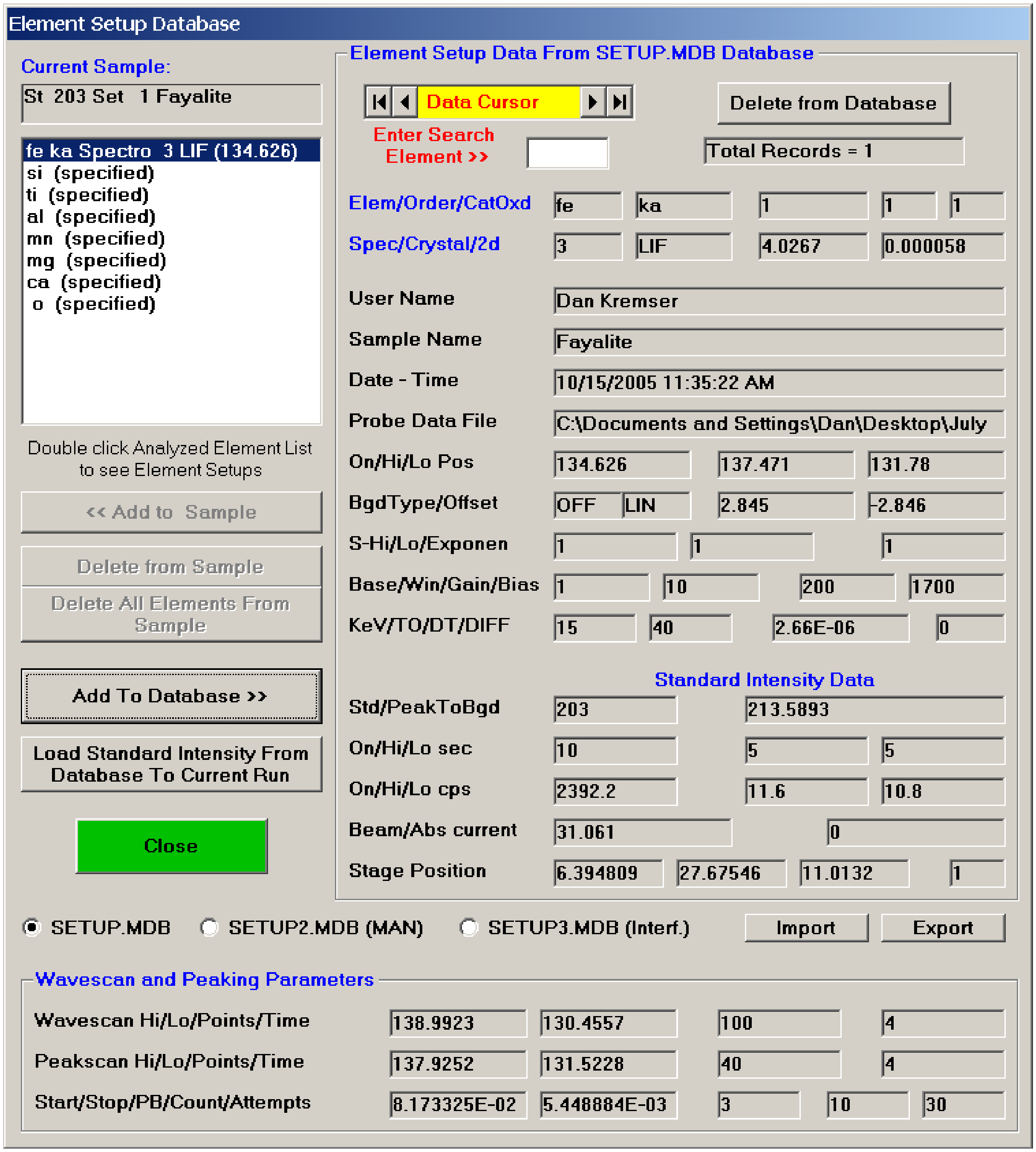
Total Records = 0

BgdType/Offset: 0 0

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

Highlight the specific element to save and click the **Add To Database**>> button. In this standard, the iron intensity is the only element to be archived, select *fe kα Spectro 3 LIF (134.626)*.

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 203 Set 1 Fayalite

fe ka Spectro 3 LIF (134.626)
si (specified)
ti (specified)
al (specified)
mn (specified)
mg (specified)
ca (specified)
o (specified)

Element Setup Data From SETUP.MDB Database

Total Records = 1

Elem/Order/CatOxd	fe	ka	1	1	1
Spec/Crystal/2d	3	LIF	4.0267	0.000058	
User Name	Dan Kremser				
Sample Name	Fayalite				
Date - Time	10/15/2005 11:35:22 AM				
Probe Data File	C:\Documents and Settings\Dan\Desktop\July				
On/Hi/Lo Pos	134.626	137.471	131.78		
BgdType/Offset	OFF	LIN	2.845	-2.846	
S-Hi/Lo/Exponen	1	1	1		
Base/Win/Gain/Bias	1	10	200	1700	
KeV/TO/DT/DIFF	15	40	2.66E-06	0	

Standard Intensity Data

Std/PeakToBgd	203	213.5893		
On/Hi/Lo sec	10	5	5	
On/Hi/Lo cps	2392.2	11.6	10.8	
Beam/Abs current	31.061	0		
Stage Position	6.394809	27.67546	11.0132	1

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

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	138.9923	130.4557	100	4	
Peakscan Hi/Lo/Points/Time	137.9252	131.5228	40	4	
Start/Stop/PB/Count/Attempts	8.173325E-02	5.448884E-03	3	10	30

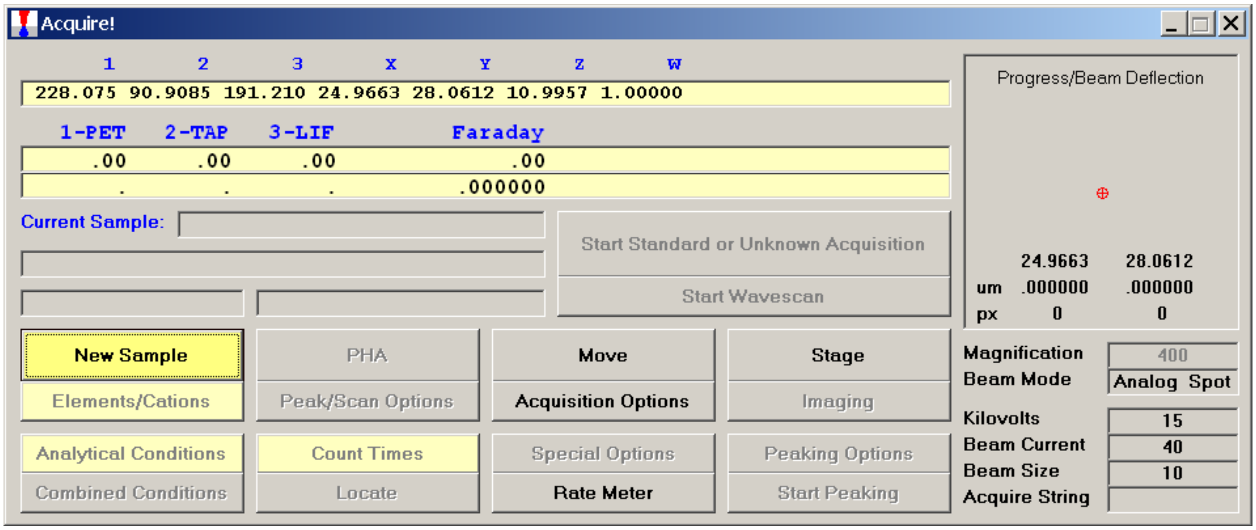
Click the **Close** button. The **Analyzed and Specified Elements** window reappears. Click the **OK** button. The **Analyze!** window returns.

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.



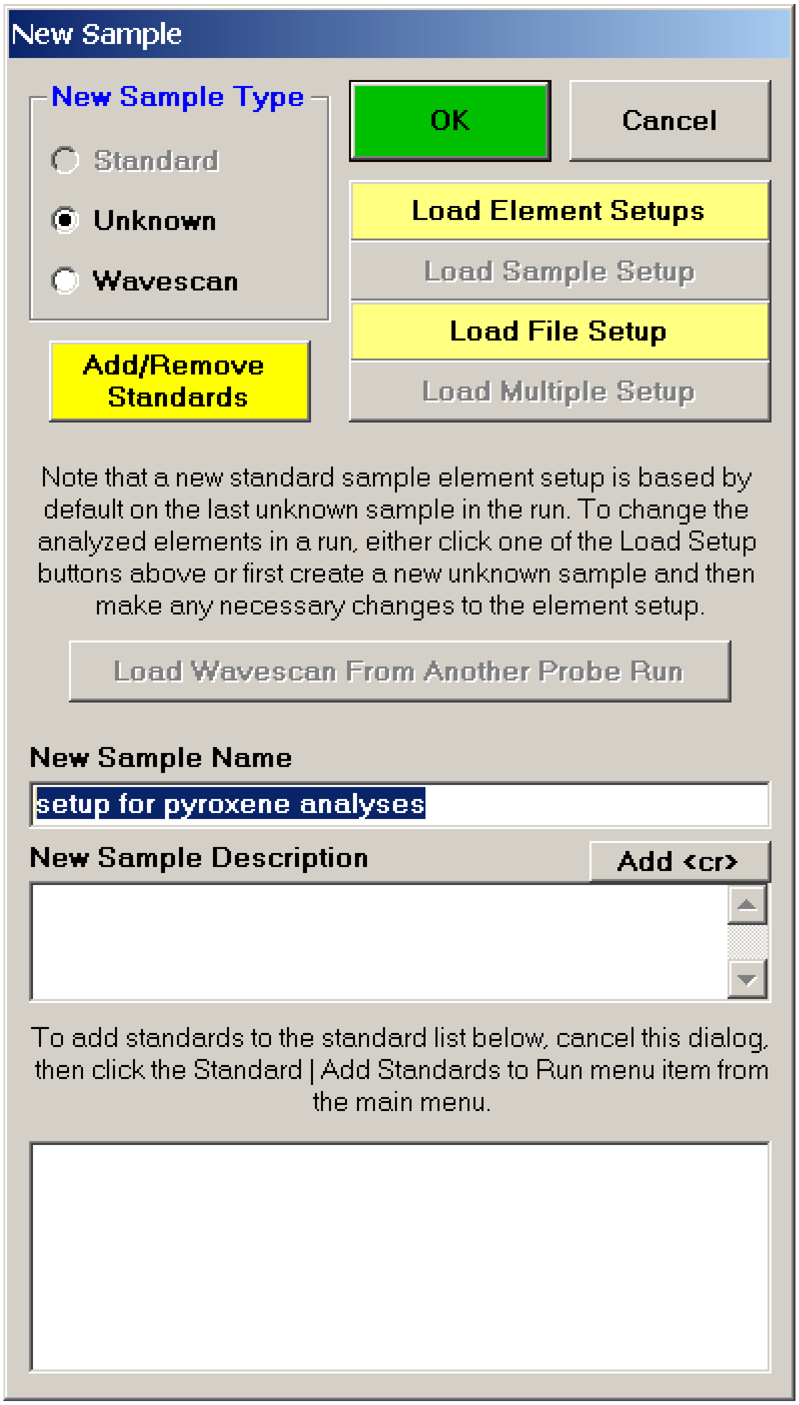
1	2	3	X	Y	Z	W
228.075	90.9085	191.210	24.9663	28.0612	10.9957	1.00000

1-PET	2-TAP	3-LIF	Faraday
.00	.00	.00	.00
.	.	.	.000000

	24.9663	28.0612
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	40
Beam Size	10
Acquire String	

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



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.

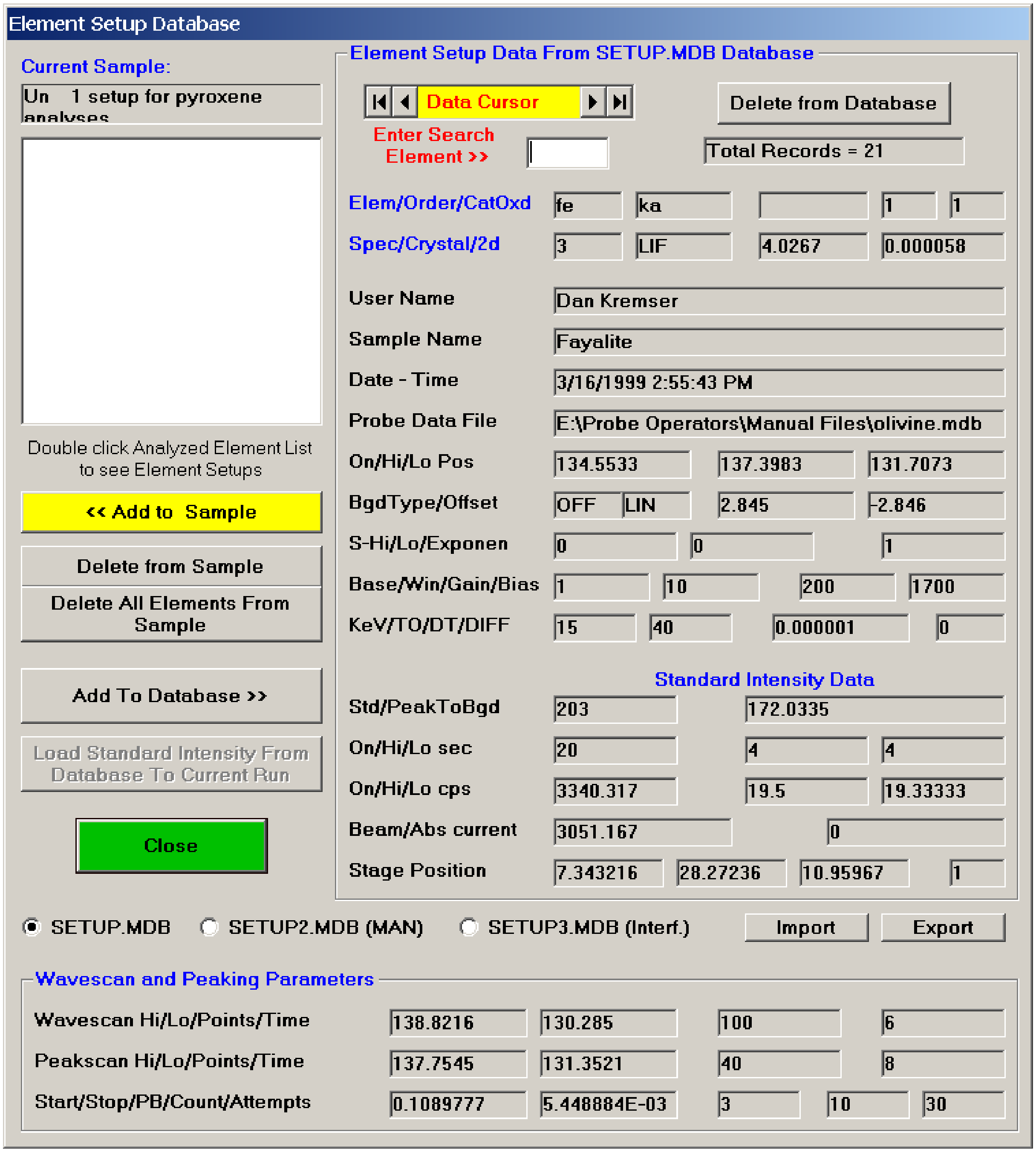
New Sample Name: setup for pyroxene analyses

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.

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

This opens the **Element Setup Database**.



Current Sample: Un 1 setup for pyroxene analyses

Total Records = 21

Elem/Order/CatOxd	fe	ka		1	1
Spec/Crystal/2d	3	LIF	4.0267	0.000058

User Name: Dan Kremser
Sample Name: Fayalite
Date - Time: 3/16/1999 2:55:43 PM
Probe Data File: E:\Probe Operators\Manual Files\olivine.mdb

On/Hi/Lo Pos	134.5533	137.3983	131.7073	
BgdType/Offset	OFF	LIN	2.845	-2.846
S-Hi/Lo/Exponen	0	0	1	
Base/Win/Gain/Bias	1	10	200	1700
KeV/TO/DT/DIFF	15	40	0.000001	0

Standard Intensity Data

Std/PeakToBgd	203	172.0335		
On/Hi/Lo sec	20	4	4	
On/Hi/Lo cps	3340.317	19.5	19.33333	
Beam/Abs current	3051.167	0		
Stage Position	7.343216	28.27236	10.95967	1

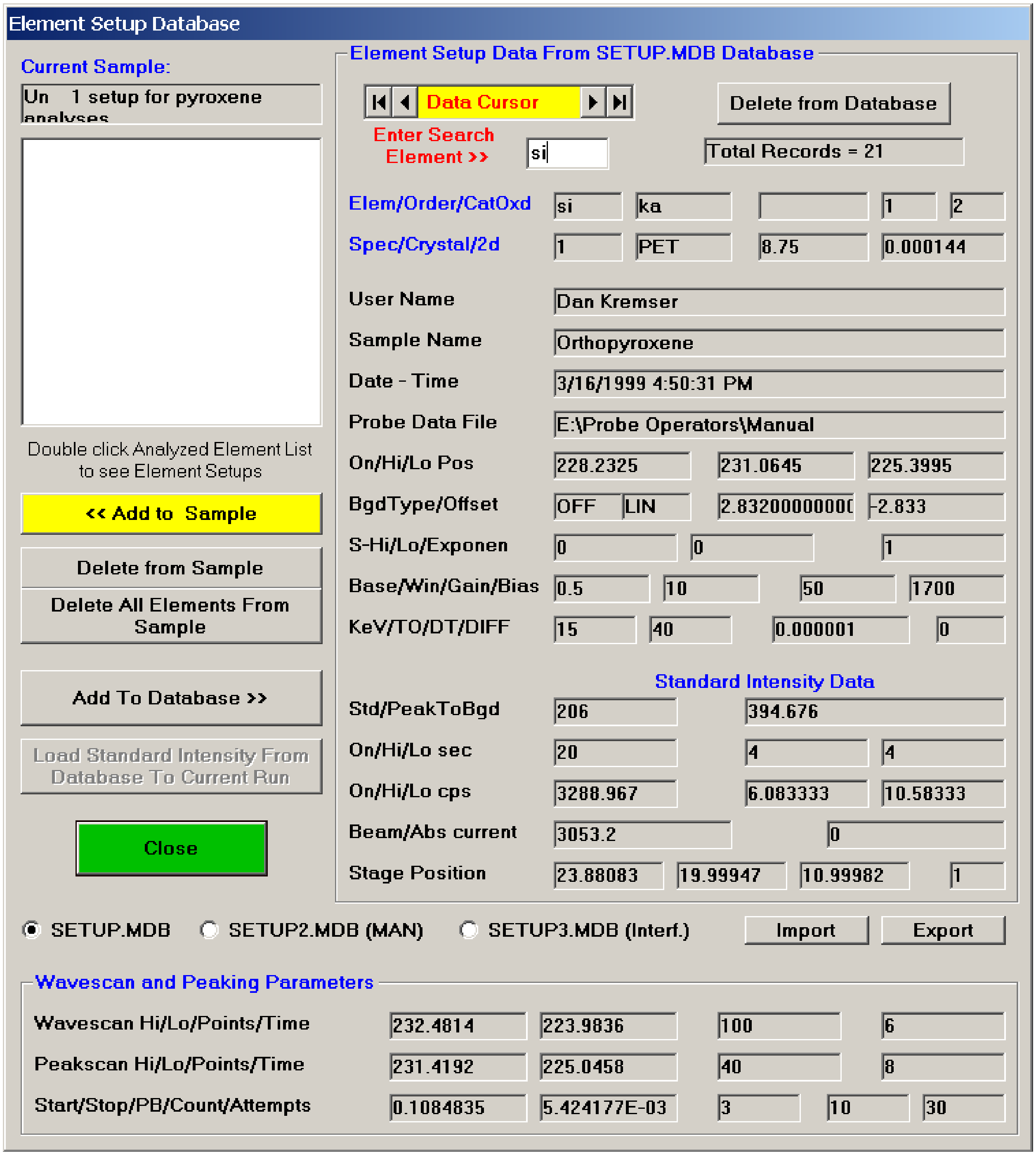
● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	138.8216	130.285	100	6	
Peakscan Hi/Lo/Points/Time	137.7545	131.3521	40	8	
Start/Stop/PB/Count/Attempts	0.1089777	5.448884E-03	3	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 1 setup for pyroxene analyses

Element Setup Data From SETUP.MDB Database

Enter Search Element >> si

Total Records = 21

Elem/Order/CatOxd	si	ka		1	2
Spec/Crystal/2d	1	PET	8.75	0.000144	
User Name	Dan Kremser				
Sample Name	Orthopyroxene				
Date - Time	3/16/1999 4:50:31 PM				
Probe Data File	E:\Probe Operators\Manual				
On/Hi/Lo Pos	228.2325	231.0645	225.3995		
BgdType/Offset	OFF	LIN	2.83200000000	-2.833	
S-Hi/Lo/Exponen	0	0	1		
Base/Win/Gain/Bias	0.5	10	50	1700	
KeV/TO/DT/DIFF	15	40	0.000001	0	

Standard Intensity Data

Std/PeakToBgd	206	394.676	
On/Hi/Lo sec	20	4	4
On/Hi/Lo cps	3288.967	6.083333	10.58333
Beam/Abs current	3053.2	0	
Stage Position	23.88083	19.99947	10.99982	1

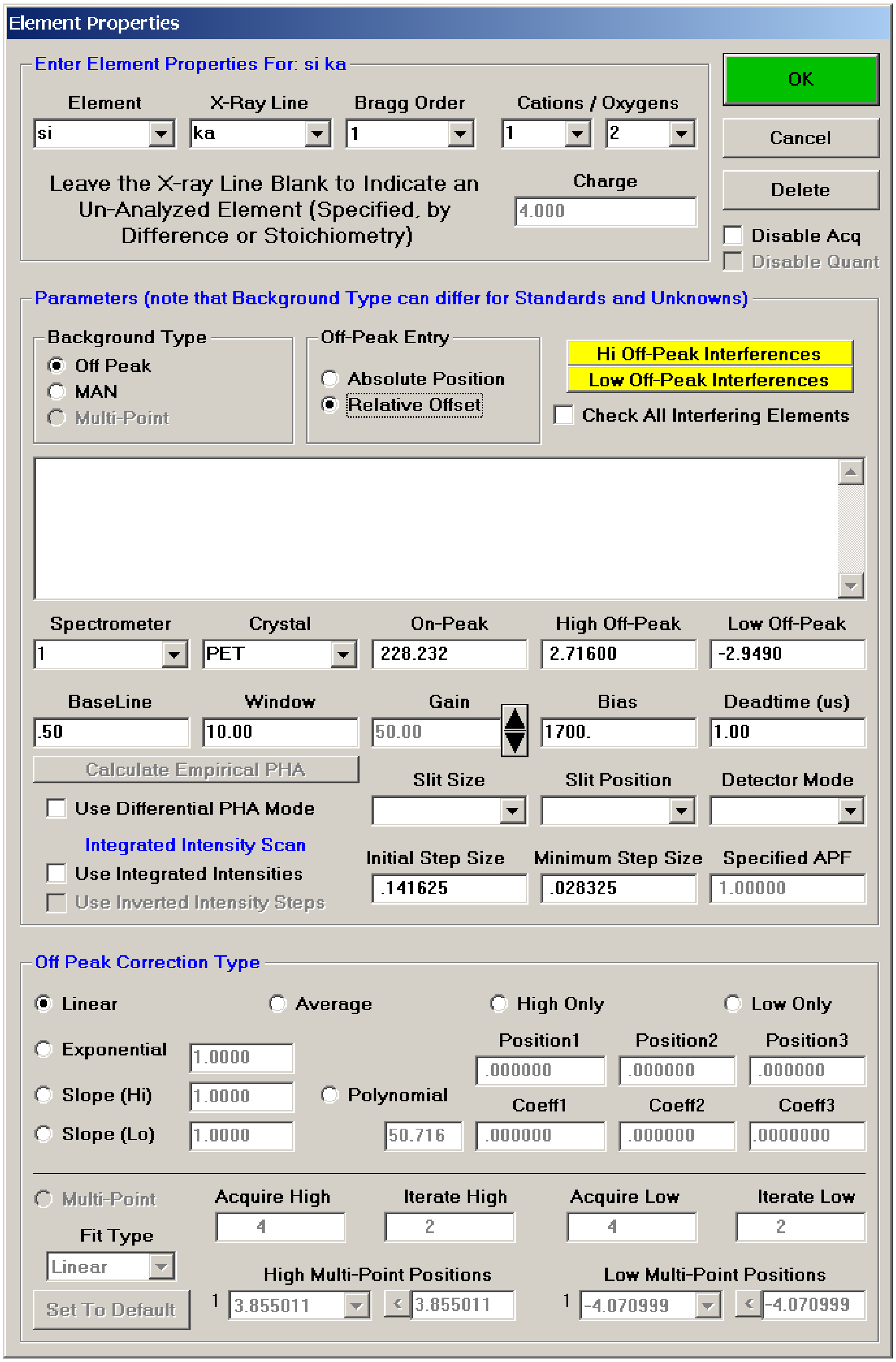
● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	232.4814	223.9836	100	6	
Peakscan Hi/Lo/Points/Time	231.4192	225.0458	40	8	
Start/Stop/PB/Count/Attempts	0.1084835	5.424177E-03	3	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 Properties

Enter Element Properties For: si ka

Element: si
X-Ray Line: ka
Bragg Order: 1
Cations / Oxygens: 1 / 2
Charge: 4.000

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

☐ Disable Acq
☐ Disable Quant

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

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

☐ Check All Interfering Elements

Spectrometer	Crystal	On-Peak	High Off-Peak	Low Off-Peak
1	PET	228.232	2.71600	-2.9490

BaseLine	Window	Gain	Bias	Deadtime (us)
.50	10.00	50.00	1700.	1.00

☐ Use Differential PHA Mode

Slit Size:
Slit Position:
Detector Mode:

Integrated Intensity Scan
☐ Use Integrated Intensities
☐ Use Inverted Intensity Steps

Initial Step Size	Minimum Step Size	Specified APF
.141625	.028325	1.00000

Off Peak Correction Type

● Linear ○ Average ○ High Only ○ Low Only

○ Exponential 1.0000
○ Slope (Hi) 1.0000
○ Slope (Lo) 1.0000
○ Polynomial 50.716

Position1	Position2	Position3
.000000	.000000	.000000

Coeff1	Coeff2	Coeff3
.000000	.000000	.0000000

○ Multi-Point

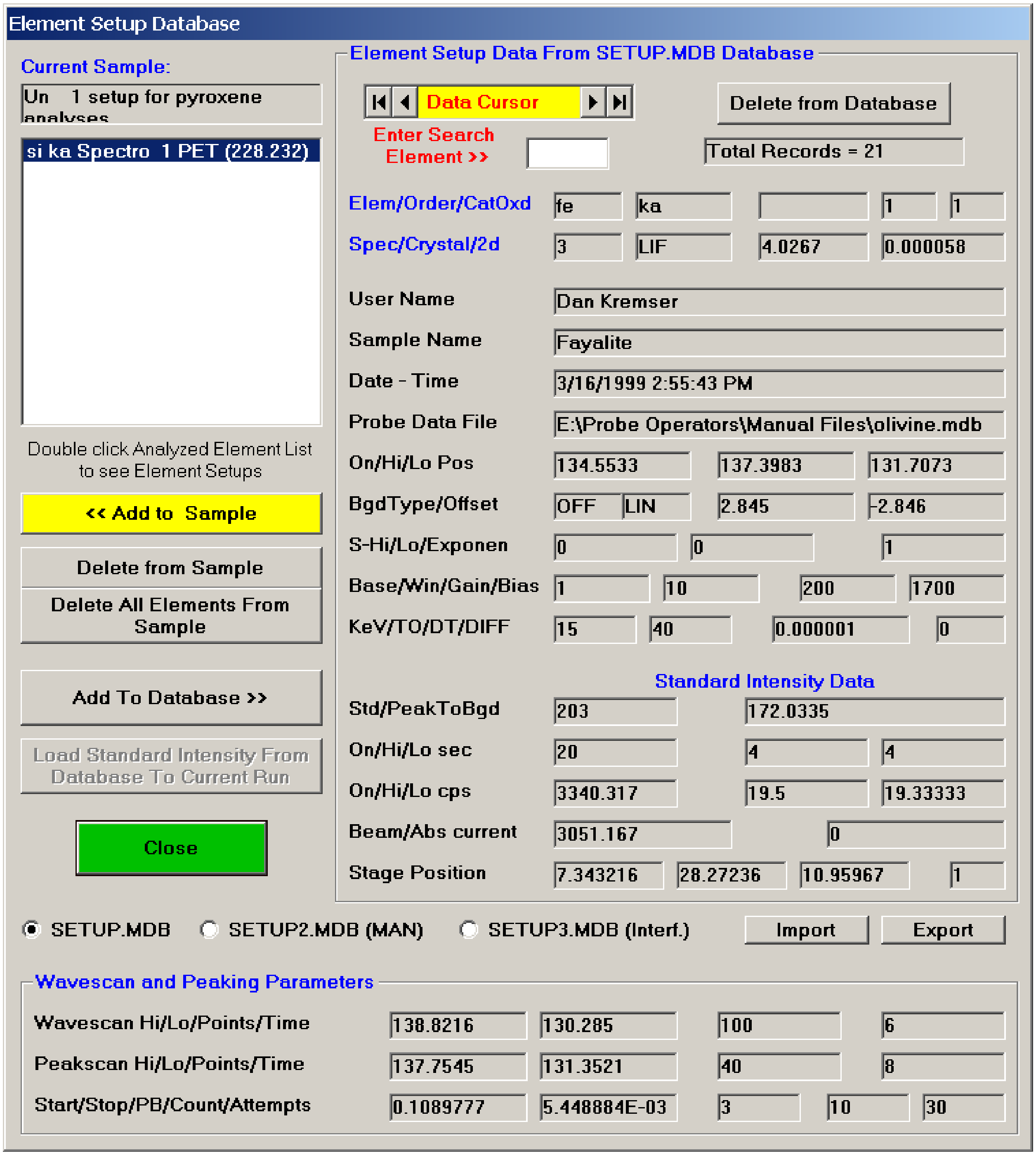
Acquire High	Iterate High	Acquire Low	Iterate Low
4	2	4	2

Fit Type: Linear

High Multi-Point Positions: 1 3.855011 3.855011
Low Multi-Point Positions: 1 -4.070999 -4.070999

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 1 setup for pyroxene analyses
si ka Spectro 1 PET (228.232)

Element Setup Data From SETUP.MDB Database
Total Records = 21
Elem/Order/CatOxd: fe | ka | | 1 | 1
Spec/Crystal/2d: 3 | LIF | 4.0267 | 0.000058
User Name: Dan Kremser
Sample Name: Fayalite
Date - Time: 3/16/1999 2:55:43 PM
Probe Data File: E:\Probe Operators\Manual Files\olivine.mdb
On/Hi/Lo Pos: 134.5533 | 137.3983 | 131.7073
BgdType/Offset: OFF | LIN | 2.845 | -2.846
S-Hi/Lo/Exponen: 0 | 0 | 1
Base/Win/Gain/Bias: 1 | 10 | 200 | 1700
KeV/TO/DT/DIFF: 15 | 40 | 0.000001 | 0

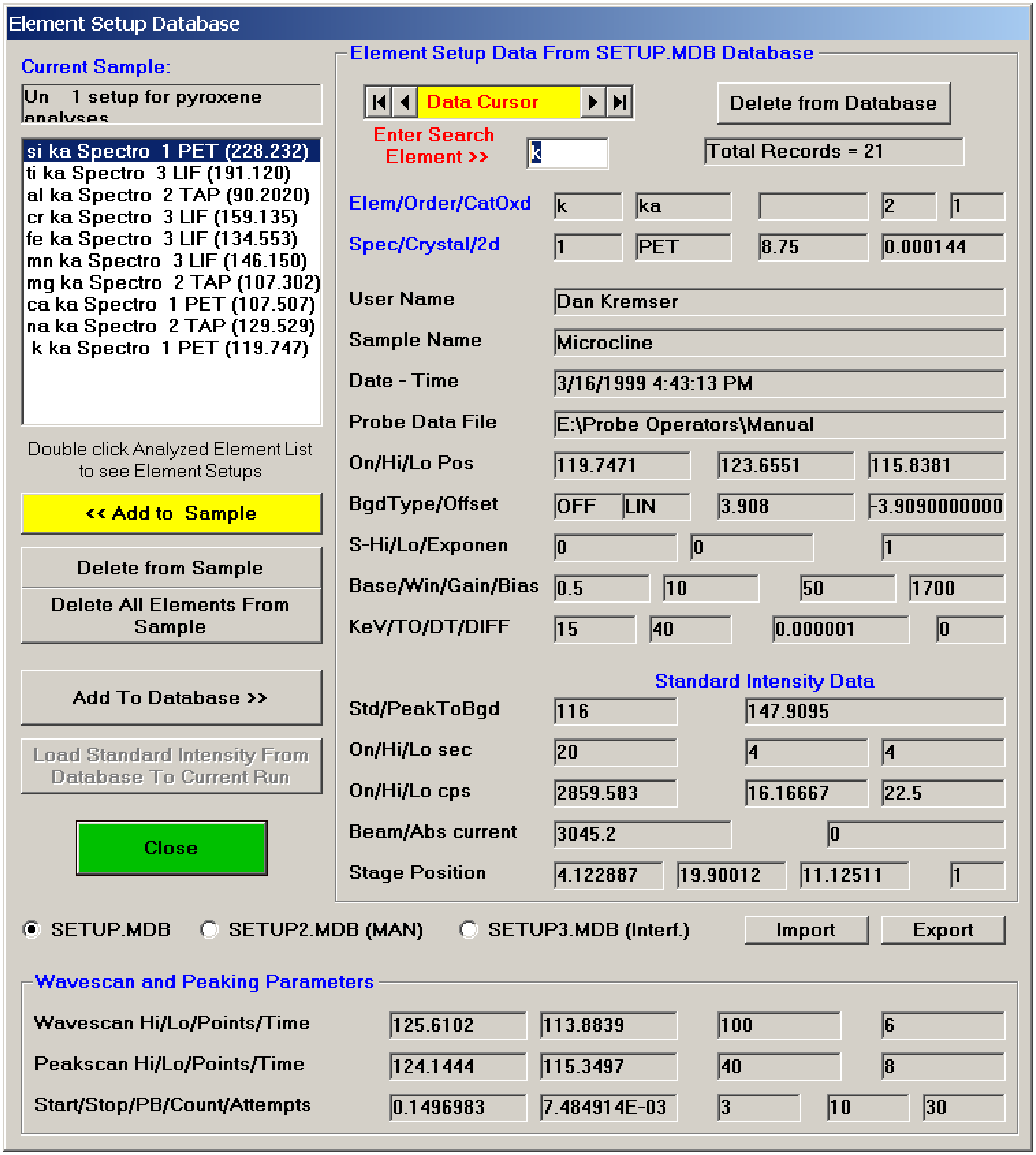
Standard Intensity Data
Std/PeakToBgd: 203 | 172.0335
On/Hi/Lo sec: 20 | 4 | 4
On/Hi/Lo cps: 3340.317 | 19.5 | 19.33333
Beam/Abs current: 3051.167 | 0
Stage Position: 7.343216 | 28.27236 | 10.95967 | 1

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

Wavescan and Peaking Parameters
Wavescan Hi/Lo/Points/Time: 138.8216 | 130.285 | 100 | 6
Peakscan Hi/Lo/Points/Time: 137.7545 | 131.3521 | 40 | 8
Start/Stop/PB/Count/Attempts: 0.1089777 | 5.448884E-03 | 3 | 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 1 setup for pyroxene analyses

si ka Spectro 1 PET (228.232)
ti ka Spectro 3 LIF (191.120)
al ka Spectro 2 TAP (90.2020)
cr ka Spectro 3 LIF (159.135)
fe ka Spectro 3 LIF (134.553)
mn ka Spectro 3 LIF (146.150)
mg ka Spectro 2 TAP (107.302)
ca ka Spectro 1 PET (107.507)
na ka Spectro 2 TAP (129.529)
k ka Spectro 1 PET (119.747)

Double click Analyzed Element List to see Element Setups

Element Setup Data From SETUP.MDB Database

Enter Search Element >> k

Total Records = 21

Elem/Order/CatOxd	k	ka		2	1
Spec/Crystal/2d	1	PET	8.75	0.000144	
User Name	Dan Kremser				
Sample Name	Microcline				
Date - Time	3/16/1999 4:43:13 PM				
Probe Data File	E:\Probe Operators\Manual				
On/Hi/Lo Pos	119.7471	123.6551	115.8381		
BgdType/Offset	OFF	LIN	3.908	-3.9090000000	
S-Hi/Lo/Exponen	0	0	1		
Base/Win/Gain/Bias	0.5	10	50	1700	
KeV/TO/DT/DIFF	15	40	0.000001	0	

Standard Intensity Data

Std/PeakToBgd	116	147.9095		
On/Hi/Lo sec	20	4	4	
On/Hi/Lo cps	2859.583	16.16667	22.5	
Beam/Abs current	3045.2	0		
Stage Position	4.122887	19.90012	11.12511	1

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

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	125.6102	113.8839	100	6	
Peakscan Hi/Lo/Points/Time	124.1444	115.3497	40	8	
Start/Stop/PB/Count/Attempts	0.1496983	7.484914E-03	3	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.

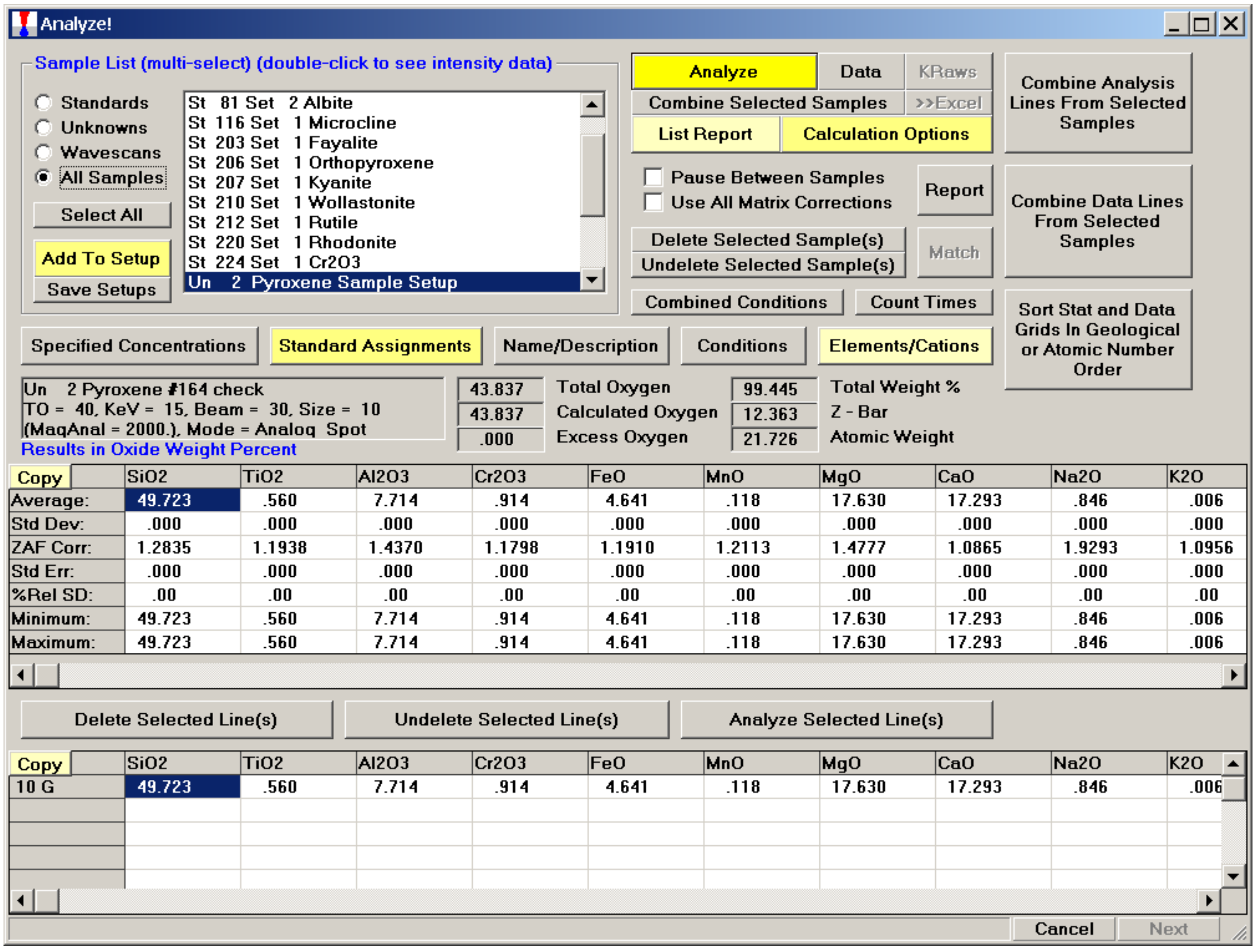
Sample Setups

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. However, because counting time and the associated unknown count factor is treated by PROBE FOR EPMA as data as opposed to setup information, it is necessary (if the user wants this information to be carried over) to acquire at least one data point with the sample setup prior to saving it as a 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. And finally, a pyroxene standard is run once to update count time information.

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



```
St  81 Set  2 Albite
St 116 Set  1 Microcline
St 203 Set  1 Fayalite
St 206 Set  1 Orthopyroxene
St 207 Set  1 Kyanite
St 210 Set  1 Wollastonite
St 212 Set  1 Rutile
St 220 Set  1 Rhodonite
St 224 Set  1 Cr2O3
Un   2 Pyroxene Sample Setup
```

```
Un    2 Pyroxene #164 check
TO =  40. KeV =  15. Beam =  30. Size =  10
(MagAnal = 2000.). Mode = Analog  Spot
```

Results in Oxide Weight Percent

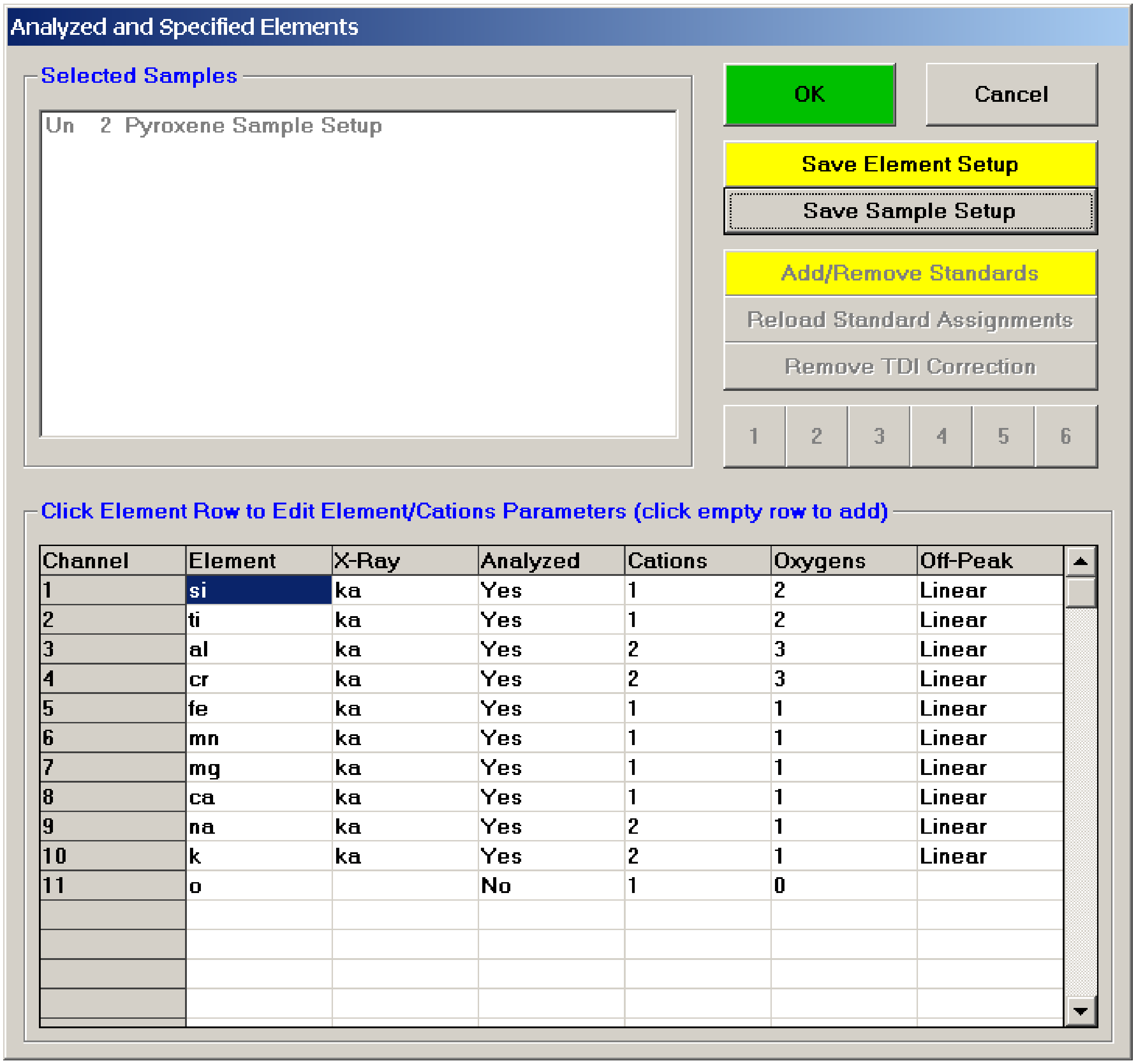
43.837	Total Oxygen	99.445	Total Weight %
43.837	Calculated Oxygen	12.363	Z - Bar
.000	Excess Oxygen	21.726	Atomic Weight

Copy	SiO2	TiO2	Al2O3	Cr2O3	FeO	MnO	MgO	CaO	Na2O	K2O
Average:	49.723	.560	7.714	.914	4.641	.118	17.630	17.293	.846	.006
Std Dev:	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
ZAF Corr:	1.2835	1.1938	1.4370	1.1798	1.1910	1.2113	1.4777	1.0865	1.9293	1.0956
Std Err:	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
%Rel SD:	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
Minimum:	49.723	.560	7.714	.914	4.641	.118	17.630	17.293	.846	.006
Maximum:	49.723	.560	7.714	.914	4.641	.118	17.630	17.293	.846	.006

Copy	SiO2	TiO2	Al2O3	Cr2O3	FeO	MnO	MgO	CaO	Na2O	K2O
10 G	49.723	.560	7.714	.914	4.641	.118	17.630	17.293	.846	.006

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

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

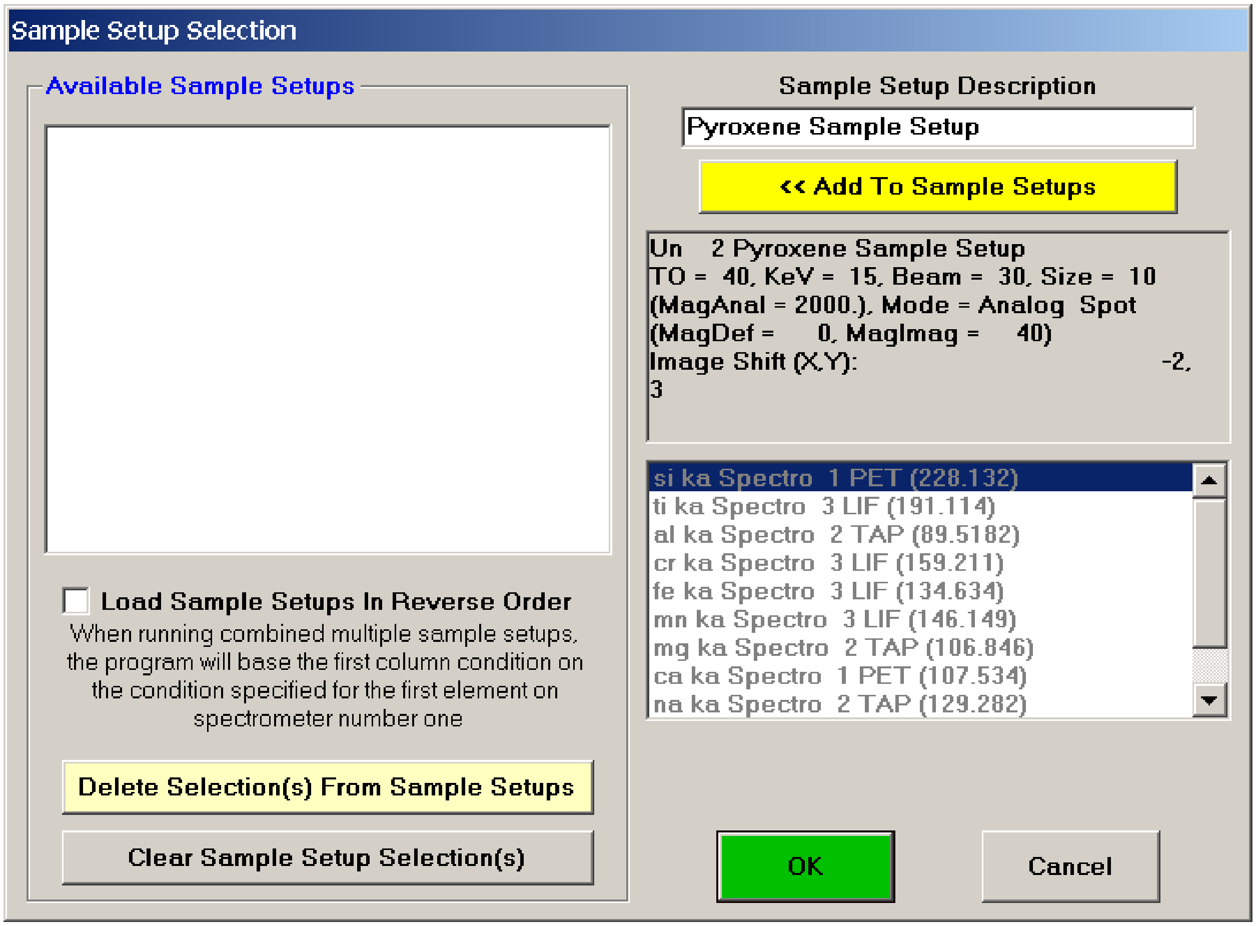


Un 2 Pyroxene Sample Setup

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	Linear
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.



Sample Setup Description: Pyroxene Sample Setup

```
Un    2 Pyroxene Sample Setup
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =      0, MagImag =     40)
Image Shift (X,Y):                         -2,
3
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
cr ka Spectro  3 LIF (159.211)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
na ka Spectro  2 TAP (129.282)
```

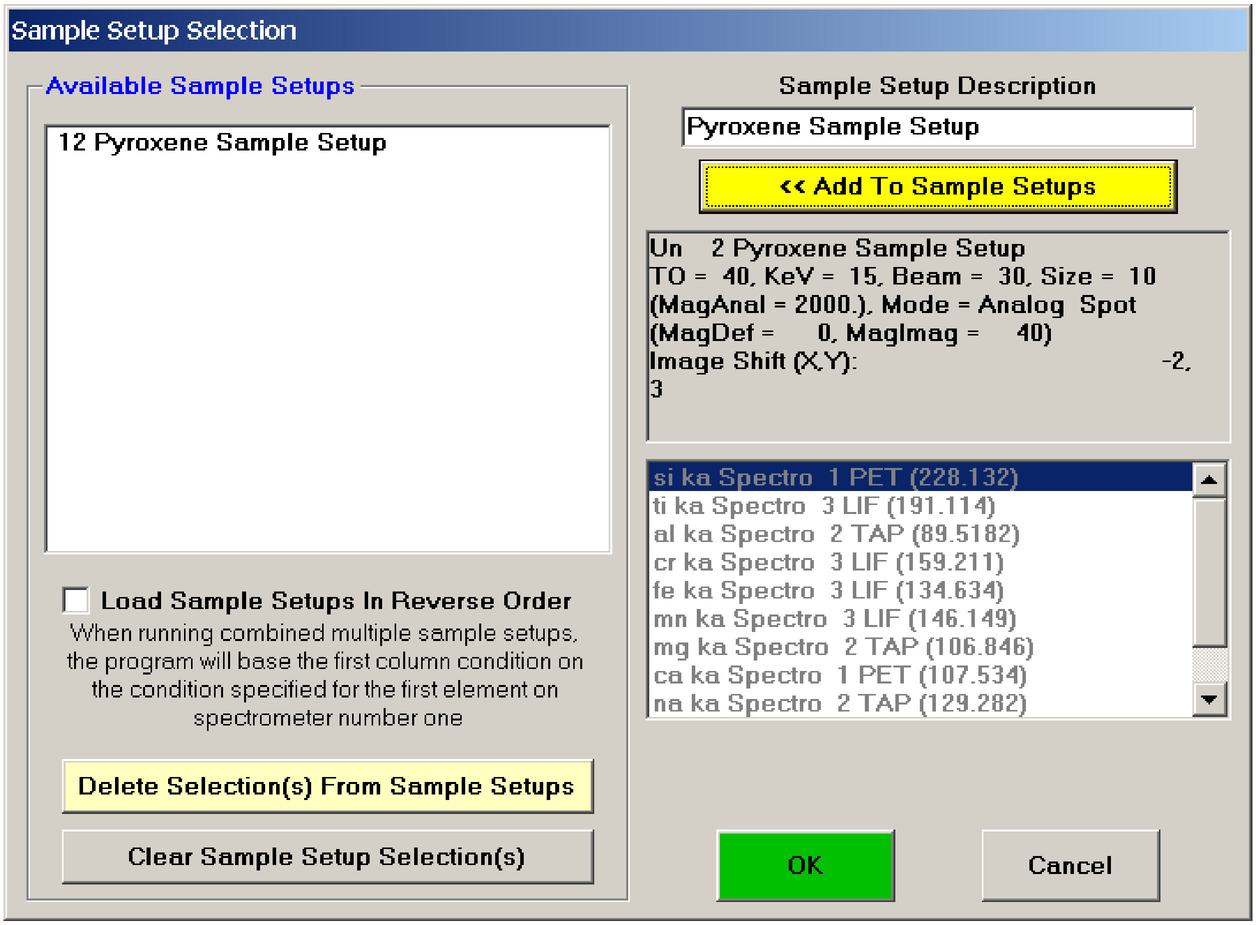
☐ Load Sample Setups In Reverse Order

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

Edit the *Sample Setup Description* text box as desired.

Click the **<< Add To Sample Setups** button.

The **Sample Setup Selection** window appears as below. Note: the first number (12) represents the sample's row number and can be seen listed using the **Run | List Sample Rows, Names, Conditions** menu.



12 Pyroxene Sample Setup

Pyroxene Sample Setup

```
Un    2 Pyroxene Sample Setup
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =      0, MagImag =     40)
Image Shift (X,Y):                           -2,
3
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
cr ka Spectro  3 LIF (159.211)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
na ka Spectro  2 TAP (129.282)
```

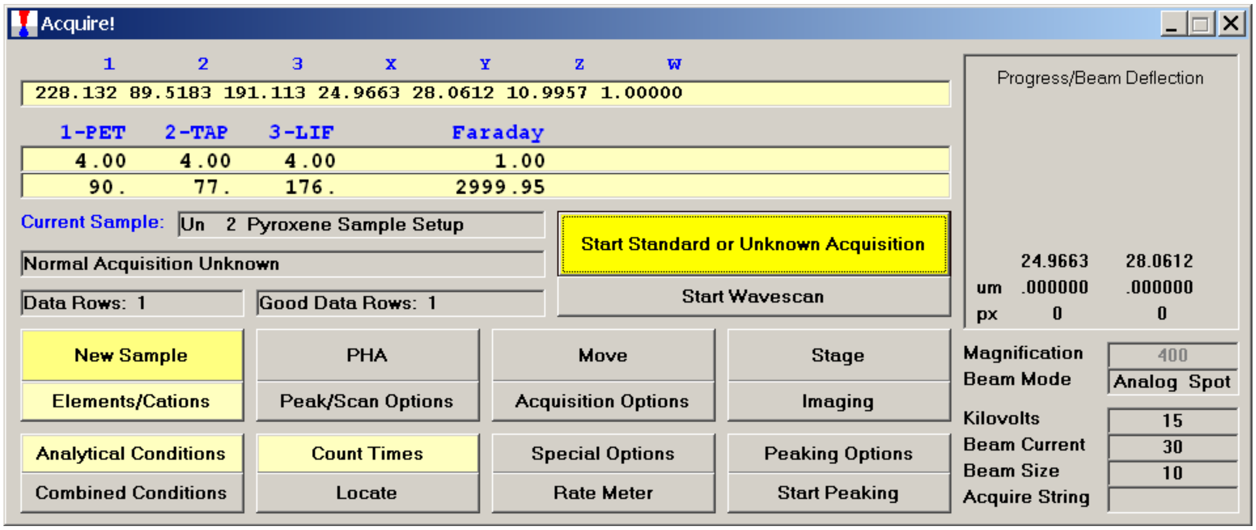
☐ Load Sample Setups In Reverse Order

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, 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.



1	2	3	X	Y	Z	W
228.132	89.5183	191.113	24.9663	28.0612	10.9957	1.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	4.00	1.00
90.	77.	176.	2999.95

Current Sample: Un 2 Pyroxene Sample Setup

Normal Acquisition Unknown

Data Rows: 1

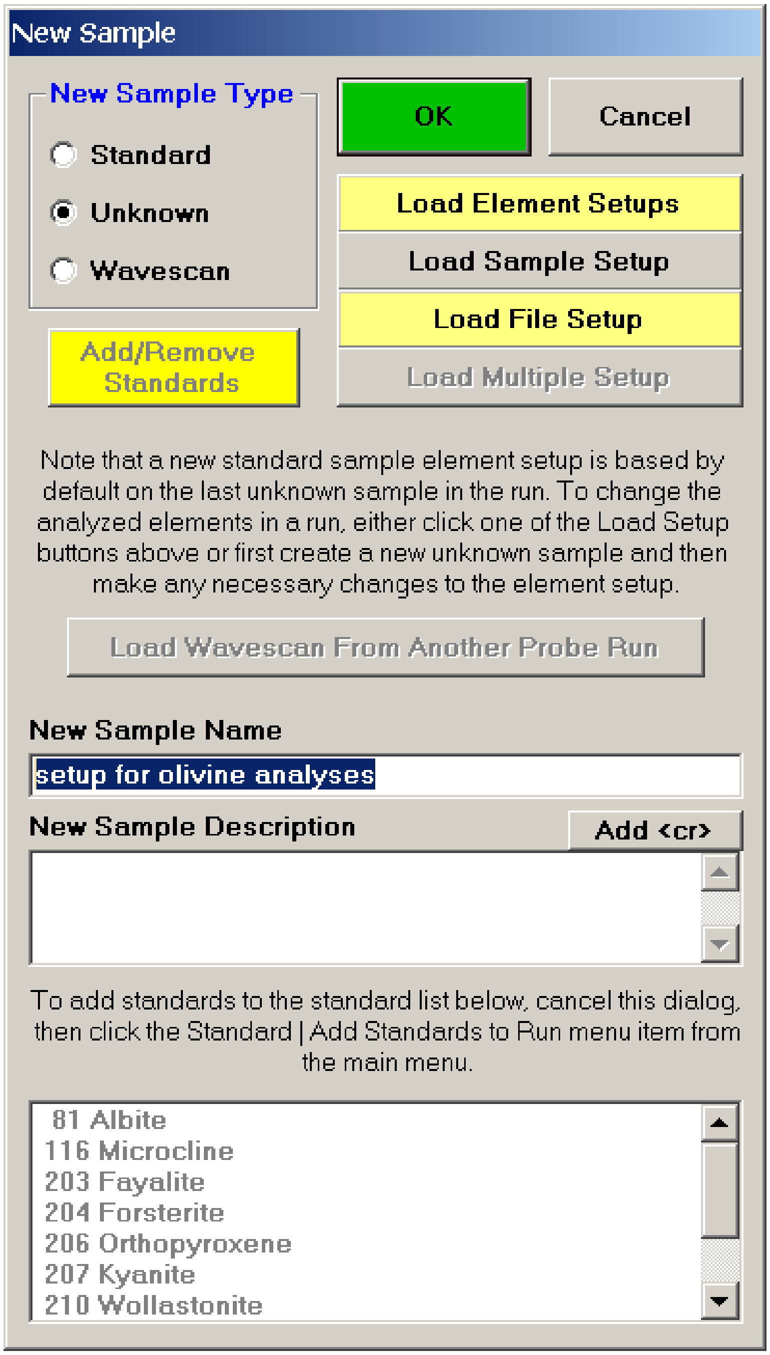
Good Data Rows: 1

	24.9663	28.0612
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	30
Beam Size	10
Acquire String	

Click the **New Sample** button.

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



○ 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: setup for olivine analyses

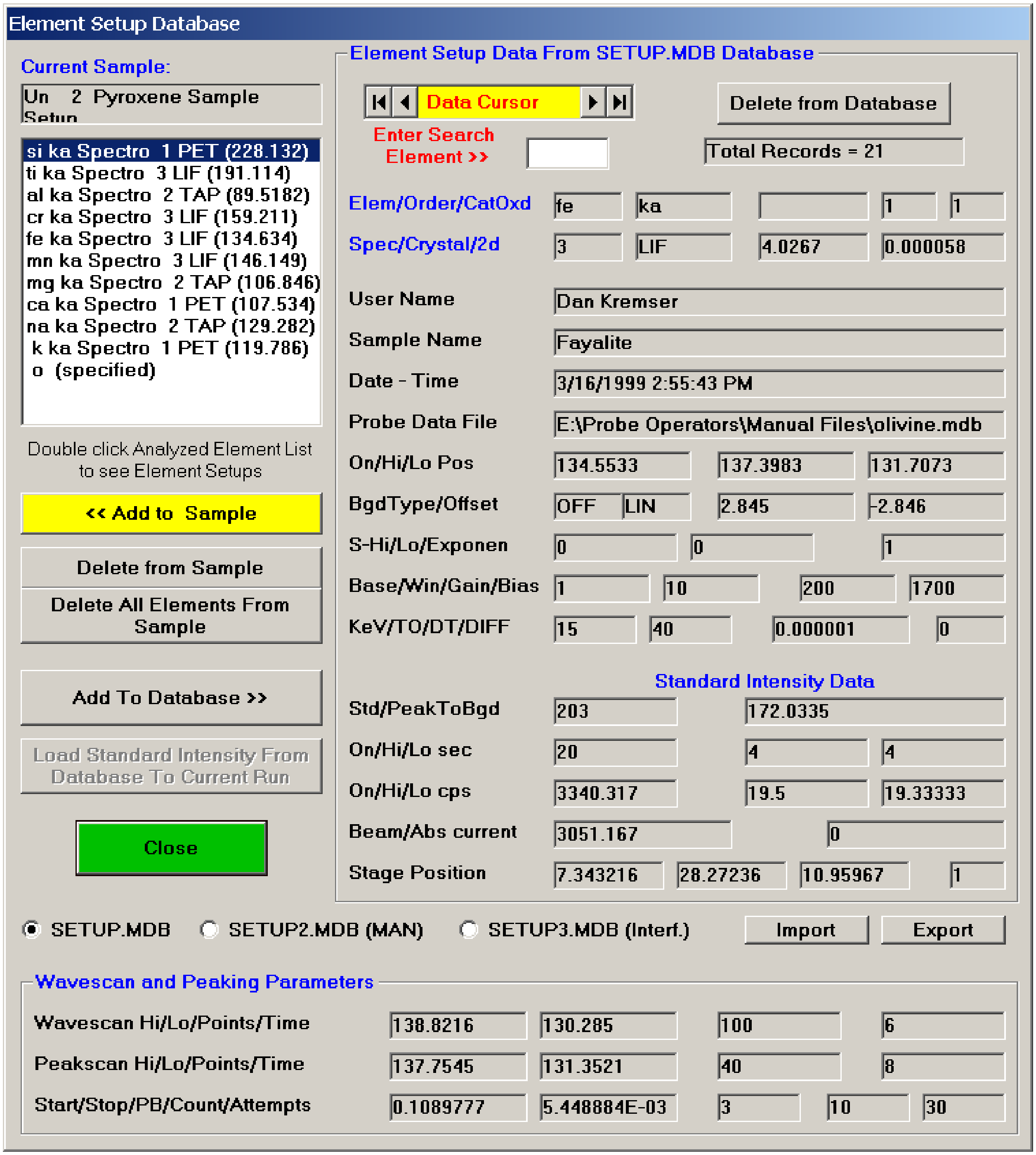
To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

81 Albite
116 Microcline
203 Fayalite
204 Forsterite
206 Orthopyroxene
207 Kyanite
210 Wollastonite

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 2 Pyroxene Sample Setup

si ka Spectro 1 PET (228.132)
ti ka Spectro 3 LIF (191.114)
al ka Spectro 2 TAP (89.5182)
cr ka Spectro 3 LIF (159.211)
fe ka Spectro 3 LIF (134.634)
mn ka Spectro 3 LIF (146.149)
mg ka Spectro 2 TAP (106.846)
ca ka Spectro 1 PET (107.534)
na ka Spectro 2 TAP (129.282)
k ka Spectro 1 PET (119.786)
o (specified)

Double click Analyzed Element List to see Element Setups

Element Setup Data From SETUP.MDB Database

Total Records = 21

Elem/Order/CatOxd	fe	ka		1	1
Spec/Crystal/2d	3	LIF	4.0267	0.000058	
User Name	Dan Kremser				
Sample Name	Fayalite				
Date - Time	3/16/1999 2:55:43 PM				
Probe Data File	E:\Probe Operators\Manual Files\olivine.mdb				
On/Hi/Lo Pos	134.5533	137.3983	131.7073		
BgdType/Offset	OFF	LIN	2.845	-2.846	
S-Hi/Lo/Exponen	0	0	1		
Base/Win/Gain/Bias	1	10	200	1700	
KeV/TO/DT/DIFF	15	40	0.000001	0	

Standard Intensity Data

Std/PeakToBgd	203	172.0335		
On/Hi/Lo sec	20	4	4	
On/Hi/Lo cps	3340.317	19.5	19.33333	
Beam/Abs current	3051.167	0		
Stage Position	7.343216	28.27236	10.95967	1

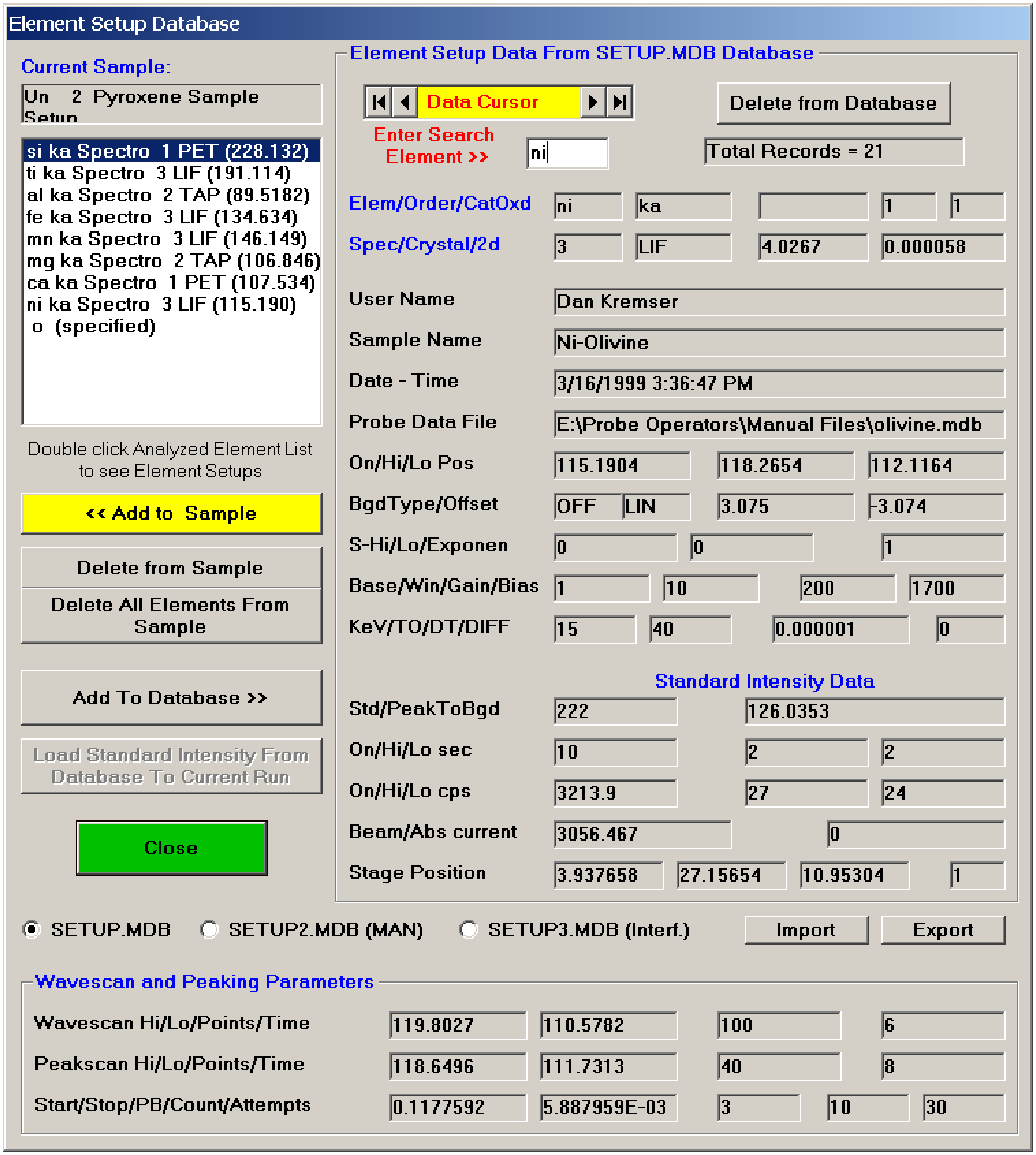
● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time	138.8216	130.285	100	6	
Peakscan Hi/Lo/Points/Time	137.7545	131.3521	40	8	
Start/Stop/PB/Count/Attempts	0.1089777	5.448884E-03	3	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).

After editing, the window appears as below.



Element Setup Database

Current Sample: Un 2 Pyroxene Sample Setup

si ka Spectro 1 PET (228.132)
ti ka Spectro 3 LIF (191.114)
al ka Spectro 2 TAP (89.5182)
fe ka Spectro 3 LIF (134.634)
mn ka Spectro 3 LIF (146.149)
mg ka Spectro 2 TAP (106.846)
ca ka Spectro 1 PET (107.534)
ni ka Spectro 3 LIF (115.190)
o (specified)

Double click Analyzed Element List to see Element Setups

Element Setup Data From SETUP.MDB Database

Enter Search Element >> ni
Total Records = 21

Elem/Order/CatOxd: ni, ka, , 1, 1
Spec/Crystal/2d: 3, LIF, 4.0267, 0.000058
User Name: Dan Kremser
Sample Name: Ni-Olivine
Date - Time: 3/16/1999 3:36:47 PM
Probe Data File: E:\Probe Operators\Manual Files\olivine.mdb
On/Hi/Lo Pos: 115.1904, 118.2654, 112.1164
BgdType/Offset: OFF, LIN, 3.075, -3.074
S-Hi/Lo/Exponen: 0, 0, 1
Base/Win/Gain/Bias: 1, 10, 200, 1700
KeV/TO/DT/DIFF: 15, 40, 0.000001, 0

Standard Intensity Data

Std/PeakToBgd: 222, 126.0353
On/Hi/Lo sec: 10, 2, 2
On/Hi/Lo cps: 3213.9, 27, 24
Beam/Abs current: 3056.467, 0
Stage Position: 3.937658, 27.15654, 10.95304, 1

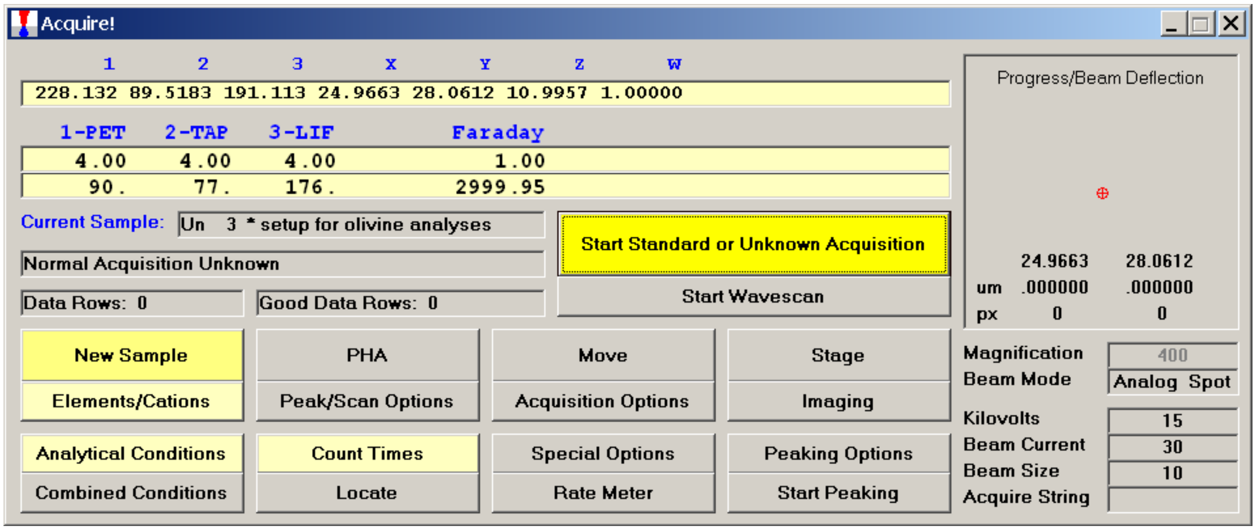
● SETUP.MDB ○ SETUP2.MDB (MAN) ○ SETUP3.MDB (Interf.)

Wavescan and Peaking Parameters

Wavescan Hi/Lo/Points/Time: 119.8027, 110.5782, 100, 6
Peakscan Hi/Lo/Points/Time: 118.6496, 111.7313, 40, 8
Start/Stop/PB/Count/Attempts: 0.1177592, 5.887959E-03, 3, 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.



1	2	3	X	Y	Z	W
228.132	89.5183	191.113	24.9663	28.0612	10.9957	1.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	4.00	1.00
90.	77.	176.	2999.95

Current Sample: Un 3 * setup for olivine analyses

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

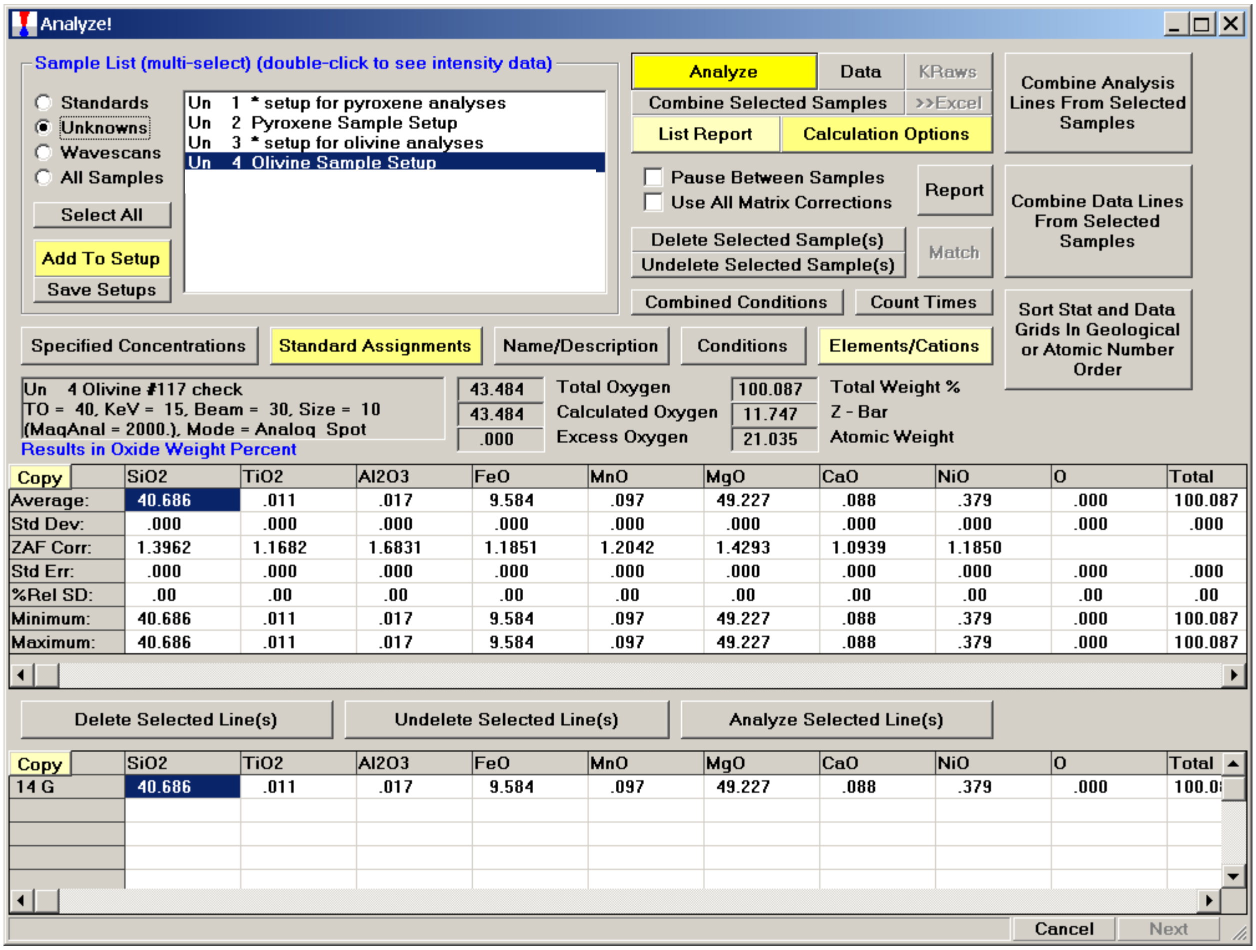
	24.9663	28.0612
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	30
Beam Size	10
Acquire String	

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. Run an olivine standard to obtain data and check the calibration.

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



Un 1 * setup for pyroxene analyses
Un 2 Pyroxene Sample Setup
Un 3 * setup for olivine analyses
Un 4 Olivine Sample Setup

Un 4 Olivine #117 check
TO = 40, KeV = 15, Beam = 30, Size = 10
(MagAnal = 2000.), Mode = Analog Spot
Results in Oxide Weight Percent

43.484 Total Oxygen
43.484 Calculated Oxygen
.000 Excess Oxygen
100.087 Total Weight %
11.747 Z - Bar
21.035 Atomic Weight

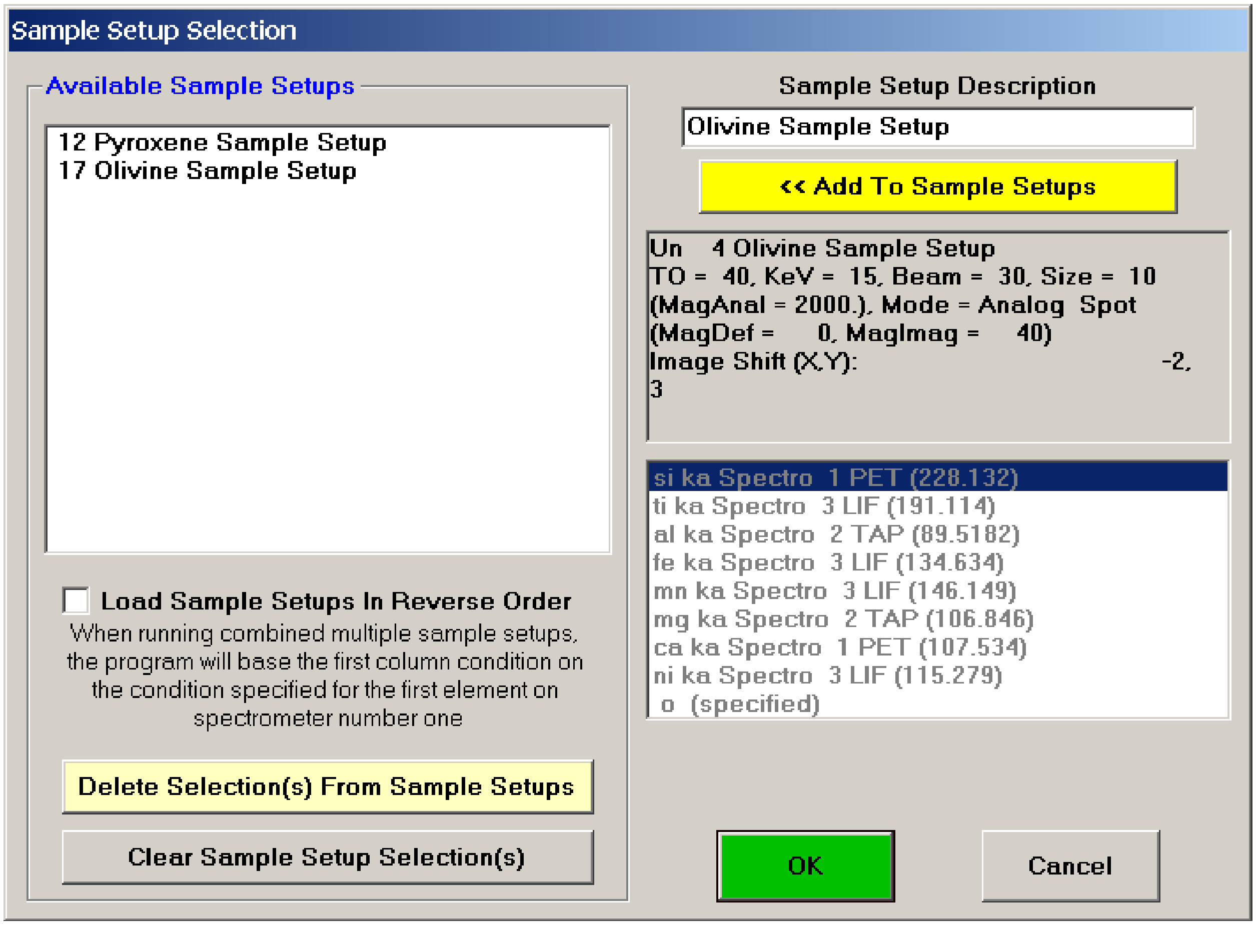
Copy	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	NiO	O	Total
Average:	40.686	.011	.017	9.584	.097	49.227	.088	.379	.000	100.087
Std Dev:	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
ZAF Corr:	1.3962	1.1682	1.6831	1.1851	1.2042	1.4293	1.0939	1.1850		
Std Err:	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
%Rel SD:	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
Minimum:	40.686	.011	.017	9.584	.097	49.227	.088	.379	.000	100.087
Maximum:	40.686	.011	.017	9.584	.097	49.227	.088	.379	.000	100.087

Copy	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	NiO	O	Total
14 G	40.686	.011	.017	9.584	.097	49.227	.088	.379	.000	100.0

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. If the user wishes to modify the *Sample Setup Description* either change the label using the **Name/Description** button in the **Analyze!** window before clicking the **Add To Sample Setups** button or from the **Sample Setup Selection** window, delete the just loaded selection (highlight the appropriate selection) and then edit the *Sample Setup Description* text field and click the **<< Add To Sample Setups** button, storing the Olivine setup along with the previously stored Pyroxene setup.



12 Pyroxene Sample Setup
17 Olivine Sample 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 Sample Setup

```
Un    4 Olivine Sample Setup
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =      0, MagImag =     40)
Image Shift (X,Y):                          -2,
3
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
ni ka Spectro  3 LIF (115.279)
 o  (specified)
```

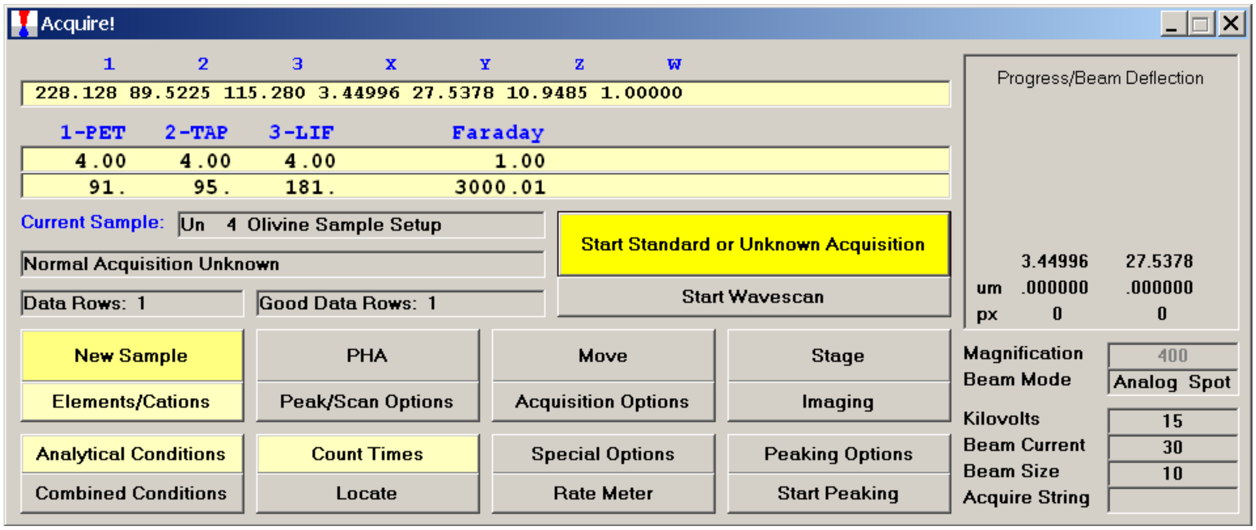
Click the **OK** button of the **Sample Setup Selection** window returning to the **Analyzed and Specified Elements** window.

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.



1	2	3	X	Y	Z	W
228.128	89.5225	115.280	3.44996	27.5378	10.9485	1.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	4.00	1.00
91.	95.	181.	3000.01

Current Sample: Un 4 Olivine Sample Setup

Normal Acquisition Unknown

Data Rows: 1

Good Data Rows: 1

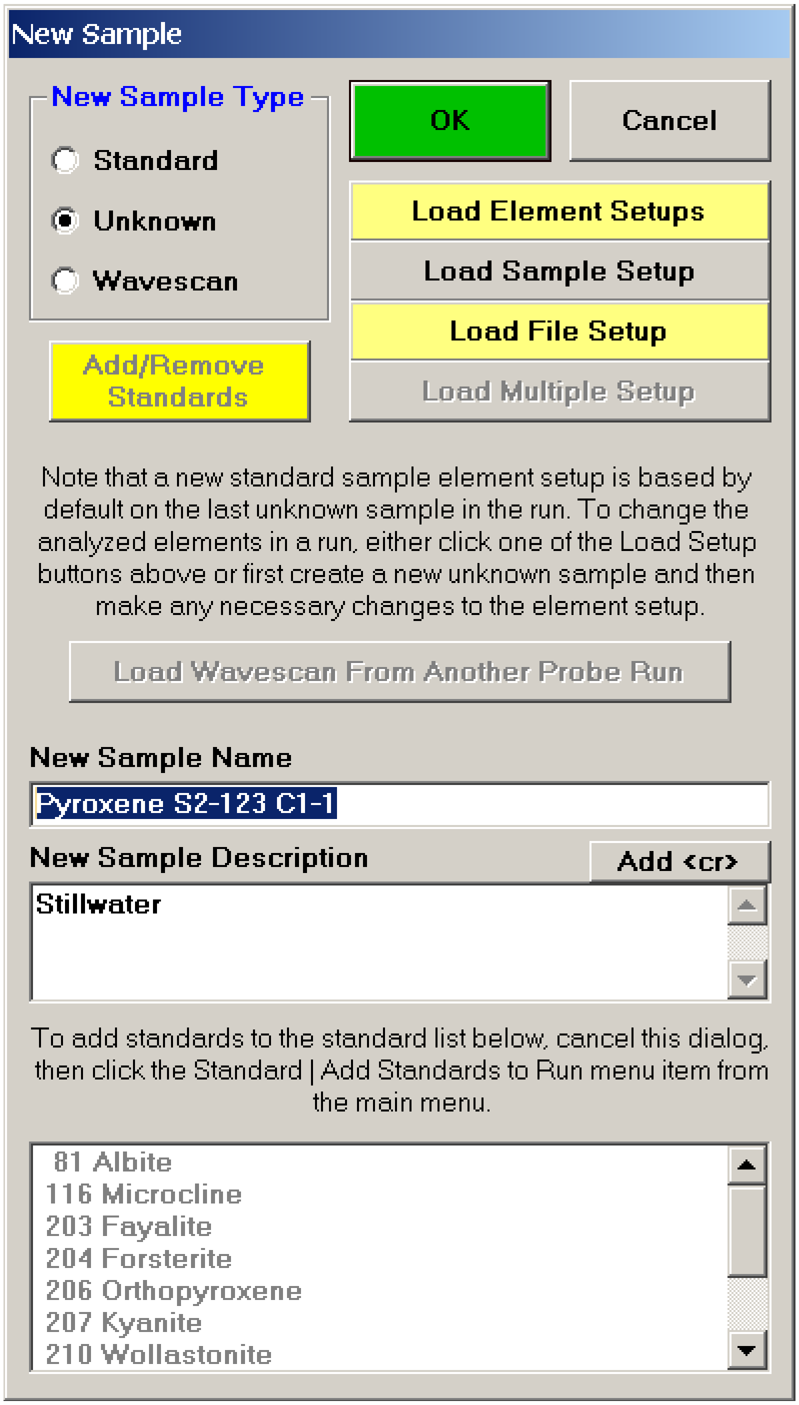
Progress/Beam Deflection

	3.44996	27.5378
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	30
Beam Size	10
Acquire String	

Click the **New Sample** button.

The **New Sample** window opens. Enter the appropriate text into the *New Sample Name* and *New Sample Description* 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: Pyroxene S2-123 C1-1

New Sample Description: Stillwater

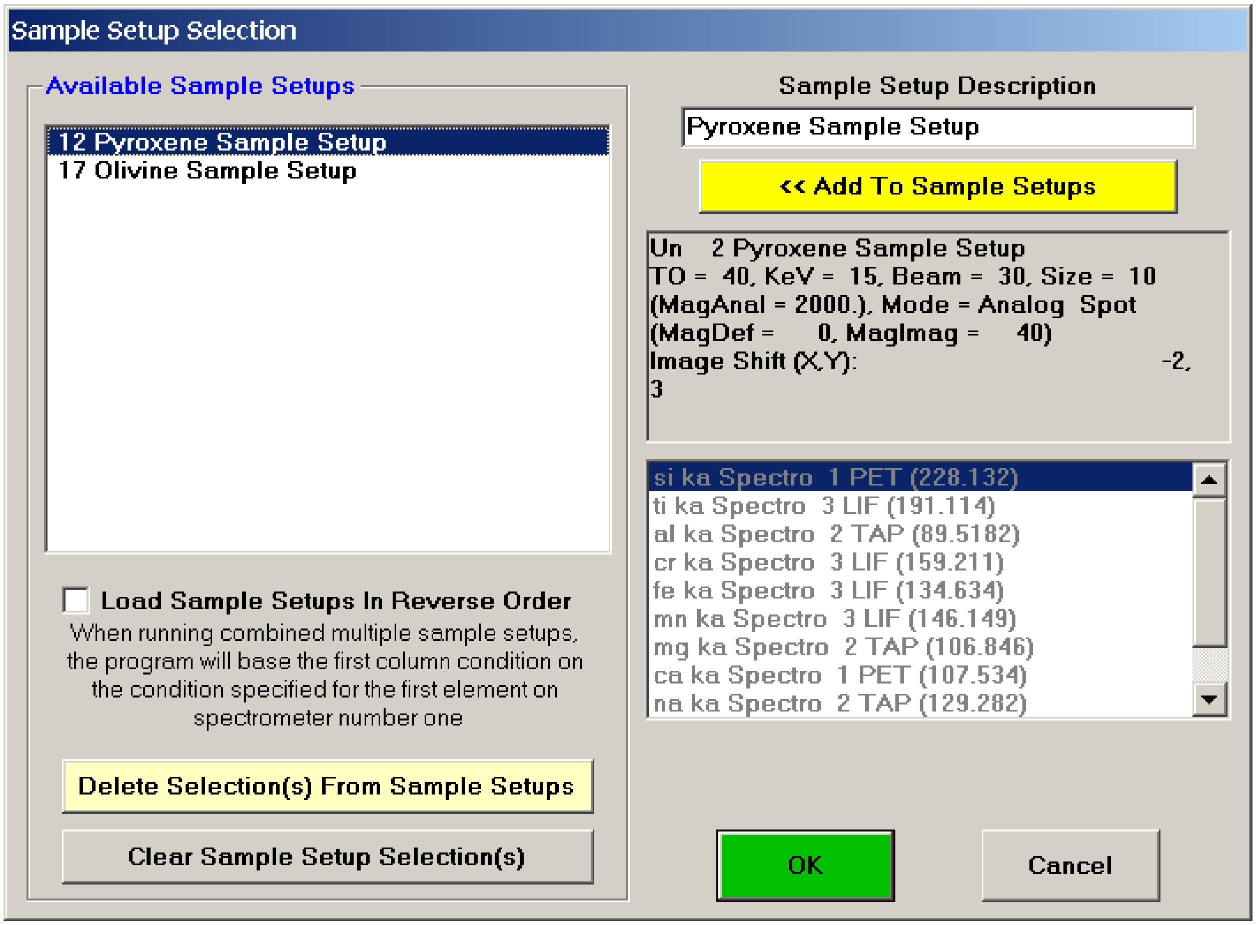
To add standards to the standard list below, cancel this dialog, then click the Standard | Add Standards to Run menu item from the main menu.

81 Albite
116 Microcline
203 Fayalite
204 Forsterite
206 Orthopyroxene
207 Kyanite
210 Wollastonite

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.



12 Pyroxene Sample Setup
17 Olivine Sample Setup

Sample Setup Description: Pyroxene Sample Setup

```
Un    2 Pyroxene Sample Setup
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =      0, MagImag =     40)
Image Shift (X,Y):                        -2,
3
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
cr ka Spectro  3 LIF (159.211)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
na ka Spectro  2 TAP (129.282)
```

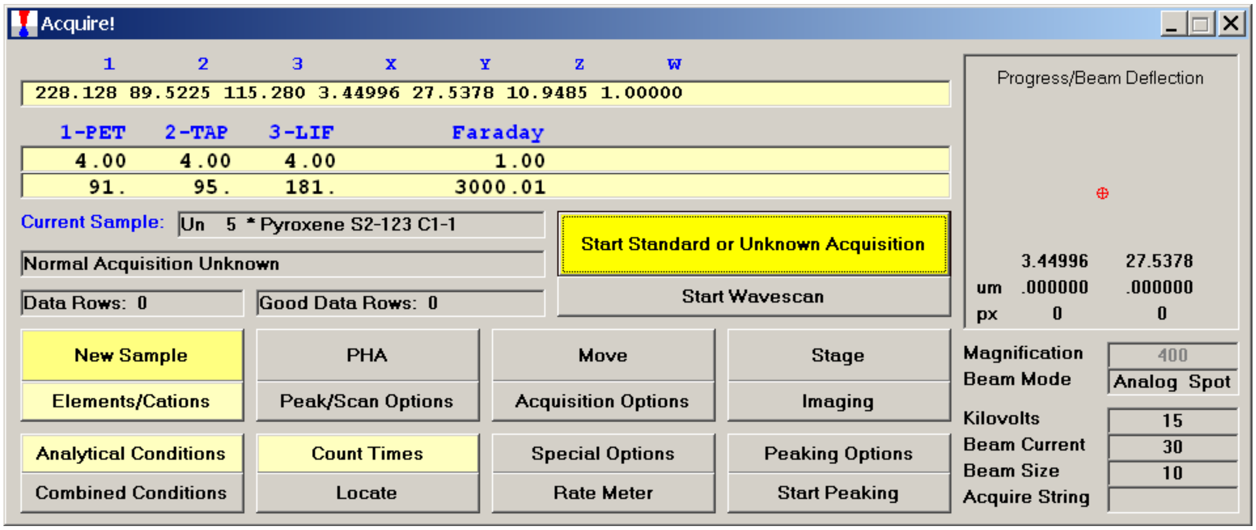
☐ Load Sample Setups In Reverse Order

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.



1	2	3	X	Y	Z	W
228.128	89.5225	115.280	3.44996	27.5378	10.9485	1.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	4.00	1.00
91.	95.	181.	3000.01

Current Sample: Un 5 * Pyroxene S2-123 C1-1

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

	3.44996	27.5378
um	.000000	.000000
px	0	0

Magnification 400

Beam Mode Analog Spot

Kilovolts 15

Beam Current 30

Beam Size 10

Acquire String

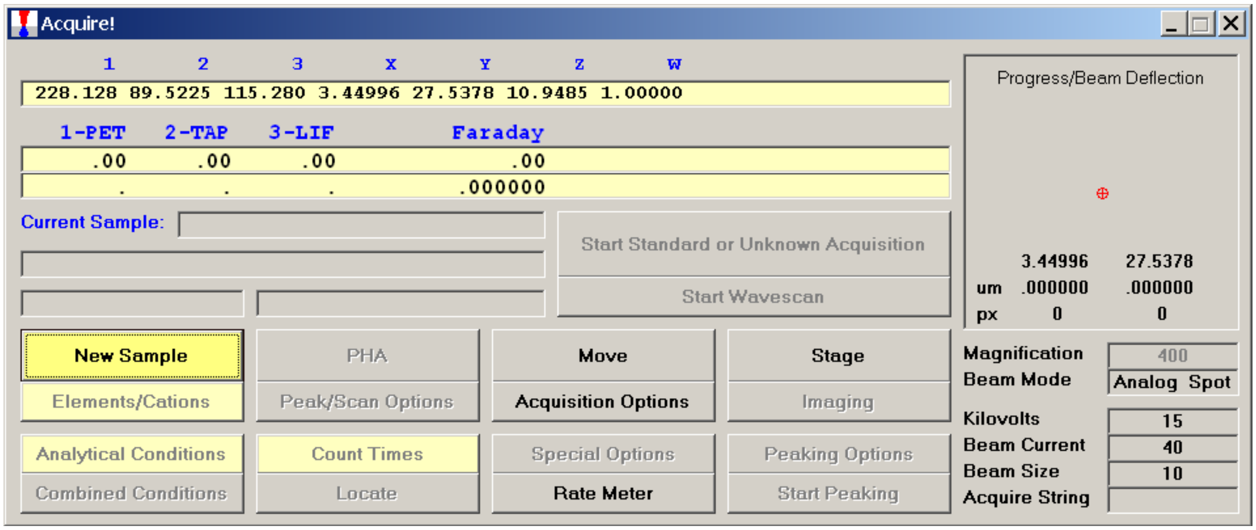
Double check your spot selection and focus and click the **Start Standard or Unknown Acquisition** button to initiate data acquisition.

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.

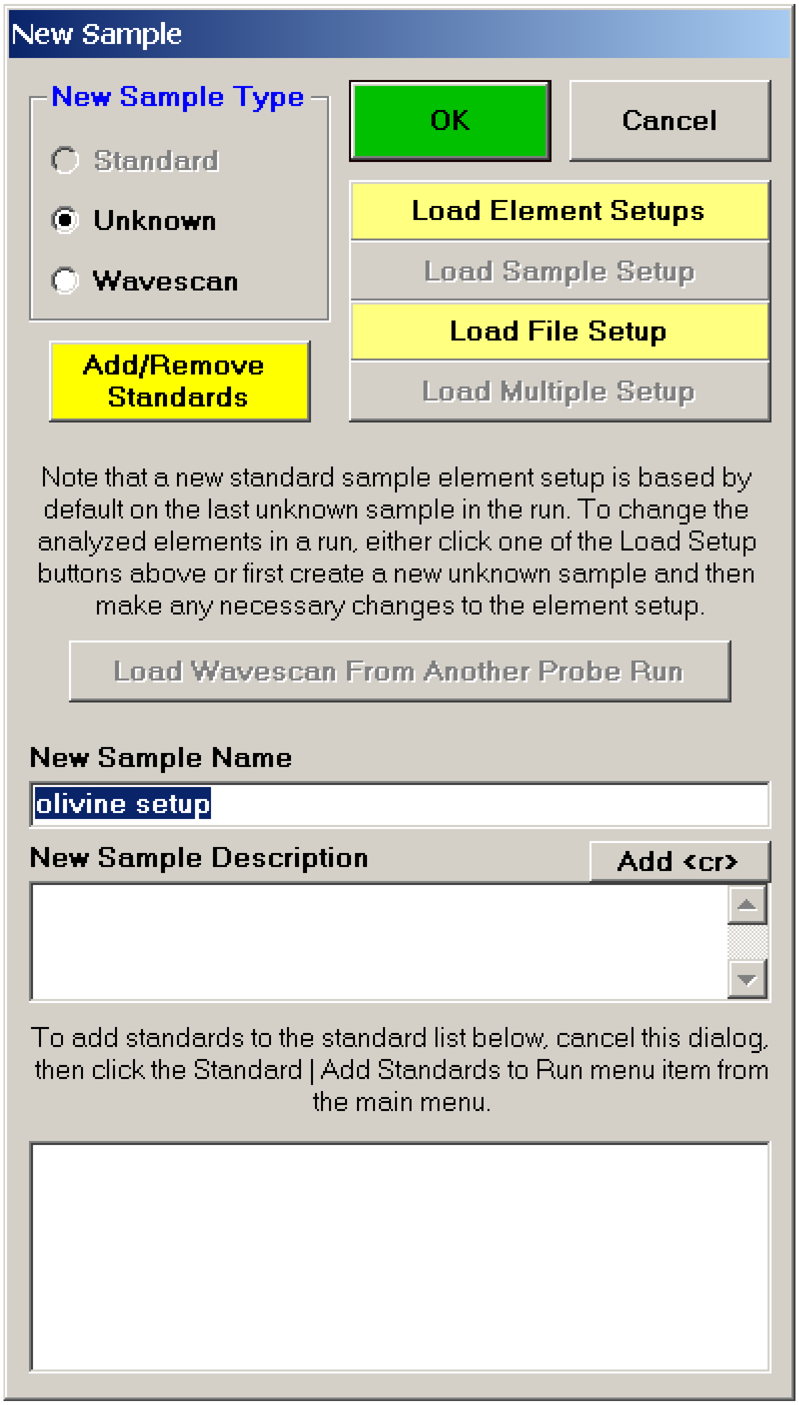


```
   1       2       3       X       Y       Z       W
228.128 89.5225 115.280 3.44996 27.5378 10.9485 1.00000

  1-PET   2-TAP   3-LIF            Faraday
     .00     .00     .00               .00
       .       .       .           .000000
```

```
      3.44996   27.5378
um    .000000   .000000
px          0         0
```

Magnification 400
Beam Mode Analog Spot
Kilovolts 15
Beam Current 40
Beam Size 10
Acquire String

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



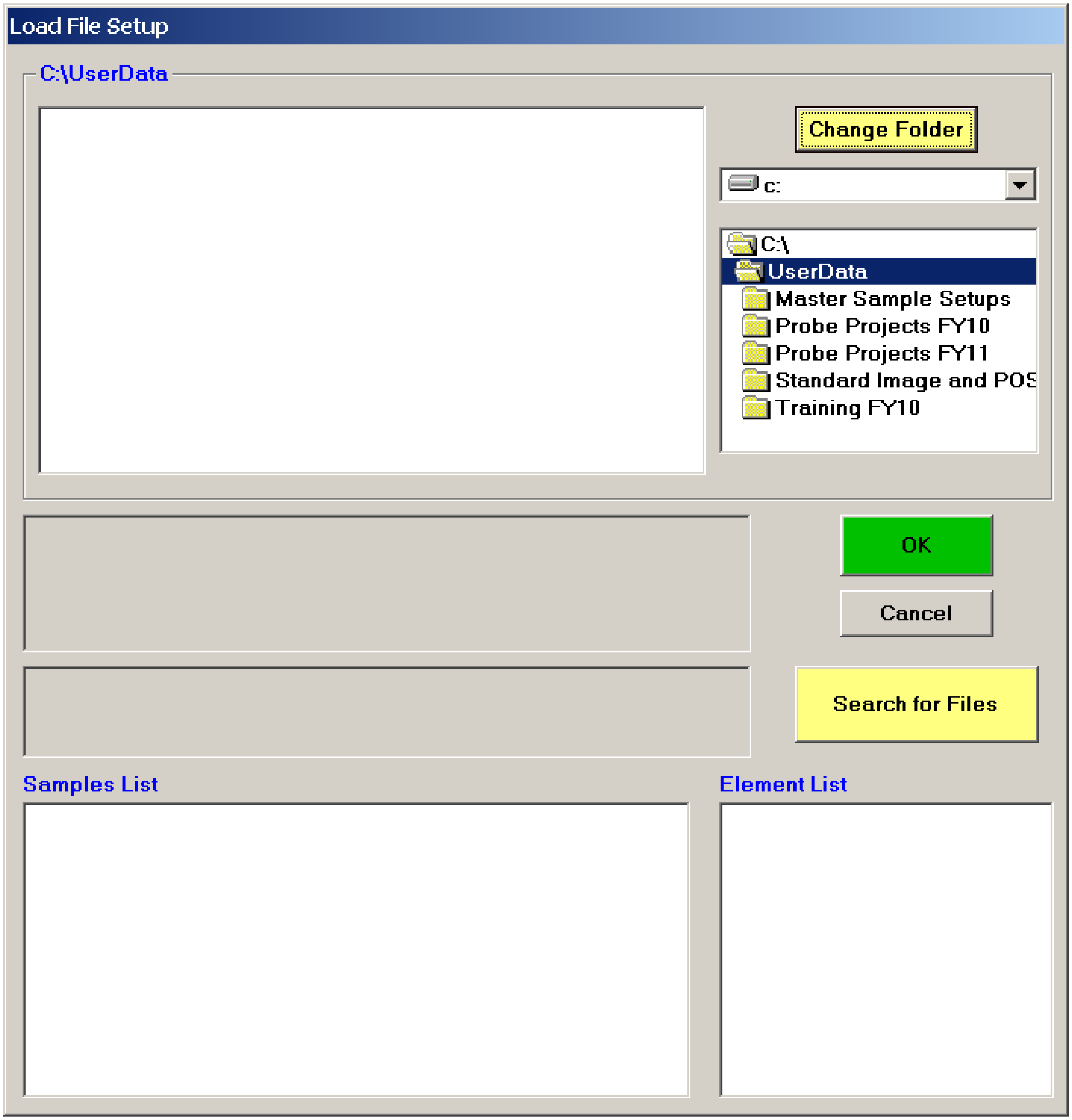
Note that a new standard sample element setup is based by default on the last unknown sample in the run. To change the analyzed elements in a run, either click one of the Load Setup buttons above or first create a new unknown sample and then make any necessary changes to the element setup.

New Sample Name: olivine setup

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.

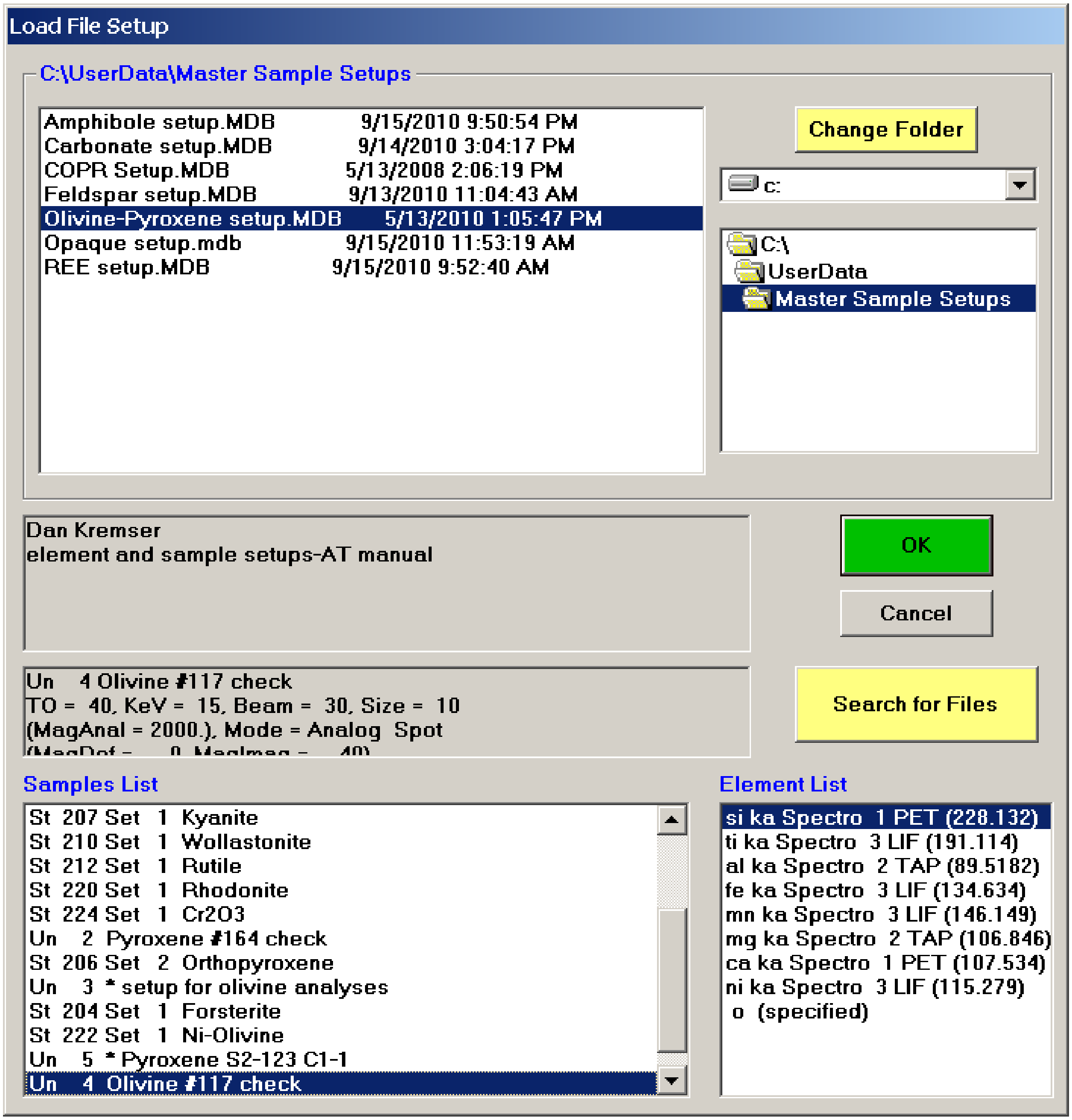
Click the **Load File Setup** button.

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.



In this example, the file STILLWATER OL-PX.MDB was newly created and the user will load both an olivine and a pyroxene sample setup into this file.

Scroll through the available Probe Run Files list and highlight the file to load from. The last sample 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.



```
Amphibole setup.MDB          9/15/2010 9:50:54 PM
Carbonate setup.MDB          9/14/2010 3:04:17 PM
COPR Setup.MDB               5/13/2008 2:06:19 PM
Feldspar setup.MDB           9/13/2010 11:04:43 AM
Olivine-Pyroxene setup.MDB   5/13/2010 1:05:47 PM
Opaque setup.mdb             9/15/2010 11:53:19 AM
REE setup.MDB                9/15/2010 9:52:40 AM
```

```
Dan Kremser
element and sample setups-AT manual
```

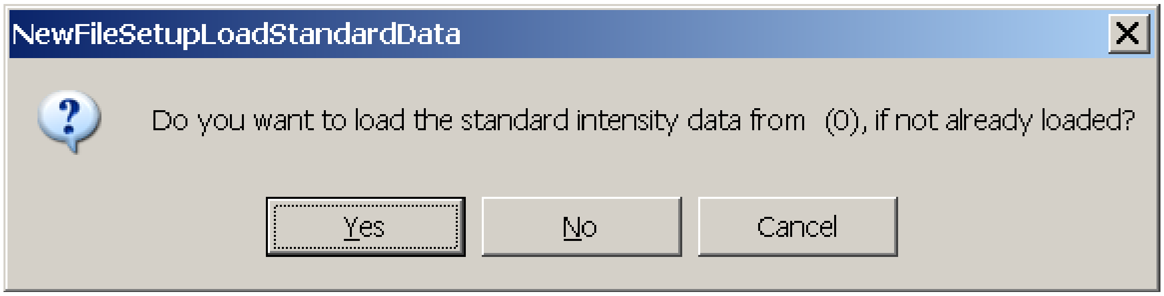
```
Un    4 Olivine #117 check
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
```

```
St  207 Set   1  Kyanite
St  210 Set   1  Wollastonite
St  212 Set   1  Rutile
St  220 Set   1  Rhodonite
St  224 Set   1  Cr2O3
Un    2  Pyroxene #164 check
St  206 Set   2  Orthopyroxene
Un    3  * setup for olivine analyses
St  204 Set   1  Forsterite
St  222 Set   1  Ni-Olivine
Un    5  * Pyroxene S2-123 C1-1
Un    4  Olivine #117 check
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
ni ka Spectro  3 LIF (115.279)
 o  (specified)
```

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

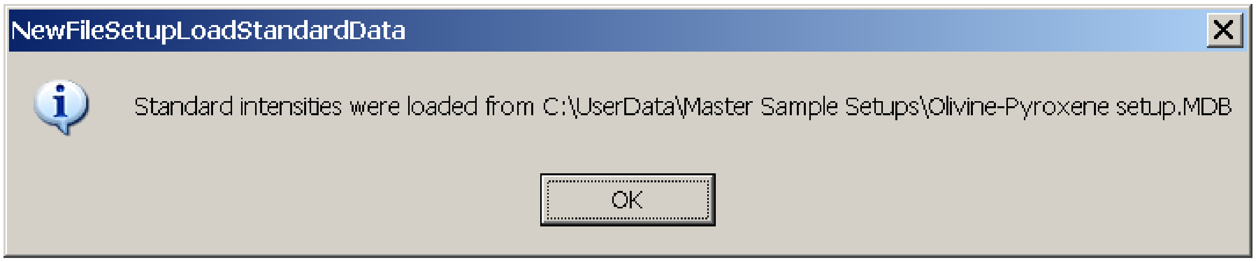
The **NewFileSetupLoadStandardData** window appears next, asking whether the user wants the previous standard intensity data to be loaded as well.



Do you want to load the standard intensity data from (0), 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.

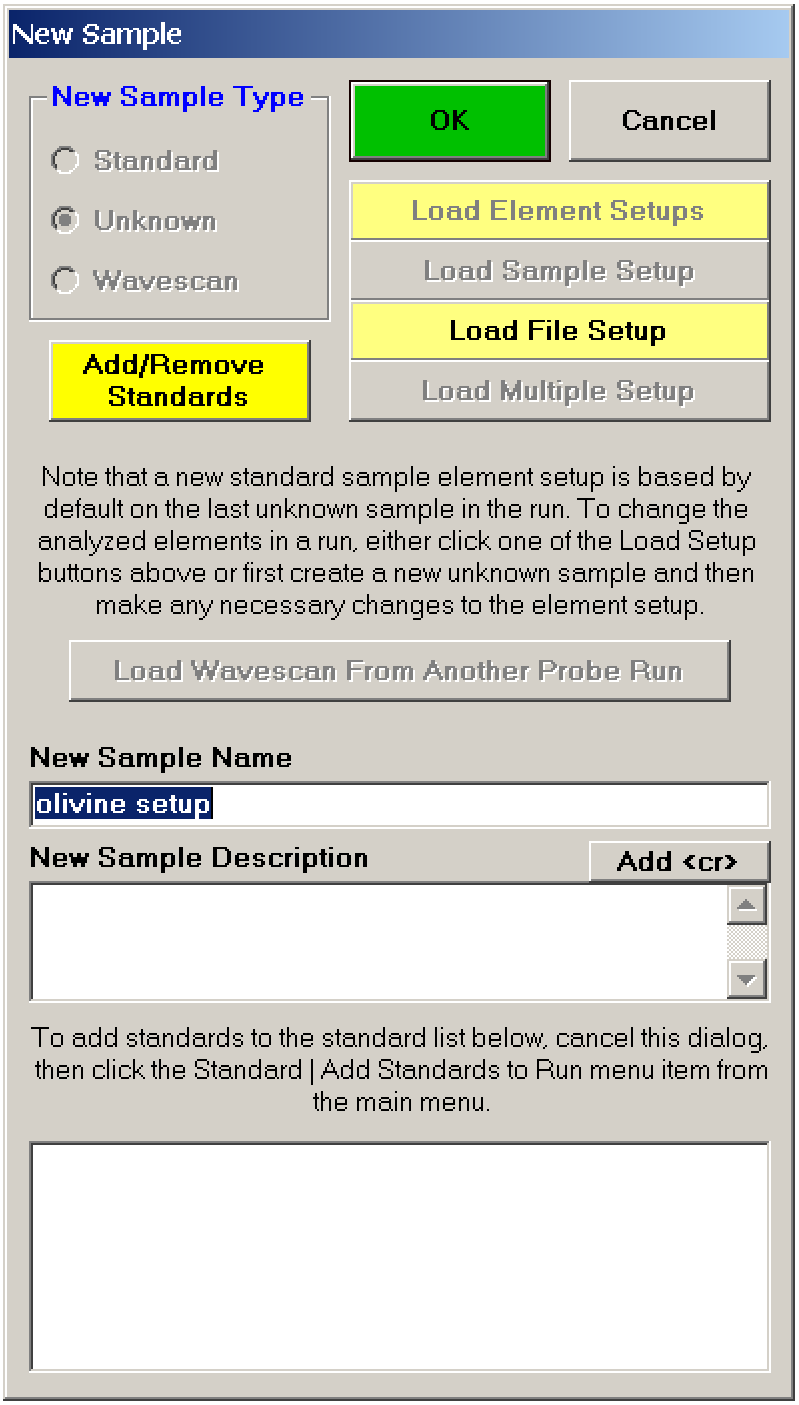
The **NewFileSetupLoadStandardData** window appears.



Standard intensities were loaded from C:\UserData\Master Sample Setups\Olivine-Pyroxene setup.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.

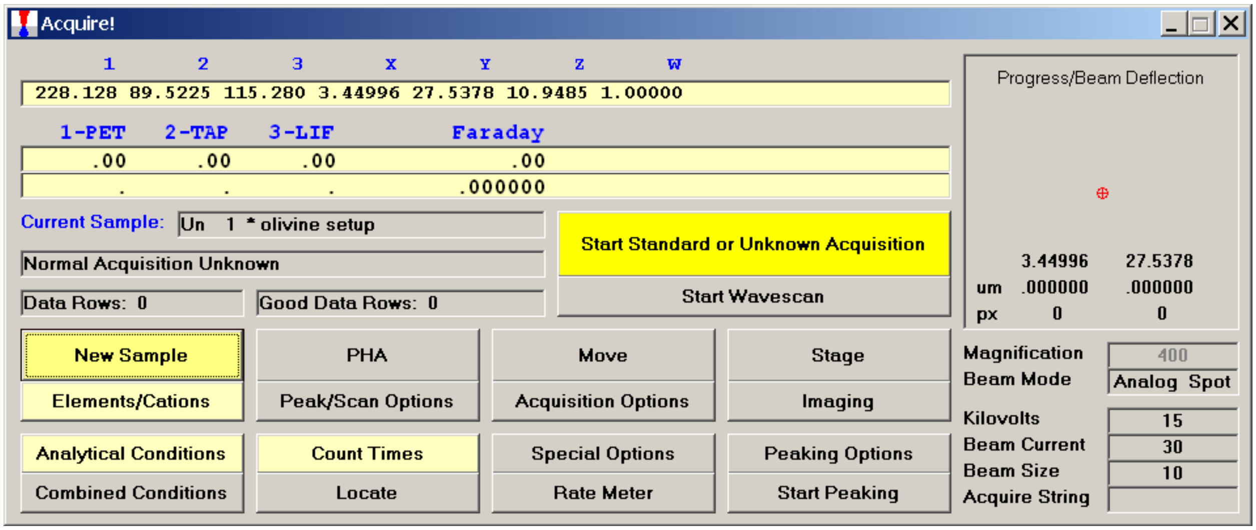
New Sample Name: olivine setup

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.

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.



```
   1        2        3        X        Y        Z        W
228.128  89.5225  115.280  3.44996  27.5378  10.9485  1.00000

  1-PET    2-TAP    3-LIF              Faraday
    .00      .00      .00                  .00
      .        .        .            .000000
```

Current Sample: Un 1 * olivine setup

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

```
        3.44996    27.5378
um     .000000    .000000
px           0          0
```

Magnification 400

Beam Mode Analog Spot

Kilovolts 15

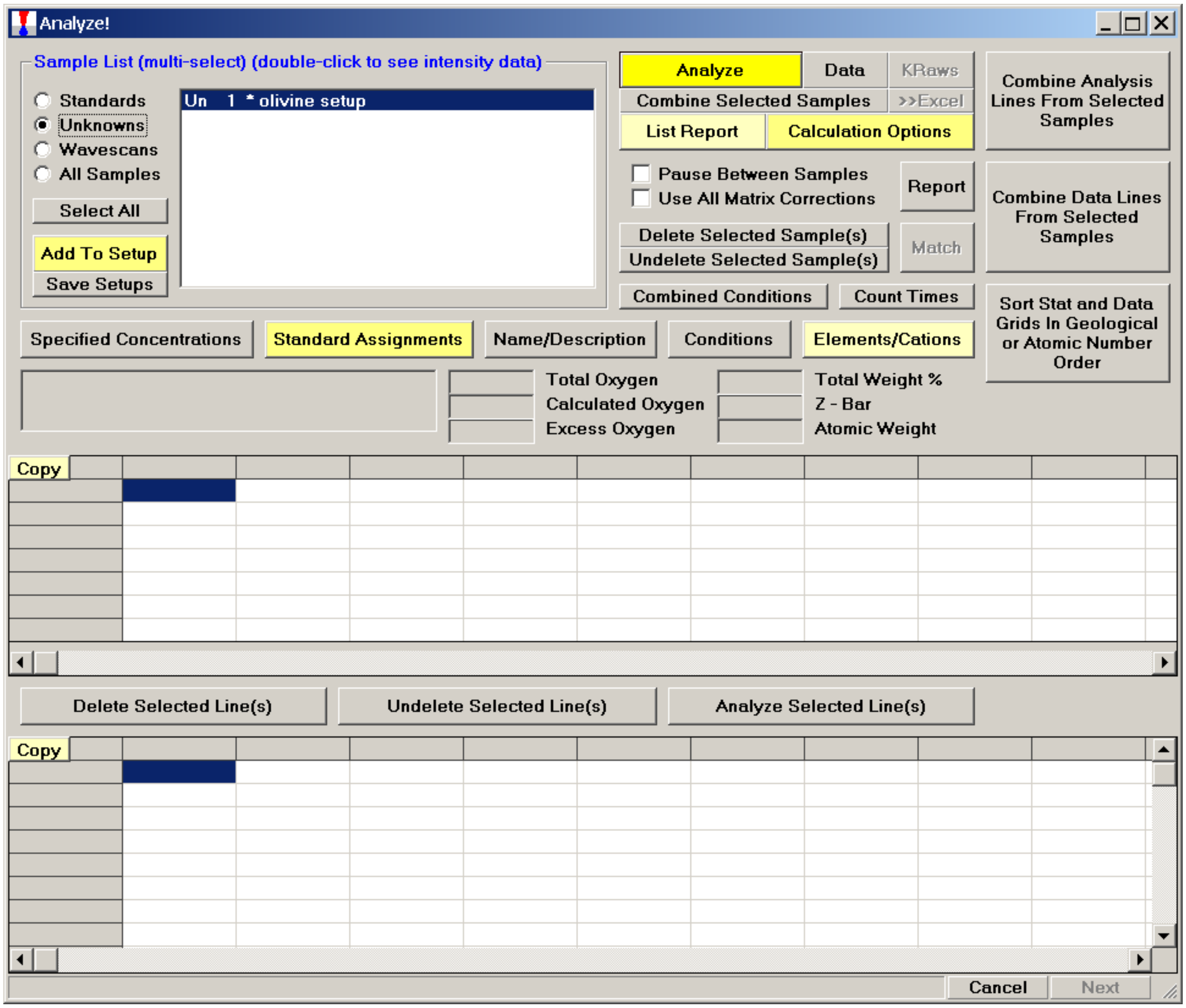
Beam Current 30

Beam Size 10

Acquire String

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.



● Unknowns

Un 1 * olivine setup

☐ Pause Between Samples

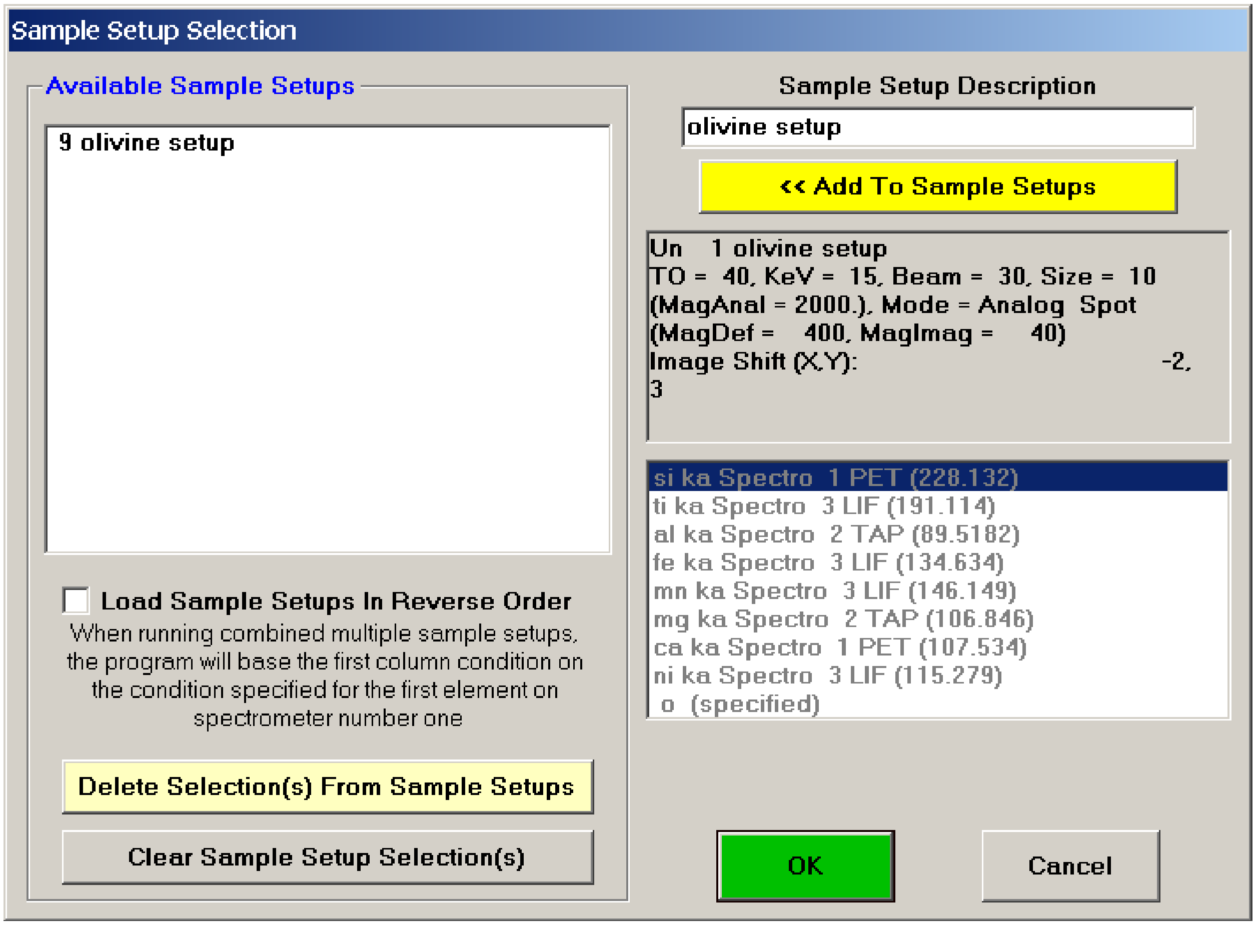
☐ Use All Matrix Corrections

Click the **Add To Setup** button.

Click the **Elements/Cations** button, opening the **Analyzed and Specified Elements** window.

Click the **Save Sample Setups** button.

The **Sample Setup Selection** window opens. Edit the *Sample Setup Description* text box and click the **<< Add To Sample Setups** button, resulting in the following window.



Sample Setup Selection

Available Sample Setups

9 olivine setup

Sample Setup Description: olivine setup

```
Un    1 olivine setup
TO =  40, KeV =  15, Beam =  30, Size =  10
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =     400, MagImag =     40)
Image Shift (X,Y):                        -2,
3
```

```
si ka Spectro  1 PET (228.132)
ti ka Spectro  3 LIF (191.114)
al ka Spectro  2 TAP (89.5182)
fe ka Spectro  3 LIF (134.634)
mn ka Spectro  3 LIF (146.149)
mg ka Spectro  2 TAP (106.846)
ca ka Spectro  1 PET (107.534)
ni ka Spectro  3 LIF (115.279)
 o  (specified)
```

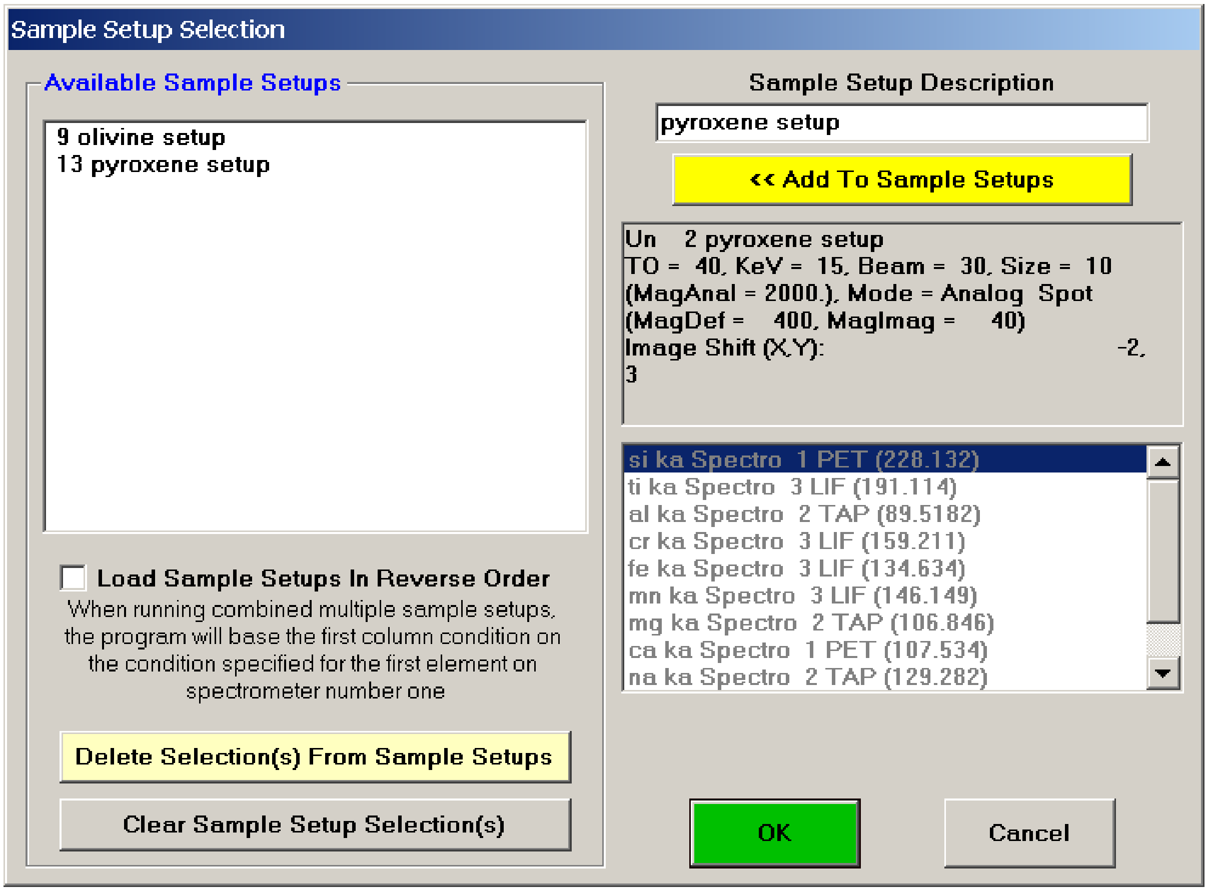
☐ Load Sample Setups In Reverse Order

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, returning to the **Analyzed and Specified Elements** window. Click this **OK** button to return to the **Analyze!** window.

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.

Remember to save each sample setup in the **Sample Setup Selection** window as described above.



Available Sample Setups:

9 olivine setup
13 pyroxene setup

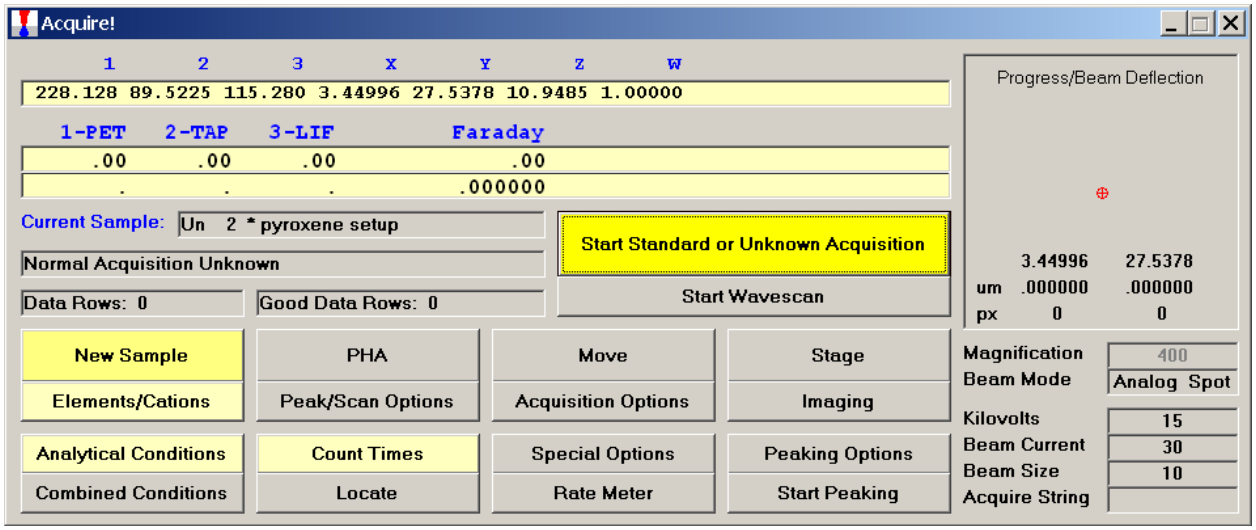
Sample Setup Description: pyroxene setup

Un 2 pyroxene setup
TO = 40, KeV = 15, Beam = 30, Size = 10
(MagAnal = 2000.), Mode = Analog Spot
(MagDef = 400, MagImag = 40)
Image Shift (X,Y): -2,
3

si ka Spectro 1 PET (228.132)
ti ka Spectro 3 LIF (191.114)
al ka Spectro 2 TAP (89.5182)
cr ka Spectro 3 LIF (159.211)
fe ka Spectro 3 LIF (134.634)
mn ka Spectro 3 LIF (146.149)
mg ka Spectro 2 TAP (106.846)
ca ka Spectro 1 PET (107.534)
na ka Spectro 2 TAP (129.282)

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

Returning to the **Acquire!** window, the user can now employ either sample setup for probe work.



1	2	3	X	Y	Z	W
228.128	89.5225	115.280	3.44996	27.5378	10.9485	1.00000

1-PET	2-TAP	3-LIF	Faraday
.00	.00	.00	.00
.	.	.	.000000

Current Sample: Un 2 * pyroxene setup

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

	3.44996	27.5378
um	.000000	.000000
px	0	0

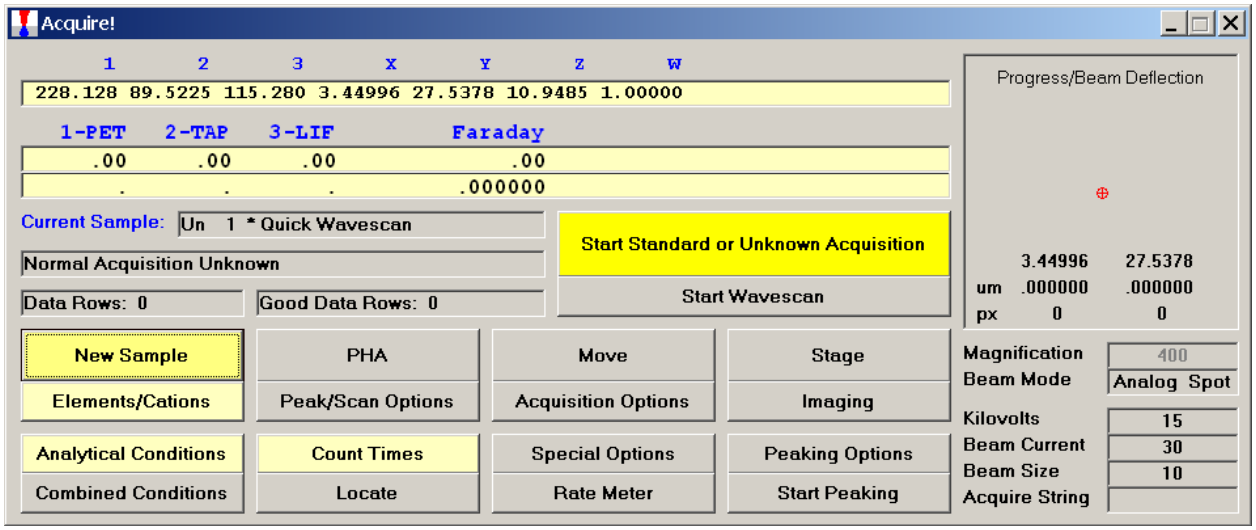
Magnification 400
Beam Mode Analog Spot
Kilovolts 15
Beam Current 30
Beam Size 10
Acquire String

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.



1	2	3	X	Y	Z	W
228.128	89.5225	115.280	3.44996	27.5378	10.9485	1.00000

1-PET	2-TAP	3-LIF	Faraday
.00	.00	.00	.00
.	.	.	.000000

Current Sample: Un 1 * Quick Wavescan

Normal Acquisition Unknown

Data Rows: 0

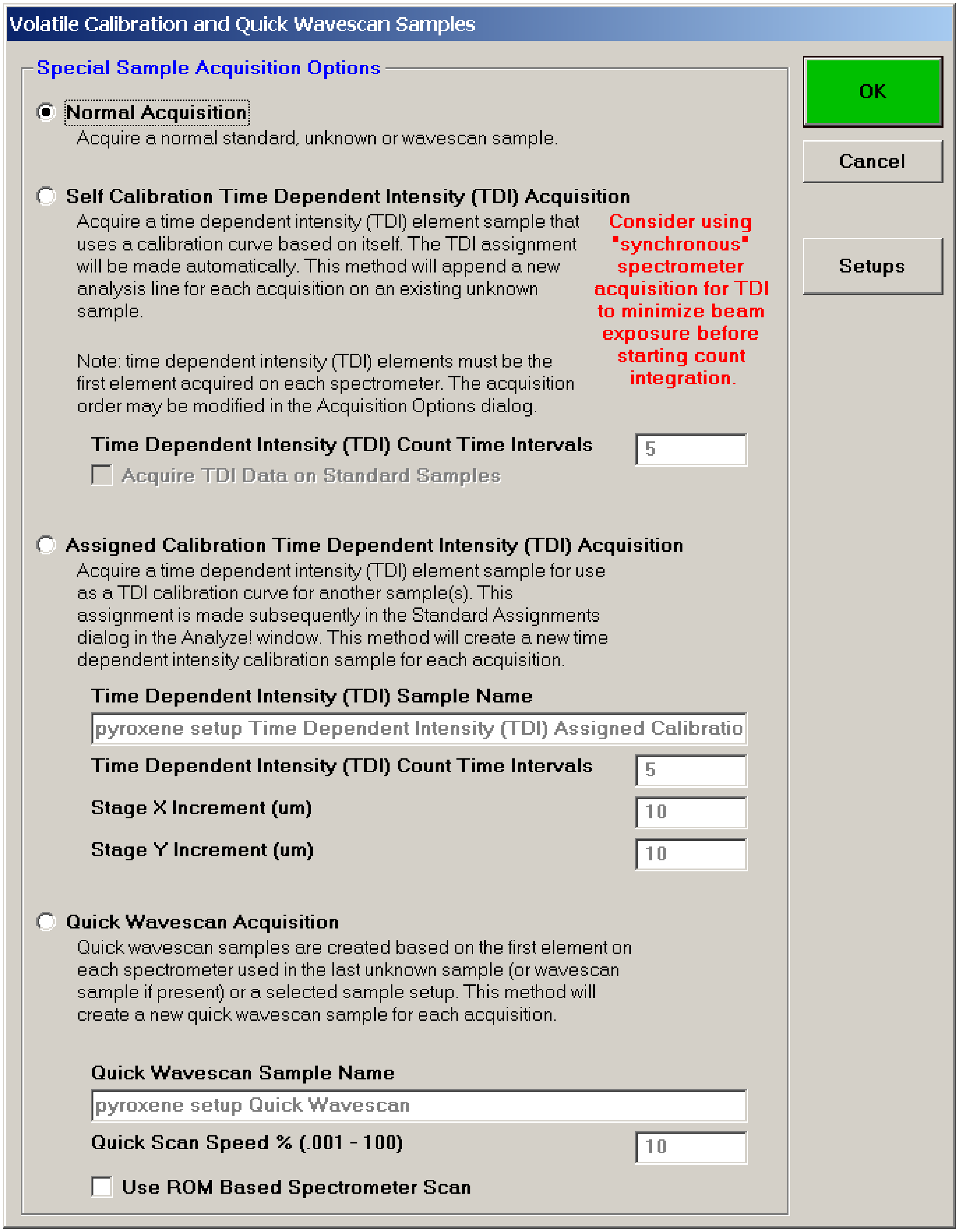
Good Data Rows: 0

Progress/Beam Deflection

	3.44996	27.5378
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	30
Beam Size	10
Acquire String	

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.

Consider using "synchronous" spectrometer acquisition for TDI to minimize beam exposure before starting count integration.

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

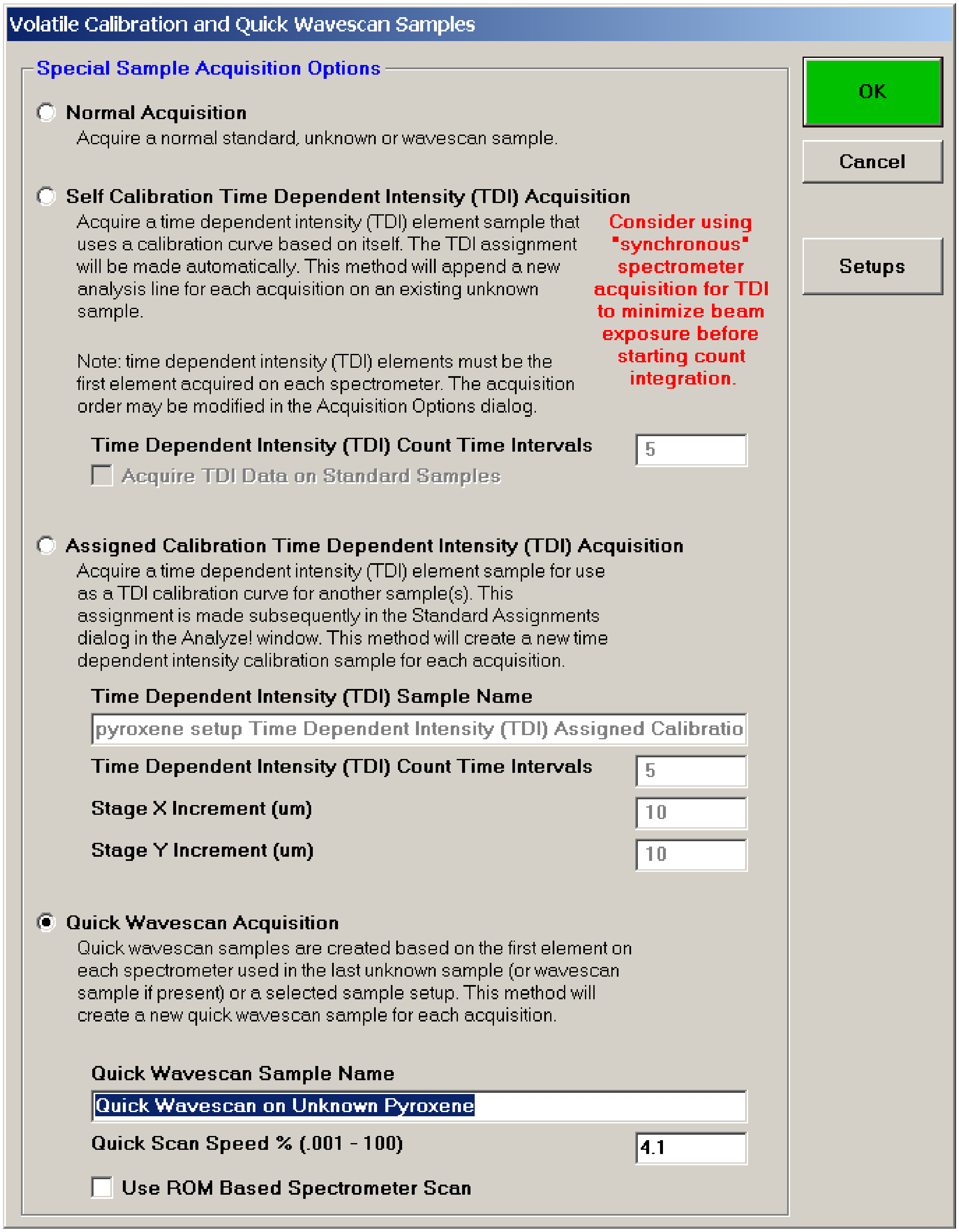
○ **Assigned Calibration Time Dependent Intensity (TDI) Acquisition**
Acquire a time dependent intensity (TDI) element sample for use as a TDI calibration curve for another sample(s). This assignment is made subsequently in the Standard Assignments dialog in the Analyze! window. This method will create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

Time Dependent Intensity (TDI) Sample Name: pyroxene setup Time Dependent Intensity (TDI) Assigned Calibratio
Time Dependent Intensity (TDI) Count Time Intervals: 5
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: pyroxene setup 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.



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.

Consider using "synchronous" spectrometer acquisition for TDI to minimize beam exposure before starting count integration.

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.

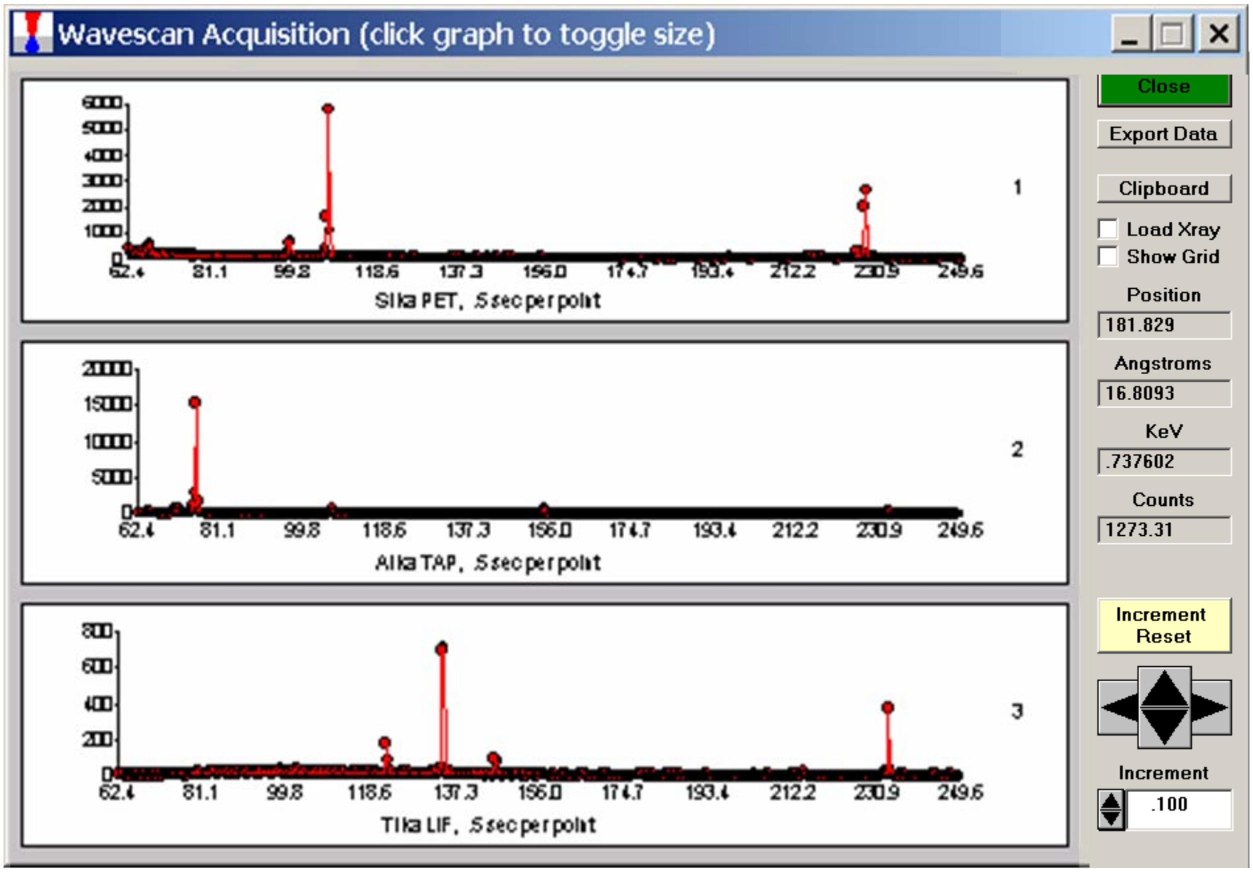
Time Dependent Intensity (TDI) Sample Name: pyroxene setup Time Dependent Intensity (TDI) Assigned Calibratio
Time Dependent Intensity (TDI) Count Time Intervals: 5
Stage X Increment (um): 10
Stage Y Increment (um): 10

● **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: Quick Wavescan on Unknown Pyroxene
Quick Scan Speed % (.001 - 100): 4.1
☐ 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 limits and proceed with the wavescan. The **Wavescan Acquisition** window opens and real time data display is viewable. A completed three-spectrometer **Wavescan Acquisition** window appears below.



Position: 181.829

Angstroms: 16.8093

KeV: .737602

Counts: 1273.31

Increment: .100

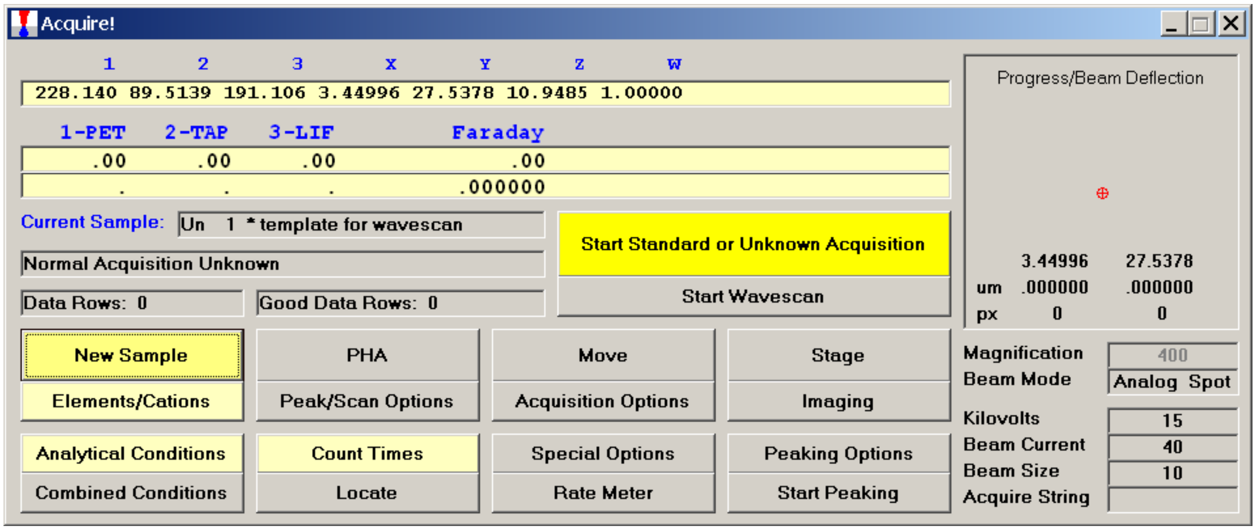
The size of each graph maybe expanded (not shown) by clicking on the relevant wavescan. Upon completion of the quick wavescan, the data may be exported via the **Export Data** button to an ASCII file or examined in more detail along with KLM marker overlay capabilities from the **Plot!** window. Printing 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.



1	2	3	X	Y	Z	W
228.140	89.5139	191.106	3.44996	27.5378	10.9485	1.00000

1-PET	2-TAP	3-LIF	Faraday
.00	.00	.00	.00
.	.	.	.000000

Current Sample: Un 1 * template for wavescan

Normal Acquisition Unknown

Data Rows: 0

Good Data Rows: 0

	3.44996	27.5378
um	.000000	.000000
px	0	0

Magnification 400

Beam Mode Analog Spot

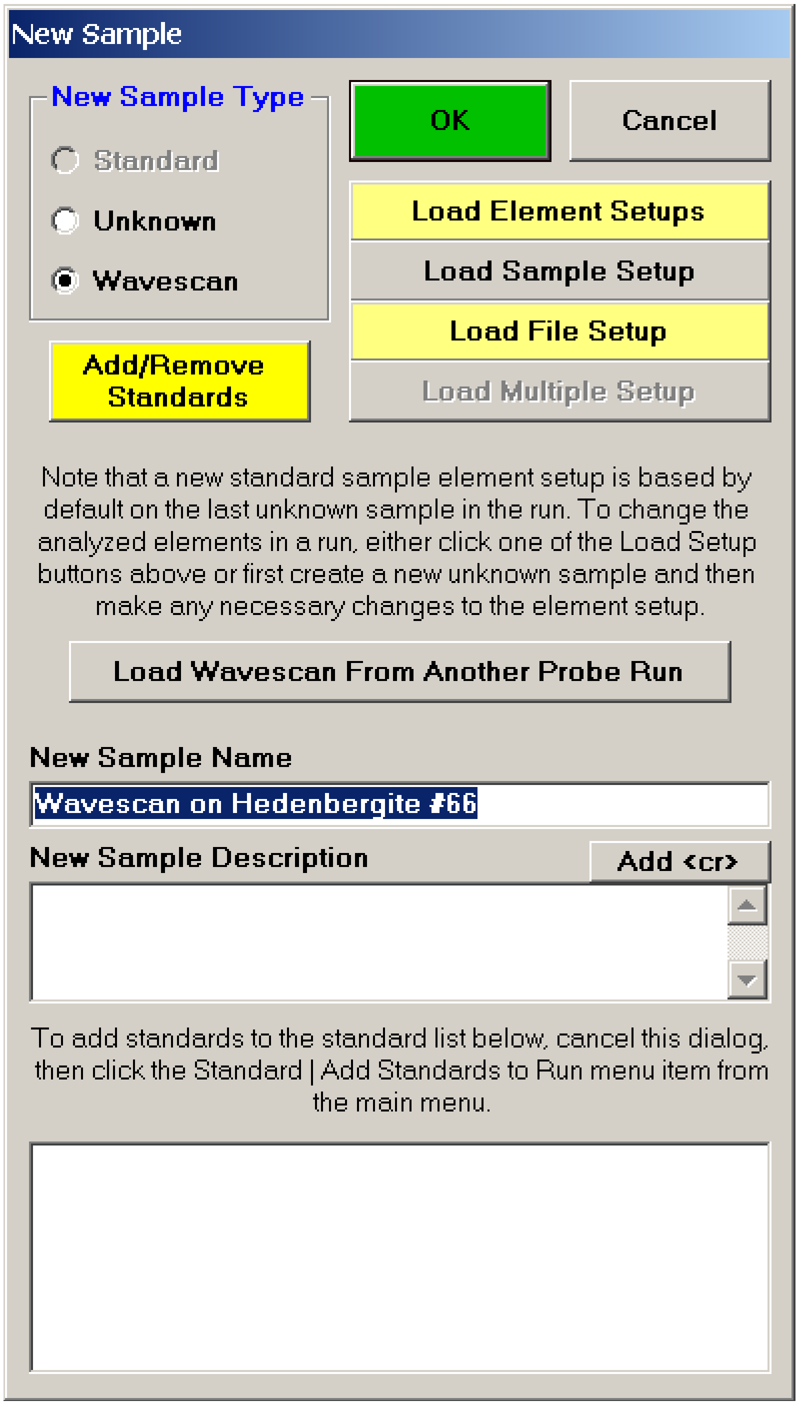
Kilovolts 15

Beam Current 40

Beam Size 10

Acquire String

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.

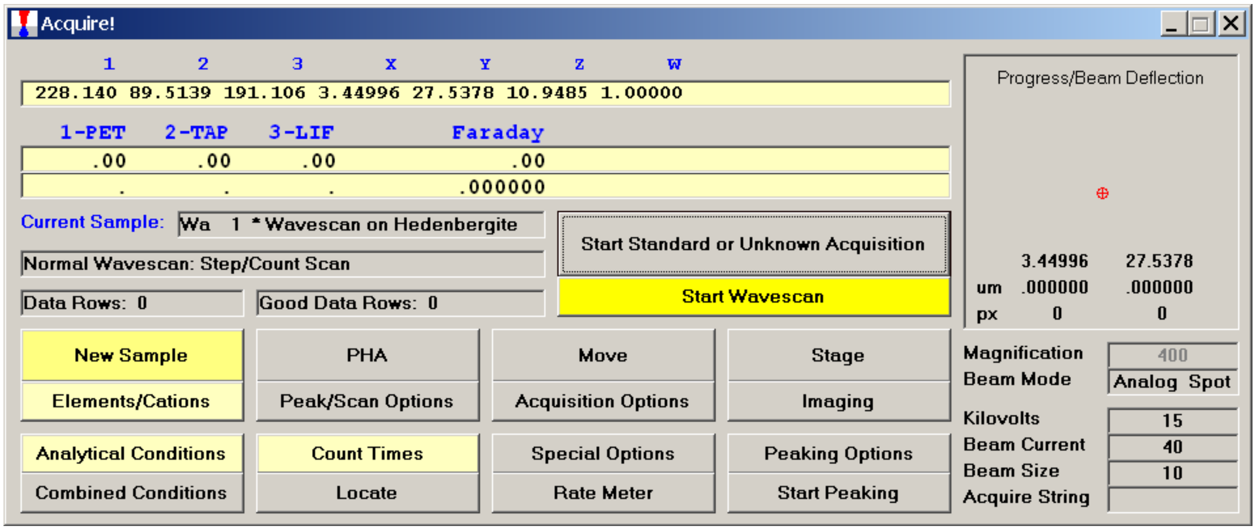
New Sample Name: Wavescan on Hedenbergite #66

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.

Click the **OK** button.

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



```
     1        2        3        X        Y        Z        W
 228.140  89.5139  191.106  3.44996  27.5378  10.9485  1.00000

   1-PET    2-TAP    3-LIF            Faraday
     .00      .00      .00                .00
       .        .        .            .000000
```

Current Sample: Wa 1 * Wavescan on Hedenbergite

Normal Wavescan: Step/Count Scan

Data Rows: 0

Good Data Rows: 0

```
     3.44996    27.5378
um   .000000    .000000
px   0          0
```

Magnification: 400

Beam Mode: Analog Spot

Kilovolts: 15

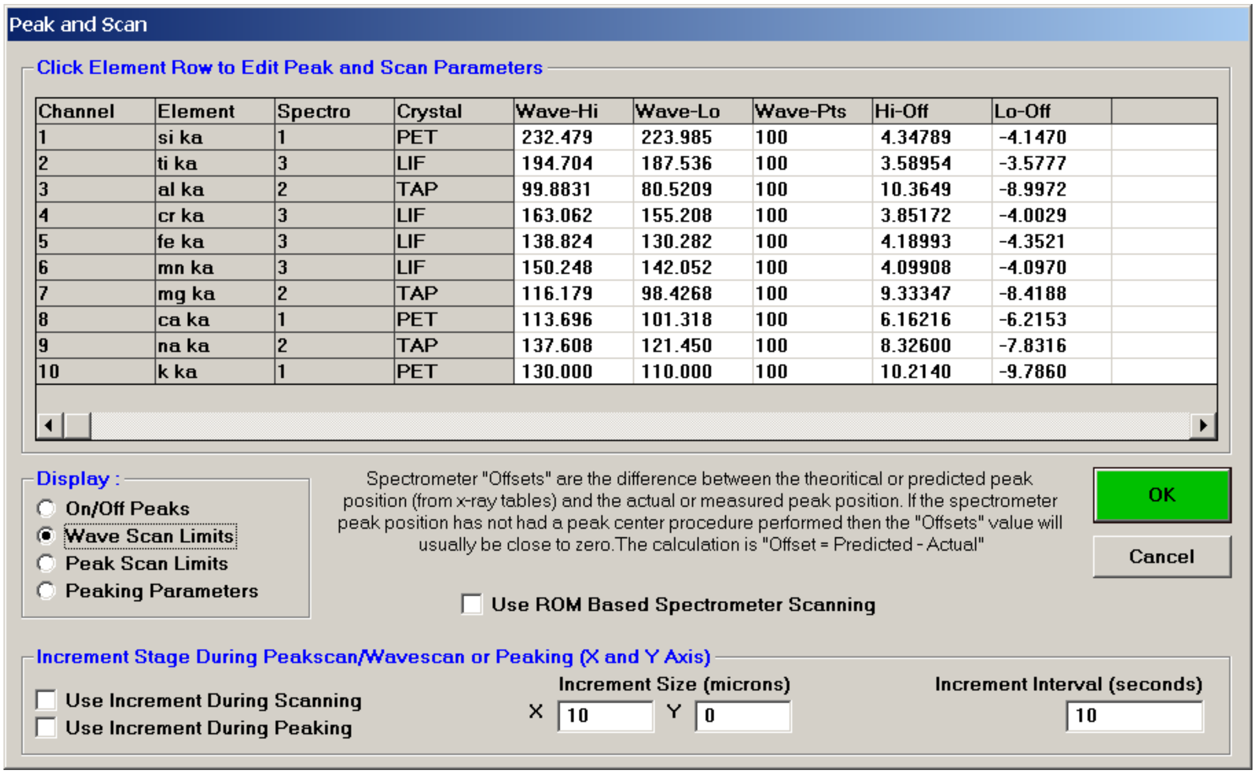
Beam Current: 40

Beam Size: 10

Acquire String:

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.



Channel	Element	Spectro	Crystal	Wave-Hi	Wave-Lo	Wave-Pts	Hi-Off	Lo-Off
1	si ka	1	PET	232.479	223.985	100	4.34789	-4.1470
2	ti ka	3	LIF	194.704	187.536	100	3.58954	-3.5777
3	al ka	2	TAP	99.8831	80.5209	100	10.3649	-8.9972
4	cr ka	3	LIF	163.062	155.208	100	3.85172	-4.0029
5	fe ka	3	LIF	138.824	130.282	100	4.18993	-4.3521
6	mn ka	3	LIF	150.248	142.052	100	4.09908	-4.0970
7	mg ka	2	TAP	116.179	98.4268	100	9.33347	-8.4188
8	ca ka	1	PET	113.696	101.318	100	6.16216	-6.2153
9	na ka	2	TAP	137.608	121.450	100	8.32600	-7.8316
10	k ka	1	PET	130.000	110.000	100	10.2140	-9.7860

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)

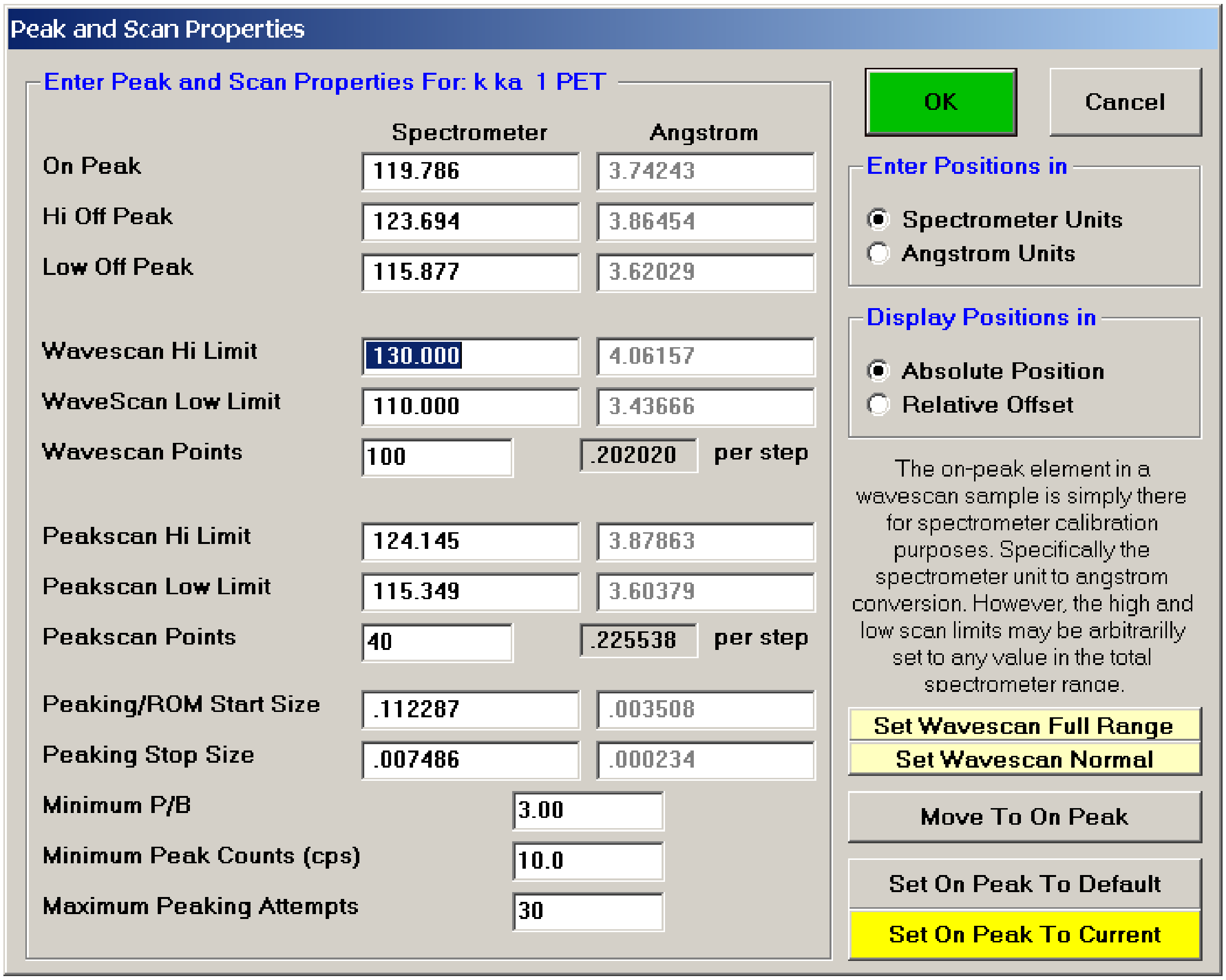
☐ Use Increment During Scanning
☐ Use Increment During Peaking

Increment Size (microns) X 10 Y 0

Increment Interval (seconds) 10

The user wishes to adjust the spectrometer start and stop values for k ka, click on the row of that element.

This opens the **Peak and Scan Properties** window. Adjust the appropriate values.


Peak and Scan Properties

Enter Peak and Scan Properties For: k ka 1 PET

	Spectrometer	Angstrom
On Peak	119.786	3.74243
Hi Off Peak	123.694	3.86454
Low Off Peak	115.877	3.62029
Wavescan Hi Limit	130.000	4.06157
WaveScan Low Limit	110.000	3.43666
Wavescan Points	100	.202020 per step
Peakscan Hi Limit	124.145	3.87863
Peakscan Low Limit	115.349	3.60379
Peakscan Points	40	.225538 per step
Peaking/ROM Start Size	.112287	.003508
Peaking Stop Size	.007486	.000234
Minimum P/B	3.00	
Minimum Peak Counts (cps)	10.0	
Maximum Peaking Attempts	30	

Enter Positions in
● Spectrometer Units
○ Angstrom Units

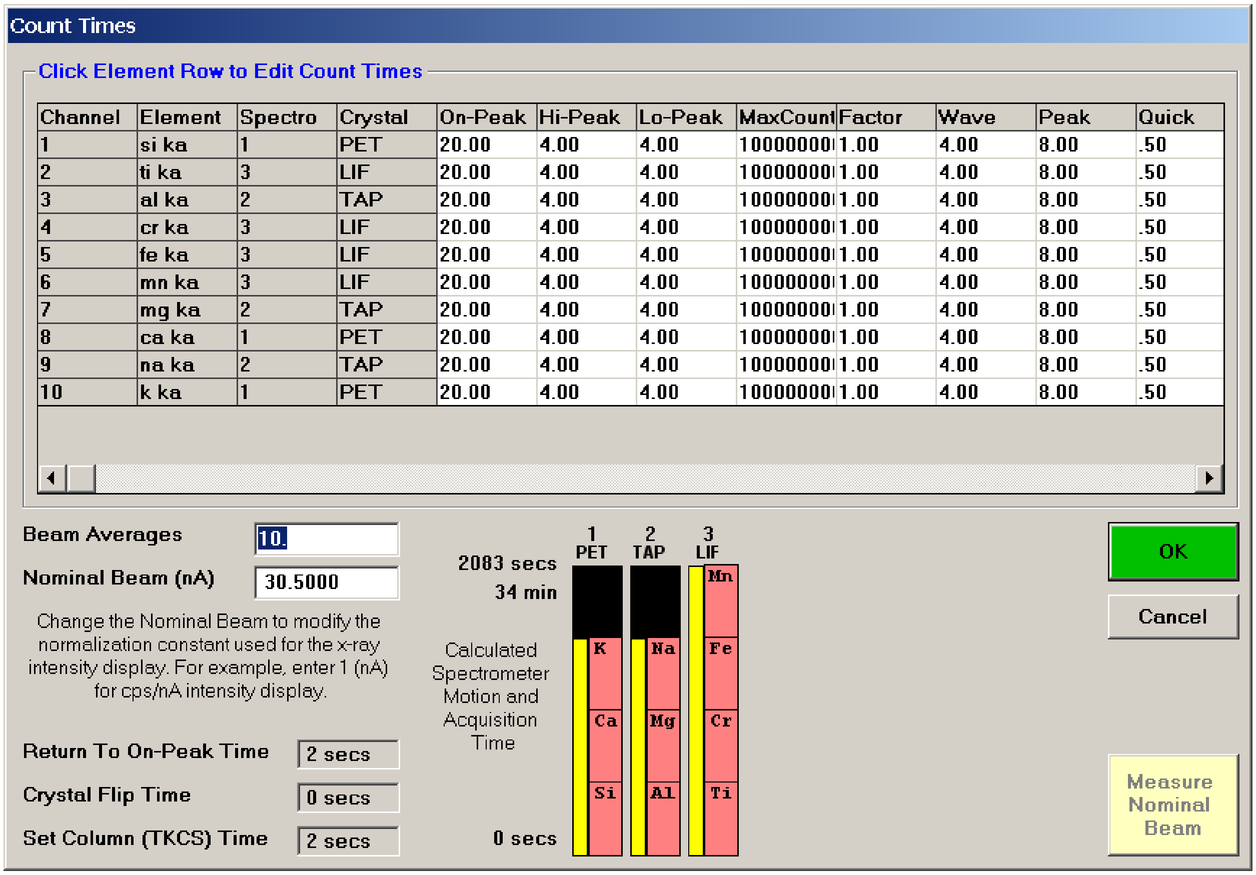
Display Positions in
● Absolute Position
○ Relative Offset

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.



Count Times

Click Element Row to Edit Count Times

Channel	Element	Spectro	Crystal	On-Peak	Hi-Peak	Lo-Peak	MaxCount	Factor	Wave	Peak	Quick
1	si ka	1	PET	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
2	ti ka	3	LIF	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
3	al ka	2	TAP	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
4	cr ka	3	LIF	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
5	fe ka	3	LIF	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
6	mn ka	3	LIF	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
7	mg ka	2	TAP	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
8	ca ka	1	PET	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
9	na ka	2	TAP	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50
10	k ka	1	PET	20.00	4.00	4.00	10000000	1.00	4.00	8.00	.50

Beam Averages: 10.

Nominal Beam (nA): 30.5000

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: 2 secs

Crystal Flip Time: 0 secs

Set Column (TKCS) Time: 2 secs

2083 secs
34 min

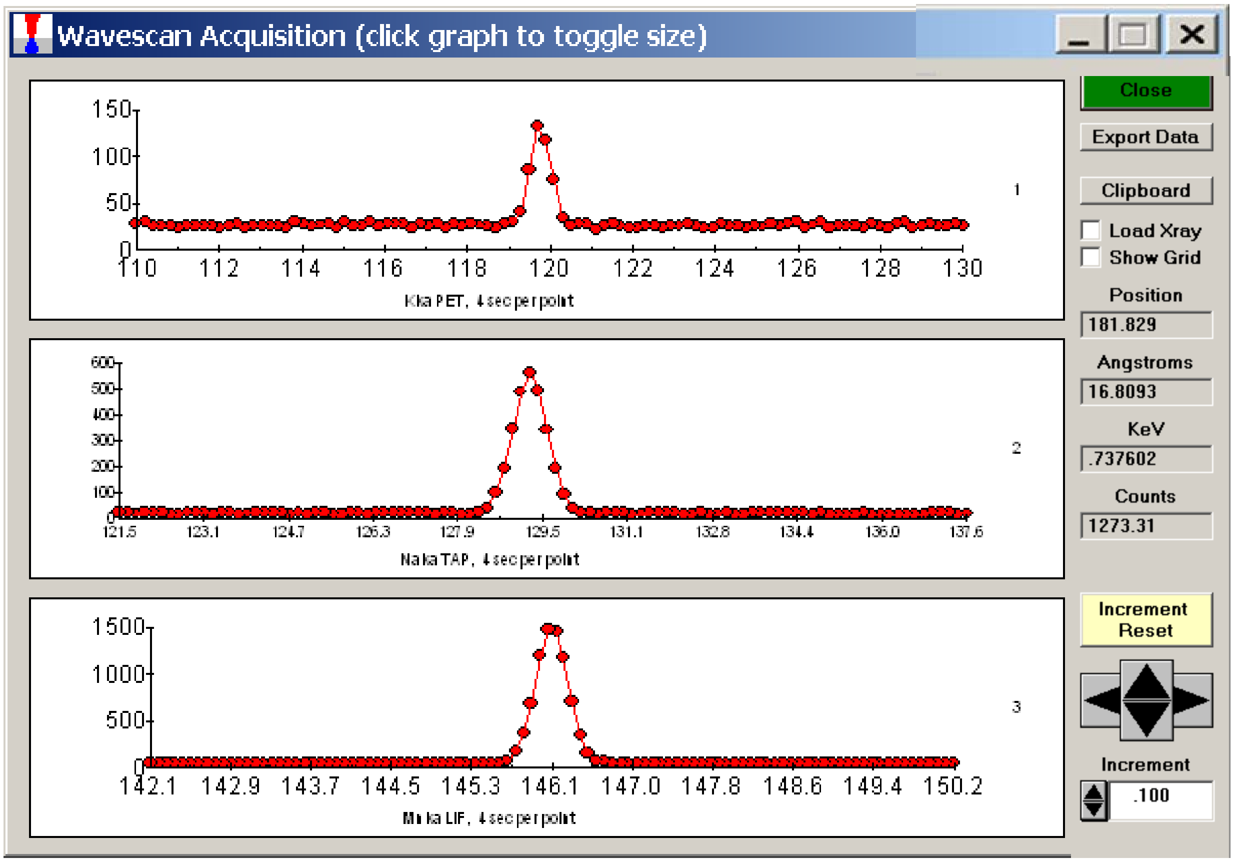
Calculated Spectrometer Motion and Acquisition Time

0 secs

Click on the appropriate element row to edit the wavescan time. Edit the **Count Time Properties** dialog box and then click it's **OK** button to close.

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 completed wavescan acquisition.



☐ Load Xray
☐ Show Grid

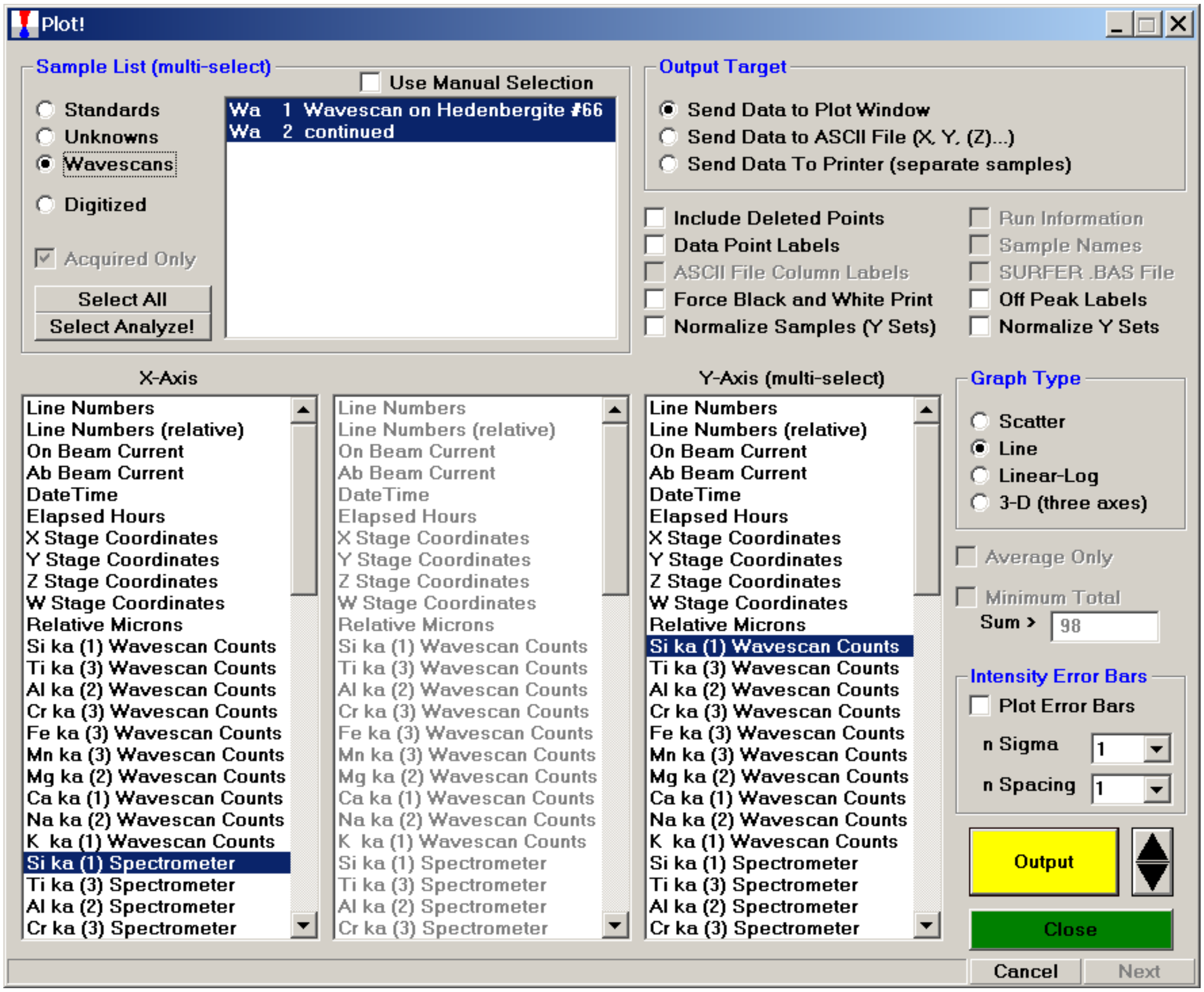
Position: 181.829
Angstroms: 16.8093
KeV: .737602
Counts: 1273.31
Increment: .100

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*.



Plot!

Sample List (multi-select)

☐ Use Manual Selection

○ Standards
○ Unknowns
● Wavescans
○ Digitized

☑ Acquired Only

Select All
Select Analyze!

Wa 1 Wavescan on Hedenbergite #66
Wa 2 continued

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		Y-Axis (multi-select)
Line Numbers	Line Numbers	Line Numbers
Line Numbers (relative)	Line Numbers (relative)	Line Numbers (relative)
On Beam Current	On Beam Current	On Beam Current
Ab Beam Current	Ab Beam Current	Ab Beam Current
DateTime	DateTime	DateTime
Elapsed Hours	Elapsed Hours	Elapsed Hours
X Stage Coordinates	X Stage Coordinates	X Stage Coordinates
Y Stage Coordinates	Y Stage Coordinates	Y Stage Coordinates
Z Stage Coordinates	Z Stage Coordinates	Z Stage Coordinates
W Stage Coordinates	W Stage Coordinates	W Stage Coordinates
Relative Microns	Relative Microns	Relative Microns
Si ka (1) Wavescan Counts	Si ka (1) Wavescan Counts	**Si ka (1) Wavescan Counts**
Ti ka (3) Wavescan Counts	Ti ka (3) Wavescan Counts	Ti ka (3) Wavescan Counts
Al ka (2) Wavescan Counts	Al ka (2) Wavescan Counts	Al ka (2) Wavescan Counts
Cr ka (3) Wavescan Counts	Cr ka (3) Wavescan Counts	Cr ka (3) Wavescan Counts
Fe ka (3) Wavescan Counts	Fe ka (3) Wavescan Counts	Fe ka (3) Wavescan Counts
Mn ka (3) Wavescan Counts	Mn ka (3) Wavescan Counts	Mn ka (3) Wavescan Counts
Mg ka (2) Wavescan Counts	Mg ka (2) Wavescan Counts	Mg ka (2) Wavescan Counts
Ca ka (1) Wavescan Counts	Ca ka (1) Wavescan Counts	Ca ka (1) Wavescan Counts
Na ka (2) Wavescan Counts	Na ka (2) Wavescan Counts	Na ka (2) Wavescan Counts
K ka (1) Wavescan Counts	K ka (1) Wavescan Counts	K ka (1) Wavescan Counts
Si ka (1) Spectrometer	Si ka (1) Spectrometer	Si ka (1) Spectrometer
Ti ka (3) Spectrometer	Ti ka (3) Spectrometer	Ti ka (3) Spectrometer
Al ka (2) Spectrometer	Al ka (2) Spectrometer	Al ka (2) Spectrometer
Cr ka (3) Spectrometer	Cr ka (3) Spectrometer	Cr ka (3) Spectrometer

Graph Type

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

☐ Average Only

☐ Minimum Total Sum > 98

Intensity Error Bars

☐ Plot Error Bars

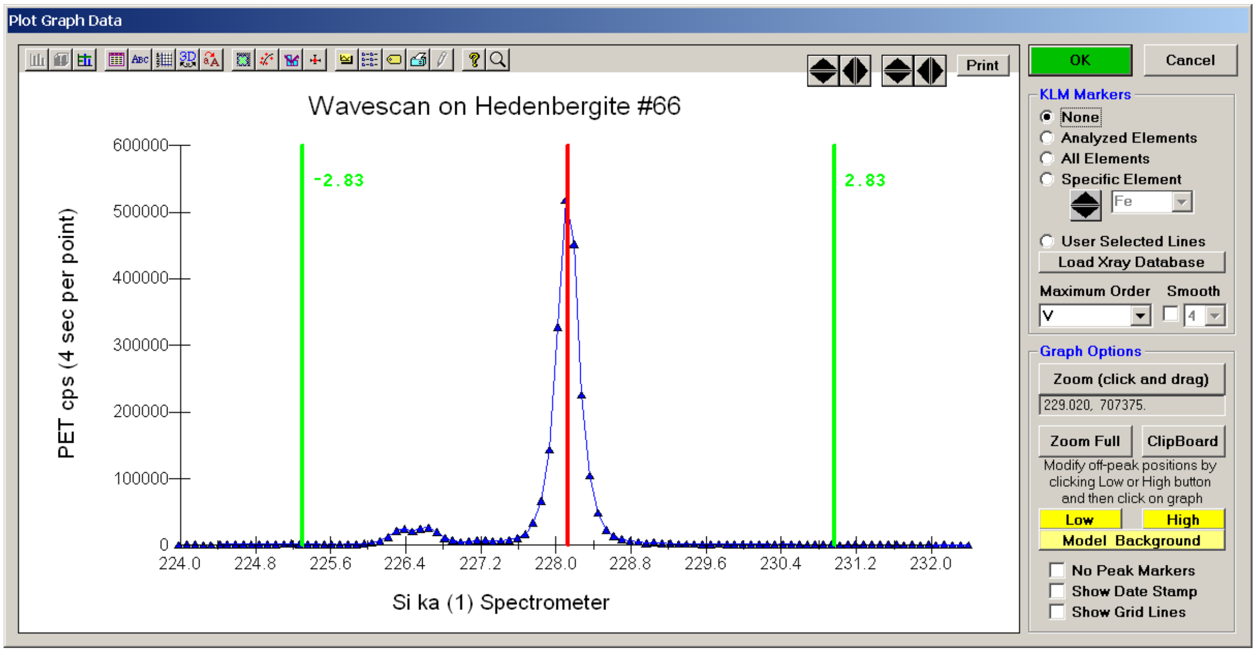
n Sigma 1

n Spacing 1

Output
Close
Cancel
Next

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).



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

Maximum Order: V
Smooth: ☐ 4

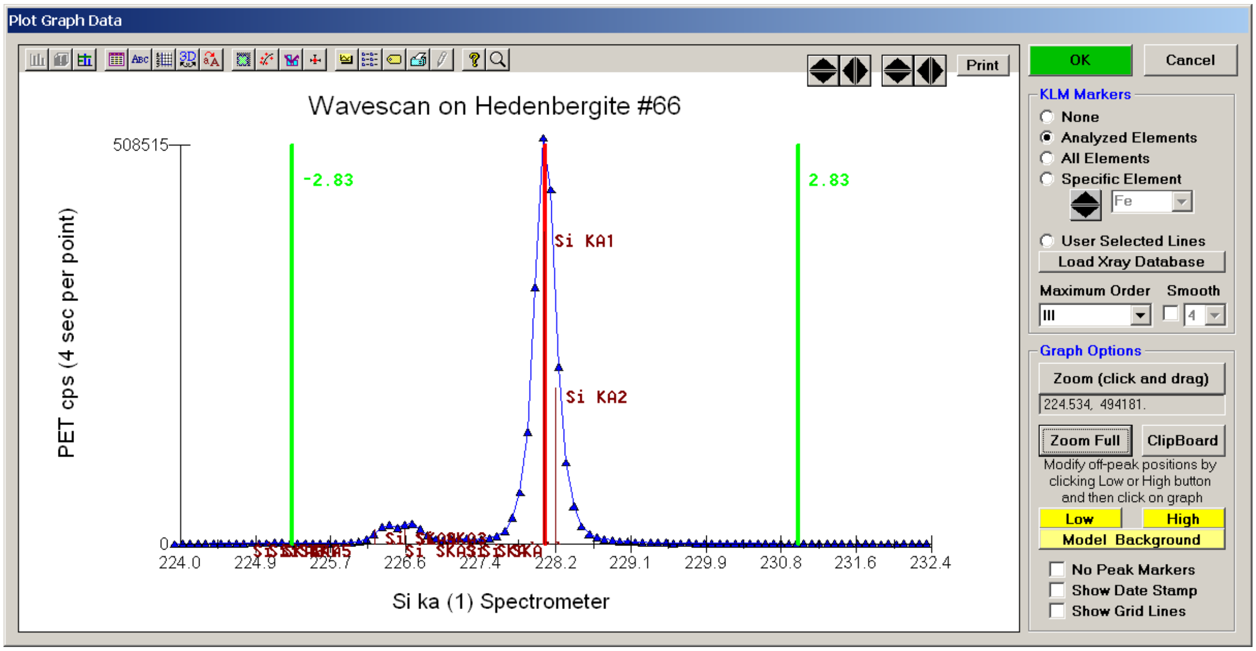
229.020, 707375.

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

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

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.

Click and drag the mouse to **Zoom** in on any portion of the graph. 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: III
Smooth: ☐ 4

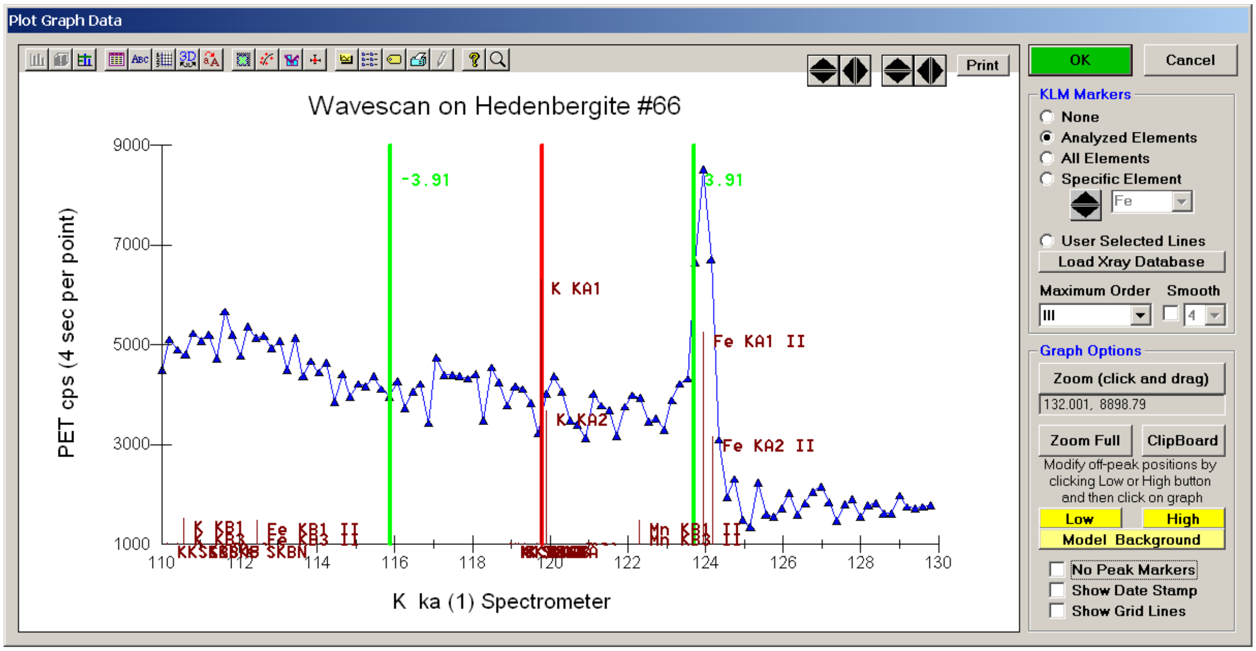
Graph Options
224.534, 494181.

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

☐ 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).

In the next screen capture, detailing *K (1) Wavescan Counts (PET cps)* versus *K (1) Spectrometer*, the user will note that the high background position falls on top of the signal from Fe K$\alpha_{1,2}$ second order. This could give an anonymously high background reading on this sample, if iron is present. Therefore, the user chooses to move the high background slightly to a lower spectrometer position.



KLM Markers

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

Maximum Order: III
Smooth: ☐ 4

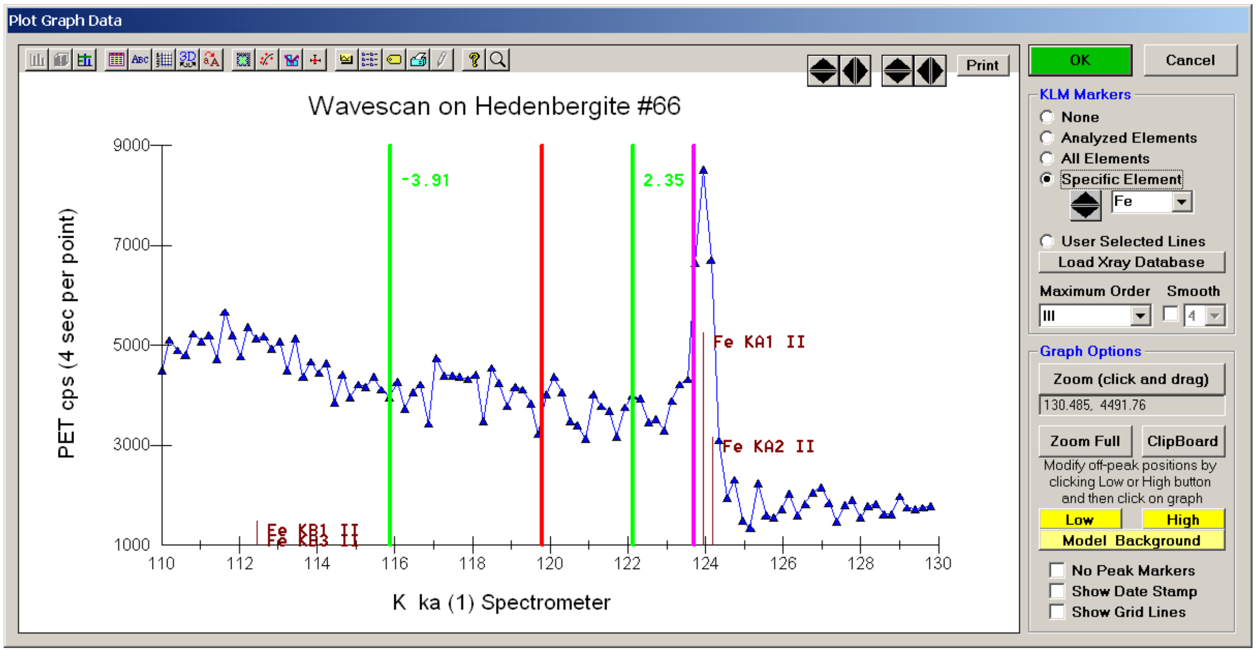
132.001, 8898.79

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

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

Click the **High** button, move the mouse cursor (note it appears as a cross on the graph) to an appropriate new position and click the graph.

The graph will update the new off-peak position (purple is the old position, green the new position).



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

Maximum Order: III
Smooth: ☐ 4

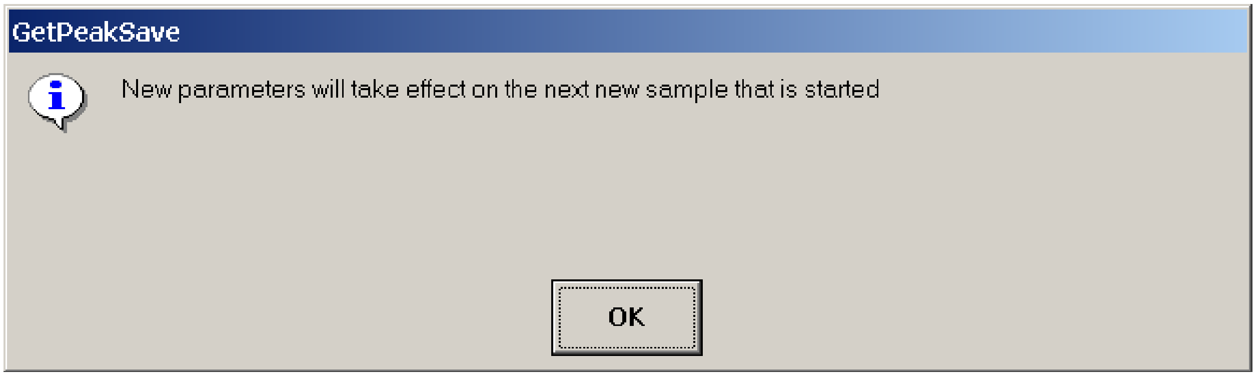
130.485, 4491.76

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

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

Click the **OK** button of the **Graph Data** window. The **GetPeakSave** window appears.

The new parameters will take effect on the next new sample that is started



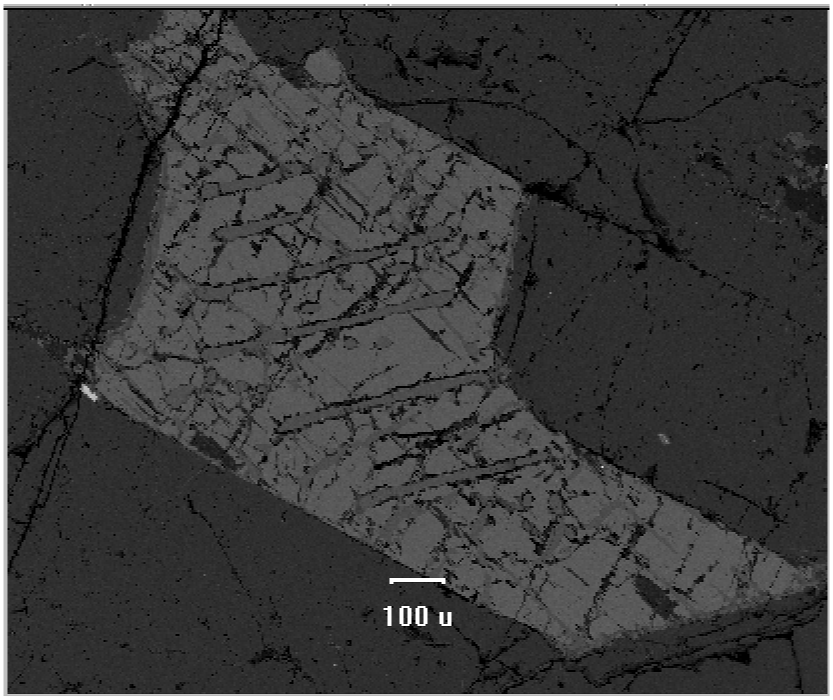
New parameters will take effect on the next new sample that is started

Click the **OK** button to accept and store the new high background position for K Kα x-rays.

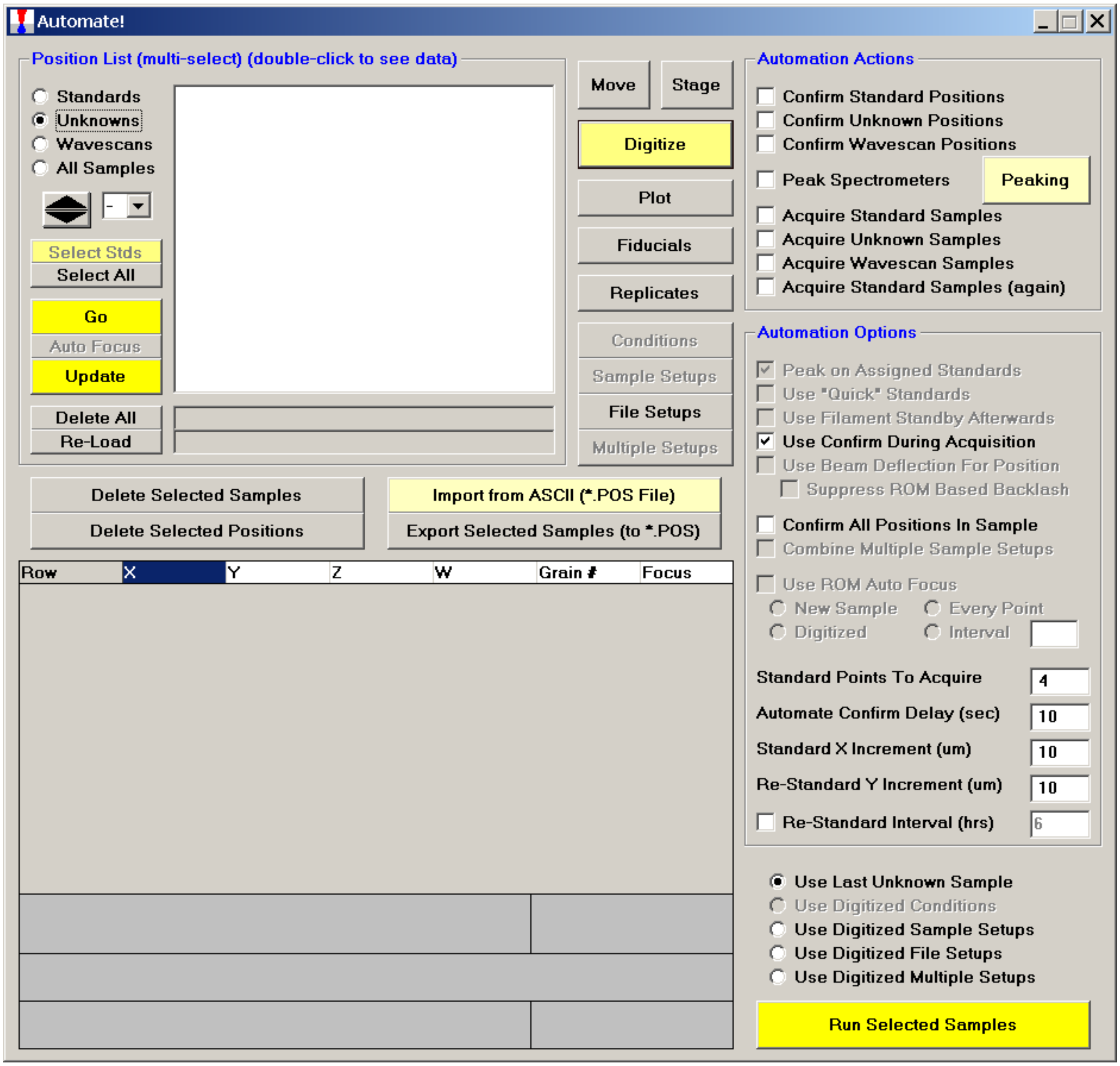
Polygon Gridding – Using Surfer Option

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 SURFER for Windows to automatically generate contour, surface and *.GRD concentration files of your data. These *.GRD files can be imported into Probe Image for viewing in false color. 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

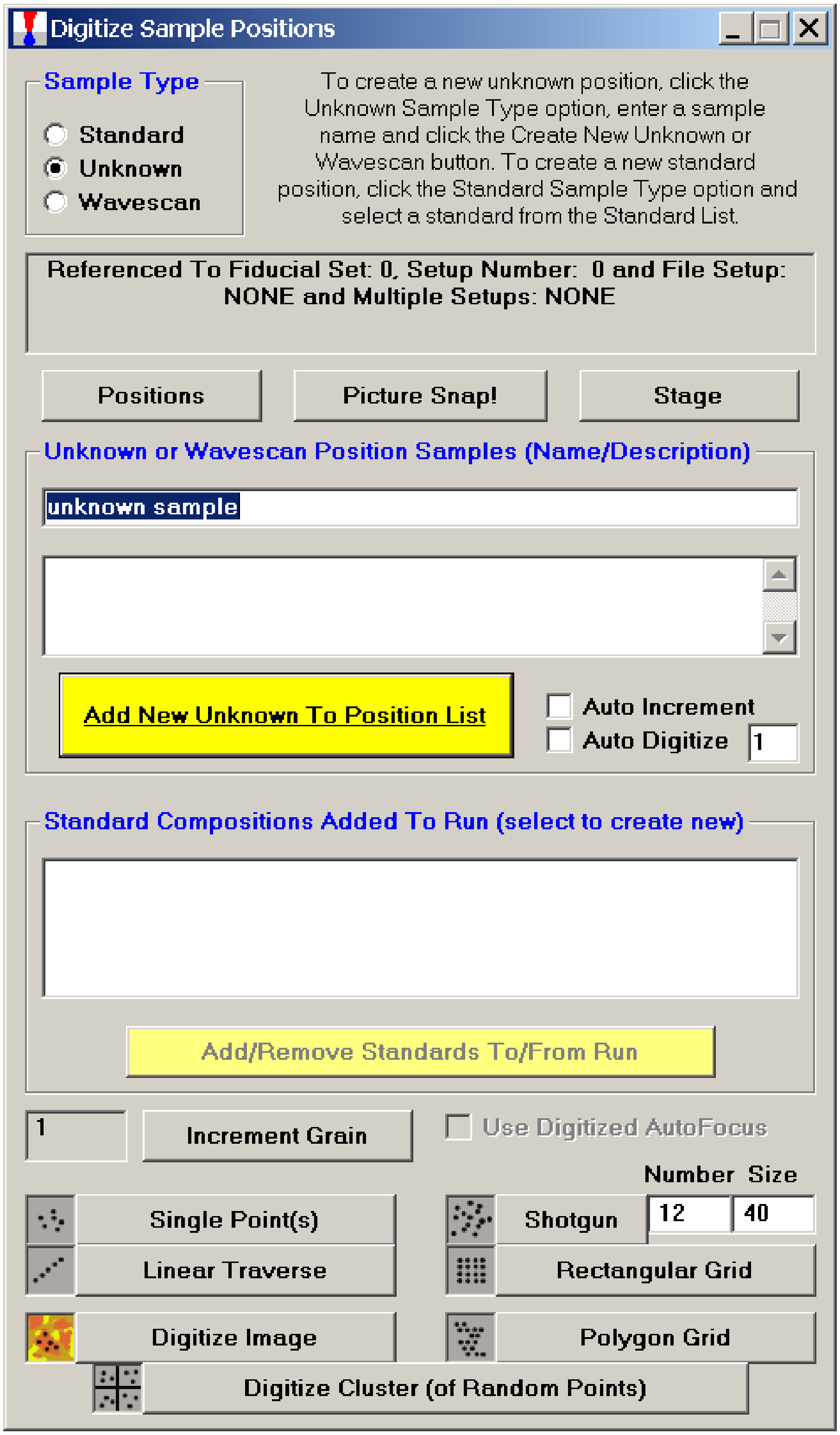
☐ Confirm Standard Positions
☐ Confirm Unknown Positions
☐ Confirm Wavescan Positions
☐ Peak Spectrometers
☐ Acquire Standard Samples
☐ Acquire Unknown Samples
☐ Acquire Wavescan Samples
☐ Acquire Standard Samples (again)

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

Standard Points To Acquire 4
Automate Confirm Delay (sec) 10
Standard X Increment (um) 10
Re-Standard Y Increment (um) 10
☐ 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.



○ Standard
● Unknown
○ Wavescan

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

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

unknown sample

☐ Auto Increment
☐ Auto Digitize 1

1

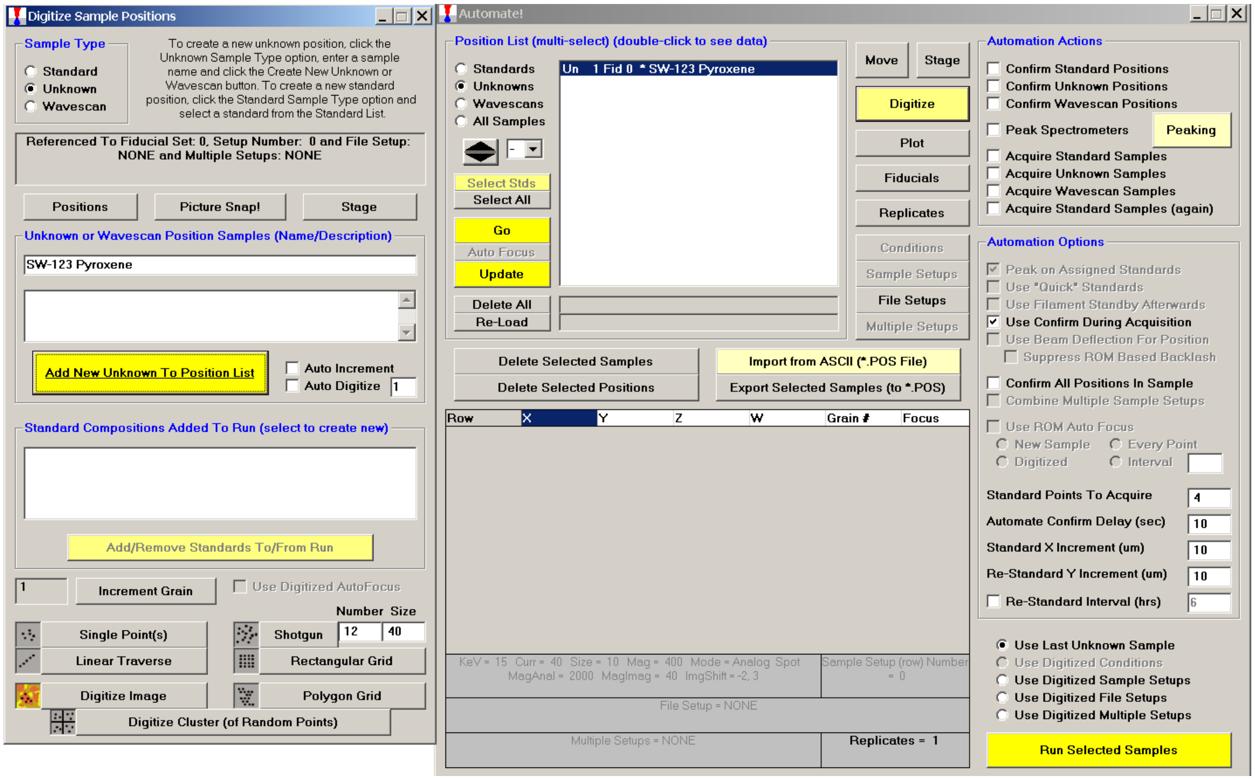
☐ Use Digitized AutoFocus

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.



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): SW-123 Pyroxene

Auto Digitize: 1

Increment Grain: 1

Shotgun Number: 12 Size: 40

Position List: Un 1 Fid 0 * SW-123 Pyroxene

KeV = 15 Curr = 40 Size = 10 Mag = 400 Mode = Analog Spot MagAnal = 2000 MagImag = 40 ImgShift = -2, 3

Sample Setup (row) Number = 0

File Setup = NONE

Multiple Setups = NONE

Replicates = 1

Standard Points To Acquire: 4

Automate Confirm Delay (sec): 10

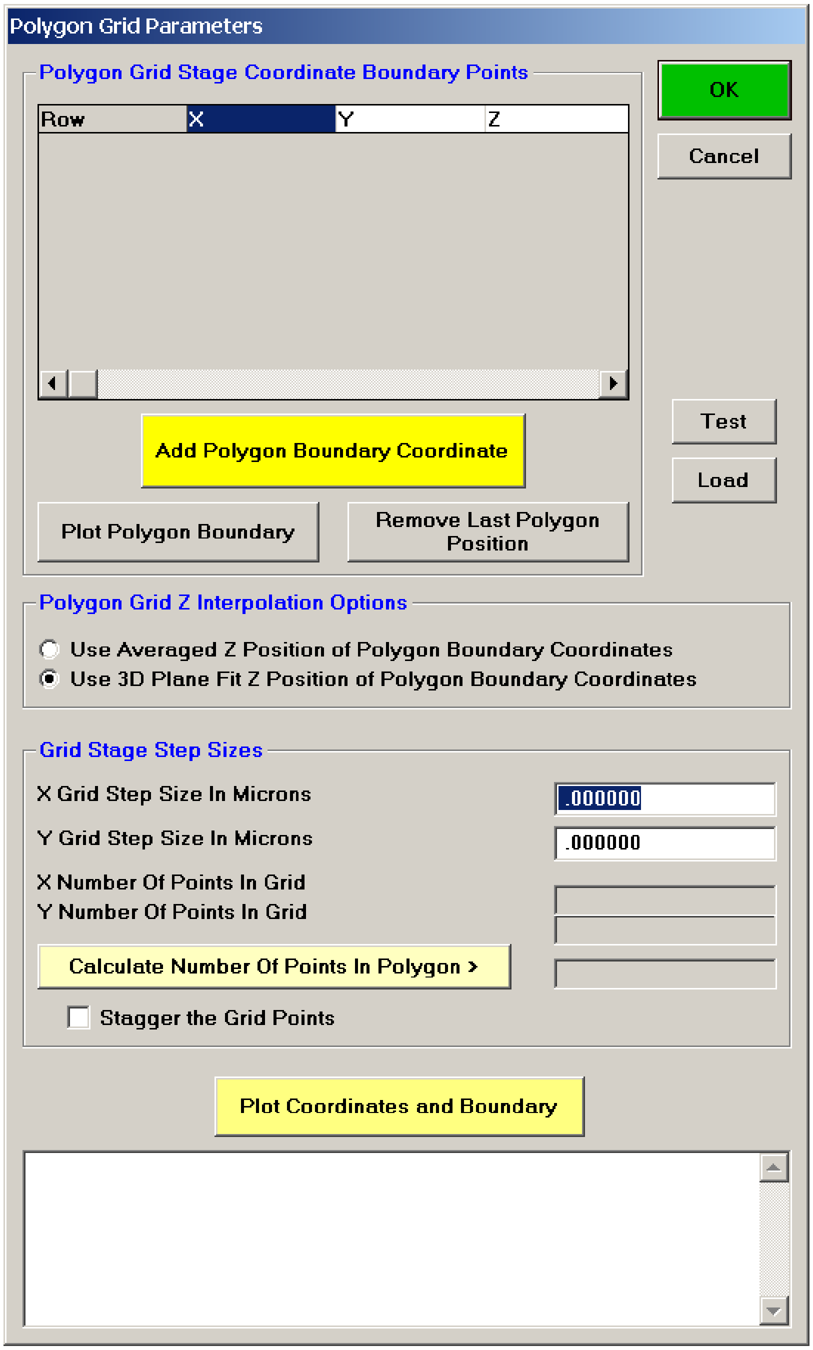
Standard X Increment (um): 10

Re-Standard Y Increment (um): 10

Re-Standard Interval (hrs): 6

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

The **Polygon Grid Parameters** window opens.



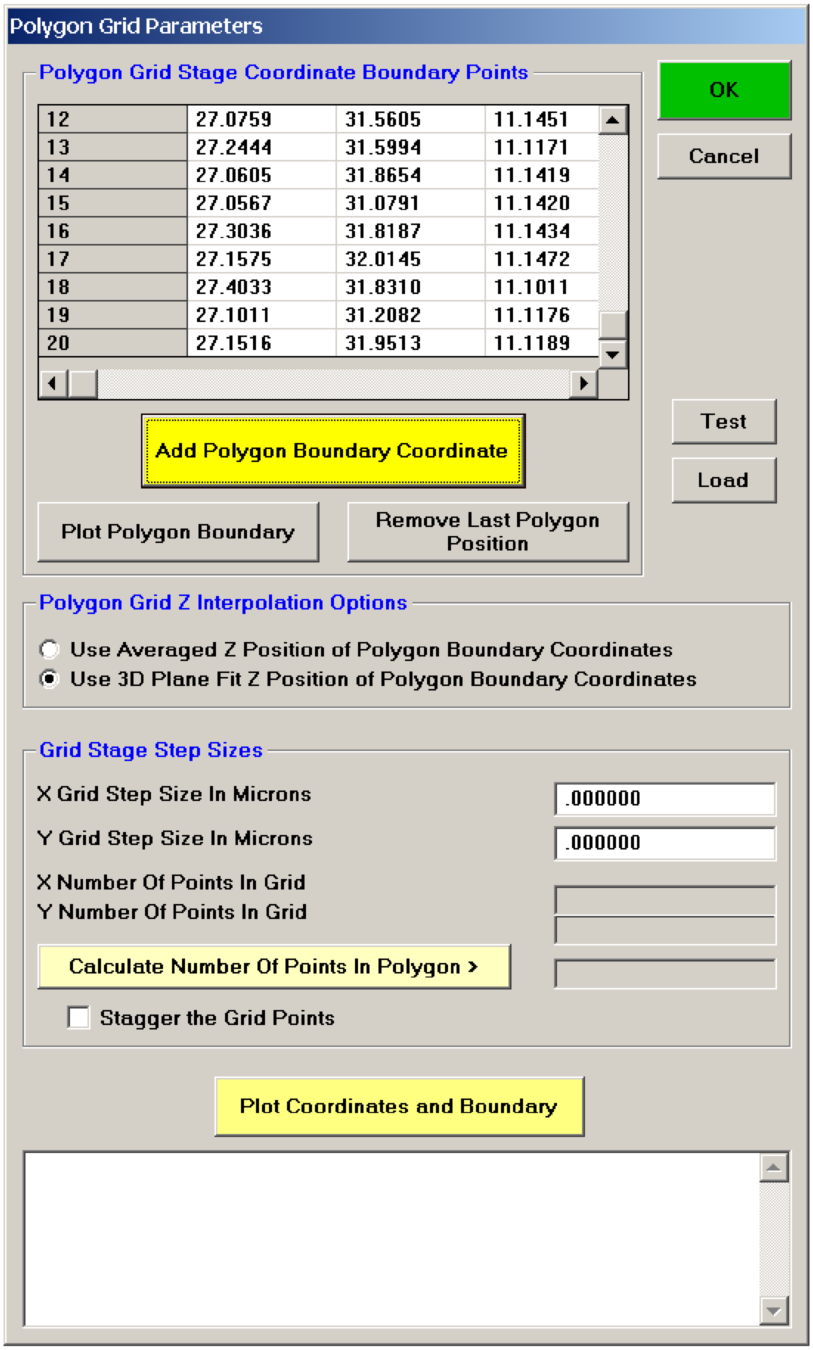
○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

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

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.

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. If a mistake is made or you simply wish to remove the previous boundary point, click the **Remove Last Polygon Position** button.



12	27.0759	31.5605	11.1451
13	27.2444	31.5994	11.1171
14	27.0605	31.8654	11.1419
15	27.0567	31.0791	11.1420
16	27.3036	31.8187	11.1434
17	27.1575	32.0145	11.1472
18	27.4033	31.8310	11.1011
19	27.1011	31.2082	11.1176
20	27.1516	31.9513	11.1189

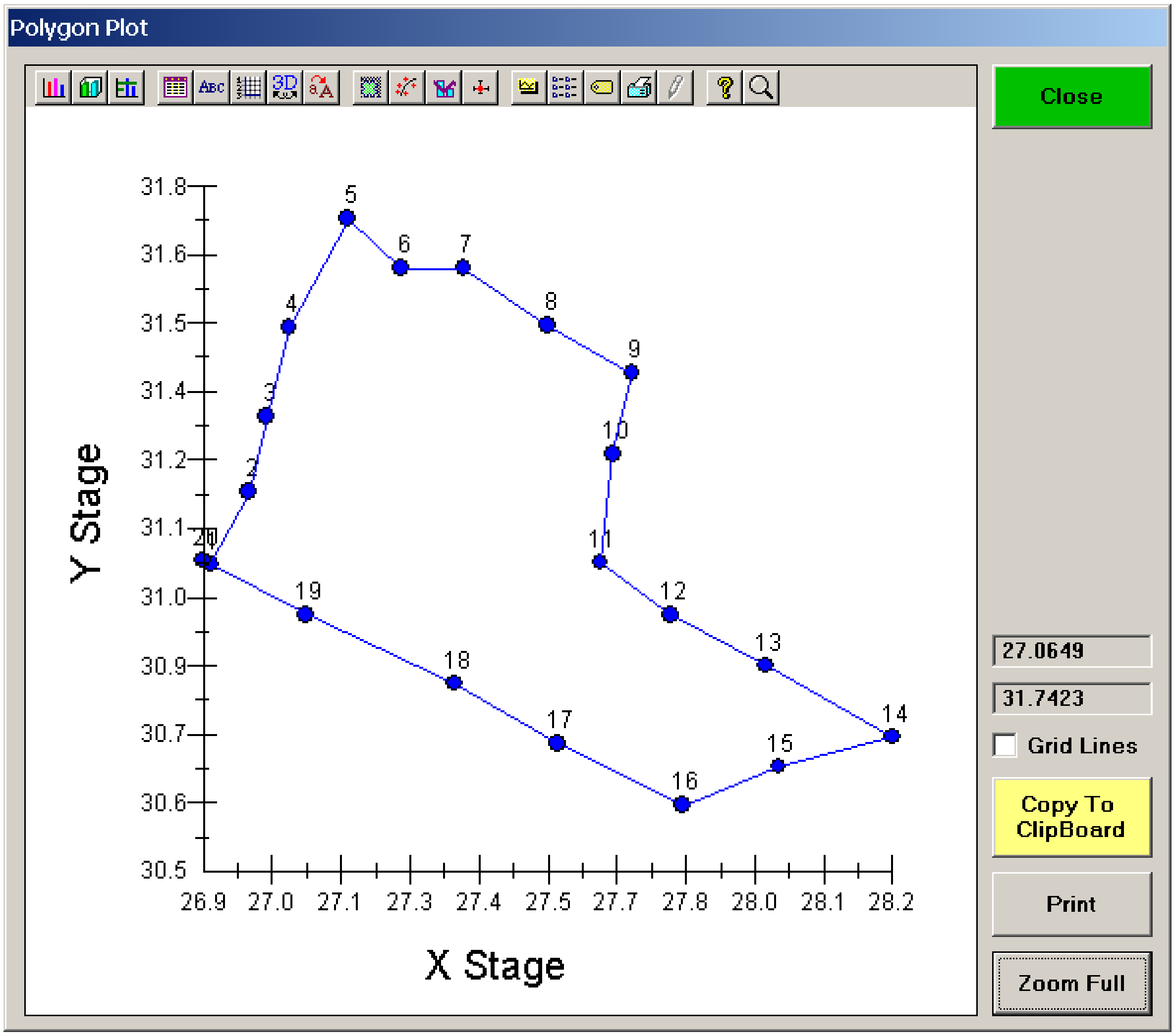
○ Use Averaged Z Position of Polygon Boundary Coordinates
● Use 3D Plane Fit Z Position of Polygon Boundary Coordinates

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.

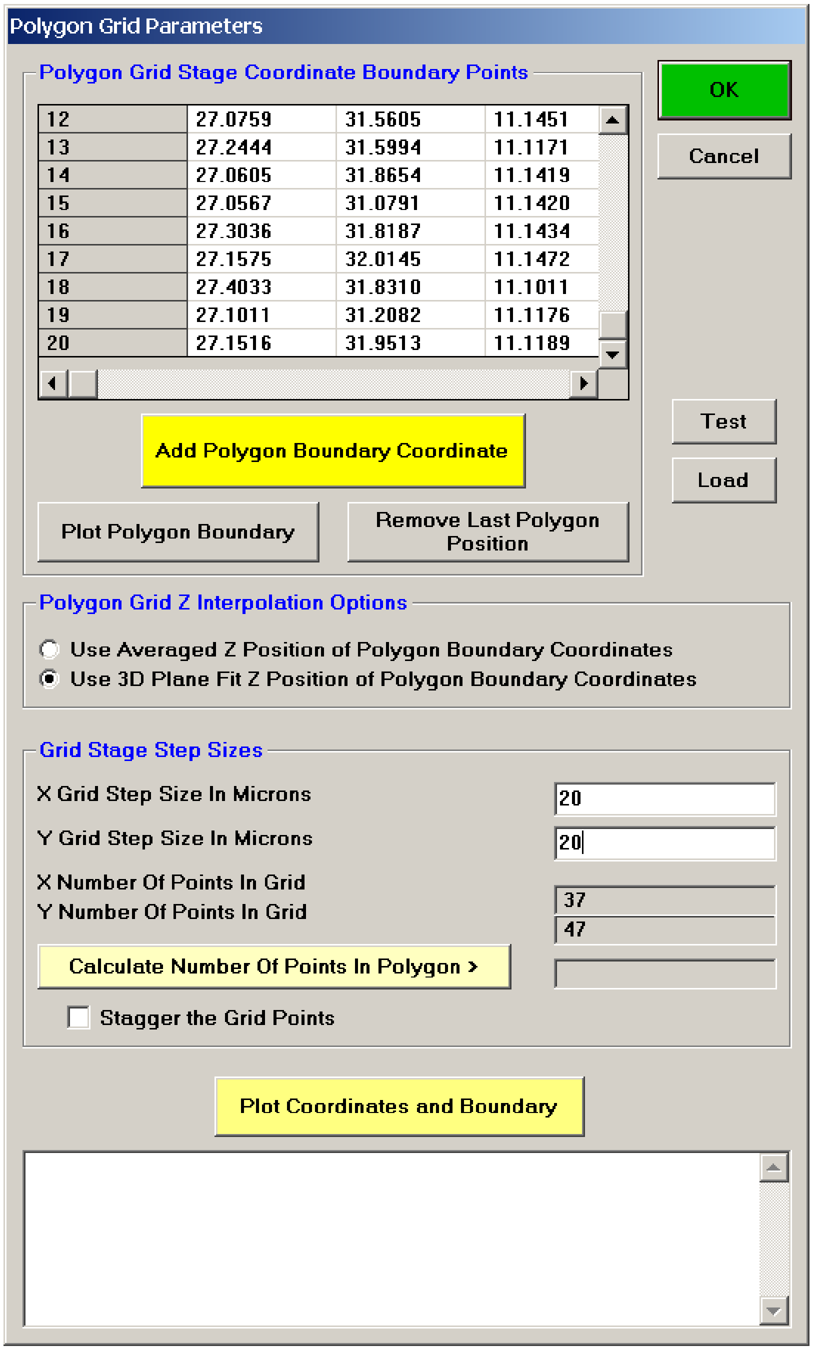


27.0649

31.7423

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

12	27.0759	31.5605	11.1451
13	27.2444	31.5994	11.1171
14	27.0605	31.8654	11.1419
15	27.0567	31.0791	11.1420
16	27.3036	31.8187	11.1434
17	27.1575	32.0145	11.1472
18	27.4033	31.8310	11.1011
19	27.1011	31.2082	11.1176
20	27.1516	31.9513	11.1189

Polygon Grid Z Interpolation Options

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

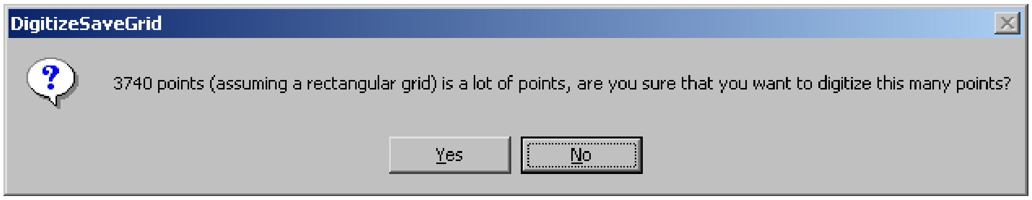
Grid Stage Step Sizes

X Grid Step Size In Microns: 20
Y Grid Step Size In Microns: 20
X Number Of Points In Grid: 37
Y Number Of Points In Grid: 47

☐ 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*.

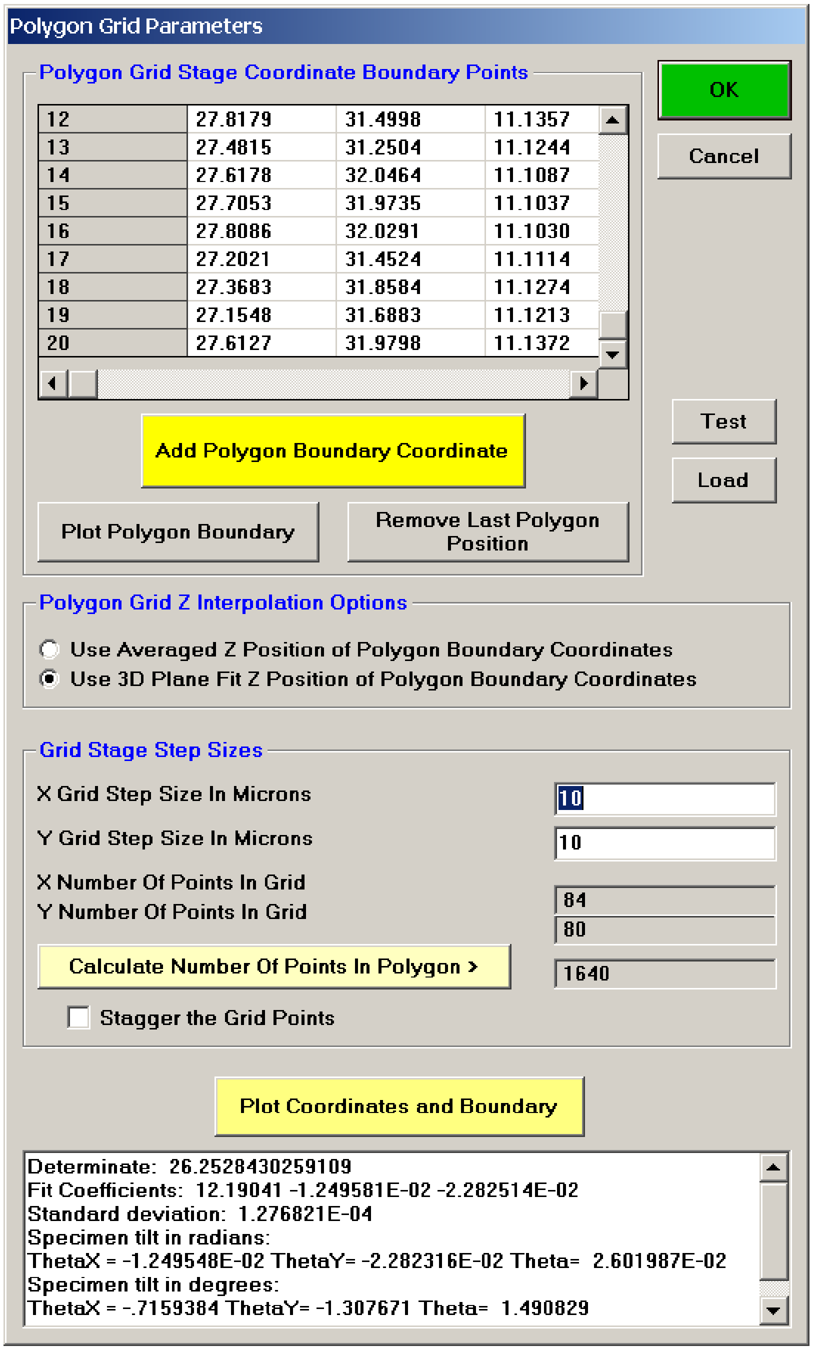
The **DigitizeSaveGrid** window appears with the number of points in an ideal rectangular grid.



DigitizeSaveGrid

3740 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 Parameters

Polygon Grid Stage Coordinate Boundary Points

12	27.8179	31.4998	11.1357
13	27.4815	31.2504	11.1244
14	27.6178	32.0464	11.1087
15	27.7053	31.9735	11.1037
16	27.8086	32.0291	11.1030
17	27.2021	31.4524	11.1114
18	27.3683	31.8584	11.1274
19	27.1548	31.6883	11.1213
20	27.6127	31.9798	11.1372

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

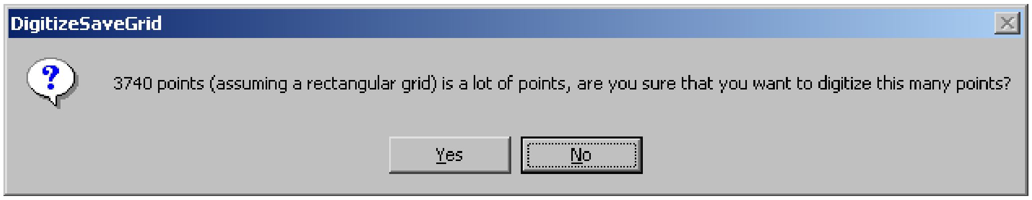
X Grid Step Size In Microns: 10
Y Grid Step Size In Microns: 10
X Number Of Points In Grid: 84
Y Number Of Points In Grid: 80
Calculate Number Of Points In Polygon >: 1640

☐ Stagger the Grid Points

```
Determinate:  26.2528430259109
Fit Coefficients:  12.19041 -1.249581E-02 -2.282514E-02
Standard deviation:  1.276821E-04
Specimen tilt in radians:
ThetaX = -1.249548E-02 ThetaY= -2.282316E-02 Theta=  2.601987E-02
Specimen tilt in degrees:
ThetaX = -.7159384 ThetaY= -1.307671 Theta=  1.490829
```

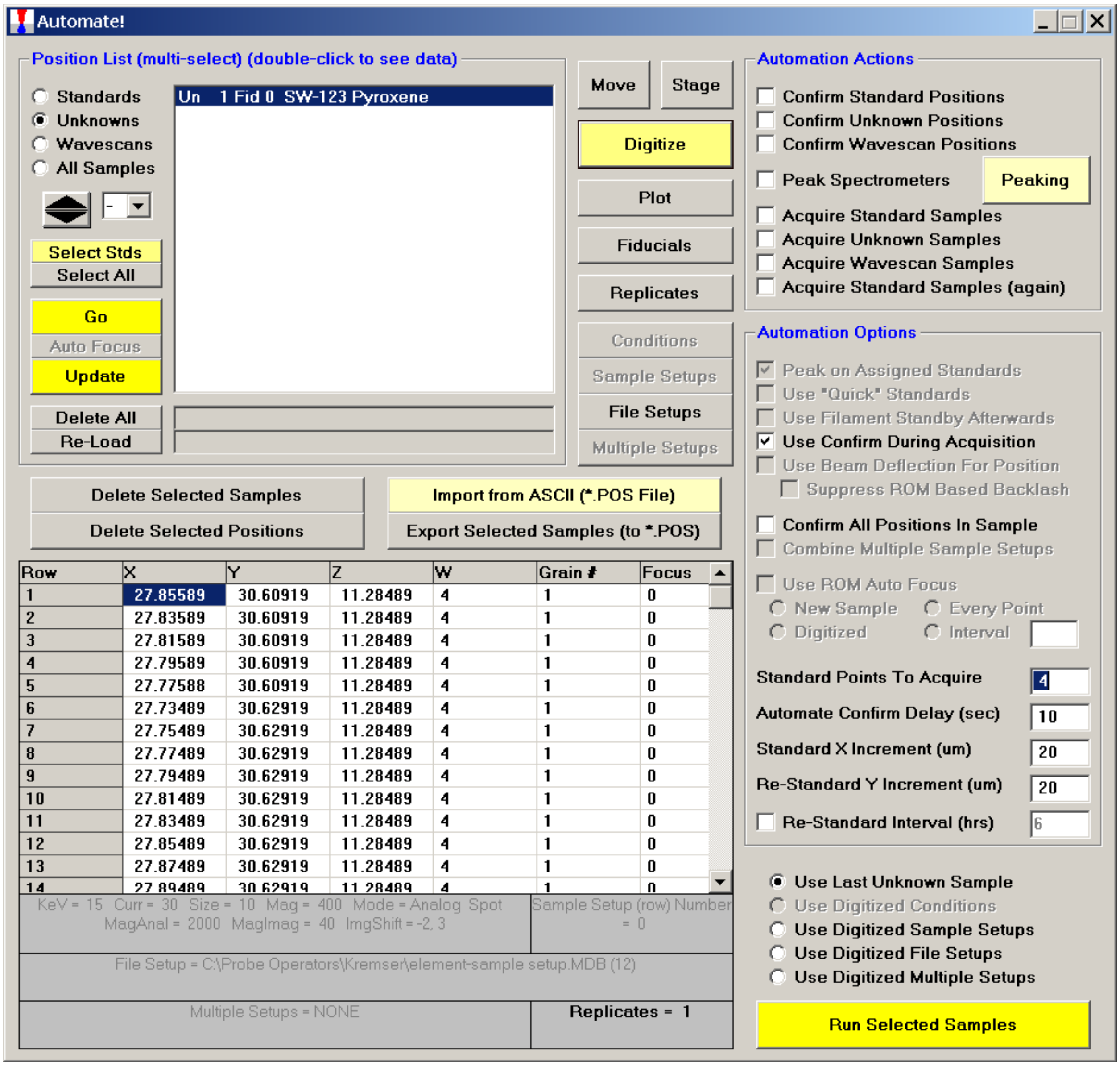
When the appropriate gridding parameters have been set, click the **OK** button, closing the **Polygon Grid Parameters** window.

The **DigitizeSaveGrid** window re-appears, click the **Yes** button.



3740 points (assuming a rectangular grid) is a lot of points, are you sure that you want to digitize this many points?

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



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

○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 Fid 0 SW-123 Pyroxene

Row	X	Y	Z	W	Grain #	Focus
1	27.85589	30.60919	11.28489	4	1	0
2	27.83589	30.60919	11.28489	4	1	0
3	27.81589	30.60919	11.28489	4	1	0
4	27.79589	30.60919	11.28489	4	1	0
5	27.77588	30.60919	11.28489	4	1	0
6	27.73489	30.62919	11.28489	4	1	0
7	27.75489	30.62919	11.28489	4	1	0
8	27.77489	30.62919	11.28489	4	1	0
9	27.79489	30.62919	11.28489	4	1	0
10	27.81489	30.62919	11.28489	4	1	0
11	27.83489	30.62919	11.28489	4	1	0
12	27.85489	30.62919	11.28489	4	1	0
13	27.87489	30.62919	11.28489	4	1	0
14	27.89489	30.62919	11.28489	4	1	0

KeV = 15 Curr = 30 Size = 10 Mag = 400 Mode = Analog Spot
MagAnal = 2000 MagImag = 40 ImgShift = -2, 3

Sample Setup (row) Number = 0

File Setup = C:\Probe Operators\Kremser\element-sample setup.MDB (12)

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)

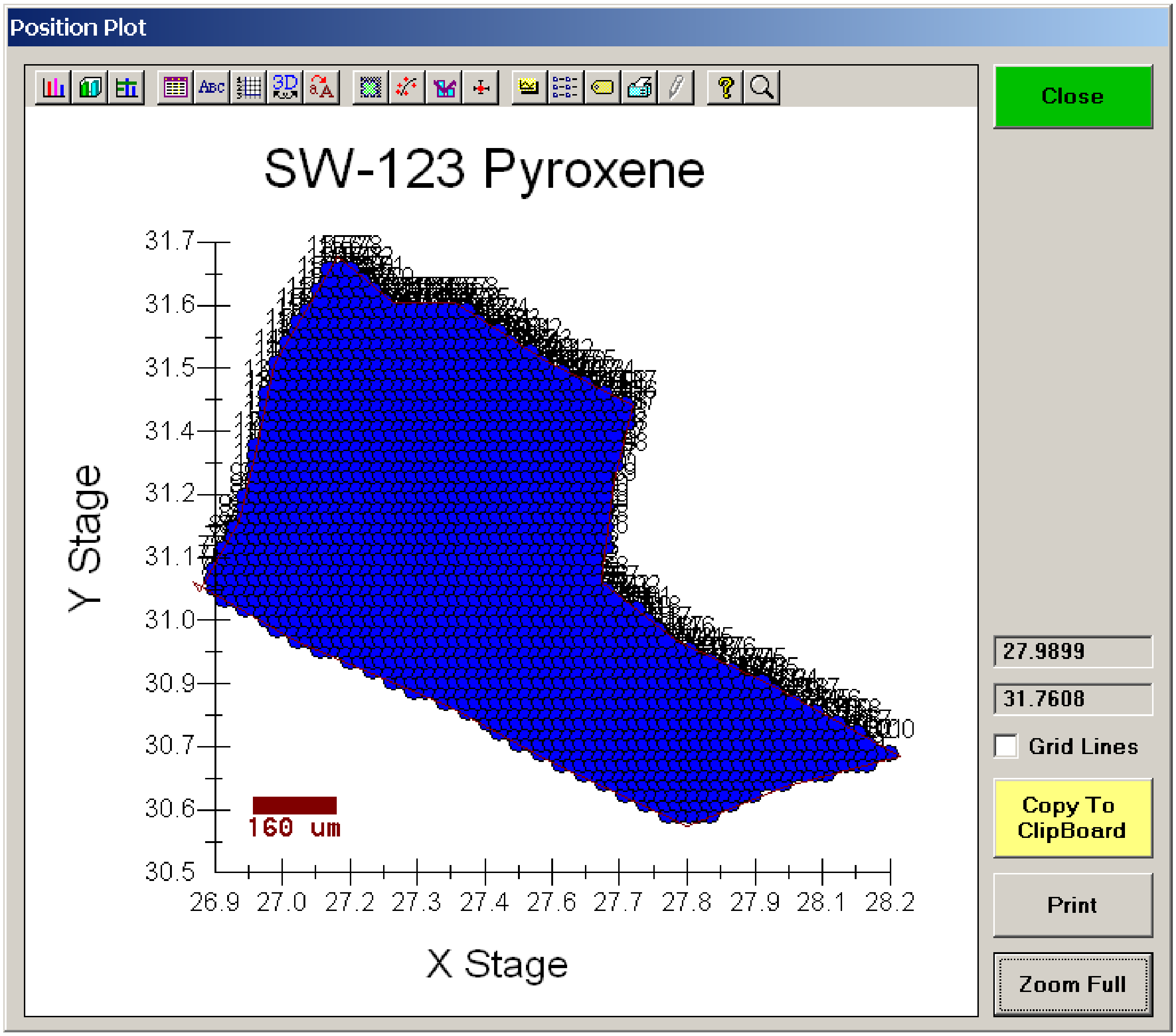
Automation Options

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

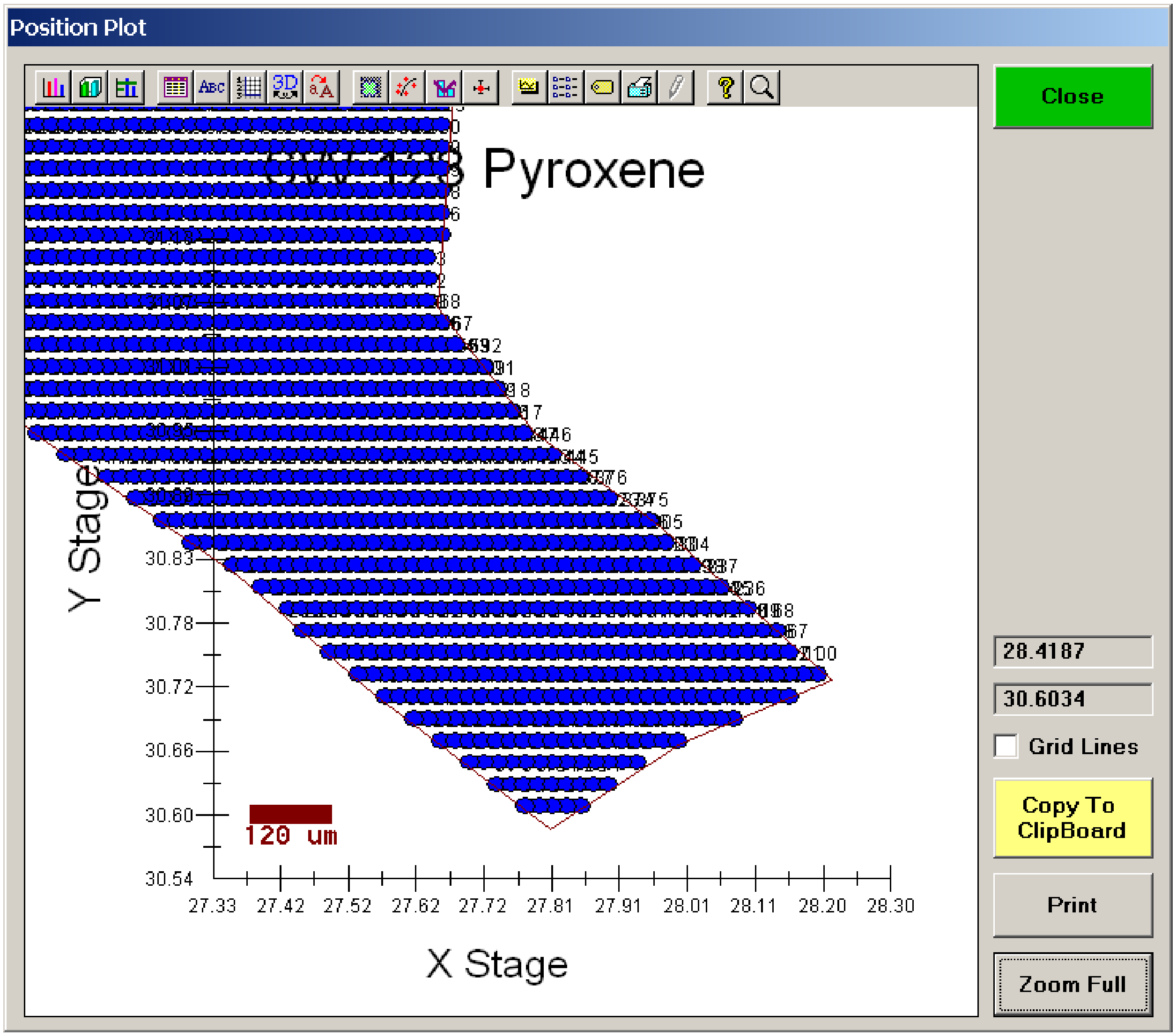
Standard Points To Acquire 4
Automate Confirm Delay (sec) 10
Standard X Increment (um) 20
Re-Standard Y Increment (um) 20
☐ Re-Standard Interval (hrs) 6

● 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. 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.



28.4187

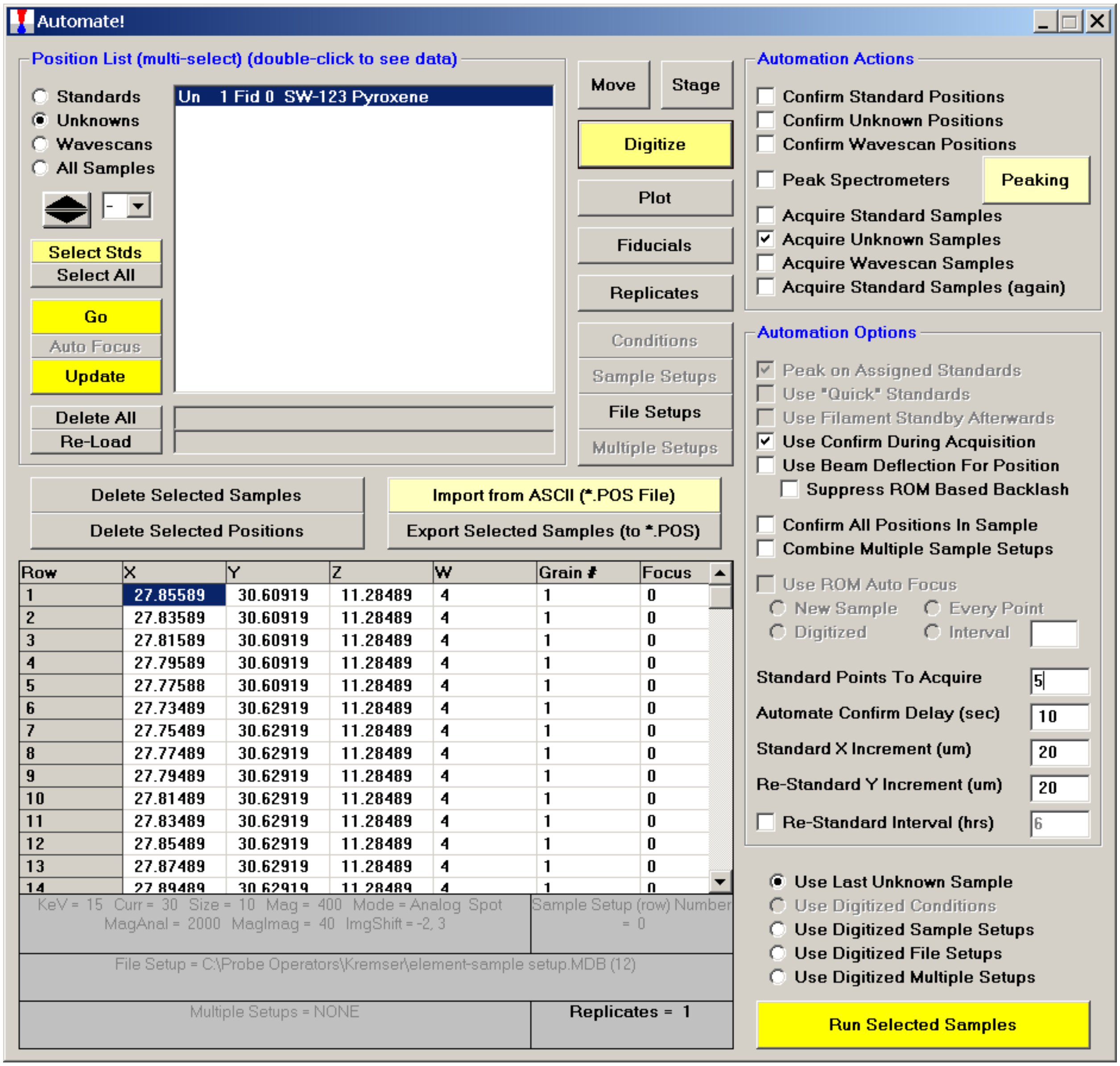
30.6034

☐ Grid Lines

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.



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

○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 Fid 0 SW-123 Pyroxene

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
☐ Suppress ROM Based Backlash
☐ Confirm All Positions In Sample
☐ Combine Multiple Sample Setups
☐ Use ROM Auto Focus
○ New Sample ○ Every Point
○ Digitized ○ Interval

Standard Points To Acquire: 5
Automate Confirm Delay (sec): 10
Standard X Increment (um): 20
Re-Standard Y Increment (um): 20
☐ Re-Standard Interval (hrs): 6

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

Row	X	Y	Z	W	Grain #	Focus
1	27.85589	30.60919	11.28489	4	1	0
2	27.83589	30.60919	11.28489	4	1	0
3	27.81589	30.60919	11.28489	4	1	0
4	27.79589	30.60919	11.28489	4	1	0
5	27.77588	30.60919	11.28489	4	1	0
6	27.73489	30.62919	11.28489	4	1	0
7	27.75489	30.62919	11.28489	4	1	0
8	27.77489	30.62919	11.28489	4	1	0
9	27.79489	30.62919	11.28489	4	1	0
10	27.81489	30.62919	11.28489	4	1	0
11	27.83489	30.62919	11.28489	4	1	0
12	27.85489	30.62919	11.28489	4	1	0
13	27.87489	30.62919	11.28489	4	1	0
14	27.89489	30.62919	11.28489	4	1	0

KeV = 15 Curr = 30 Size = 10 Mag = 400 Mode = Analog Spot
MagAnal = 2000 MagImag = 40 ImgShift = -2, 3

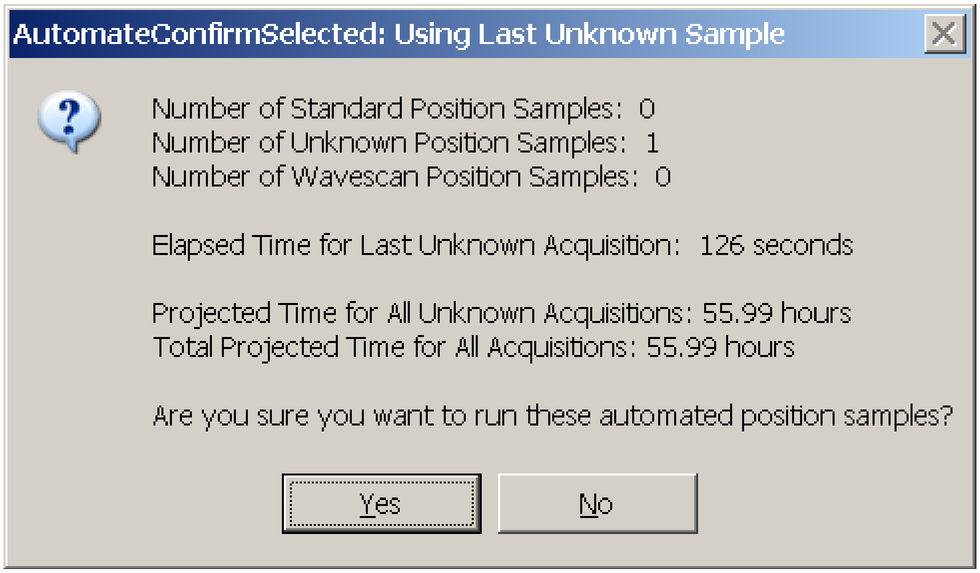
Sample Setup (row) Number = 0

File Setup = C:\Probe Operators\Kremser\element-sample setup.MDB (12)

Multiple Setups = NONE

Replicates = 1

The **AutomateConfirmSelected** window opens and the user clicks the **Yes** button to activate the acquisition.



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

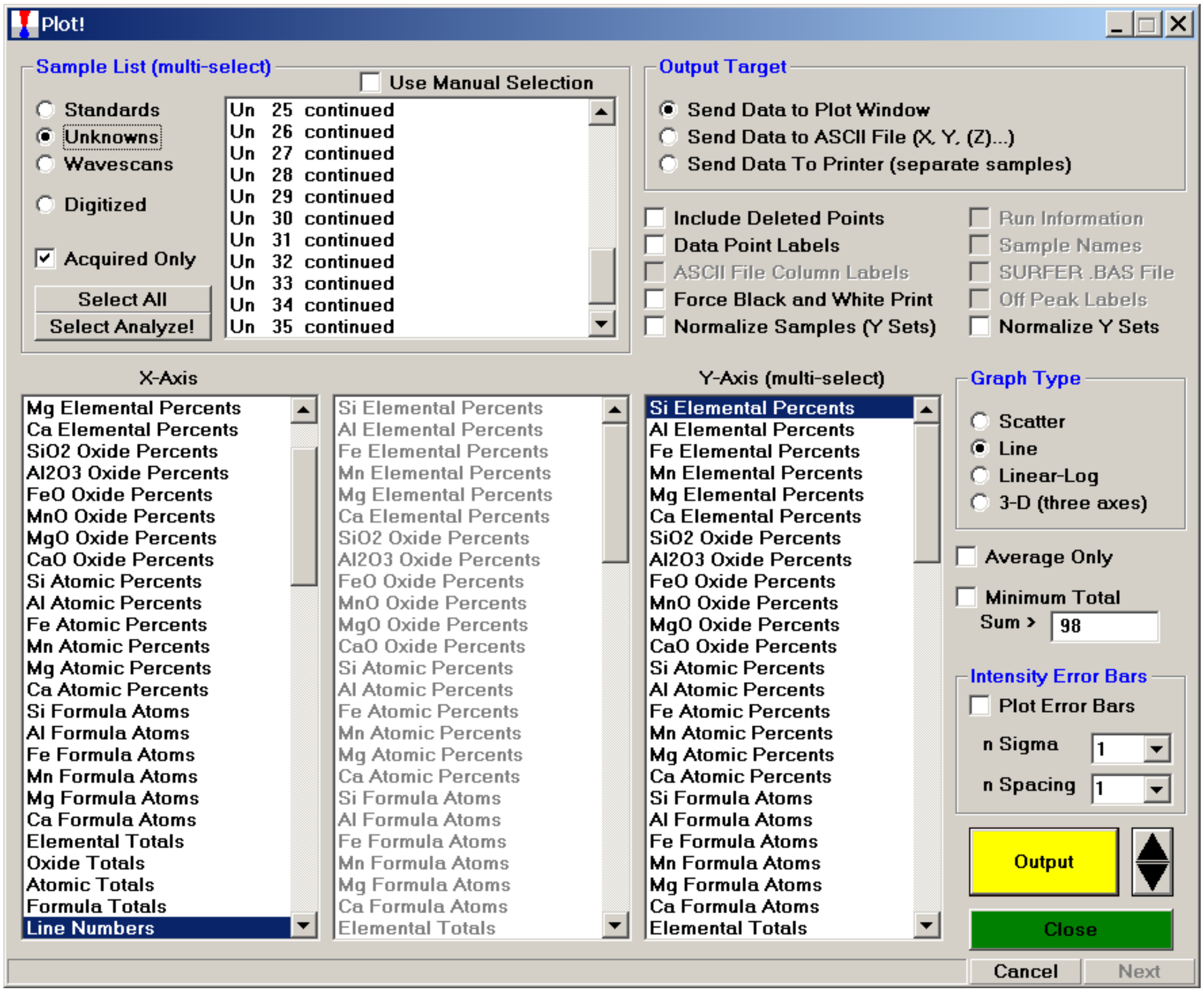
Elapsed Time for Last Unknown Acquisition: 126 seconds

Projected Time for All Unknown Acquisitions: 55.99 hours
Total Projected Time for All Acquisitions: 55.99 hours

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

Note, acquisition time is now calculated.

Upon completion of the data acquisition, open the **Plot!** window.



Sample List (multi-select)

☐ Use Manual Selection

○ Standards
● Unknowns
○ Wavescans
○ Digitized

☑ 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

Y-Axis (multi-select)

Graph Type

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

☐ Average Only

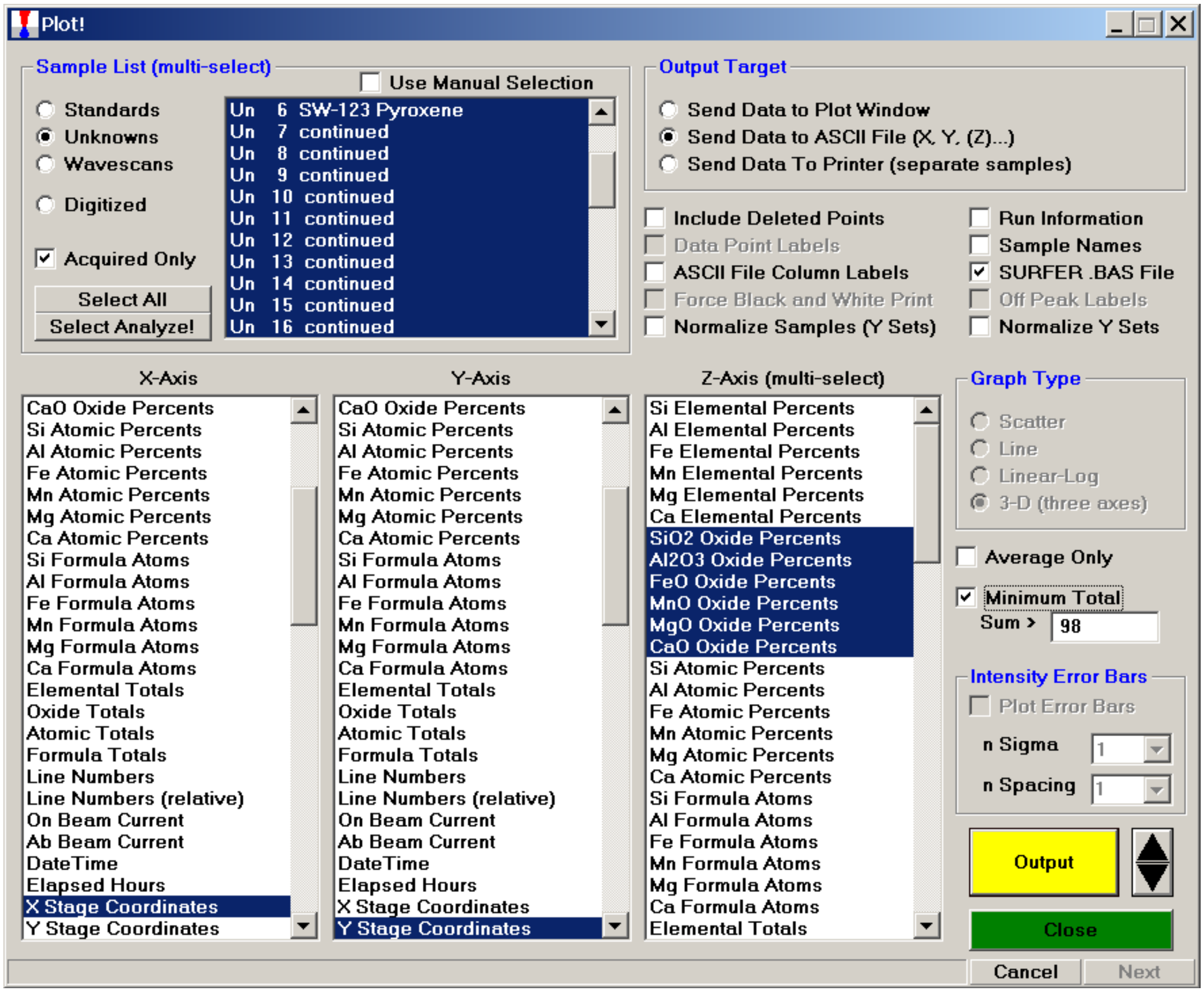
☐ Minimum Total
Sum > 98

Intensity Error Bars

☐ Plot Error Bars
n Sigma 1
n Spacing 1

Select (highlight) all of the unknown digitized points (Un6-35 in this example). 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 the other check boxes listed here. Click the *SURFER.BAS File* check box and select an *X-Axis, Y-Axis* and *Z-Axis (multi-select)* parameters to plot.



Plot!

Sample List (multi-select)

☐ Use Manual Selection

○ Standards
● Unknowns
○ Wavescans
○ Digitized

☑ Acquired Only

Select All
Select Analyze!

Un 6 SW-123 Pyroxene
Un 7 continued
Un 8 continued
Un 9 continued
Un 10 continued
Un 11 continued
Un 12 continued
Un 13 continued
Un 14 continued
Un 15 continued
Un 16 continued

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

CaO Oxide Percents
Si Atomic Percents
Al Atomic Percents
Fe Atomic Percents
Mn Atomic Percents
Mg Atomic Percents
Ca Atomic Percents
Si Formula Atoms
Al Formula Atoms
Fe Formula Atoms
Mn Formula Atoms
Mg Formula Atoms
Ca Formula Atoms
Elemental Totals
Oxide Totals
Atomic Totals
Formula Totals
Line Numbers
Line Numbers (relative)
On Beam Current
Ab Beam Current
DateTime
Elapsed Hours
X Stage Coordinates
Y Stage Coordinates

Y-Axis

CaO Oxide Percents
Si Atomic Percents
Al Atomic Percents
Fe Atomic Percents
Mn Atomic Percents
Mg Atomic Percents
Ca Atomic Percents
Si Formula Atoms
Al Formula Atoms
Fe Formula Atoms
Mn Formula Atoms
Mg Formula Atoms
Ca Formula Atoms
Elemental Totals
Oxide Totals
Atomic Totals
Formula Totals
Line Numbers
Line Numbers (relative)
On Beam Current
Ab Beam Current
DateTime
Elapsed Hours
X Stage Coordinates
Y Stage Coordinates

Z-Axis (multi-select)

Si Elemental Percents
Al Elemental Percents
Fe Elemental Percents
Mn Elemental Percents
Mg Elemental Percents
Ca Elemental Percents
SiO2 Oxide Percents
Al2O3 Oxide Percents
FeO Oxide Percents
MnO Oxide Percents
MgO Oxide Percents
CaO Oxide Percents
Si Atomic Percents
Al Atomic Percents
Fe Atomic Percents
Mn Atomic Percents
Mg Atomic Percents
Ca Atomic Percents
Si Formula Atoms
Al Formula Atoms
Fe Formula Atoms
Mn Formula Atoms
Mg Formula Atoms
Ca Formula Atoms
Elemental Totals

Graph Type

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

☐ Average Only
☑ Minimum Total
Sum > 98

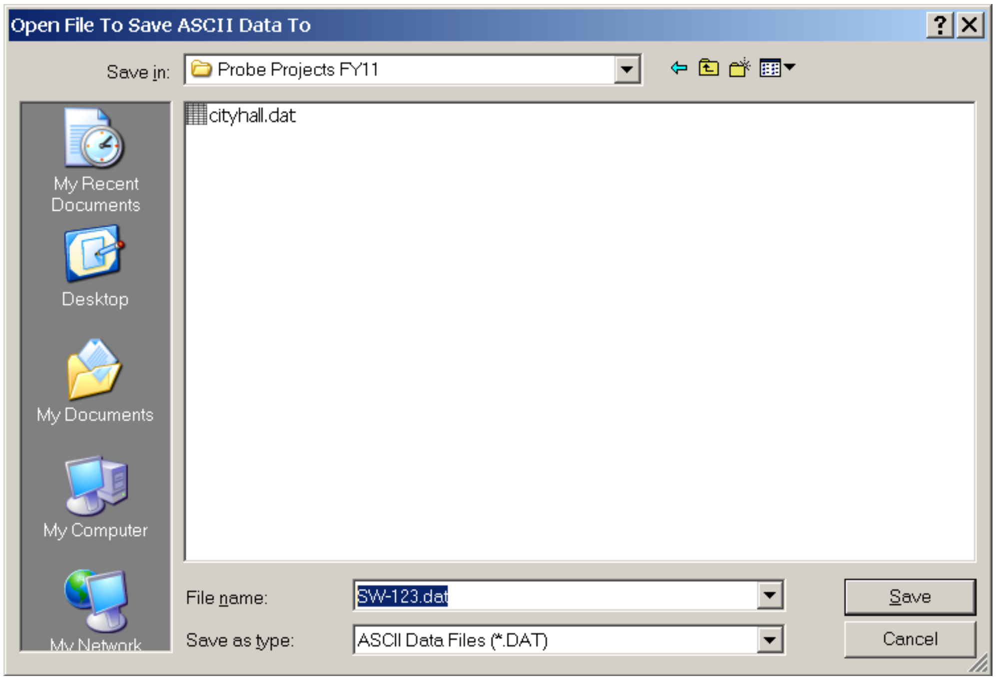
Intensity Error Bars

☐ Plot Error Bars
n Sigma 1
n Spacing 1

Output
Close
Cancel
Next

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: Probe Projects FY11

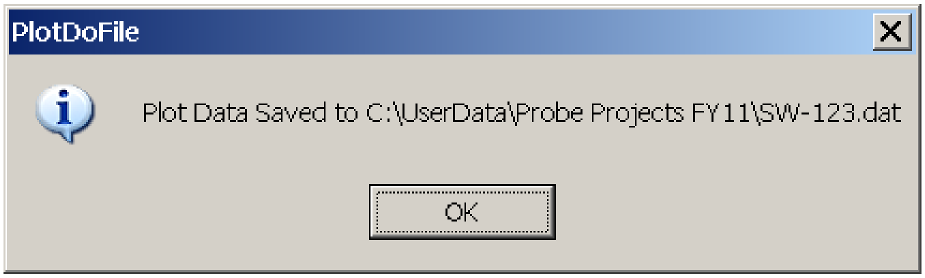
cityhall.dat

File name: SW-123.dat

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

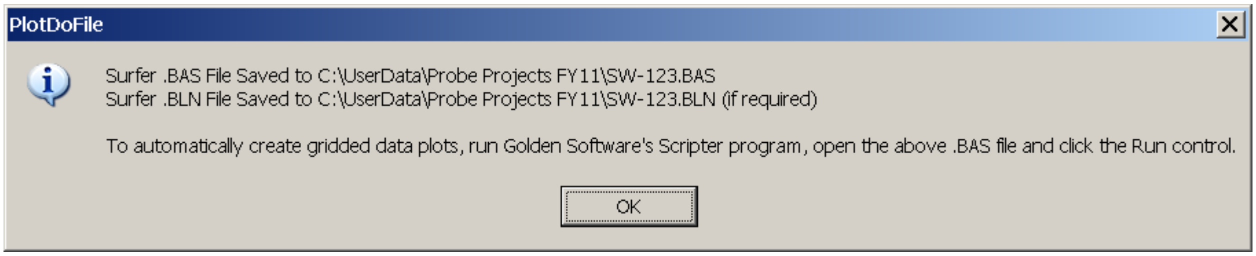
Click the **Save** button.

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



Plot Data Saved to C:\UserData\Probe Projects FY11\SW-123.dat

Another **PlotDoFile** window appears.



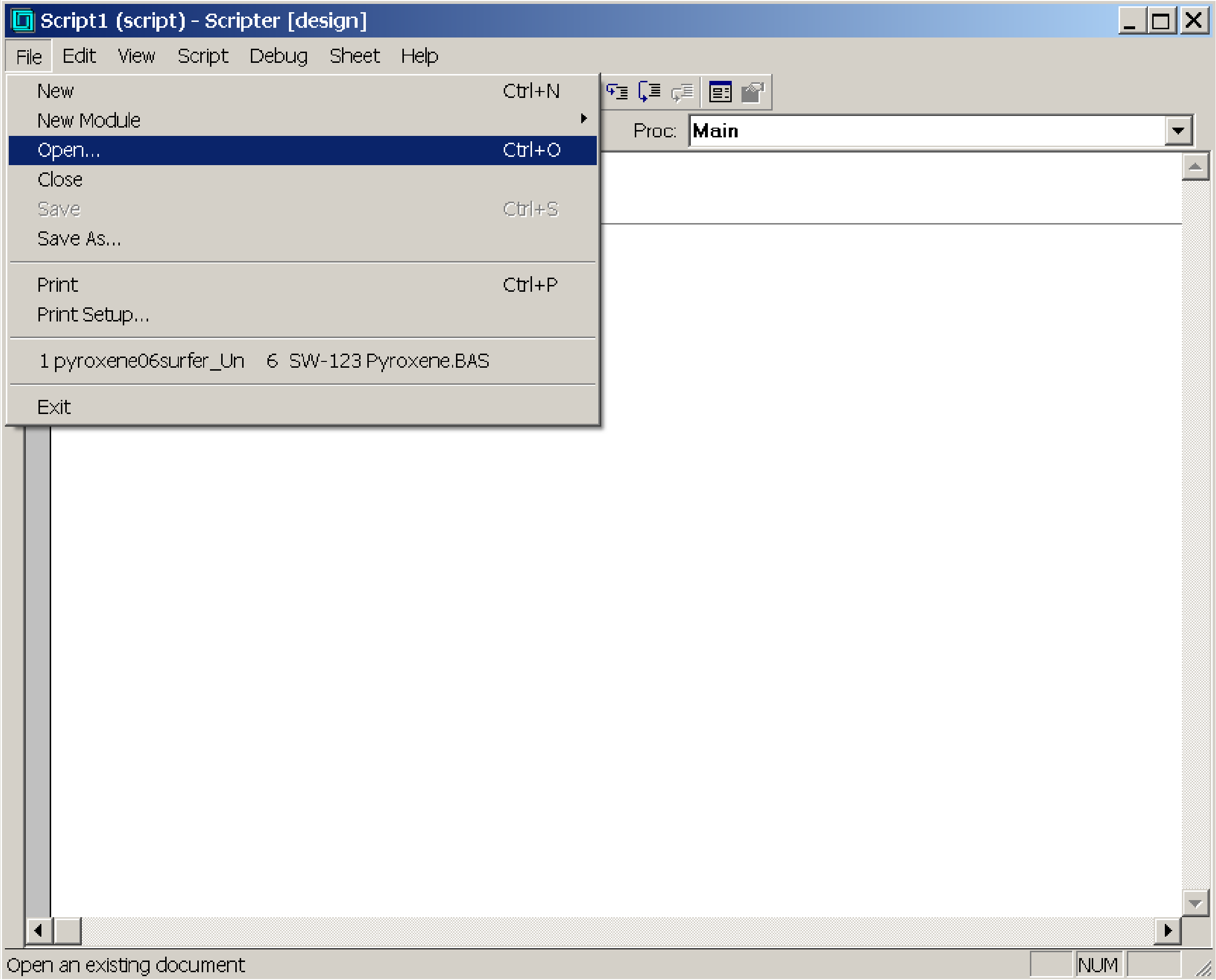
Surfer .BAS File Saved to C:\UserData\Probe Projects FY11\SW-123.BAS
Surfer .BLN File Saved to C:\UserData\Probe Projects FY11\SW-123.BLN (if required)

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

Click the **OK** button to create these files.

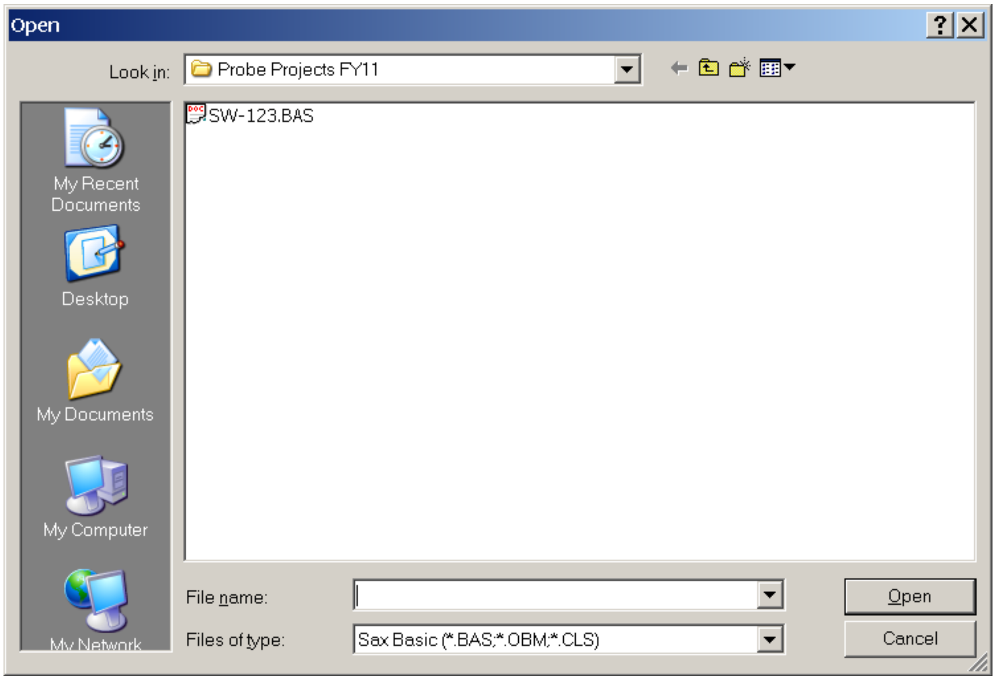
The SW123.BAS script file created above contains the OLE code for generating contour and surface plots of the digitized probe data.

To run the SW123.BAS script file, double click on the **GS Scripter32** icon in the PROBE FOR EPMA Software folder on the desktop. Select the **File | Open** menu.



The **Open Document** window appears.

Edit the *Look in:* directory to identify the location of the SW123.BAS file.



Look in: Probe Projects FY11

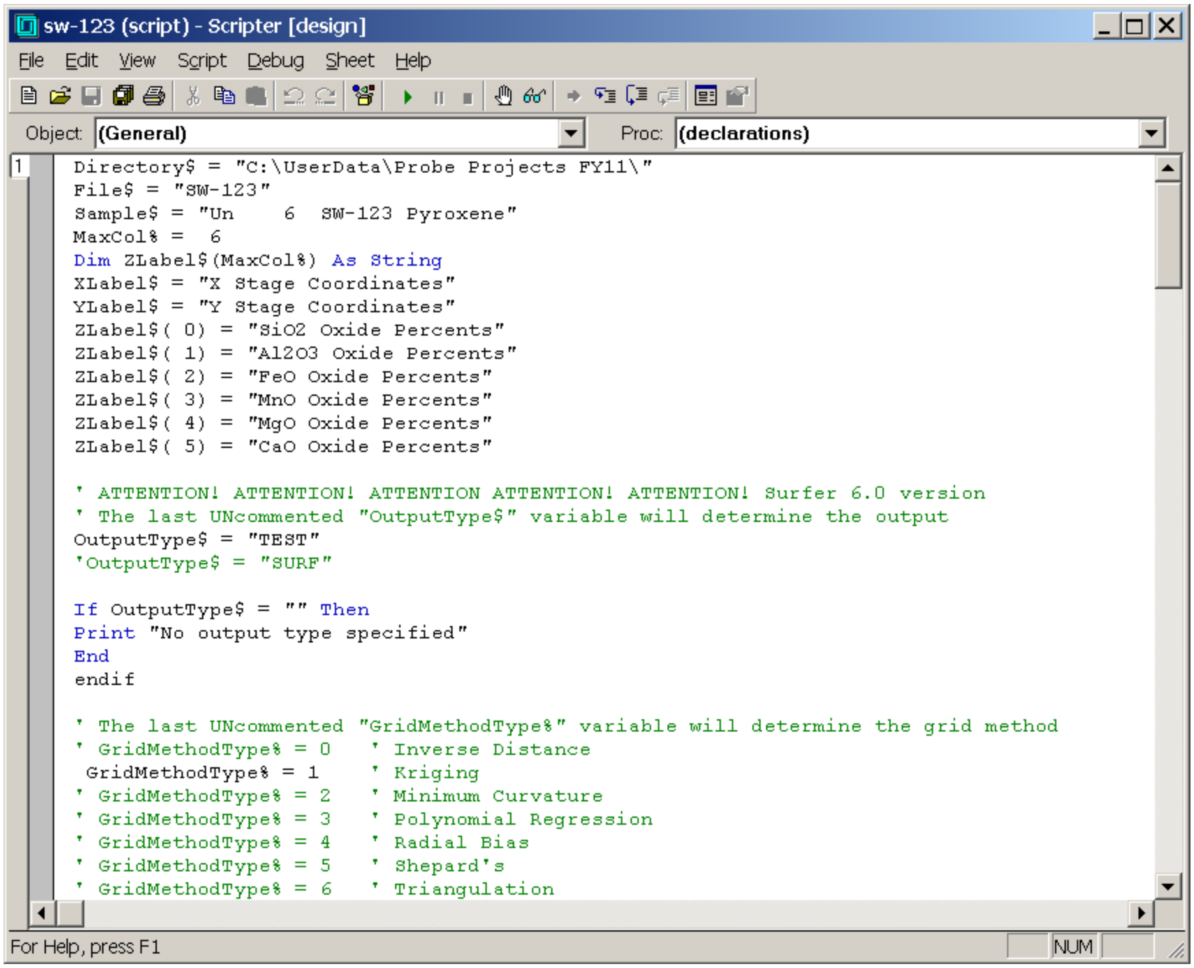
SW-123.BAS

File name:

Files of type: Sax Basic (*.BAS;*.OBM;*.CLS)

Click the **Open** button.

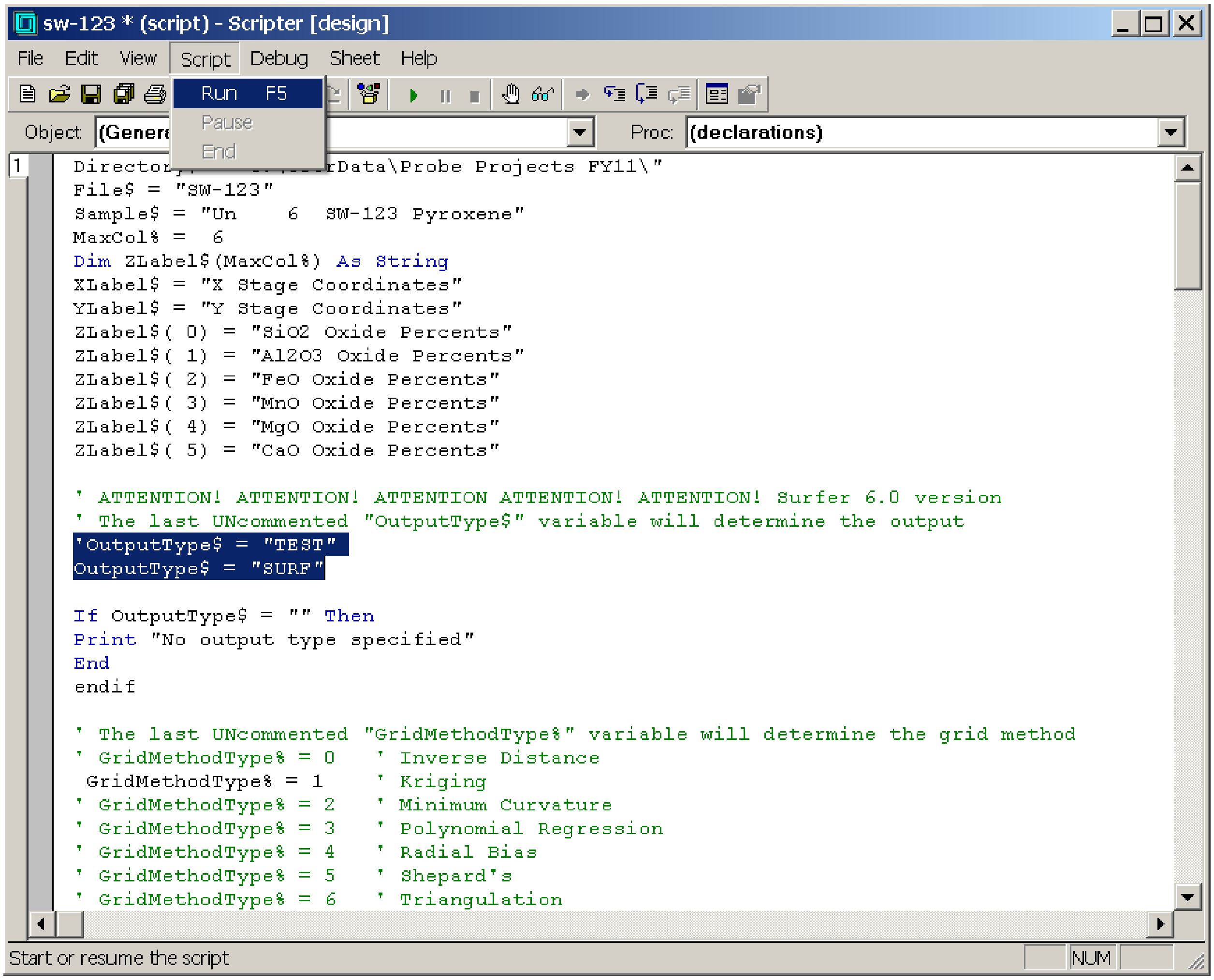
GS Scripter now details the open SW123.BAS file, of which a portion is illustrated below.



```
Directory$ = "C:\UserData\Probe Projects FY11\"
File$ = "SW-123"
Sample$ = "Un     6   SW-123 Pyroxene"
MaxCol% =   6
Dim ZLabel$(MaxCol%) As String
XLabel$ = "X Stage Coordinates"
YLabel$ = "Y Stage Coordinates"
ZLabel$( 0) = "SiO2 Oxide Percents"
ZLabel$( 1) = "Al2O3 Oxide Percents"
ZLabel$( 2) = "FeO Oxide Percents"
ZLabel$( 3) = "MnO Oxide Percents"
ZLabel$( 4) = "MgO Oxide Percents"
ZLabel$( 5) = "CaO Oxide Percents"

' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! Surfer 6.0 version
' The last UNcommented "OutputType$" variable will determine the output
OutputType$ = "TEST"
'OutputType$ = "SURF"

If OutputType$ = "" Then
Print "No output type specified"
End
endif

' The last UNcommented "GridMethodType%" variable will determine the grid method
' GridMethodType% = 0    ' Inverse Distance
 GridMethodType% = 1     ' Kriging
' GridMethodType% = 2    ' Minimum Curvature
' GridMethodType% = 3    ' Polynomial Regression
' GridMethodType% = 4    ' Radial Bias
' GridMethodType% = 5    ' Shepard's
' GridMethodType% = 6    ' Triangulation
```

The default output mode of the script file is "TEST", which will only output the plots to the screen. To produce output to the default printer, comment out the line OutputType$ = "TEST" by placing a single quote in front of the line and uncomment the line OutputType$ = "SURF" by removing the single quote in front of it (highlighted in next screen capture).

Click **Run | Start** menu to begin the automated plotting.

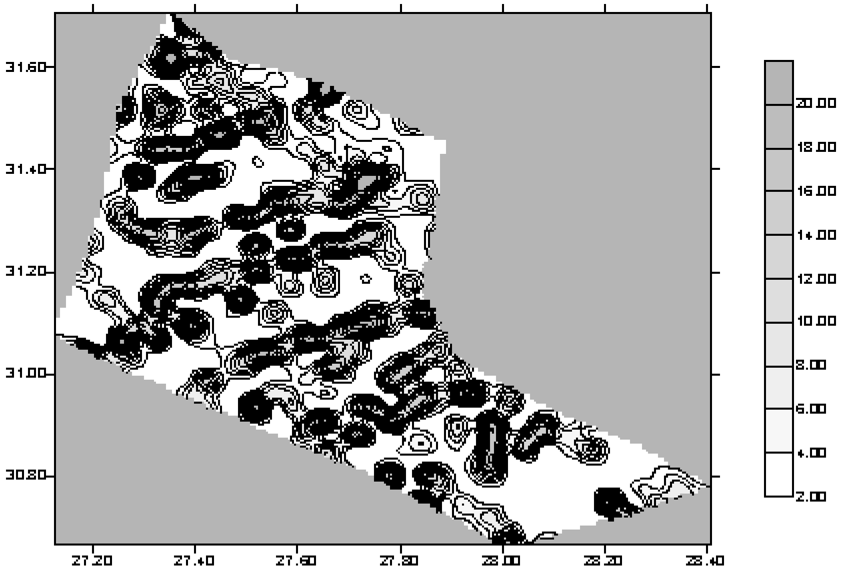


```
Director             rData\Probe Projects FY11\"
File$ = "SW-123"
Sample$ = "Un     6   SW-123 Pyroxene"
MaxCol% =  6
Dim ZLabel$(MaxCol%) As String
XLabel$ = "X Stage Coordinates"
YLabel$ = "Y Stage Coordinates"
ZLabel$( 0) = "SiO2 Oxide Percents"
ZLabel$( 1) = "Al2O3 Oxide Percents"
ZLabel$( 2) = "FeO Oxide Percents"
ZLabel$( 3) = "MnO Oxide Percents"
ZLabel$( 4) = "MgO Oxide Percents"
ZLabel$( 5) = "CaO Oxide Percents"

' ATTENTION! ATTENTION! ATTENTION ATTENTION! ATTENTION! Surfer 6.0 version
' The last UNcommented "OutputType$" variable will determine the output
'OutputType$ = "TEST"
OutputType$ = "SURF"

If OutputType$ = "" Then
Print "No output type specified"
End
endif

' The last UNcommented "GridMethodType%" variable will determine the grid method
' GridMethodType% = 0    ' Inverse Distance
 GridMethodType% = 1     ' Kriging
' GridMethodType% = 2    ' Minimum Curvature
' GridMethodType% = 3    ' Polynomial Regression
' GridMethodType% = 4    ' Radial Bias
' GridMethodType% = 5    ' Shepard's
' GridMethodType% = 6    ' Triangulation
```

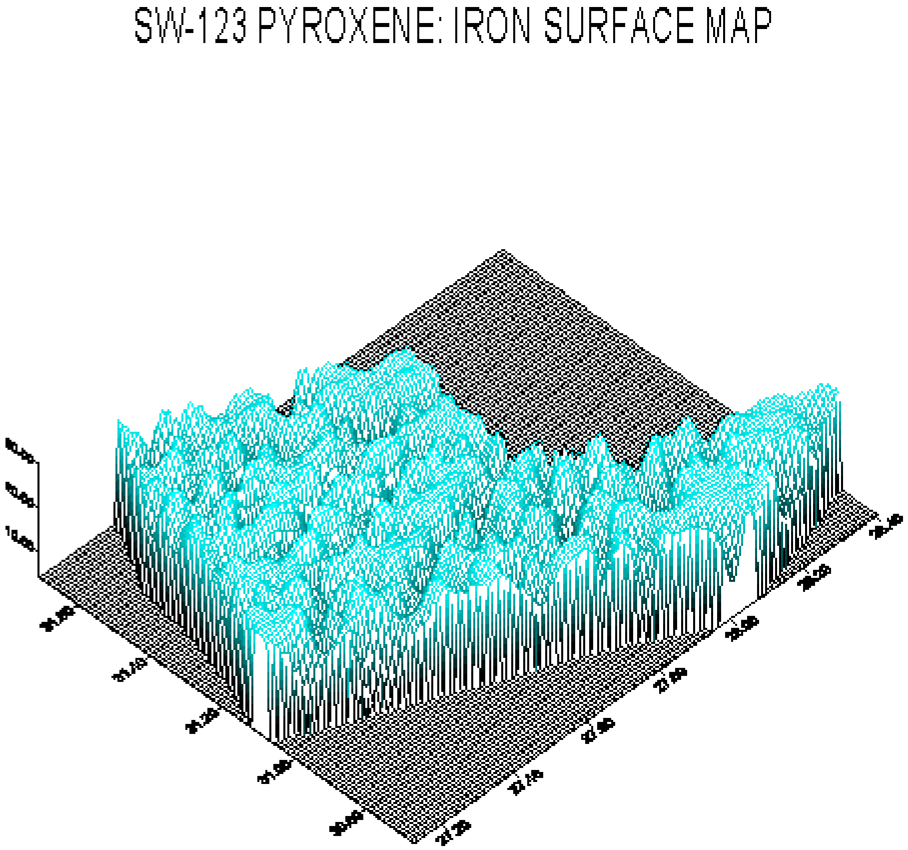
Basic contour and surface maps will be output to the printer. Raw data concentration (*.GRD) files will also be created; these may be opened in SURFER for further modification and output.

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.



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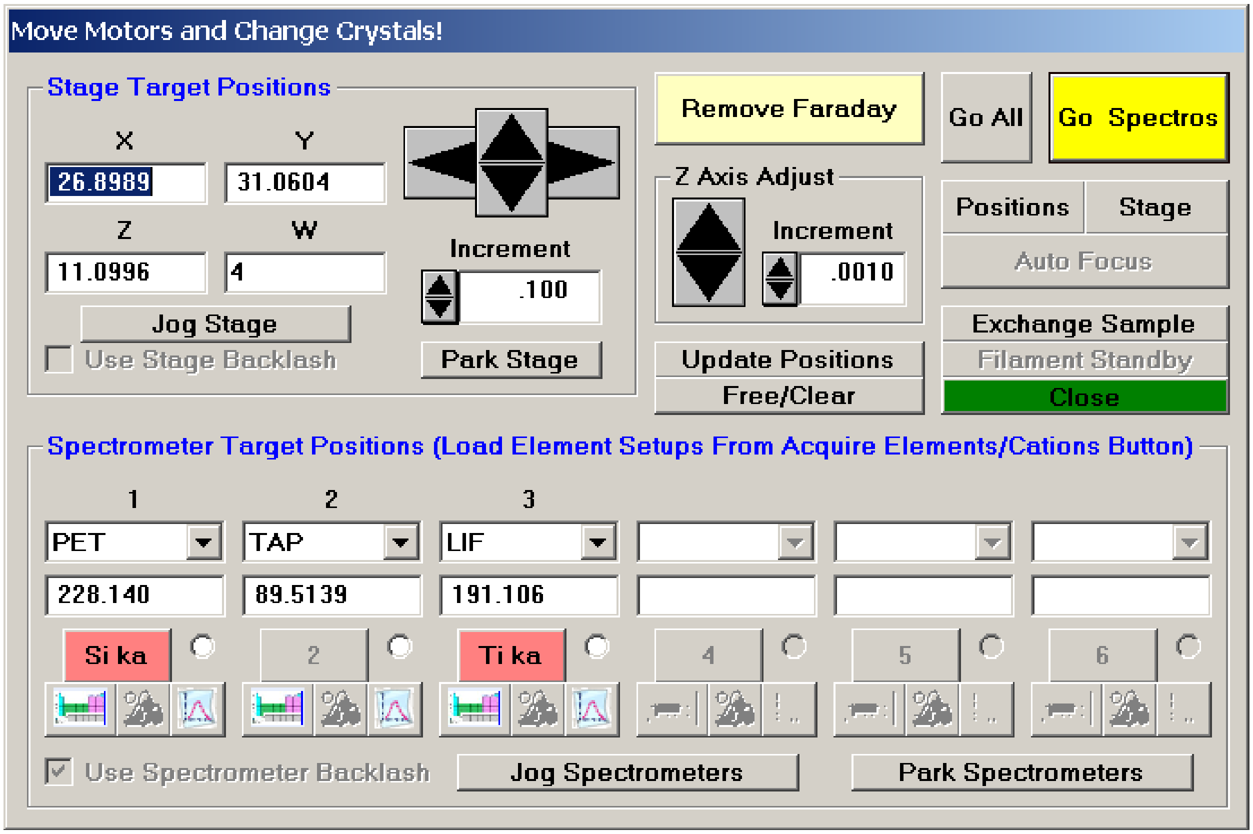
Stage Bit Maps and Picture Snap! Feature

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 the JEOL 733 microprobe the user has several options for searching for analysis or standard locations. An optical image (reflected or transmitted light) or a video feed of the same image is available but at only one relatively high magnification, about 400 times. Additionally, one can search for the area of interest utilizing the secondary or backscattered detectors on the microprobe at variable magnifications (ranging as low as 40 times), 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 and used to effectively narrow the search for the analysis position.

Now, navigation around and exact positioning is easily accomplished using the stage bit map and Picture Snap! features in PROBE FOR EPMA. 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: 26.8989
Y: 31.0604
Z: 11.0996
W: 4
Increment: .100
☐ Use Stage Backlash

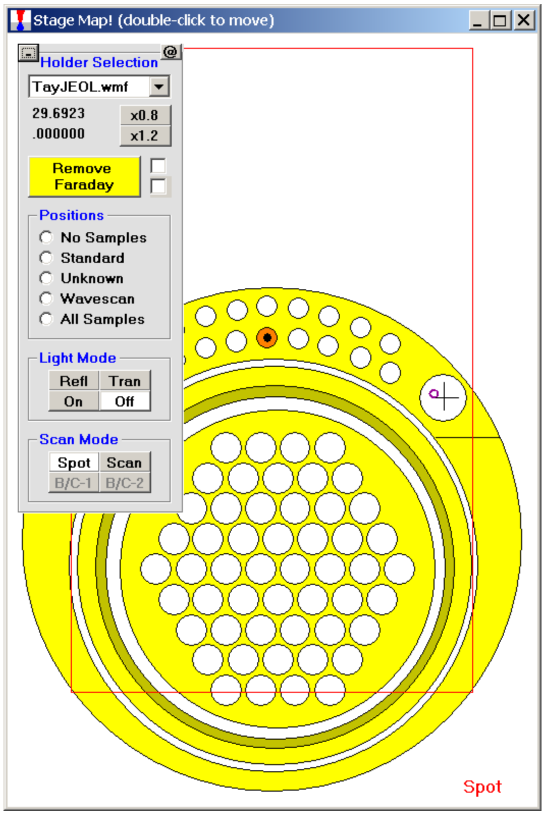
Z Axis Adjust
Increment: .0010

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

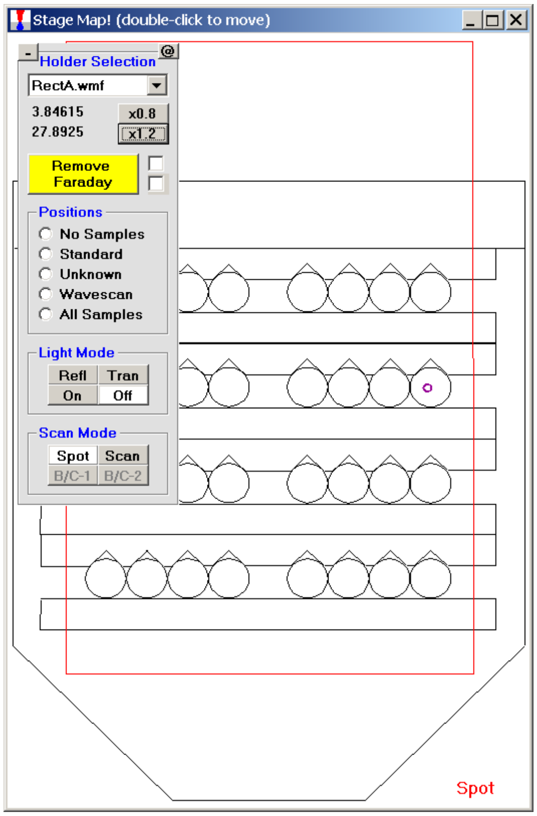
1	2	3			
PET	TAP	LIF			
228.140	89.5139	191.106			
Si ka	2	Ti ka	4	5	6

☑ Use Spectrometer Backlash

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



TayJEOL.wmf
29.6923
.000000



RectA.wmf
3.84615
27.8925

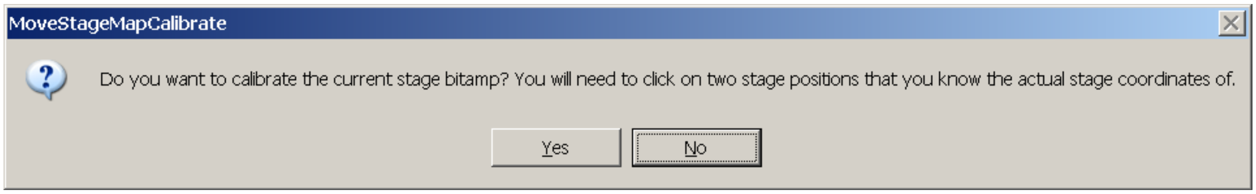
To select another *Holder Selection* image, simply select the file from the drop-down list box. Image files (windows metafiles (*.WMF)) and coordinate limits are specified in the Standards section of the PROBEWIN.INI file. The entire map maybe reduced or enlarged retaining scale using the **x0.8** or **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 (Micrografx Designer or the shareware program Metafile Companion[1]) 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.

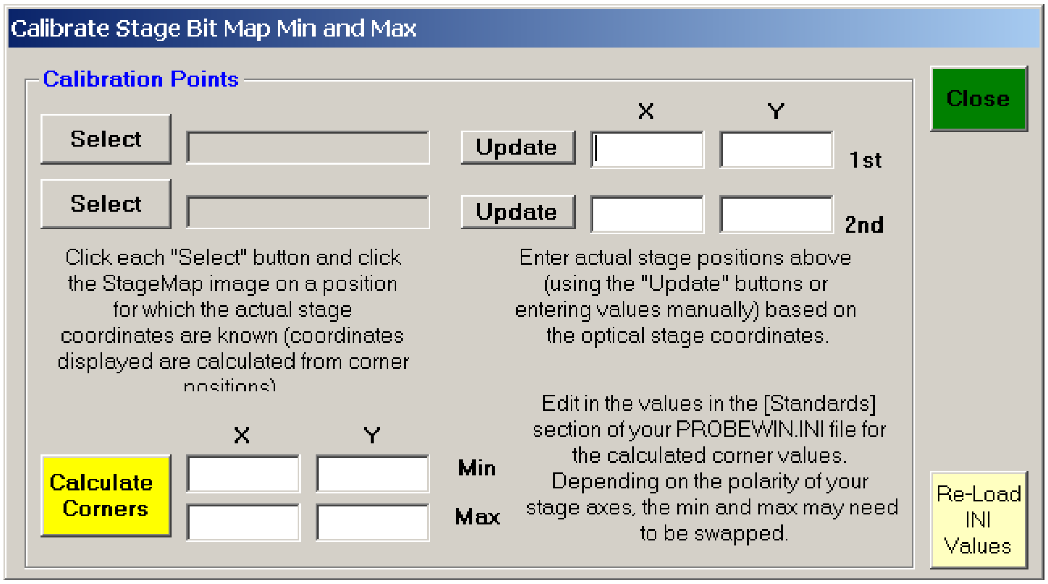
[1] Mention of specific third party software products does not imply their endorsement.

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

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.

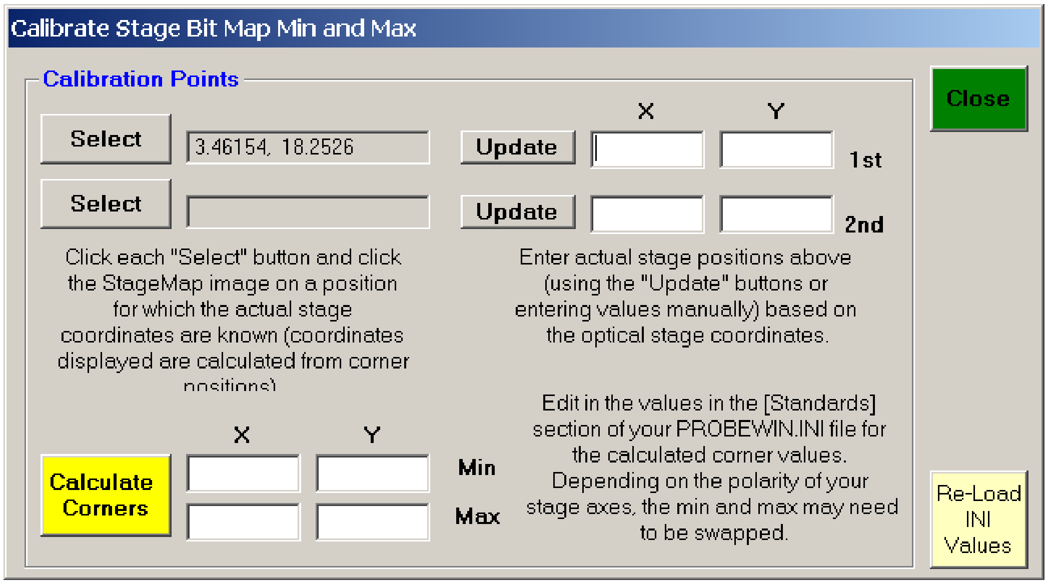
Click the top **Select** button, opening the **Stage Select** window.


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.


Calibrate Stage Bit Map Min and Max

Calibration Points

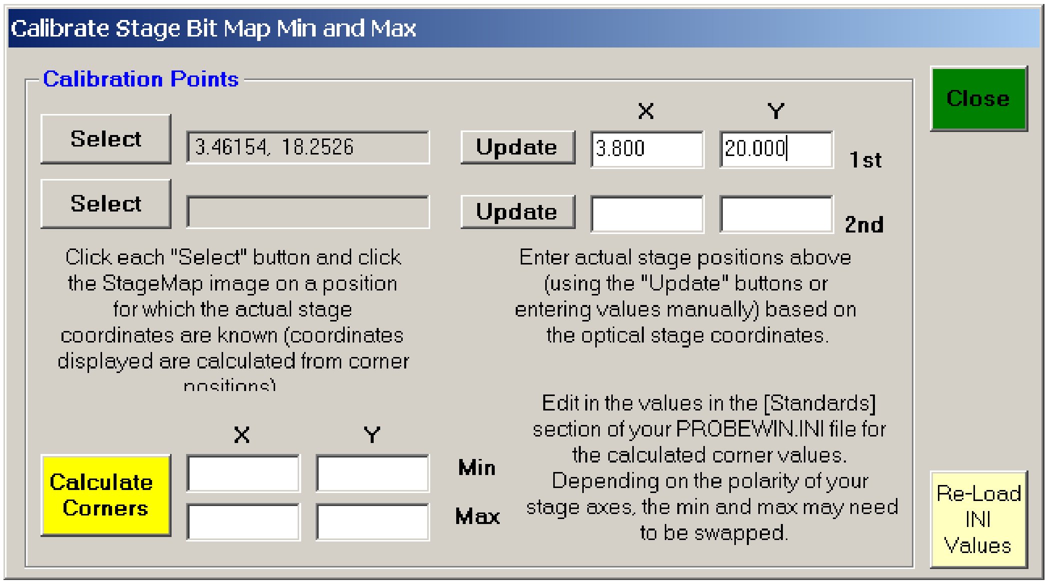
3.46154, 18.2526

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.


Calibrate Stage Bit Map Min and Max

Calibration Points

3.46154, 18.2526

X: 3.800

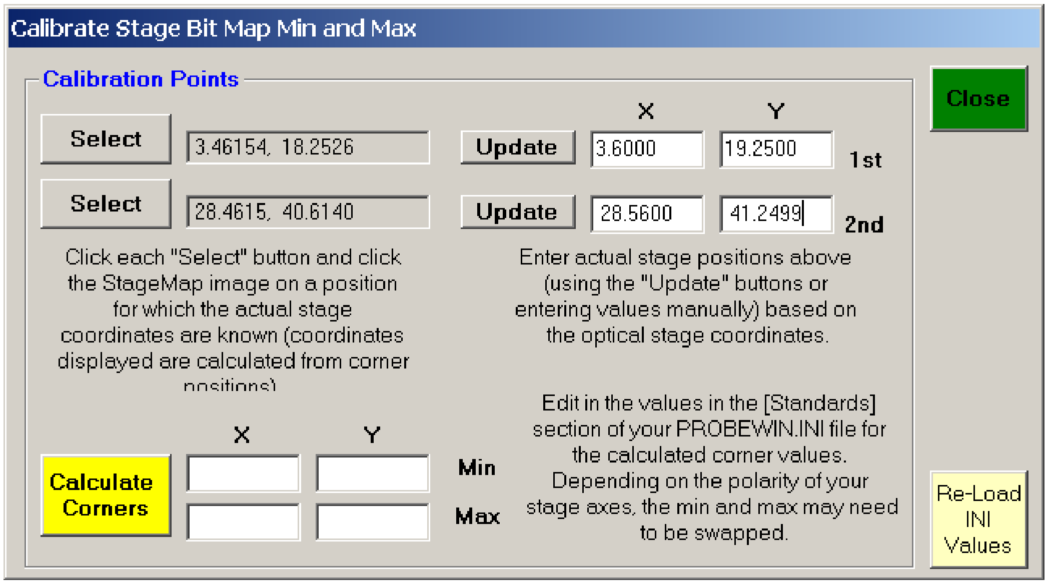
Y: 20.000

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.


Calibrate Stage Bit Map Min and Max

Calibration Points

			X	Y	
Select	3.46154, 18.2526	Update	3.6000	19.2500	1st
Select	28.4615, 40.6140	Update	28.5600	41.2499	2nd

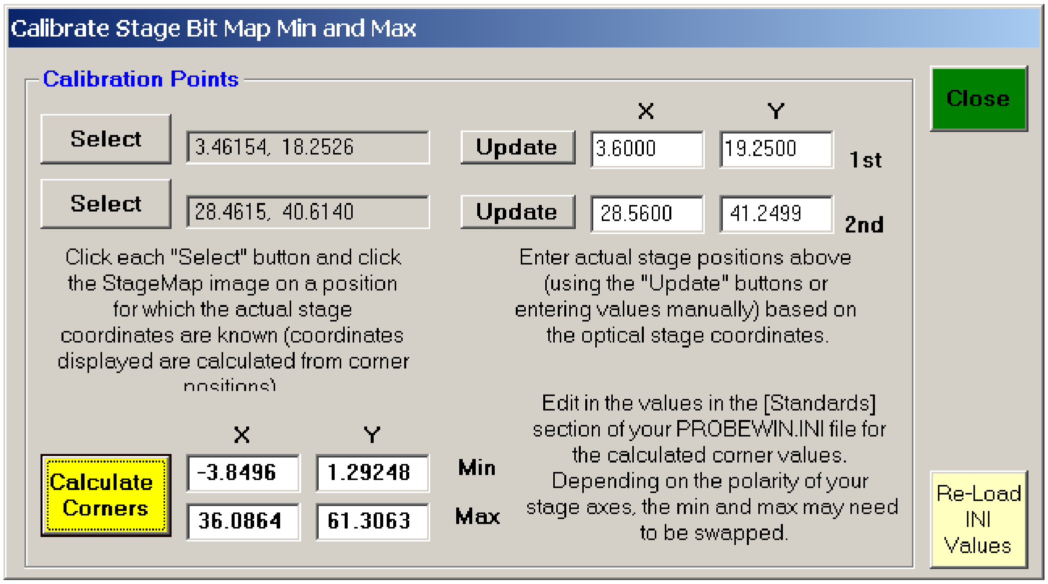
Click each "Select" button and click the StageMap image on a position for which the actual stage coordinates are known (coordinates displayed are calculated from corner positions)

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

	X	Y
Min		
Max		

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 **Calculate Corners** button to obtain the correct corner values to calibrate your Stage Map. These values min and max values are entered into the Standards section of the PROBEWIN.INI file.


Calibrate Stage Bit Map Min and Max

Calibration Points

			X	Y	
Select	3.46154, 18.2526	Update	3.6000	19.2500	1st
Select	28.4615, 40.6140	Update	28.5600	41.2499	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.

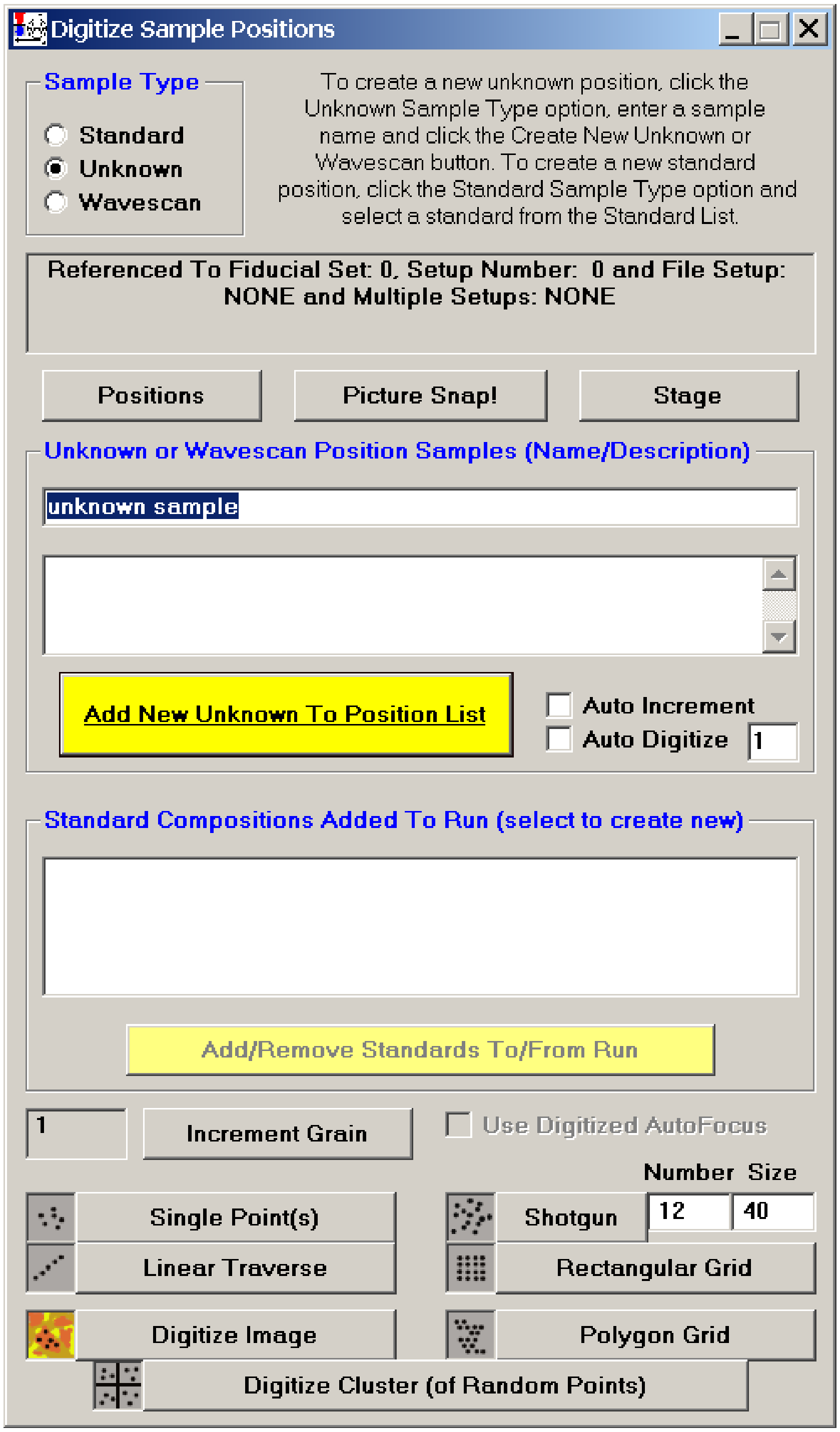
	X	Y
Min	-3.8496	1.29248
Max	36.0864	61.3063

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.

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

The new **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 **Digitize Sample Positions** window.



Sample Type
○ Standard
● Unknown
○ Wavescan

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

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

unknown sample

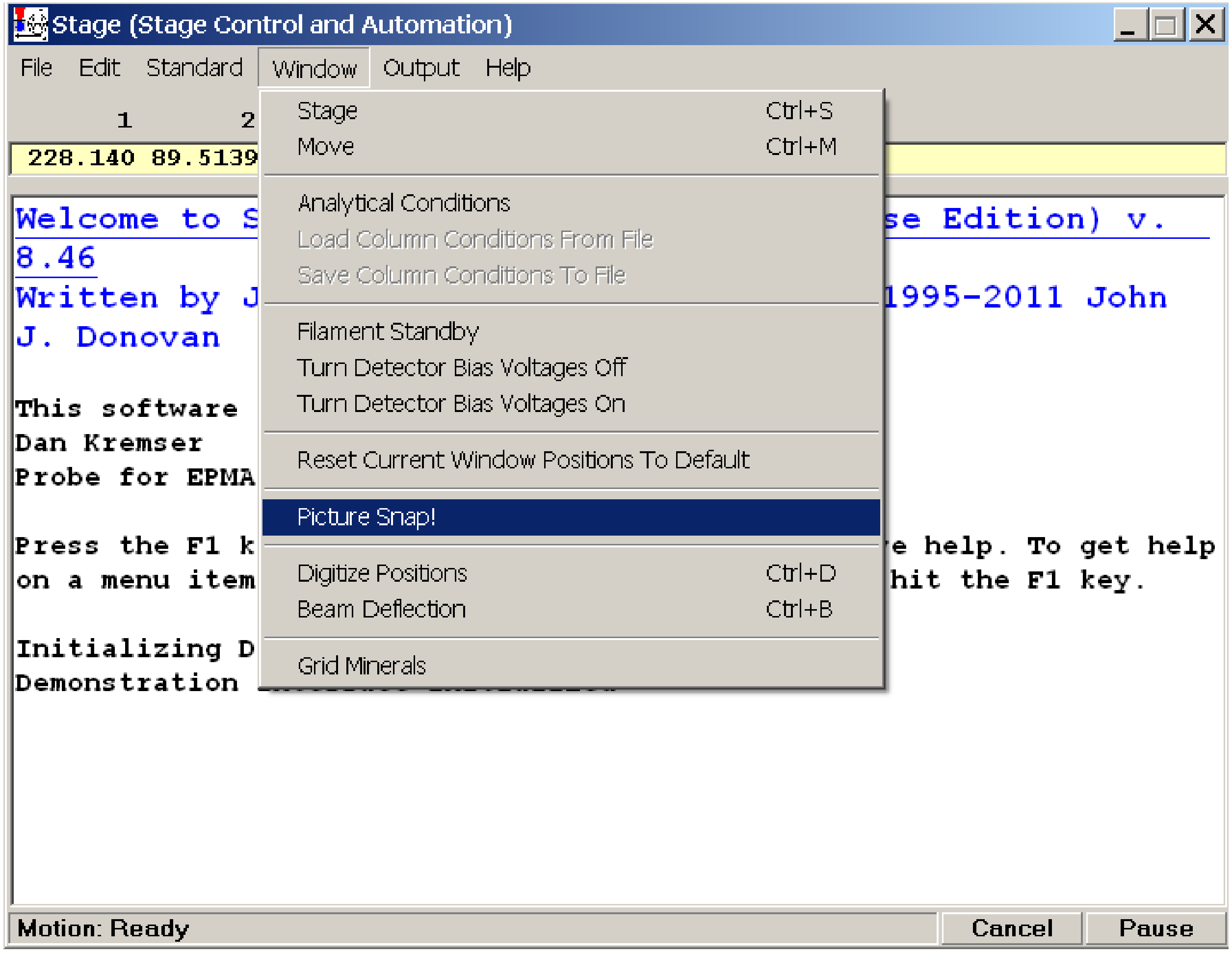
☐ Auto Increment
☐ Auto Digitize 1

1

☐ Use Digitized AutoFocus

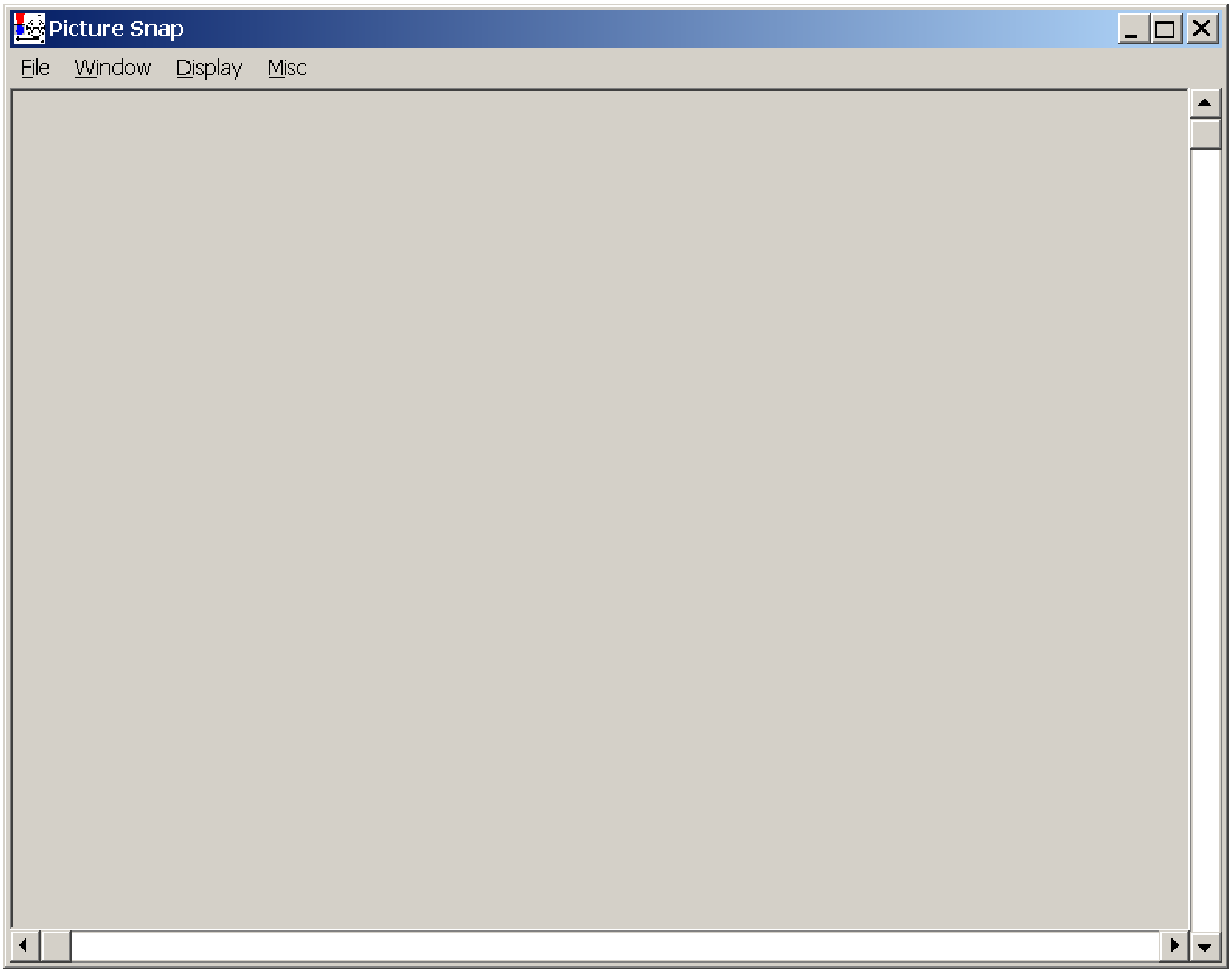
Number 12, Size 40

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

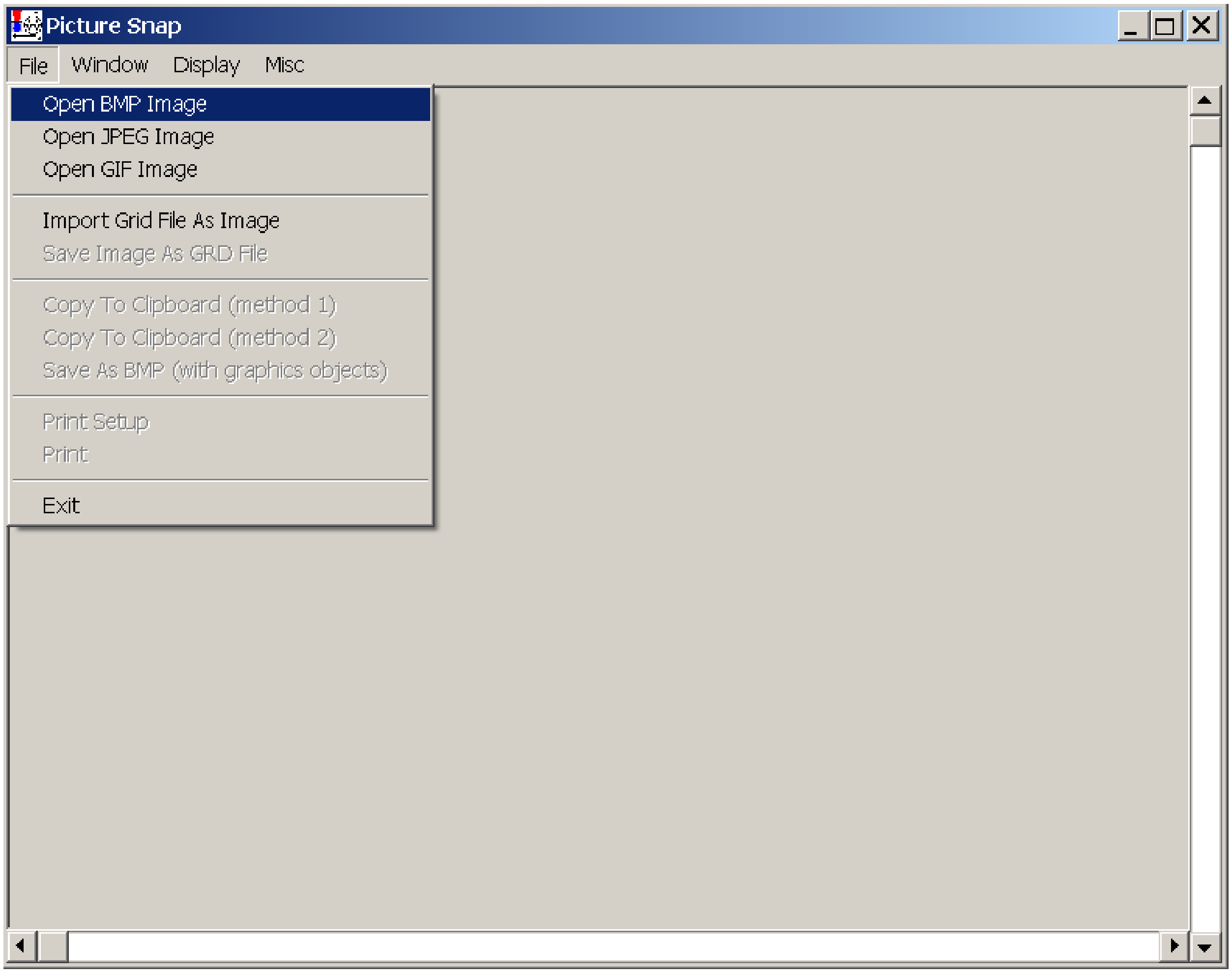


```
Welcome to S                                  se Edition) v.
8.46
Written by J                                  1995-2011 John
J. Donovan

This software
Dan Kremser
Probe for EPMA

Press the F1 k                                e help. To get help
on a menu item                                 hit the F1 key.

Initializing D
Demonstration
```

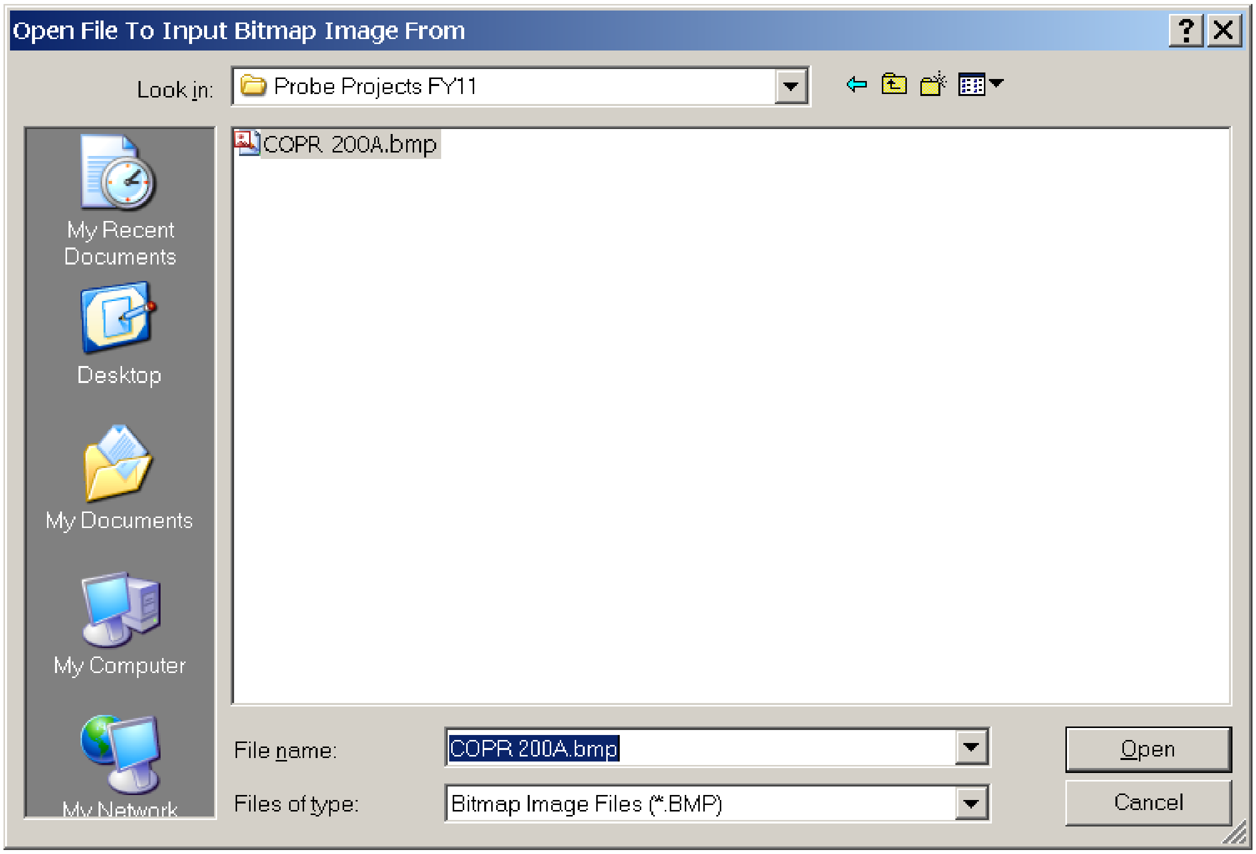
The main **Picture Snap!** window appears.



Select the **File** menu and open the appropriate image file.



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



Look in: Probe Projects FY11

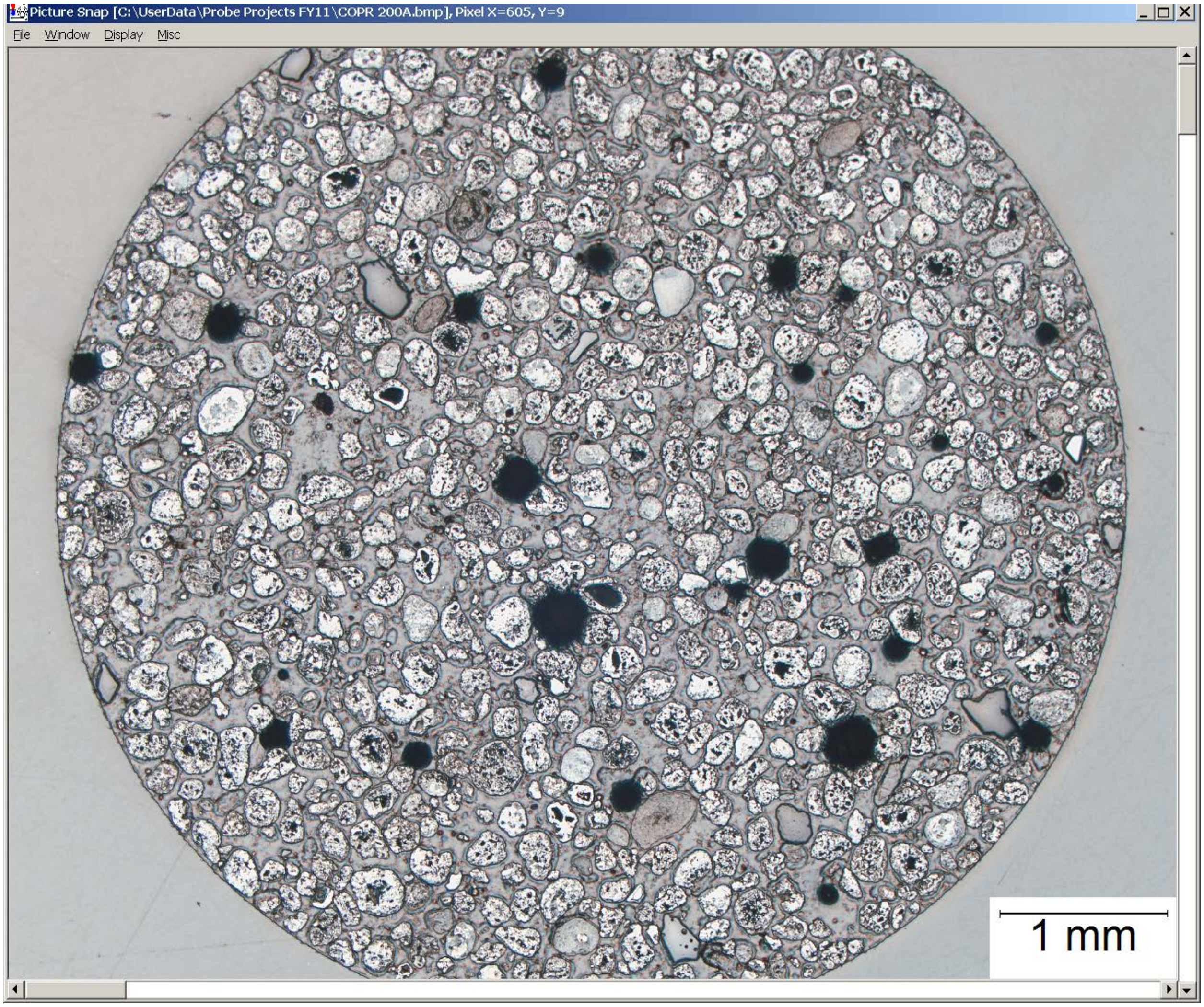
COPR 200A.bmp

File name: COPR 200A.bmp

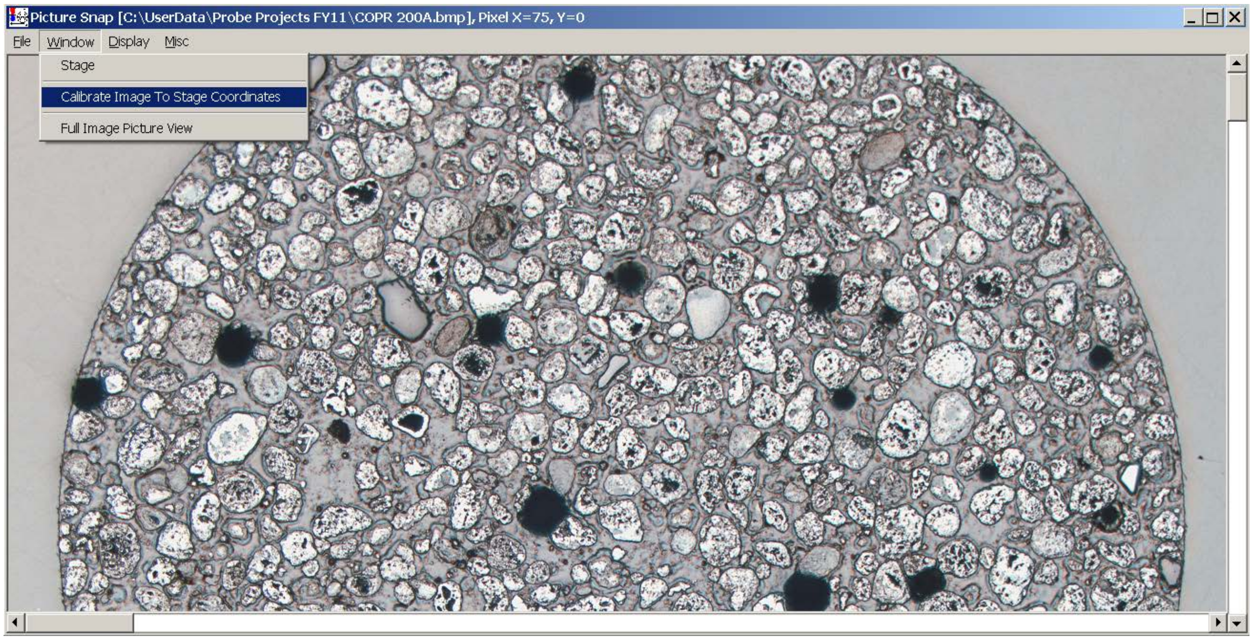
Files of type: Bitmap Image Files (*.BMP)

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

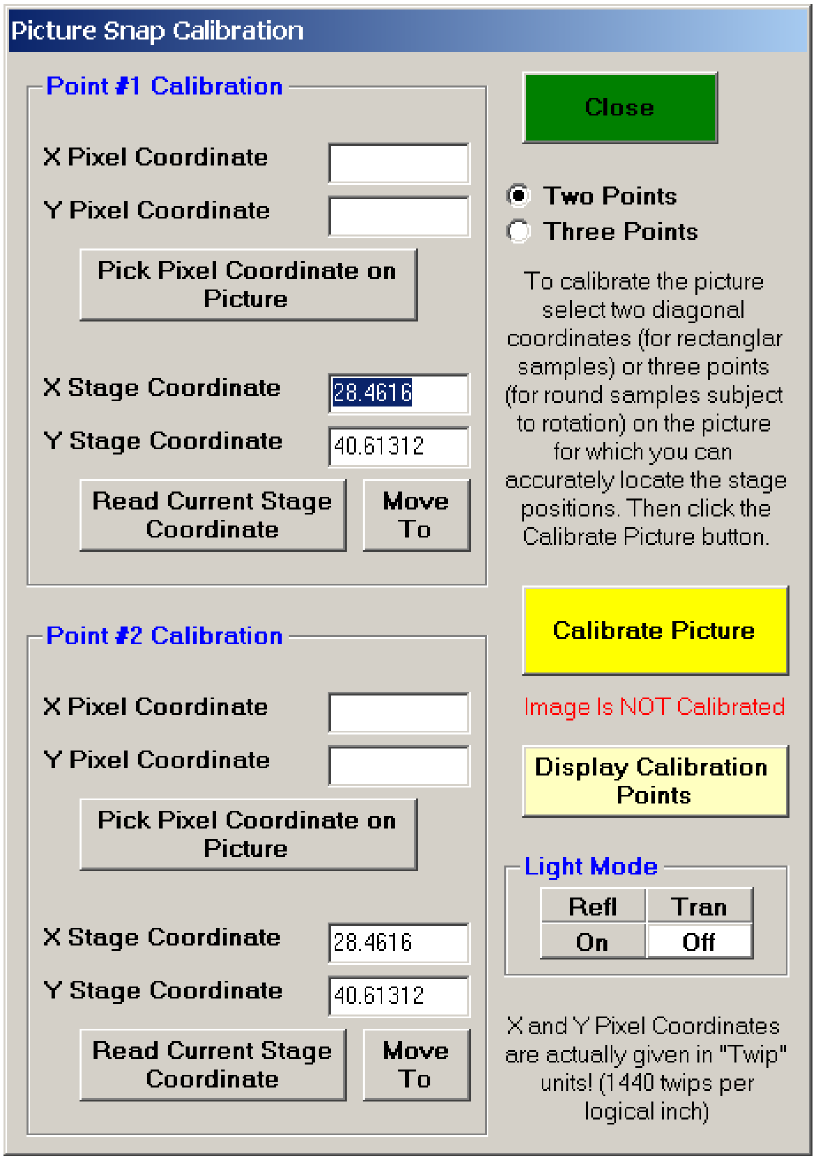
The image is displayed in the **Picture Snap!** window.



Select the **Window | Calibrate** menu.



The **Picture Snap Calibration** window appears.



Point #1 Calibration

X Pixel Coordinate:
Y Pixel Coordinate:
X Stage Coordinate: 28.4616
Y Stage Coordinate: 40.61312

Point #2 Calibration

X Pixel Coordinate:
Y Pixel Coordinate:
X Stage Coordinate: 28.4616
Y Stage Coordinate: 40.61312

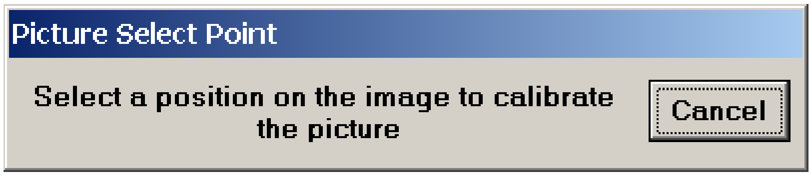
● Two Points
○ Three Points

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

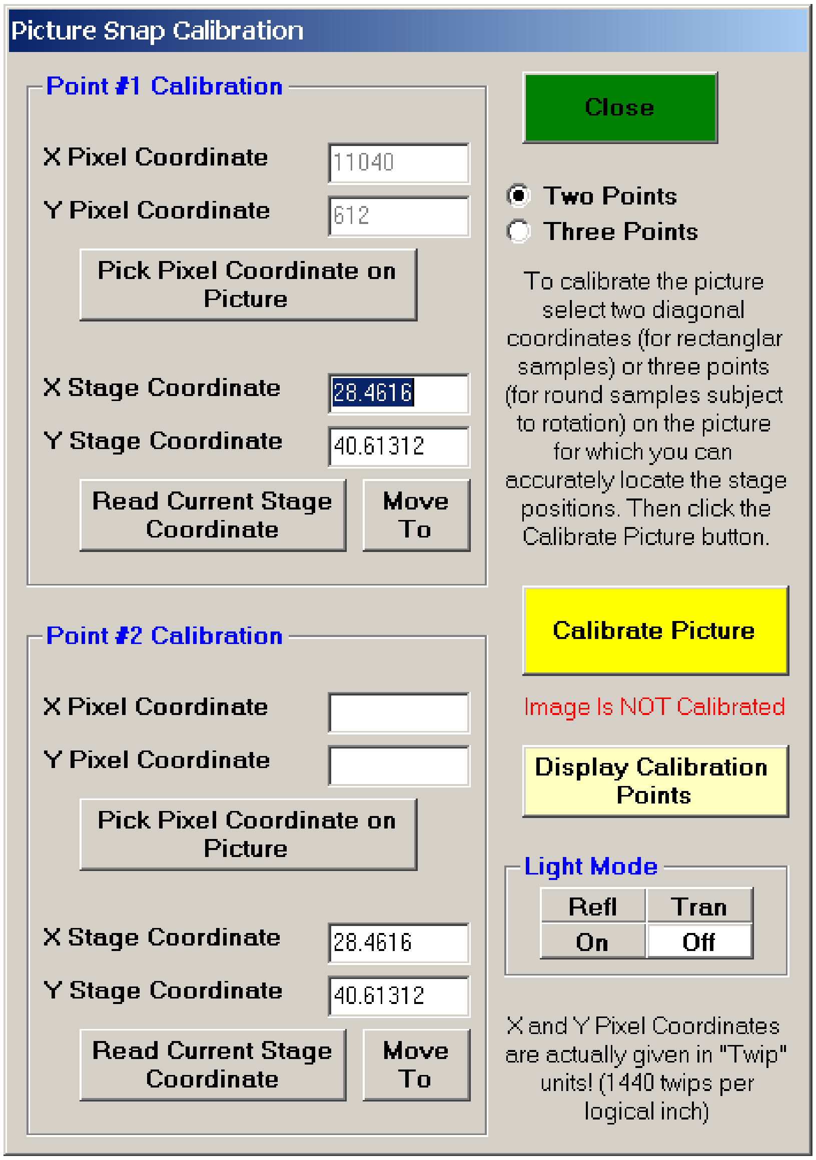
X and Y Pixel Coordinates are actually given in "Twip" units! (1440 twips per logical inch)

Image calibration is accomplished using a two point method for rectangular mounts or a three point calibration when importing round images subject to rotation. 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: 11040

Y Pixel Coordinate: 612

X Stage Coordinate: 28.4616

Y Stage Coordinate: 40.61312

Point #2 Calibration

X Pixel Coordinate:

Y Pixel Coordinate:

X Stage Coordinate: 28.4616

Y Stage Coordinate: 40.61312

● Two Points
○ Three Points

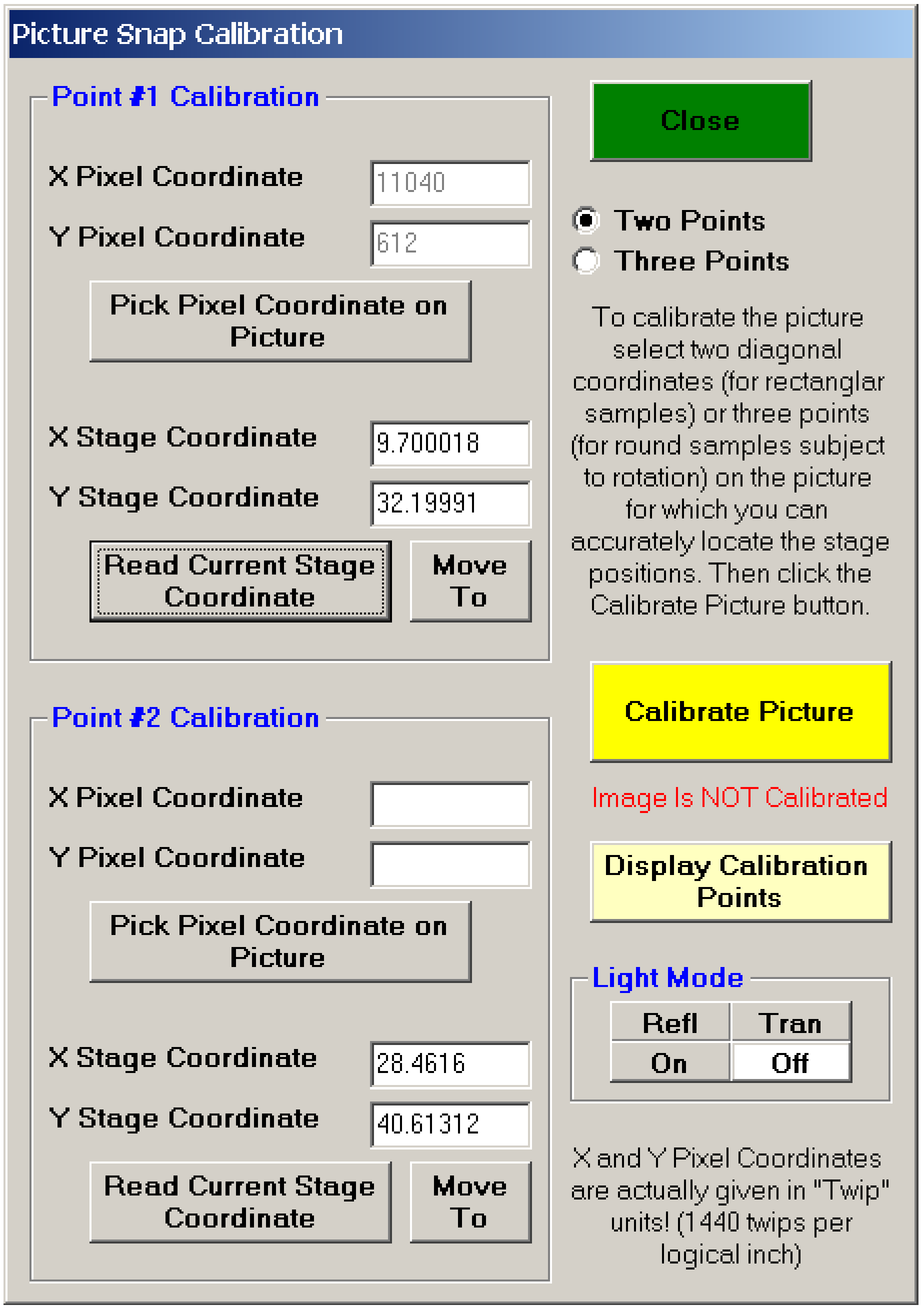
To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

Image Is NOT Calibrated

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

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.

The stage location for the first calibration point is entered.



Point #1 Calibration

X Pixel Coordinate: 11040

Y Pixel Coordinate: 612

X Stage Coordinate: 9.700018

Y Stage Coordinate: 32.19991

Point #2 Calibration

X Pixel Coordinate:

Y Pixel Coordinate:

X Stage Coordinate: 28.4616

Y Stage Coordinate: 40.61312

● Two Points

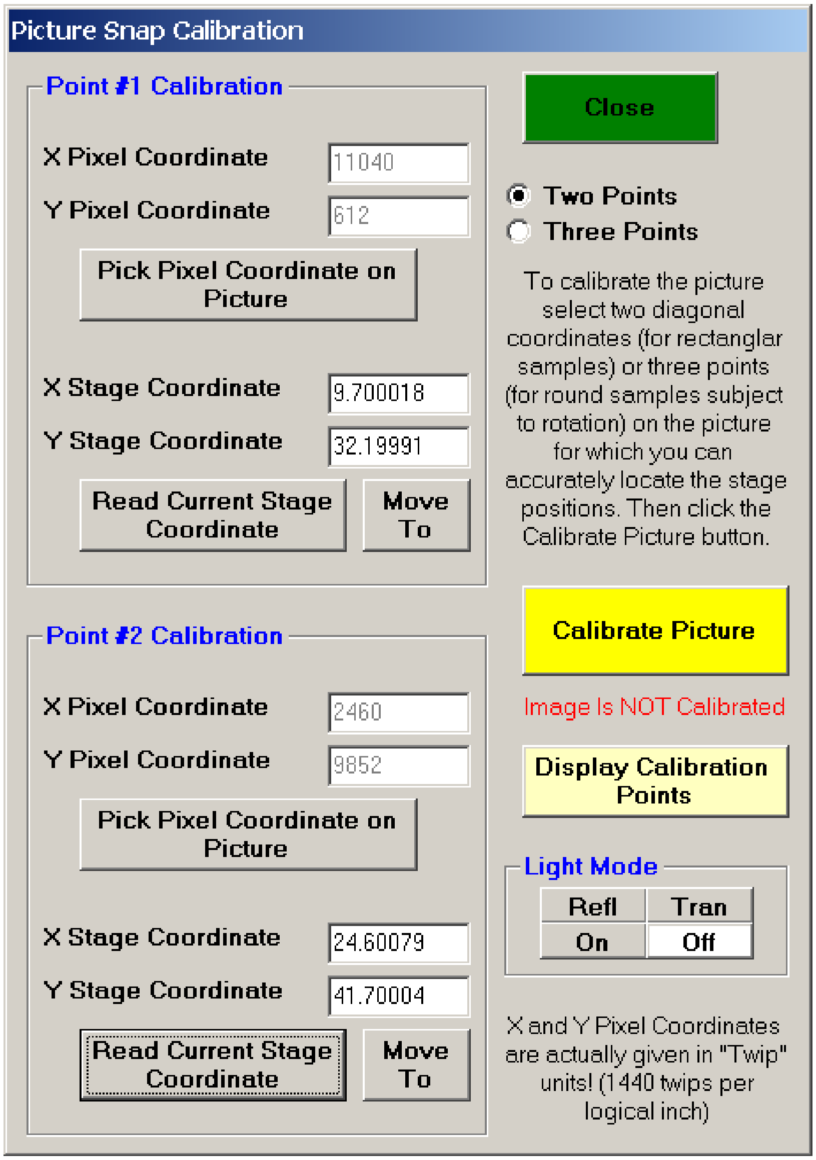
○ Three Points

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)

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



Point #1 Calibration
X Pixel Coordinate 11040
Y Pixel Coordinate 612
X Stage Coordinate 9.700018
Y Stage Coordinate 32.19991

Point #2 Calibration
X Pixel Coordinate 2460
Y Pixel Coordinate 9852
X Stage Coordinate 24.60079
Y Stage Coordinate 41.70004

● Two Points
○ Three Points

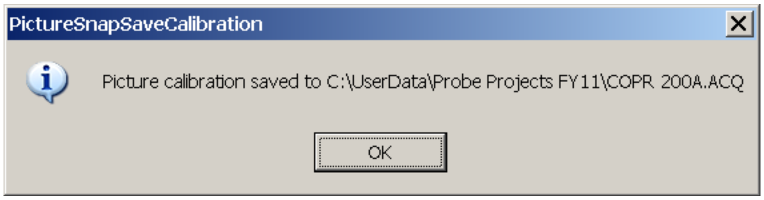
To calibrate the picture select two diagonal coordinates (for rectanglar samples) or three points (for round samples subject to rotation) on the picture for which you can accurately locate the stage positions. Then click the Calibrate Picture button.

Image Is NOT Calibrated

Light Mode: Refl On, Tran Off

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

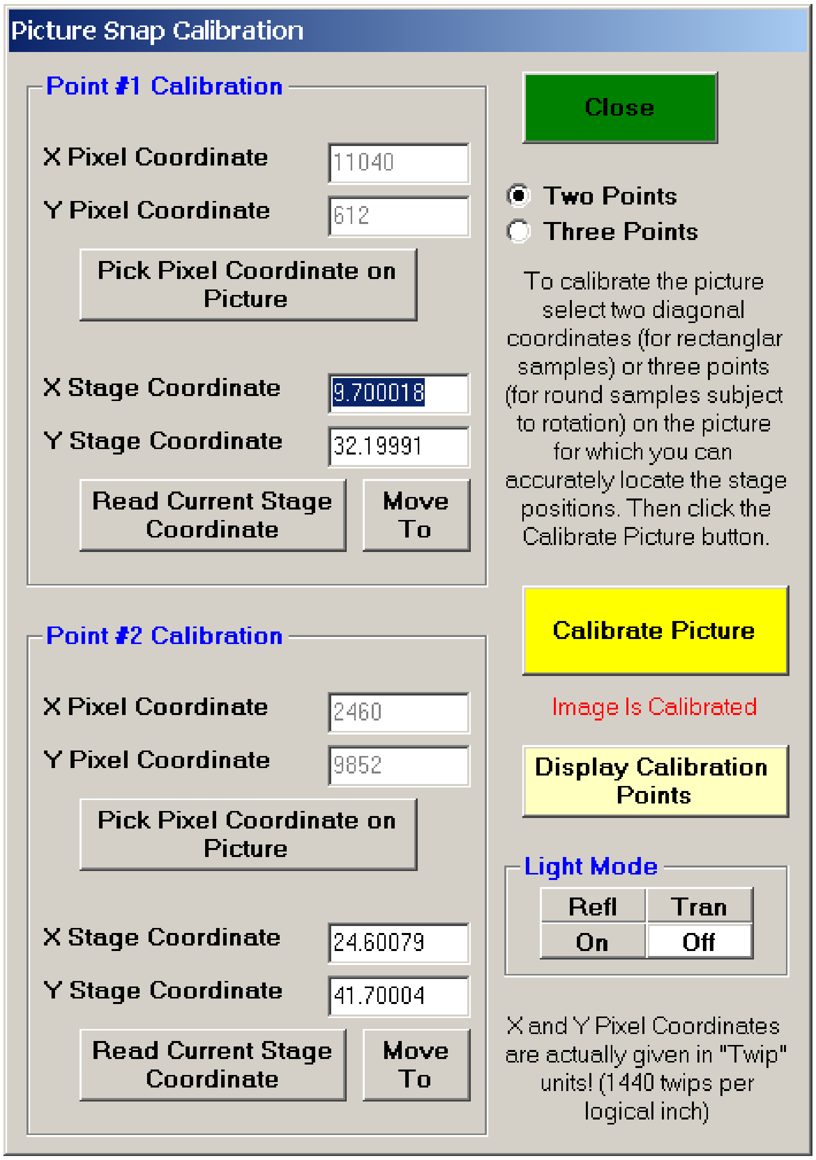
Finally, click the **Calibrate Picture** button opening the **PictureSnapSaveCalibration** window.


PictureSnapSaveCalibration

Picture calibration saved to C:\UserData\Probe Projects FY11\COPR 200A.ACQ

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

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


Picture Snap Calibration

Point #1 Calibration

X Pixel Coordinate: 11040

Y Pixel Coordinate: 612

X Stage Coordinate: 9.700018

Y Stage Coordinate: 32.19991

Point #2 Calibration

X Pixel Coordinate: 2460

Y Pixel Coordinate: 9852

X Stage Coordinate: 24.60079

Y Stage Coordinate: 41.70004

● 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

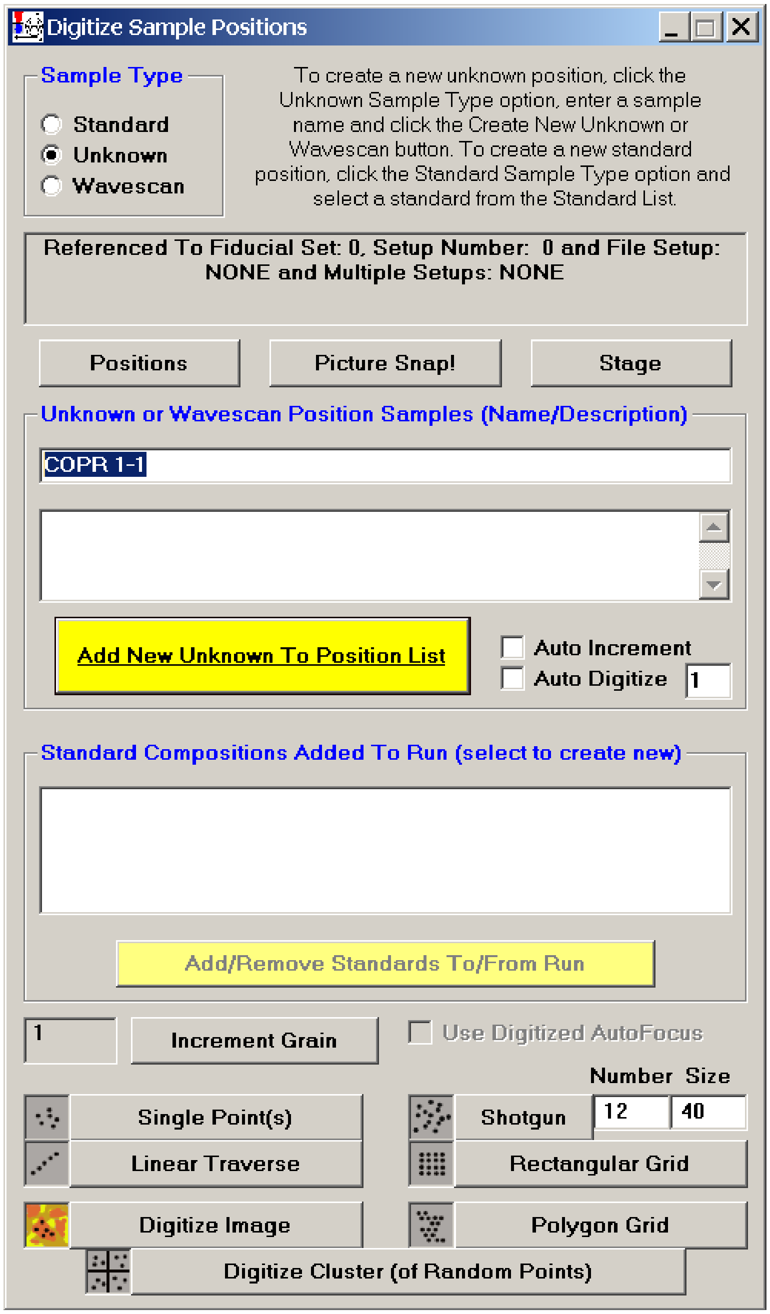
Light Mode: Refl On, Tran Off

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.



○ 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

COPR 1-1

☐ Auto Increment
☐ Auto Digitize 1

1 Increment Grain

☐ Use Digitized AutoFocus

Number 12 Size 40

Create a new unknown. Double click on the spot for the first analysis point on the just calibrated image to drive the stage to those coordinates. Click the **Random Point(s)** button to digitize that sample location. Additional points maybe saved. All analysis locations can be viewed from the **Display | Unknown Position Samples** menu. All analysis locations can be 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.

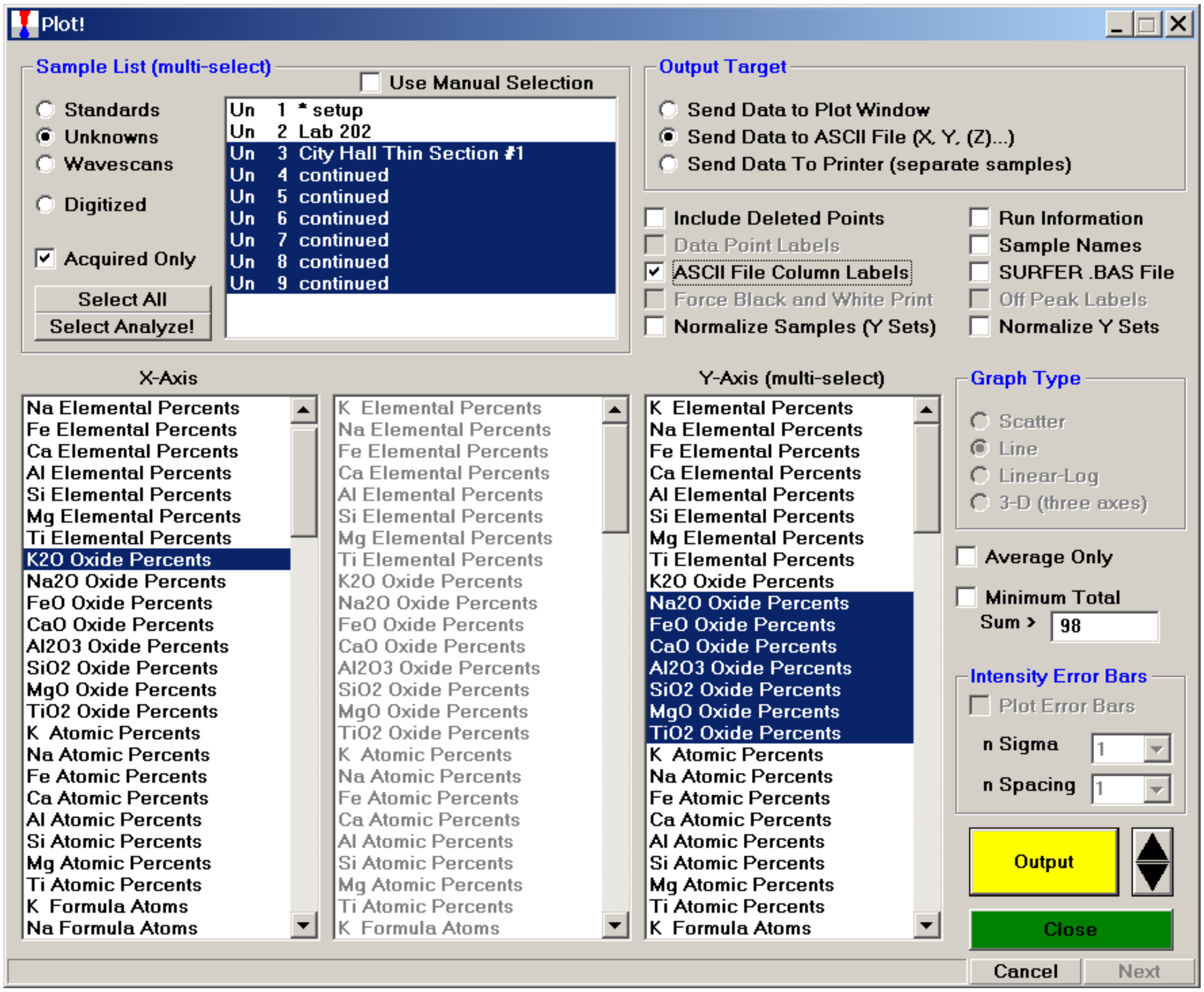
After data collection has been completed, open the **Plot!** window.

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)

☐ Use Manual Selection

○ Standards
● Unknowns
○ Wavescans
○ Digitized
☑ Acquired Only

Un 1 * setup
Un 2 Lab 202
Un 3 City Hall Thin Section #1
Un 4 continued
Un 5 continued
Un 6 continued
Un 7 continued
Un 8 continued
Un 9 continued

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: K2O Oxide Percents

Y-Axis (multi-select): Na2O Oxide Percents, FeO Oxide Percents, CaO Oxide Percents, Al2O3 Oxide Percents, SiO2 Oxide Percents, MgO Oxide Percents, TiO2 Oxide Percents

Graph Type

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

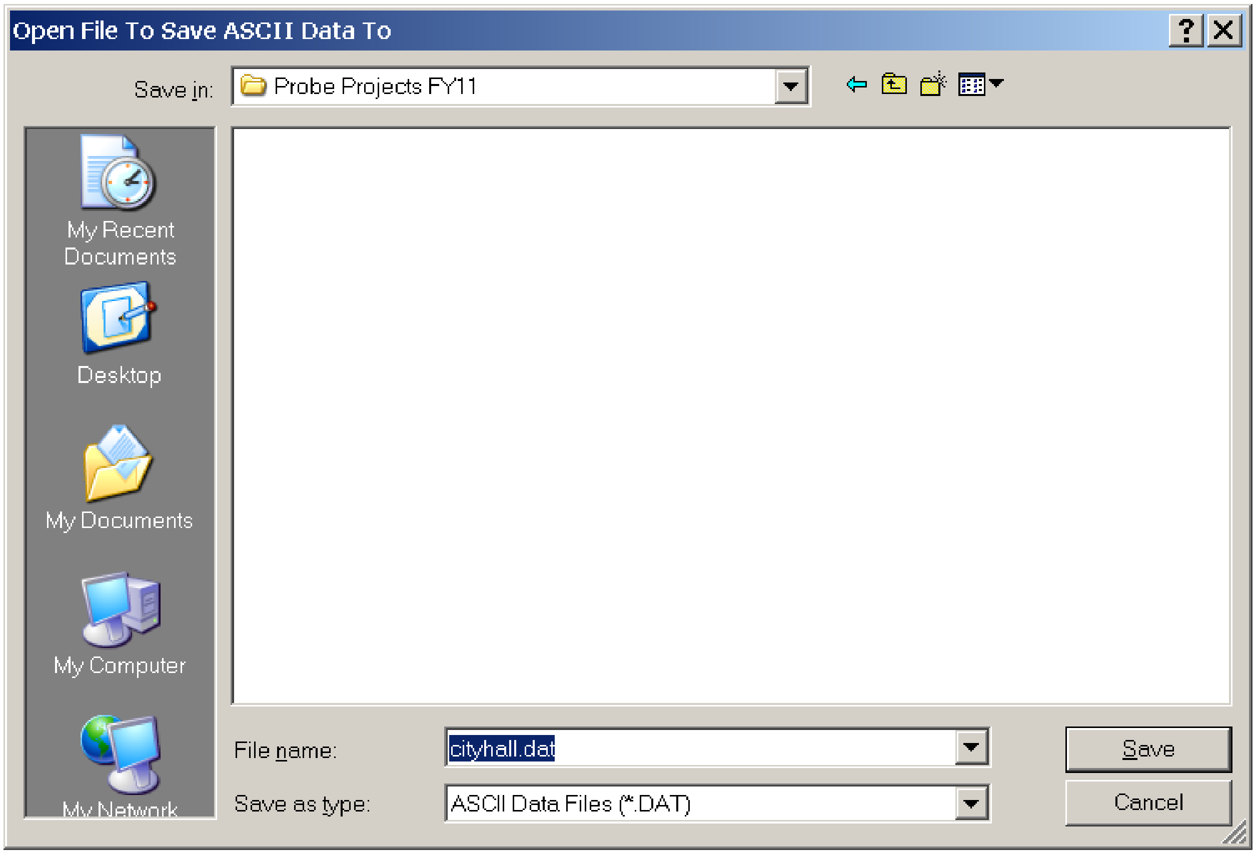
☐ Average Only
☐ Minimum Total Sum > 98

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.



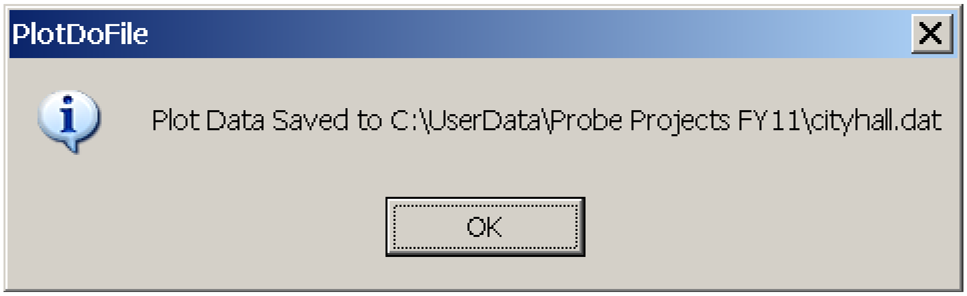
Save in: Probe Projects FY11

File name: cityhall.dat

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

Click the **Save** button.

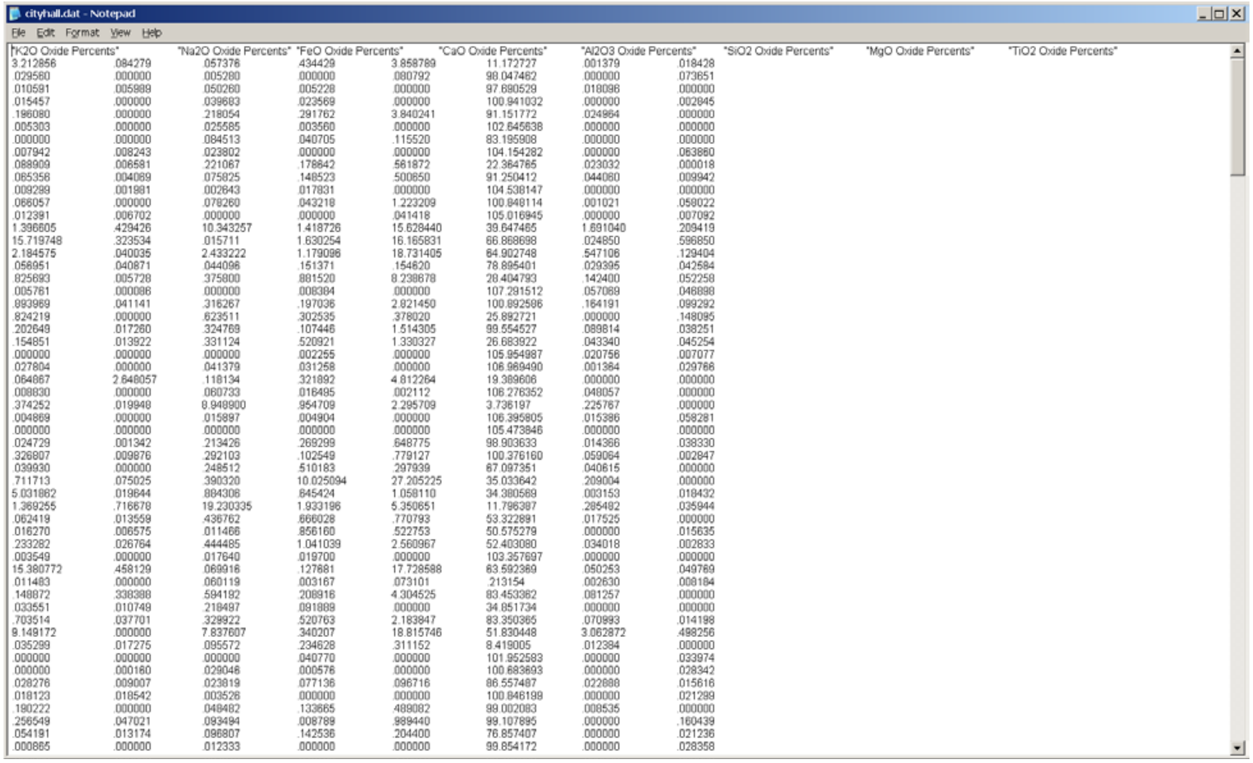
The **PlotDoFile** window appears, indicating that the data was saved.



Plot Data Saved to C:\UserData\Probe Projects FY11\cityhall.dat

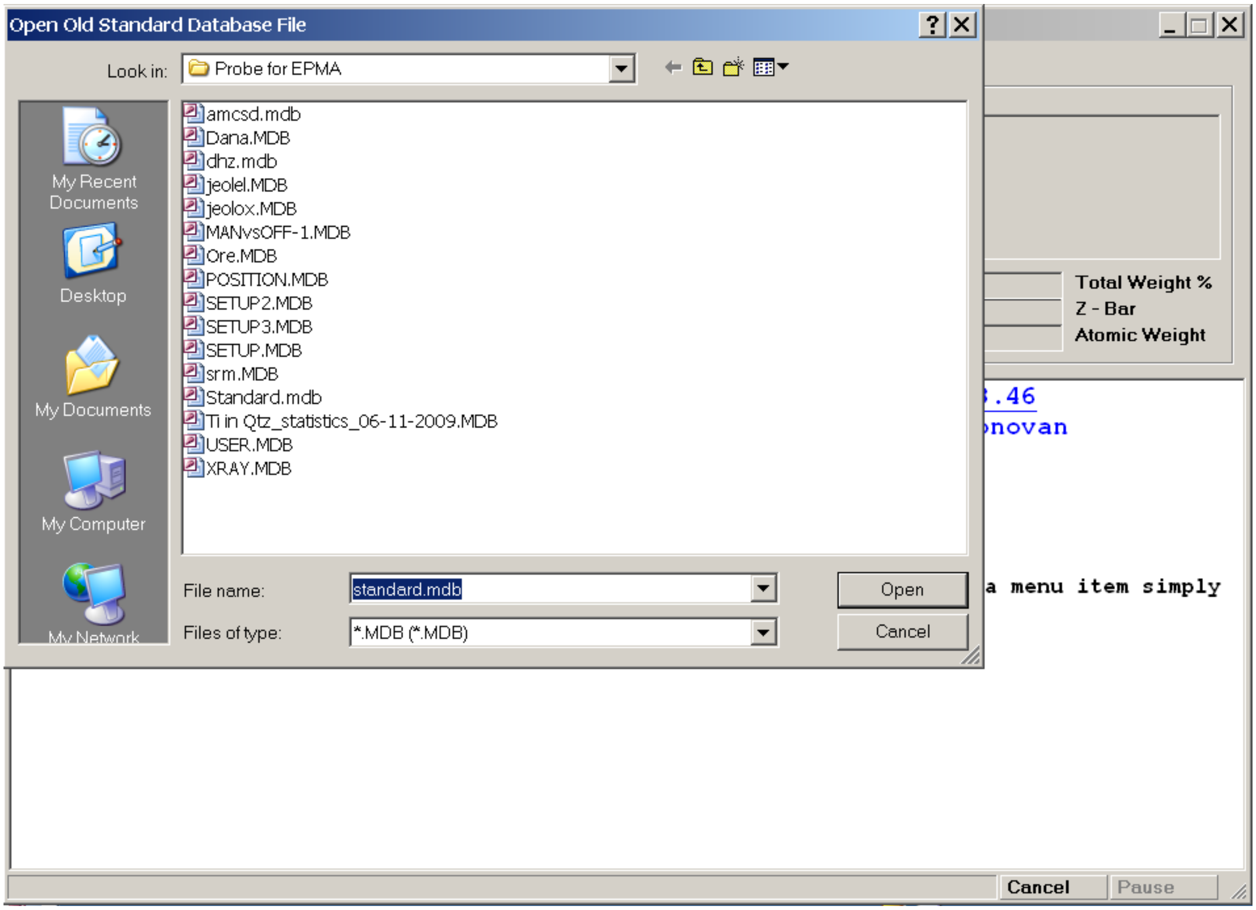
Click the **OK** button.

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     .005889     .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     .178842     .561872     22.364765   .023032     .000018
.065356     .004089     .075825     .148523     .500650     91.250412   .044060     .009942
.009289     .001881     .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    1.179096    18.731405   64.902748   .547106     .129404
.056951     .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
.064867     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. Open the program **Standard** from the PROBE for EPMA Software folder on the desktop.


Open Old Standard Database File

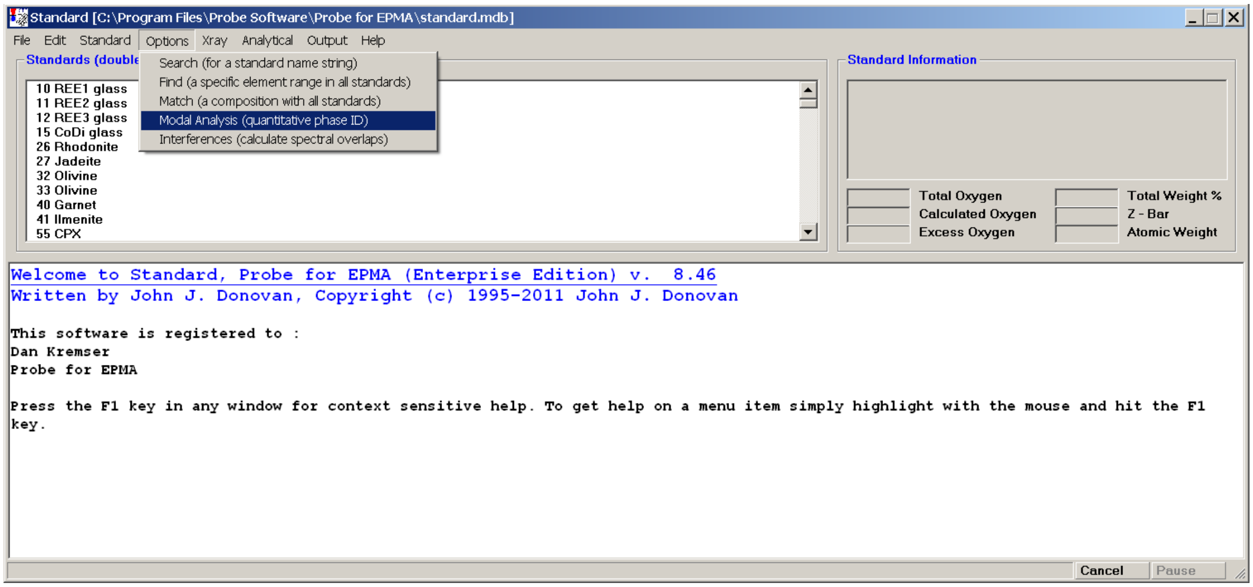
Look in: Probe for EPMA

File name: standard.mdb

Files of type: *.MDB (*.MDB)

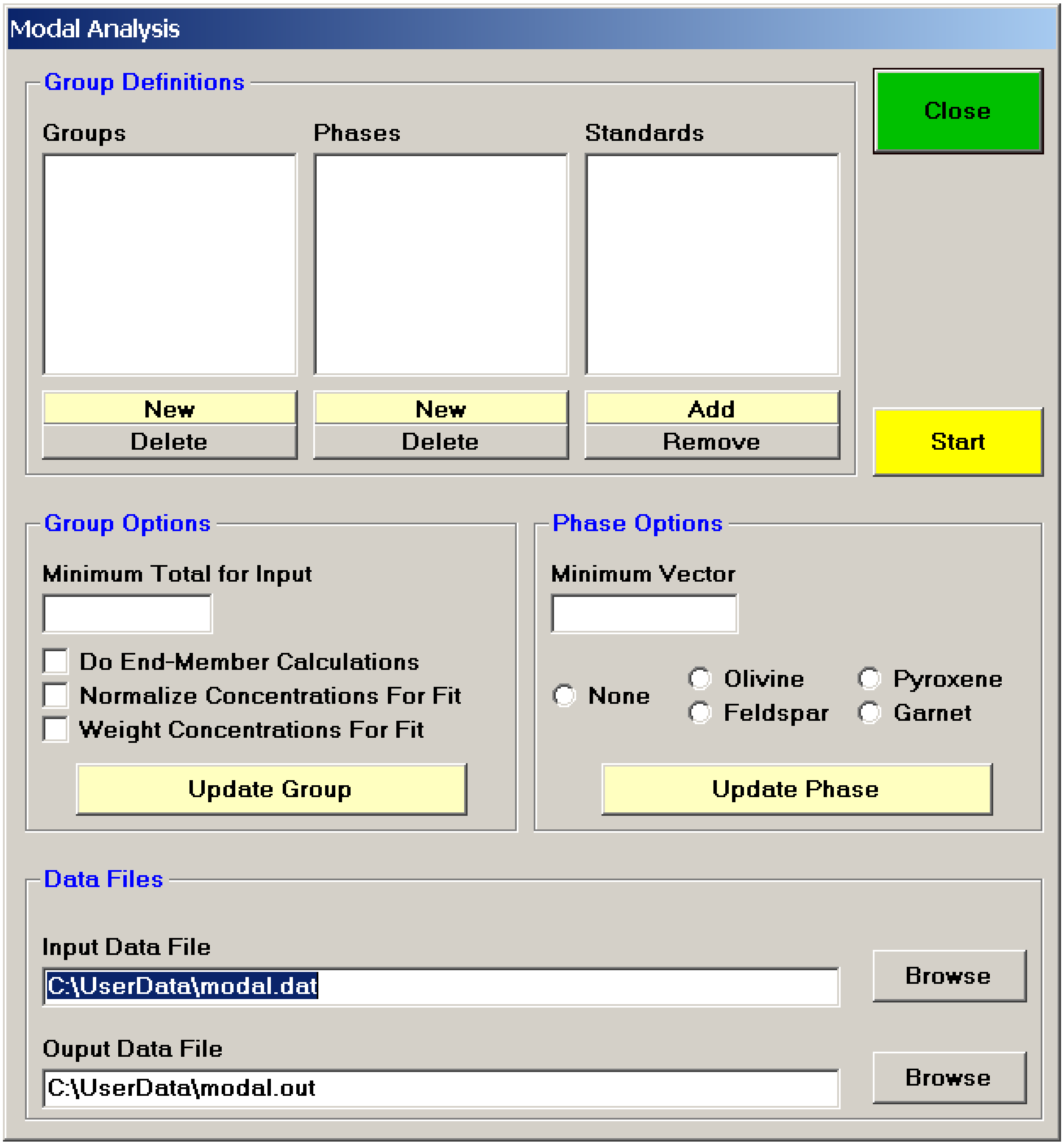
Select (highlight) a standard database that will be used to define the modal phases. Click the **Open** button to load this database.

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



```
Welcome to Standard, Probe for EPMA (Enterprise Edition) v.  8.46
Written by John J. Donovan, Copyright (c) 1995-2011 John J. Donovan

This software is registered to :
Dan Kremser
Probe for EPMA

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.



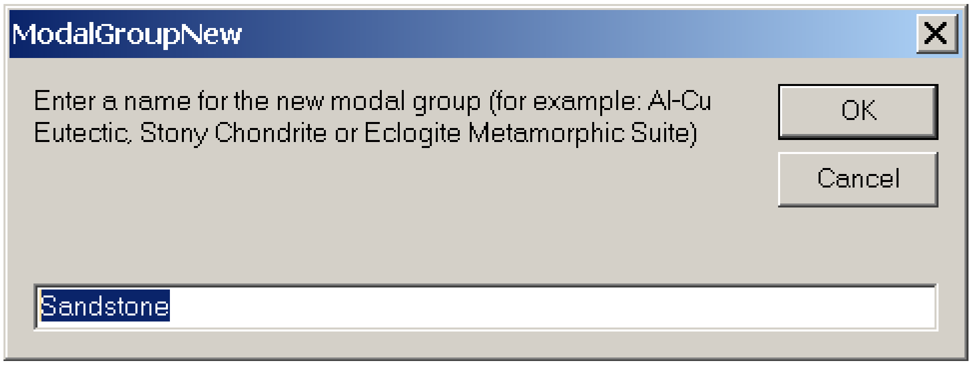
☐ Do End-Member Calculations
☐ Normalize Concentrations For Fit
☐ Weight Concentrations For Fit

Input Data File: C:\UserData\modal.dat

Ouput Data File: C:\UserData\modal.out

Start by defining an overall Group, click the **New** button under *Groups*.

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



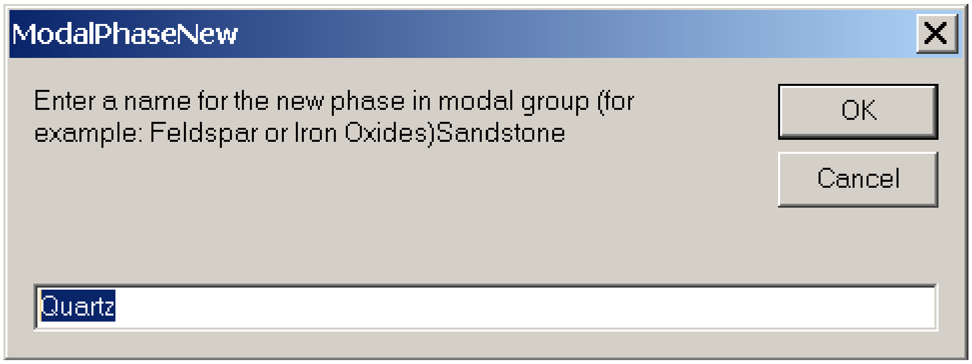
Enter a name for the new modal group (for example: Al-Cu Eutectic, Stony Chondrite or Eclogite Metamorphic Suite)

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.

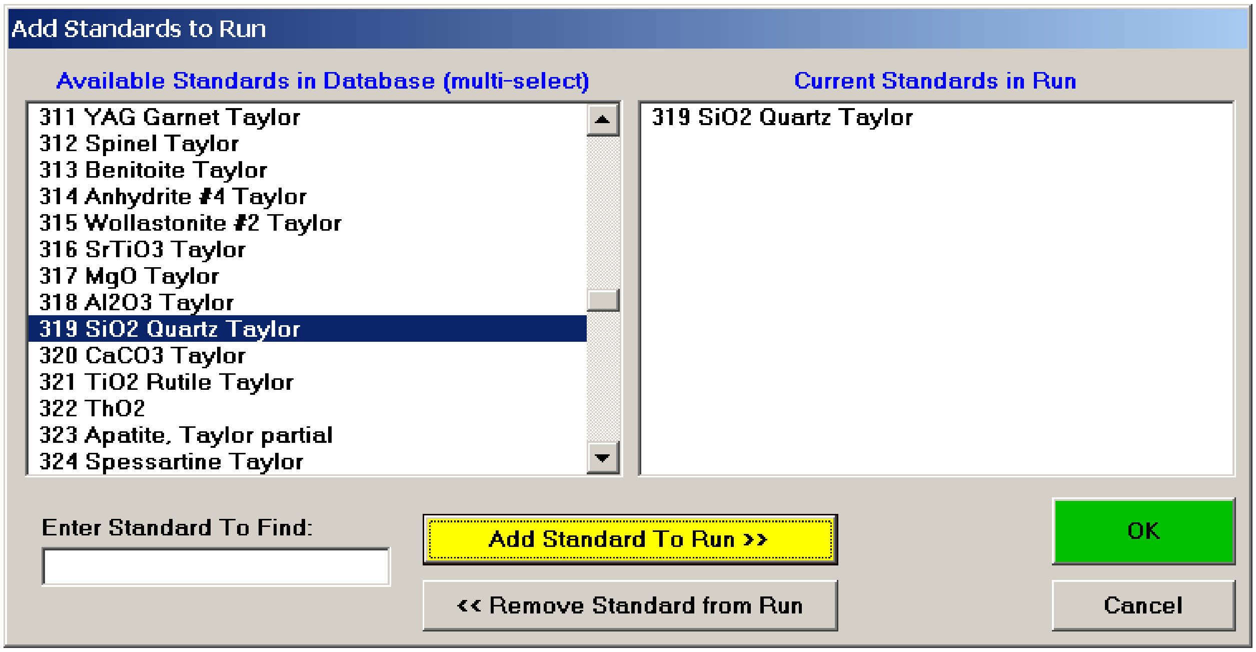


Enter a name for the new phase in modal group (for example: Feldspar or Iron Oxides)Sandstone

Quartz

Click the **OK** button.

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

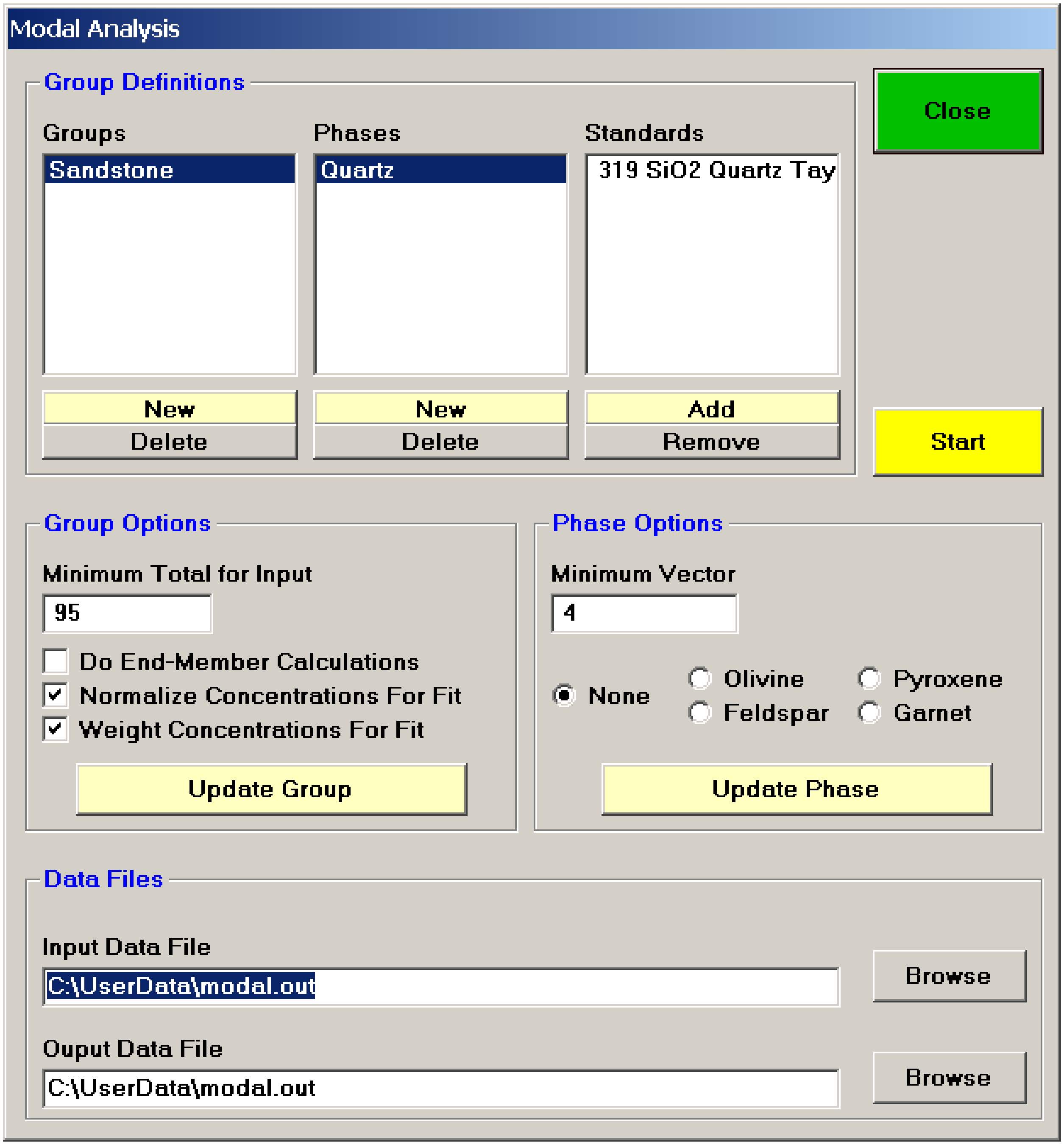


311 YAG Garnet Taylor
312 Spinel Taylor
313 Benitoite Taylor
314 Anhydrite #4 Taylor
315 Wollastonite #2 Taylor
316 SrTiO3 Taylor
317 MgO Taylor
318 Al2O3 Taylor
319 SiO2 Quartz Taylor
320 CaCO3 Taylor
321 TiO2 Rutile Taylor
322 ThO2
323 Apatite, Taylor partial
324 Spessartine Taylor

319 SiO2 Quartz Taylor

Choose standards to define this modal 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: 319 SiO2 Quartz Tay

Minimum Total for Input: 95

☐ Do End-Member Calculations

☑ Normalize Concentrations For Fit

☑ Weight Concentrations For Fit

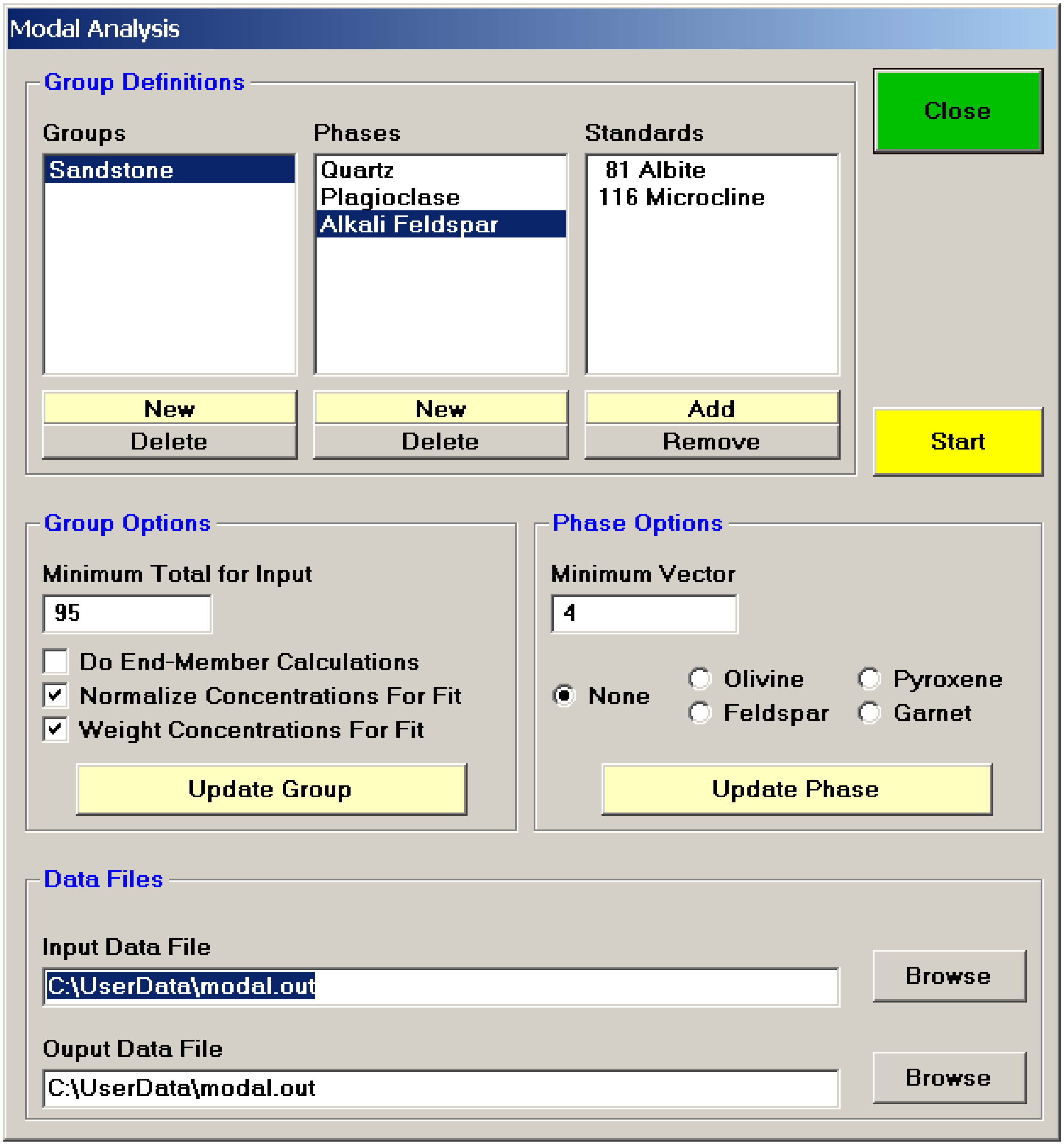
Minimum Vector: 4

● None

Input Data File: C:\UserData\modal.out

Ouput Data File: C:\UserData\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:
81 Albite
116 Microcline

Minimum Total for Input: 95

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

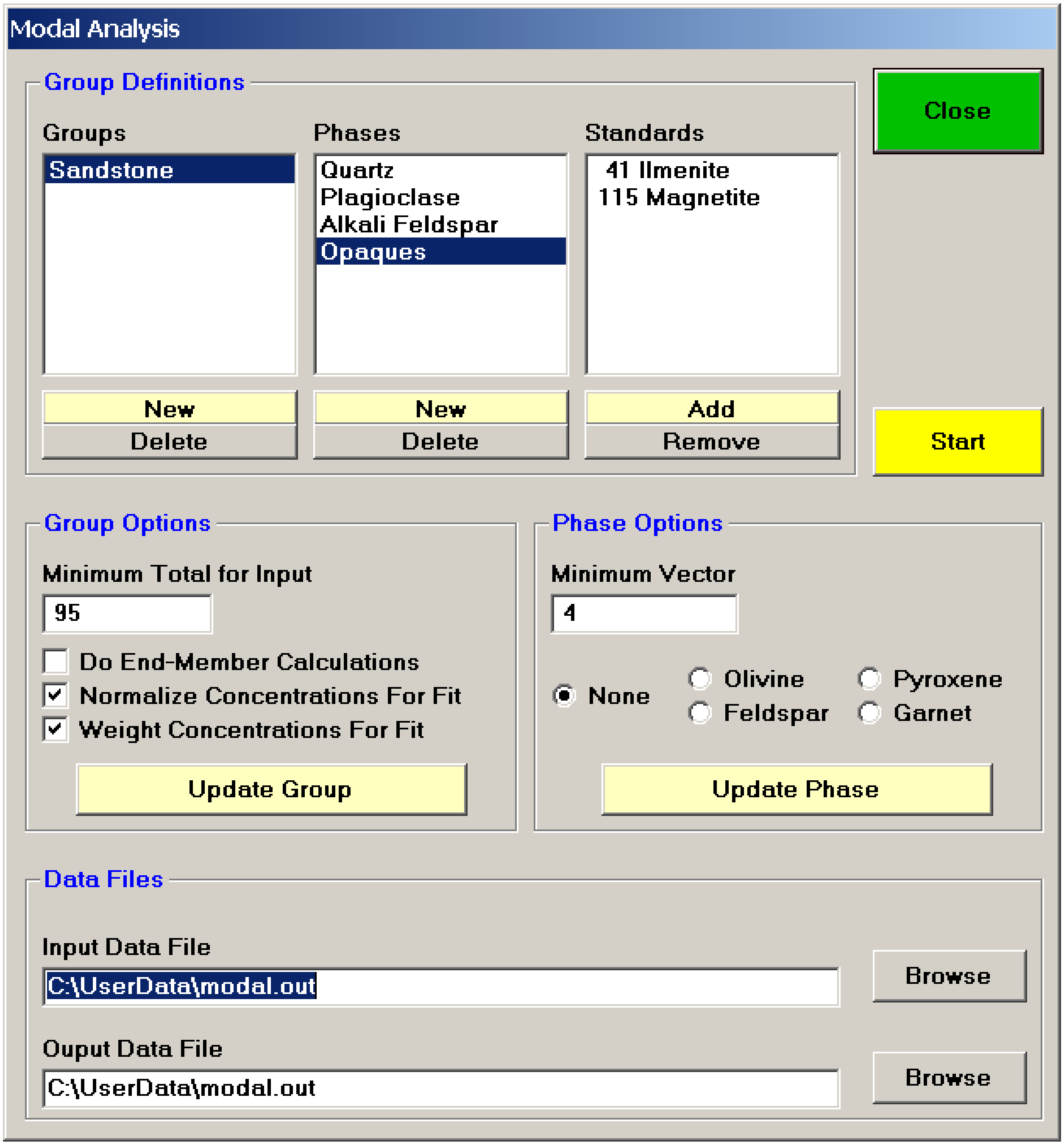
Minimum Vector: 4

● None ○ Olivine ○ Pyroxene ○ Feldspar ○ Garnet

Input Data File: C:\UserData\modal.out

Ouput Data File: C:\UserData\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
41 Ilmenite
115 Magnetite

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:\UserData\modal.out

Ouput Data File
C:\UserData\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.

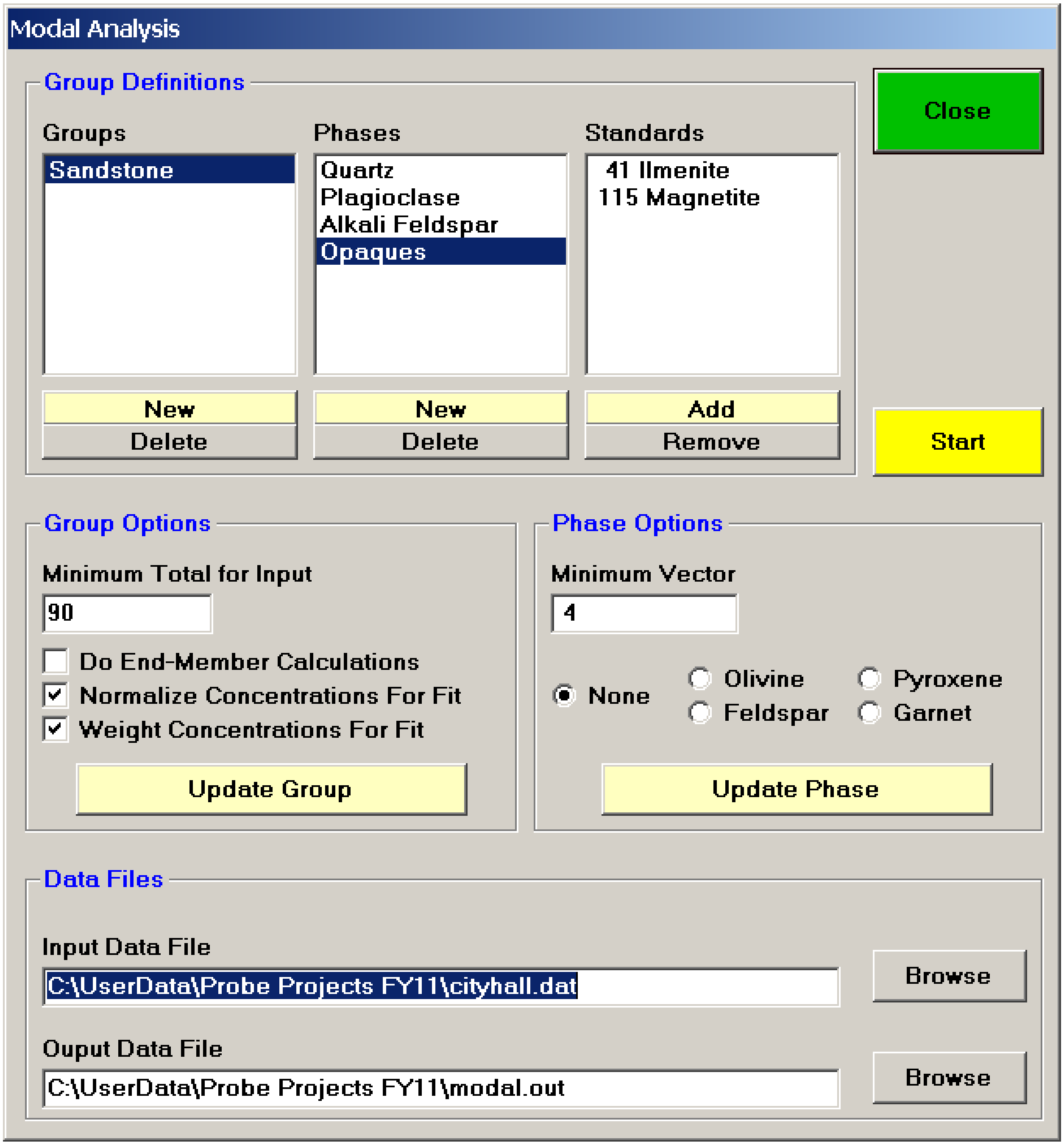
Select the *Do End-Member Calculations* option and check the appropriate mineral name under *Phase Options* to perform end-member calculations as listed.

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.



Groups: Sandstone

Phases: Quartz, Plagioclase, Alkali Feldspar, Opaques

Standards: 41 Ilmenite, 115 Magnetite

Minimum Total for Input: 90

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

Minimum Vector: 4

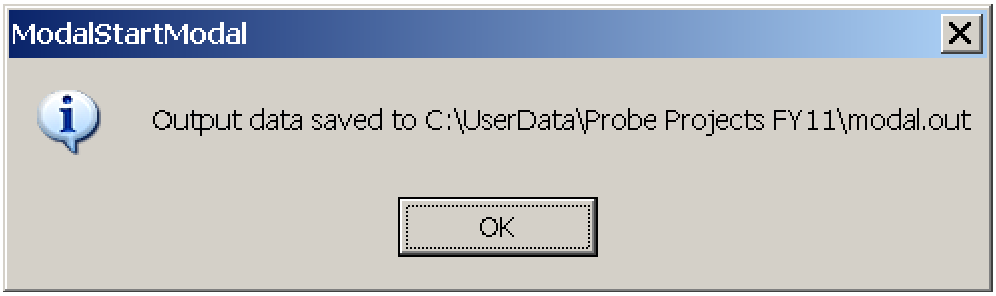
● None ○ Olivine ○ Pyroxene ○ Feldspar ○ Garnet

Input Data File: C:\UserData\Probe Projects FY11\cityhall.dat

Ouput Data File: C:\UserData\Probe Projects FY11\modal.out

Click the **Start** button to initiate the modal analysis calculation on each data point.

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:\UserData\Probe Projects FY11\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.

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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:

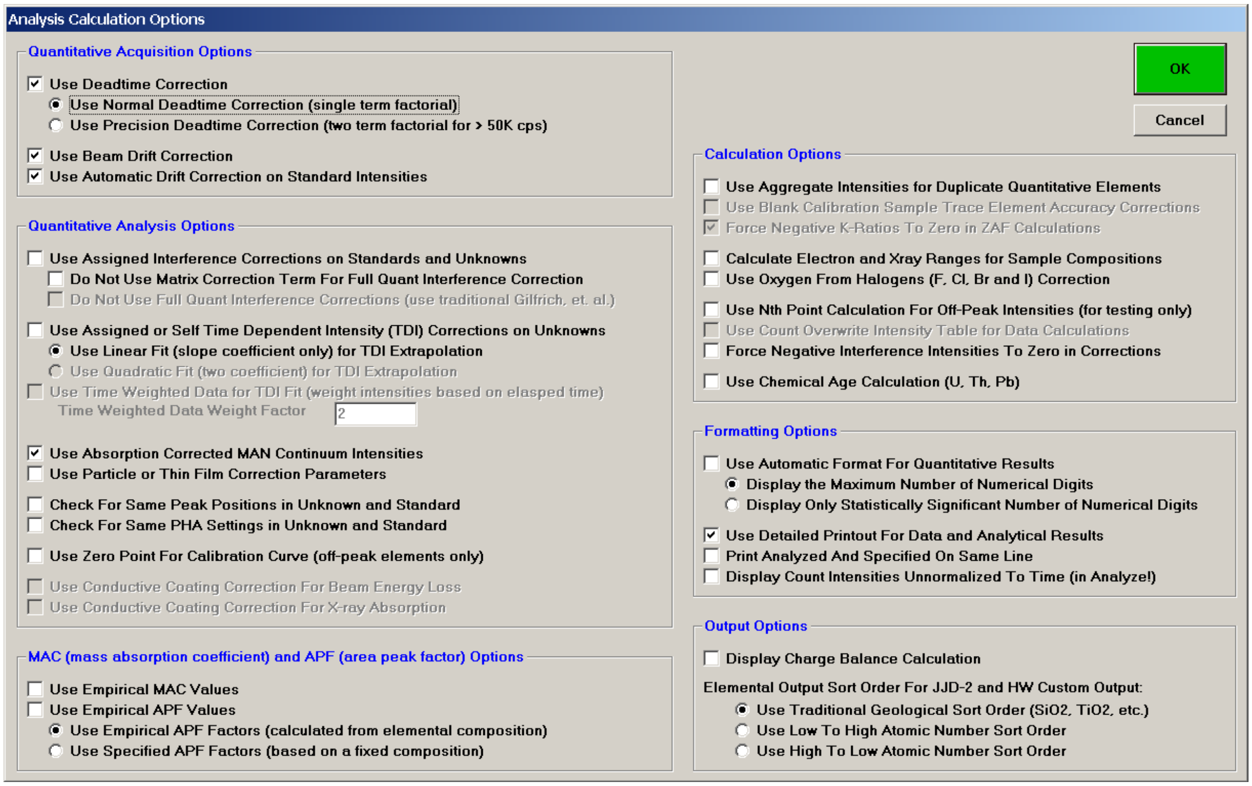
$$\frac{n'}{i} = k(1 - \tau n') \quad (2)$$

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:

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

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

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)

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!)

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 in the JEOL 733). 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.

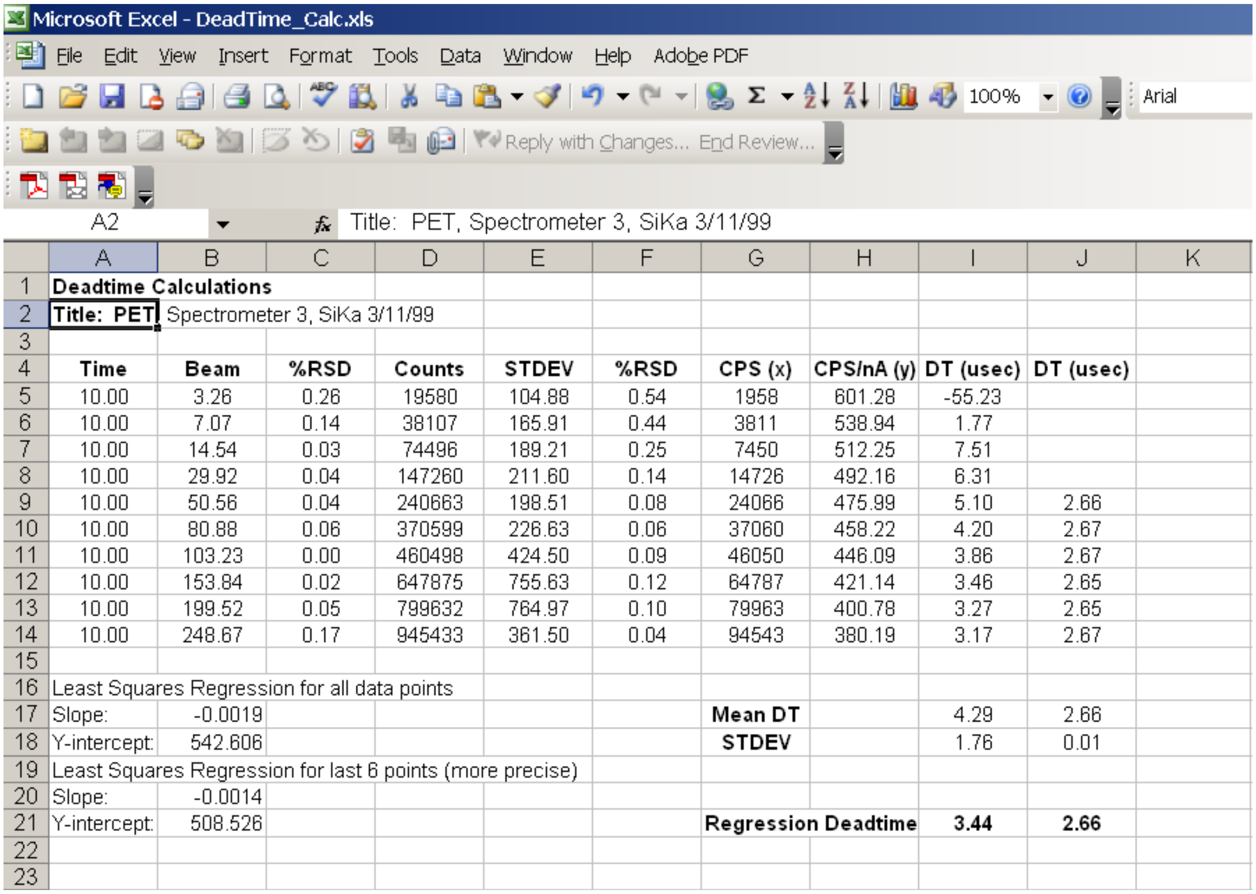
Time	Beam	1	2	3
10	3.259	22083	79765	19470
10	3.263	22069	79995	19590
10	3.247	21755	80091	19679
10	7.08	42503	154130	37952
10	7.06	42642	154665	38087
10	7.072	42168	154182	38282
10	14.547	83163	293002	74572
10	14.539	83315	292602	74281
10	14.543	82998	293326	74636
10	29.911	162904	547744	147492
10	29.917	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.

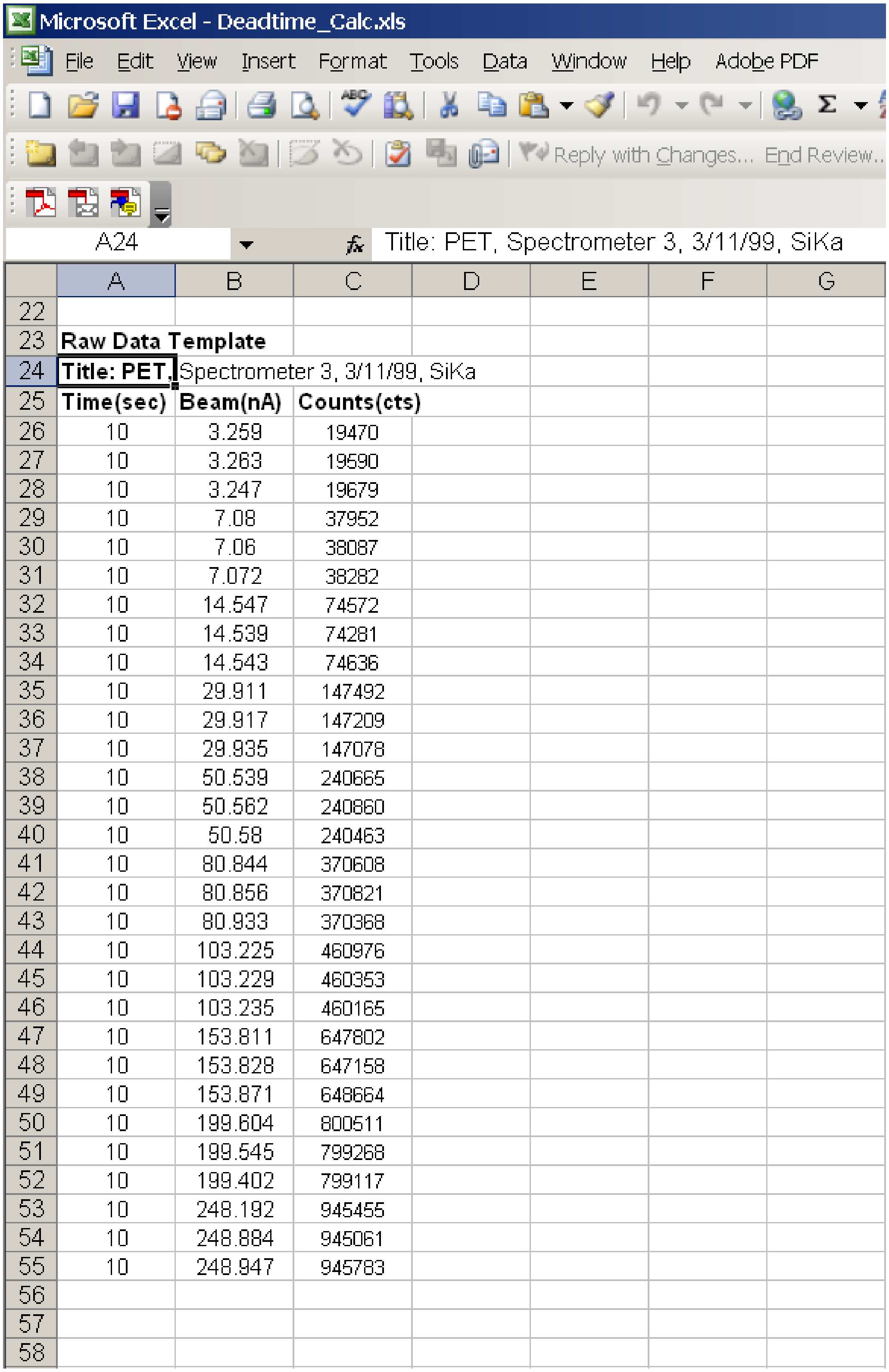
Below is the calculation portion of the Excel template.



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.



	A	B	C	D	E	F	G
22							
23	**Raw Data Template**						
24	**Title: PET,** Spectrometer 3, 3/11/99, SiKa						
25	**Time(sec)**	**Beam(nA)**	**Counts(cts)**				
26	10	3.259	19470				
27	10	3.263	19590				
28	10	3.247	19679				
29	10	7.08	37952				
30	10	7.06	38087				
31	10	7.072	38282				
32	10	14.547	74572				
33	10	14.539	74281				
34	10	14.543	74636				
35	10	29.911	147492				
36	10	29.917	147209				
37	10	29.935	147078				
38	10	50.539	240665				
39	10	50.562	240860				
40	10	50.58	240463				
41	10	80.844	370608				
42	10	80.856	370821				
43	10	80.933	370368				
44	10	103.225	460976				
45	10	103.229	460353				
46	10	103.235	460165				
47	10	153.811	647802				
48	10	153.828	647158				
49	10	153.871	648664				
50	10	199.604	800511				
51	10	199.545	799268				
52	10	199.402	799117				
53	10	248.192	945455				
54	10	248.884	945061				
55	10	248.947	945783				
56							
57							
58							

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 SCALARS.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.

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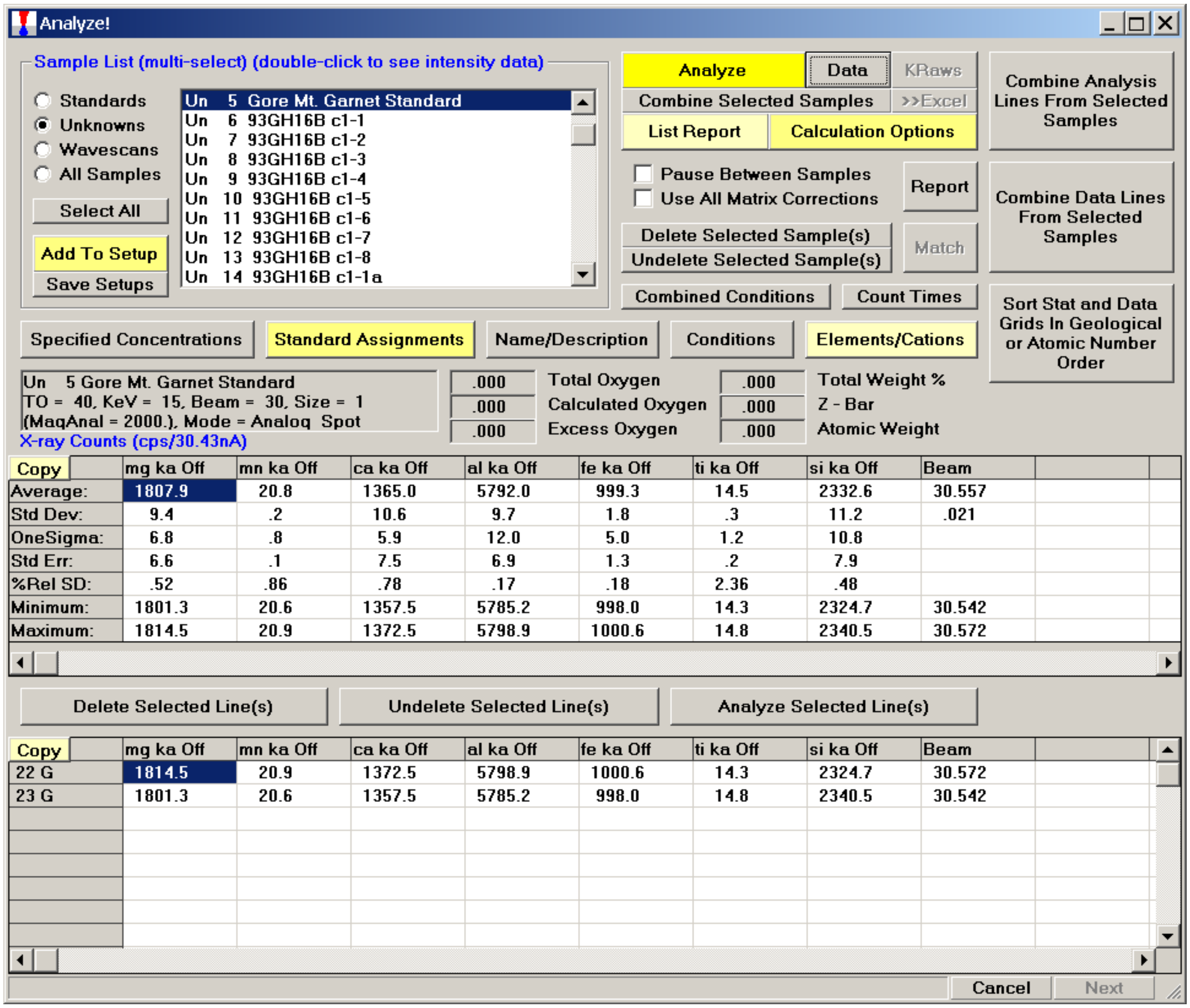
Calculation Options

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.



Un 5 Gore Mt. Garnet Standard
Un 6 93GH16B c1-1
Un 7 93GH16B c1-2
Un 8 93GH16B c1-3
Un 9 93GH16B c1-4
Un 10 93GH16B c1-5
Un 11 93GH16B c1-6
Un 12 93GH16B c1-7
Un 13 93GH16B c1-8
Un 14 93GH16B c1-1a

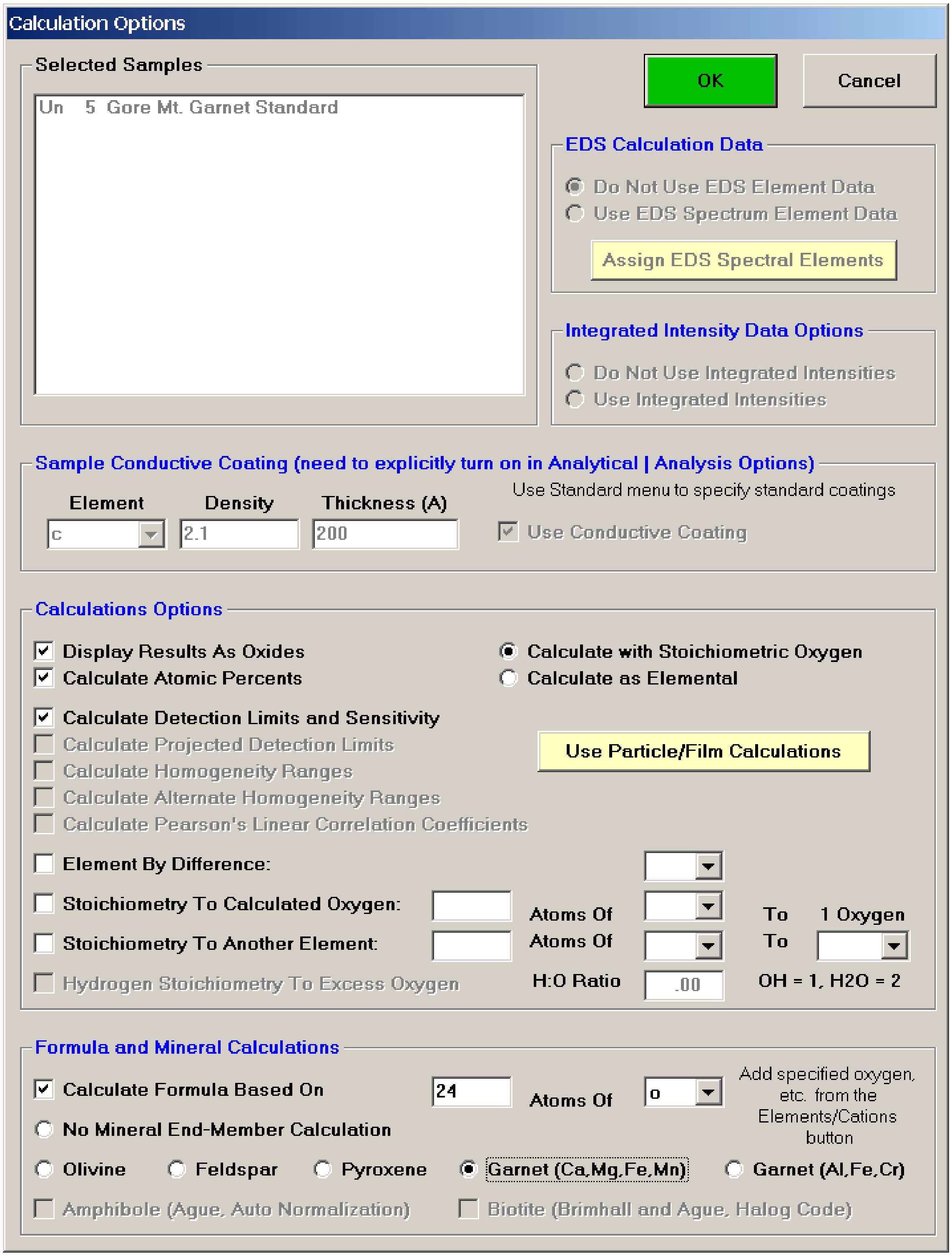
Un 5 Gore Mt. Garnet Standard
TO = 40, KeV = 15, Beam = 30, Size = 1
(MagAnal = 2000.), Mode = Analog Spot
X-ray Counts (cps/30.43nA)

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

Copy	mg ka Off	mn ka Off	ca ka Off	al ka Off	fe ka Off	ti ka Off	si ka Off	Beam
Average:	1807.9	20.8	1365.0	5792.0	999.3	14.5	2332.6	30.557
Std Dev:	9.4	.2	10.6	9.7	1.8	.3	11.2	.021
OneSigma:	6.8	.8	5.9	12.0	5.0	1.2	10.8	
Std Err:	6.6	.1	7.5	6.9	1.3	.2	7.9	
%Rel SD:	.52	.86	.78	.17	.18	2.36	.48	
Minimum:	1801.3	20.6	1357.5	5785.2	998.0	14.3	2324.7	30.542
Maximum:	1814.5	20.9	1372.5	5798.9	1000.6	14.8	2340.5	30.572

Copy	mg ka Off	mn ka Off	ca ka Off	al ka Off	fe ka Off	ti ka Off	si ka Off	Beam
22 G	1814.5	20.9	1372.5	5798.9	1000.6	14.3	2324.7	30.572
23 G	1801.3	20.6	1357.5	5785.2	998.0	14.8	2340.5	30.542

The **Calculation Options** window opens.



Selected Samples

Un 5 Gore Mt. Garnet Standard

EDS Calculation Data

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

Use Standard menu to specify standard coatings

Element	Density	Thickness (A)
c	2.1	200

☑ Use 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
☐ Element By Difference:
☐ 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 24 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)

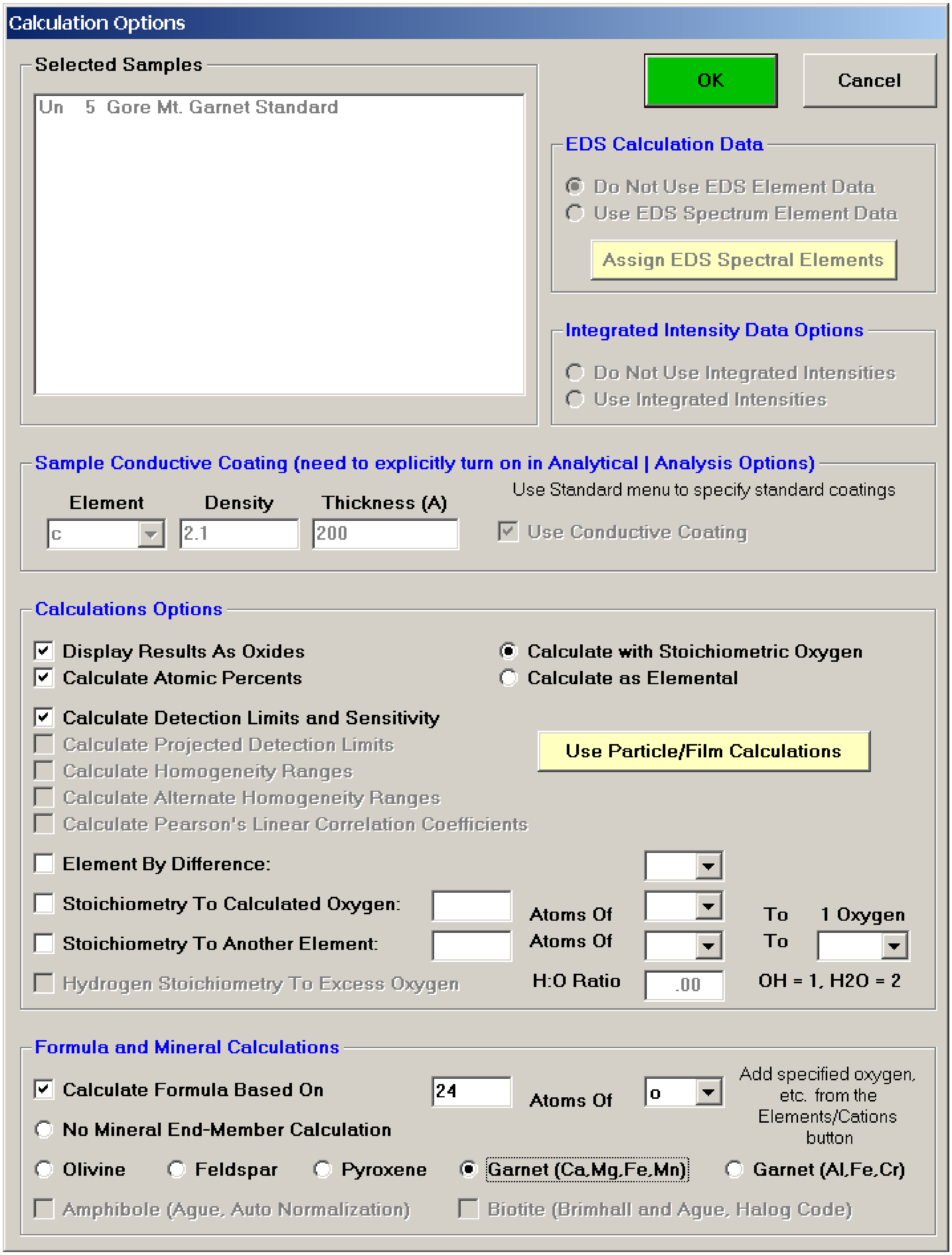
Each of the selected options in the above window will be briefly discussed in conjunction with the data output for the selected sample *Un   5 Gore Mt. Garnet Standard*.

```
Un    5 Gore Mt. Garnet Standard
TakeOff = 40.0  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

Std 40
Number of Data Lines:   2             Number of 'Good' Data Lines:   2
First/Last Date-Time: 11/21/1996 10:51:22 AM to 11/21/1996 10:55:35 AM
WARNING- Forcing negative k-ratios to zero

Average Total Oxygen:       42.298     Average Total Weight%:  100.752
Average Calculated Oxygen:  42.298     Average Atomic Number:   13.652
Average Excess Oxygen:        .000     Average Atomic Weight:   22.871
Average ZAF Iteration:        4.00     Average Quant Iterate:     2.00

Oxygen Calculated by Cation Stoichiometry and Included in the Matrix Correction

Un    5 Gore Mt. Garnet Standard, Results in Elemental Weight Percents

SPEC:        O
TYPE:     CALC

AVER:   42.298
SDEV:     .027

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
BGDS:      LIN     LIN     LIN     LIN     LIN     LIN     LIN
TIME:    40.00   40.00   40.00   40.00   40.00   40.00   20.00
BEAM:    30.56   30.56   30.56   30.56   30.56   30.56   30.56

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si   SUM
    22   5.229    .418   5.345  11.932  17.024    .065  18.474 100.765
    23   5.189    .413   5.287  11.896  16.982    .067  18.588 100.740

AVER:    5.209    .415   5.316  11.914  17.003    .066  18.531 100.752
SDEV:     .028    .004    .041    .025    .029    .002    .081    .018
SERR:     .020    .003    .029    .018    .021    .001    .057
%RSD:      .54     .85     .76     .21     .17    2.36     .44
STDS:       40      26      40      40      40      41      40

STKF:    .0330   .3086   .0499   .0841   .1468   .2898   .1370
STCT:   1818.5  1807.9  1356.0  5863.6   993.9  7261.9  2319.7

UNKF:    .0328   .0035   .0502   .0831   .1476   .0006   .1377
UNCT:   1807.9    20.8  1365.0  5792.0   999.3    14.5  2332.6
UNBG:     31.0     7.3    33.8    59.4    11.7    46.8     6.3

ZCOR:   1.5892  1.1716  1.0580  1.4339  1.1517  1.1330  1.3457
KRAW:    .9941   .0115  1.0066   .9878  1.0054   .0020  1.0055
PKBG:    59.27    3.87   41.44   98.54   86.43    1.31  375.63
```

```
Un    5 Gore Mt. Garnet Standard, Results in Oxide Weight Percents

SPEC:        O
TYPE:     CALC

AVER:     .000
SDEV:     .000

ELEM:      MgO     MnO     CaO   Al2O3     FeO    TiO2    SiO2   SUM
    22   8.671    .539   7.478  22.545  21.901    .108  39.522 100.765
    23   8.605    .533   7.398  22.478  21.848    .112  39.767 100.740

AVER:    8.638    .536   7.438  22.512  21.874    .110  39.645 100.752
SDEV:     .047    .005    .057    .048    .038    .003    .174    .018
SERR:     .033    .003    .040    .034    .027    .002    .123
%RSD:      .54     .85     .76     .21     .17    2.36     .44

Un    5 Gore Mt. Garnet Standard, Results in Atomic Percents

SPEC:        O
TYPE:     CALC

AVER:   60.010
SDEV:     .026

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si   SUM
    22   4.884    .173   3.027  10.040   6.921    .031  14.933 100.000
    23   4.846    .170   2.994  10.007   6.902    .032  15.021 100.000

AVER:    4.865    .172   3.011  10.023   6.911    .031  14.977 100.000
SDEV:     .027    .001    .024    .023    .013    .001    .063    .000
SERR:     .019    .001    .017    .017    .009    .001    .044
%RSD:      .56     .87     .78     .23     .19    2.34     .42

Un    5 Gore Mt. Garnet Standard, Results Based on 24 Atoms of o

SPEC:        O
TYPE:     CALC

AVER:   24.000
SDEV:     .000

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si   SUM
    22   1.954    .069   1.211   4.016   2.769    .012   5.974  40.005
    23   1.937    .068   1.197   4.001   2.759    .013   6.006  39.981

AVER:    1.946    .069   1.204   4.009   2.764    .012   5.990  39.993
SDEV:     .012    .001    .010    .011    .007    .000    .022    .017
SERR:     .008    .000    .007    .008    .005    .000    .016
%RSD:      .61     .92     .83     .28     .24    2.30     .37

Garnet Mineral End-Member Calculations (Ca, Mg, Fe, Mn)

           Gro     Pyr     Alm      Sp
    22    20.2    32.6    46.1     1.2
    23    20.1    32.5    46.3     1.1

AVER:     20.1    32.5    46.2     1.1
SDEV:       .1      .0      .1      .0

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

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
    22    .012    .039    .017    .012    .043    .023    .023
    23    .012    .041    .017    .012    .044    .023    .020

AVER:     .012    .040    .017    .012    .044    .023    .021
SDEV:     .000    .001    .000    .000    .001    .000    .002
SERR:     .000    .001    .000    .000    .000    .000    .001
```

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

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
    22      .4     5.1      .4      .2      .5    14.6      .5
    23      .4     5.3      .4      .2      .5    14.4      .5

AVER:       .4     5.2      .4      .2      .5    14.5      .5
SDEV:       .0      .1      .0      .0      .0      .2      .0
SERR:       .0      .1      .0      .0      .0      .1      .0

Range of Homogeneity (t-test) in +/- Elemental Weight Percent (Average of Sample):

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci    .025    .004    .035    .023    .025    .001    .077
  80ci    .055    .009    .078    .052    .056    .003    .172
  90ci    .113    .019    .159    .107    .114    .007    .353
  95ci    .228    .038    .321    .214    .230    .014    .710
  99ci   1.142    .189   1.607   1.074   1.151    .069   3.556

Test of Homogeneity (t-test) at 1.0 % Precision (Average of Sample):

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci     yes     yes     yes     yes     yes      no     yes
  80ci      no      no      no     yes     yes      no     yes
  90ci      no      no      no     yes     yes      no      no
  95ci      no      no      no      no      no      no      no
  99ci      no      no      no      no      no      no      no

Level of Homogeneity (t-test) in +/- Percent (Average of Sample):

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci      .5     1.0      .7      .2      .1     2.3      .4
  80ci     1.1     2.2     1.5      .4      .3     5.1      .9
  90ci     2.2     4.5     3.0      .9      .7    10.4     1.9
  95ci     4.4     9.1     6.0     1.8     1.4    21.0     3.8
  99ci    21.9    45.5    30.2     9.0     6.8   105.2    19.2

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

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci     ---    .008     ---     ---     ---    .008     ---
  80ci     ---    .017     ---     ---     ---    .018     ---
  90ci     ---    .035     ---     ---     ---    .037     ---
  95ci     ---    .070     ---     ---     ---    .075     ---
  99ci     ---    .349     ---     ---     ---    .374     ---

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

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci    .035    .006    .049    .033    .035    .002    .109
  80ci    .078    .013    .110    .073    .079    .005    .243
  90ci    .160    .027    .225    .151    .161    .010    .499
  95ci    .322    .053    .454    .303    .325    .020   1.004
  99ci   1.615    .267   2.272   1.519   1.628    .098   5.029
```

```
Range of Ideal Homogeneity (t-test) in +/- Elemental Weight Percent (Average of Sample)
(Meisenkothen and Donovan):

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci    .026    .017    .031    .034    .116    .002    .118
  80ci    .059    .038    .069    .075    .260    .004    .263
  90ci    .121    .078    .141    .155    .532    .008    .539
  95ci    .243    .157    .285    .311   1.072    .017   1.085
  99ci   1.219    .788   1.427   1.560   5.368    .084   5.436

Range of Actual Homogeneity (t-test) in +/- Elemental Weight Percent (Average of Sample)
(Meisenkothen and Donovan):

ELEM:       Mg      Mn      Ca      Al      Fe      Ti      Si
  60ci    .035    .006    .049    .033    .035    .002    .109
  80ci    .078    .013    .110    .073    .079    .005    .243
  90ci    .160    .027    .225    .151    .161    .010    .499
  95ci    .322    .053    .454    .303    .325    .020   1.004
  99ci   1.615    .267   2.272   1.519   1.628    .098   5.029
```



Calculation Options

Selected Samples

Un 5 Gore Mt. Garnet Standard

EDS Calculation Data

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

Use Standard menu to specify standard coatings

Element: c
Density: 2.1
Thickness (A): 200

☑ Use 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

☐ Element By Difference:
☐ 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 24 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 *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.

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. Each must be added as a "not analyzed" element; click any empty row in the element list, type in the element symbol and leave the x-ray line blank. 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 *Formula and Mineral Calculation* fields at the base 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).

$$C_{\mathrm{MDL}} = (\mathrm{ZAF}) \frac{3\sqrt{\mathrm{I_B}/t}}{\mathrm{I_S}} \cdot 100$$

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

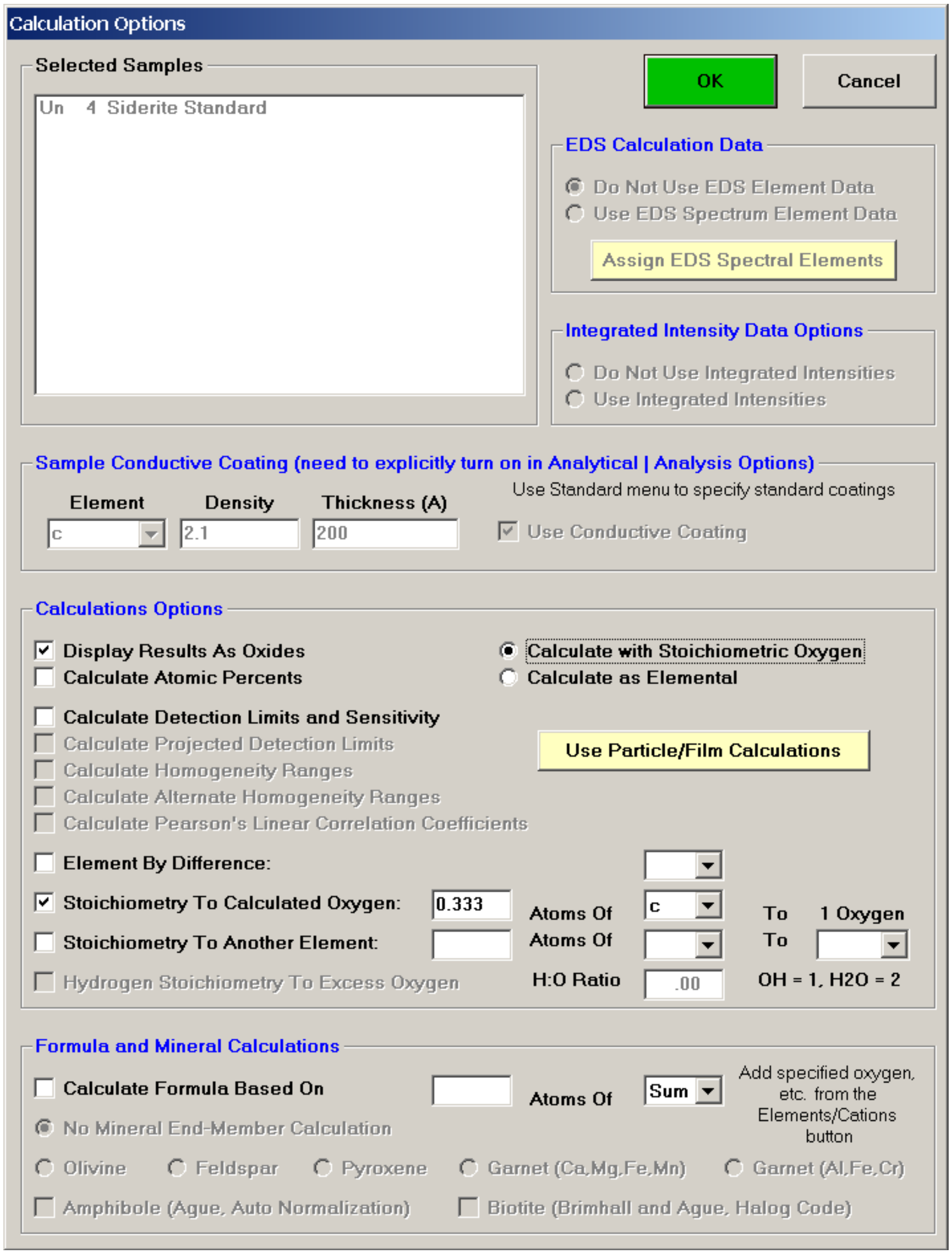
The homogeneity test compares the 99% confidence range of homogeneity value with 1% of the sample concentration for each element. If the range of homogeneity is less than 1% of the sample concentration then the sample may be considered to be homogenous within 1%. The detection limit calculation here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



Calculation Options

Selected Samples

Un 4 Siderite Standard

EDS Calculation Data

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

Use Standard menu to specify standard coatings

Element: c
Density: 2.1
Thickness (A): 200
☑ Use 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

☐ Element By Difference:
☑ Stoichiometry To Calculated Oxygen: 0.333 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.

```
Un    4 Siderite Standard
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
First/Last Date-Time: 07/26/1999 02:45:52 PM to 07/26/1999 02:51:12 PM
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

Un    4 Siderite Standard, 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

Un    4 Siderite Standard, 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
```

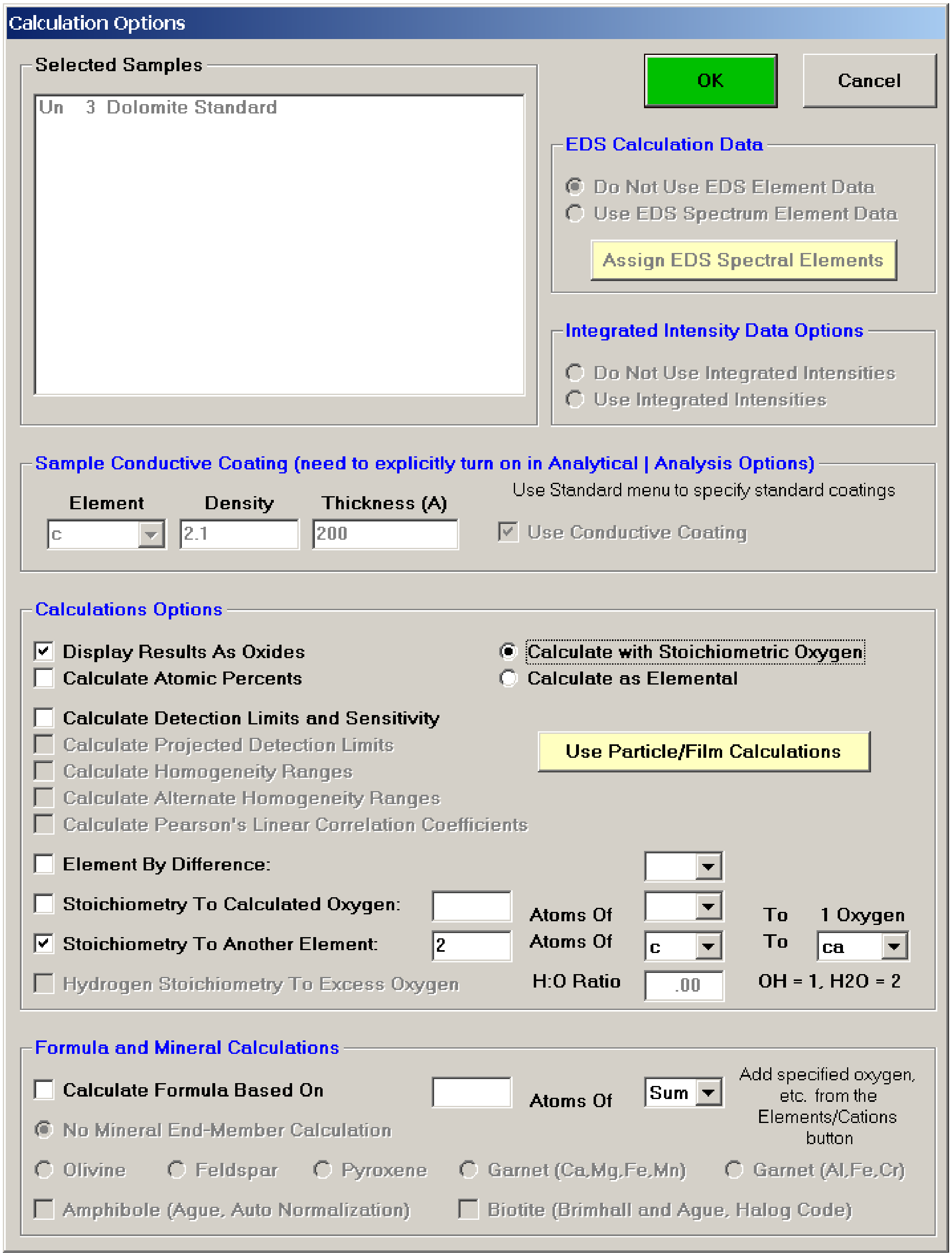
```
AVER:      .012    .119   2.984  58.981 100.042
SDEV:      .011    .008    .091    .192    .192
SERR:      .006    .005    .053    .111
%RSD:     86.77    6.95    3.06     .33
```

Another interesting example demonstrating this feature is nicely documented in the User's Guide and Reference documentation (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.



Calculation Options

Selected Samples

Un 3 Dolomite Standard

EDS Calculation Data

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

Use Standard menu to specify standard coatings

Element	Density	Thickness (A)
c	2.1	200

☑ Use 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

☐ Element By Difference:
☐ Stoichiometry To Calculated Oxygen: Atoms Of 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

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 resulting carbonate output is seen next.

```
Un    3 Dolomite Standard
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
First/Last Date-Time: 07/26/1999 02:36:45 PM to 07/26/1999 02:42:40 PM
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

Un    3 Dolomite Standard, 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

Un    3 Dolomite Standard, 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
```

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Linear Calibration - Curve Method

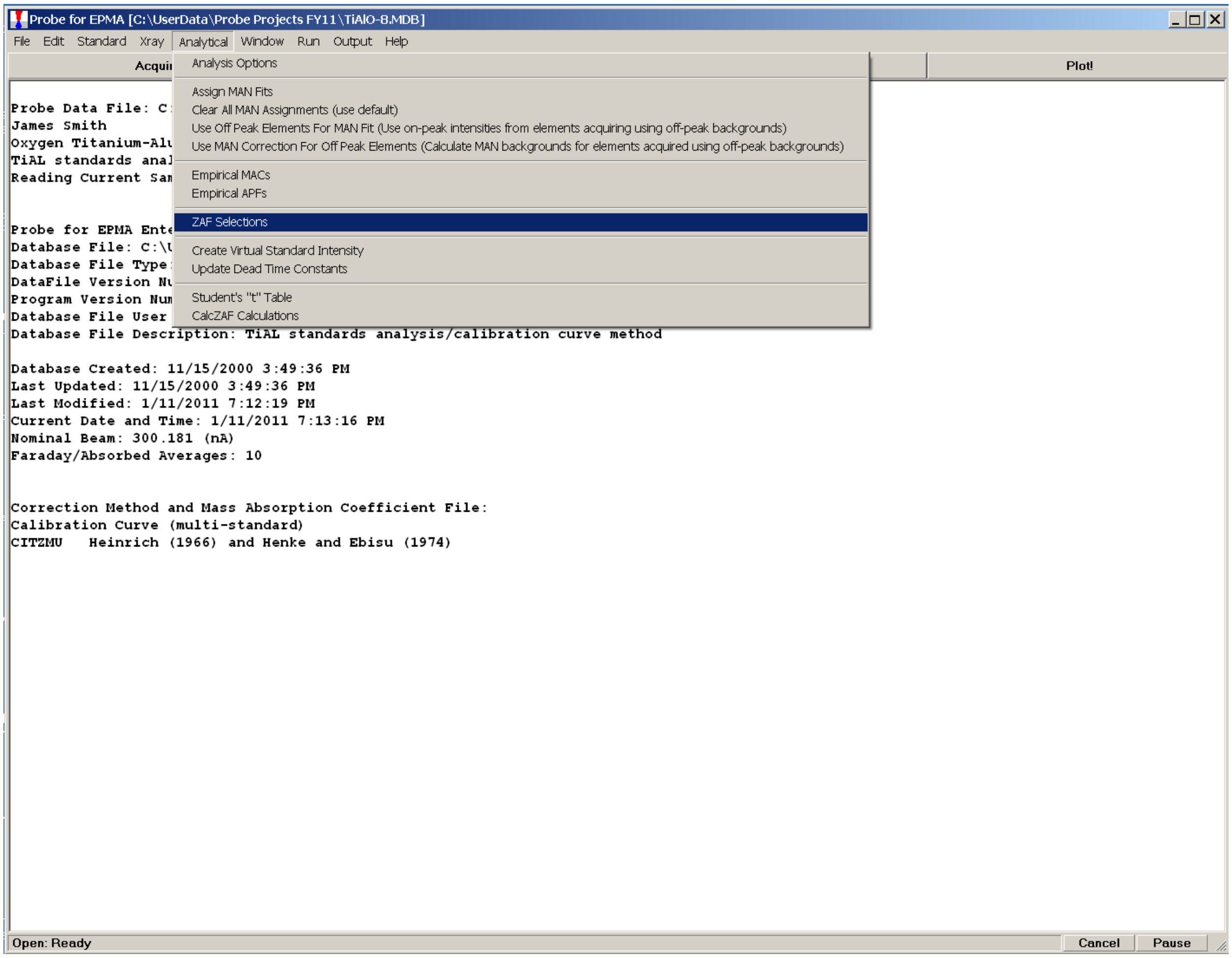
PROBE FOR EPMA offers a sophisticated calibration curve (multi-standard) method for correcting x-ray data. It is based on a second order polynomial fit to multiple standard intensity data. This option has been utilized in special situations such as the analysis of trace carbon in steels and when a suitable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

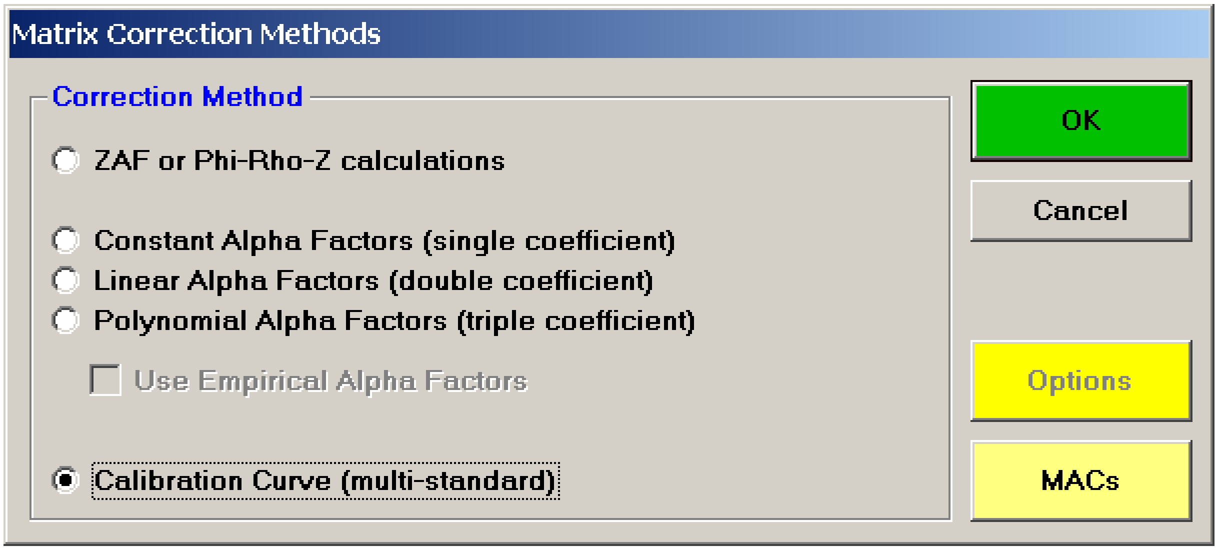
Aluminum, titanium and oxygen were peaked on the appropriate standards and count rate data (five spots each) were acquired on each of the nine standards. The count rate data was then examined in the **Analyze!** window to ascertain the precision of the five data points on each standard, deleting any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



```
Probe Data File: C:
James Smith
Oxygen Titanium-Alu
TiAL standards anal
Reading Current Sam


Probe for EPMA Ente
Database File: C:\U
Database File Type:
DataFile Version Nu
Program Version Num
Database File User
Database File Description: TiAL standards analysis/calibration curve method

Database Created: 11/15/2000 3:49:36 PM
Last Updated: 11/15/2000 3:49:36 PM
Last Modified: 1/11/2011 7:12:19 PM
Current Date and Time: 1/11/2011 7:13:16 PM
Nominal Beam: 300.181 (nA)
Faraday/Absorbed Averages: 10


Correction Method and Mass Absorption Coefficient File:
Calibration Curve (multi-standard)
CITZMU   Heinrich (1966) and Henke and Ebisu (1974)
```

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



Matrix Correction Methods

Correction Method

○ ZAF or Phi-Rho-Z calculations

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

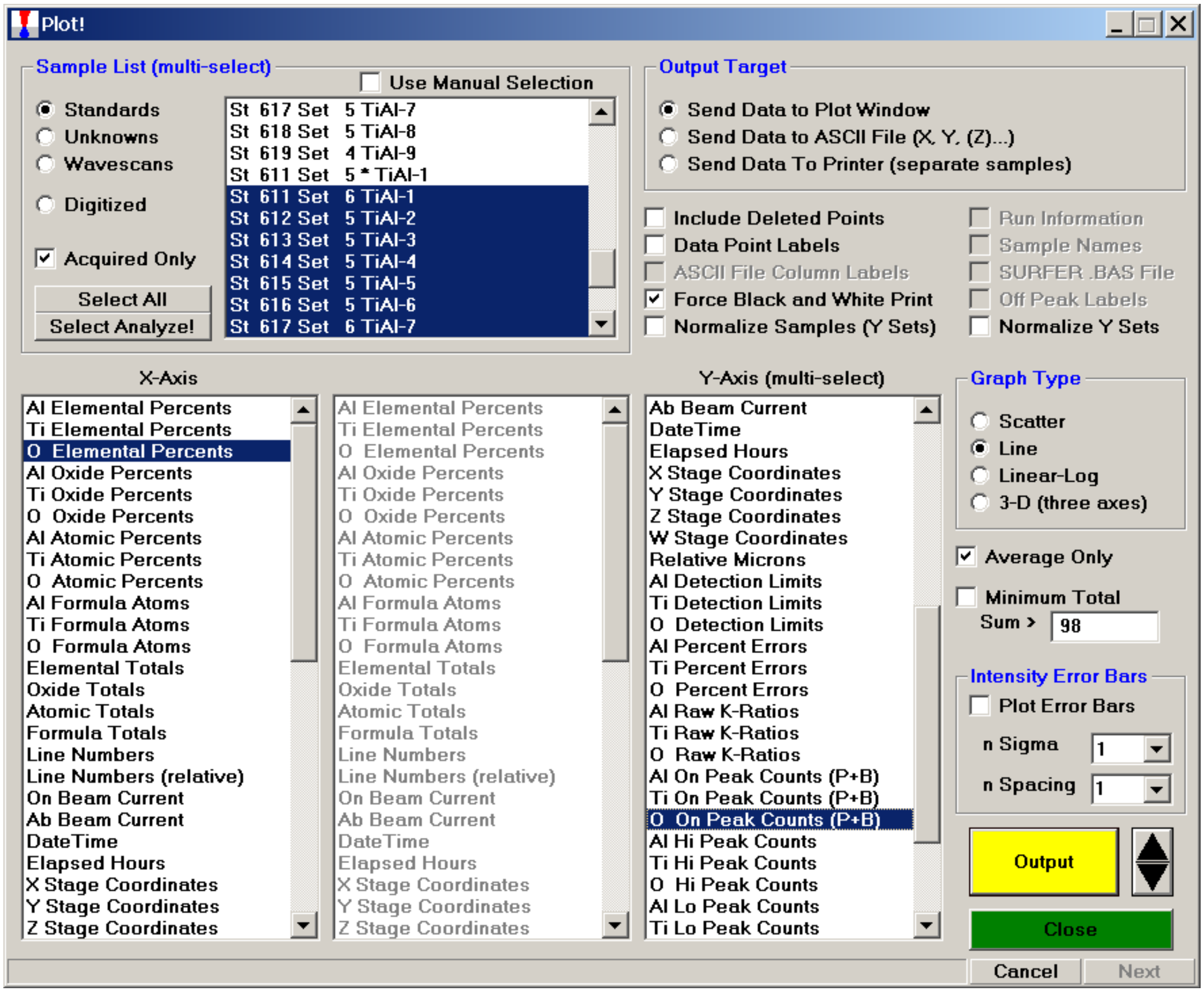
☐ Use Empirical Alpha Factors

● 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. Open the **Plot!** window. Select all nine titanium-aluminide alloy standards to plot. Note, the check box for *Force Black and White Print* was selected. If the user wants to output and archive the graphed data, this option causes the printer to create a clean black and white print, without gray background (see discussion below). Select a *Graph Type*. Check the *Average Only* check box to use the average value of each standard sample.

Finally, plot *O Elemental Percents* versus *O On Peak Counts (P+B)*.



Plot!

Sample List (multi-select)

☐ Use Manual Selection

● Standards
○ Unknowns
○ Wavescans
○ Digitized
☑ Acquired Only

St 617 Set 5 TiAl-7
St 618 Set 5 TiAl-8
St 619 Set 4 TiAl-9
St 611 Set 5 * TiAl-1
St 611 Set 6 TiAl-1
St 612 Set 5 TiAl-2
St 613 Set 5 TiAl-3
St 614 Set 5 TiAl-4
St 615 Set 5 TiAl-5
St 616 Set 5 TiAl-6
St 617 Set 6 TiAl-7

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
O Elemental Percents

Y-Axis (multi-select)
O On Peak Counts (P+B)

Graph Type

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

☑ Average Only
☐ Minimum Total Sum > 98

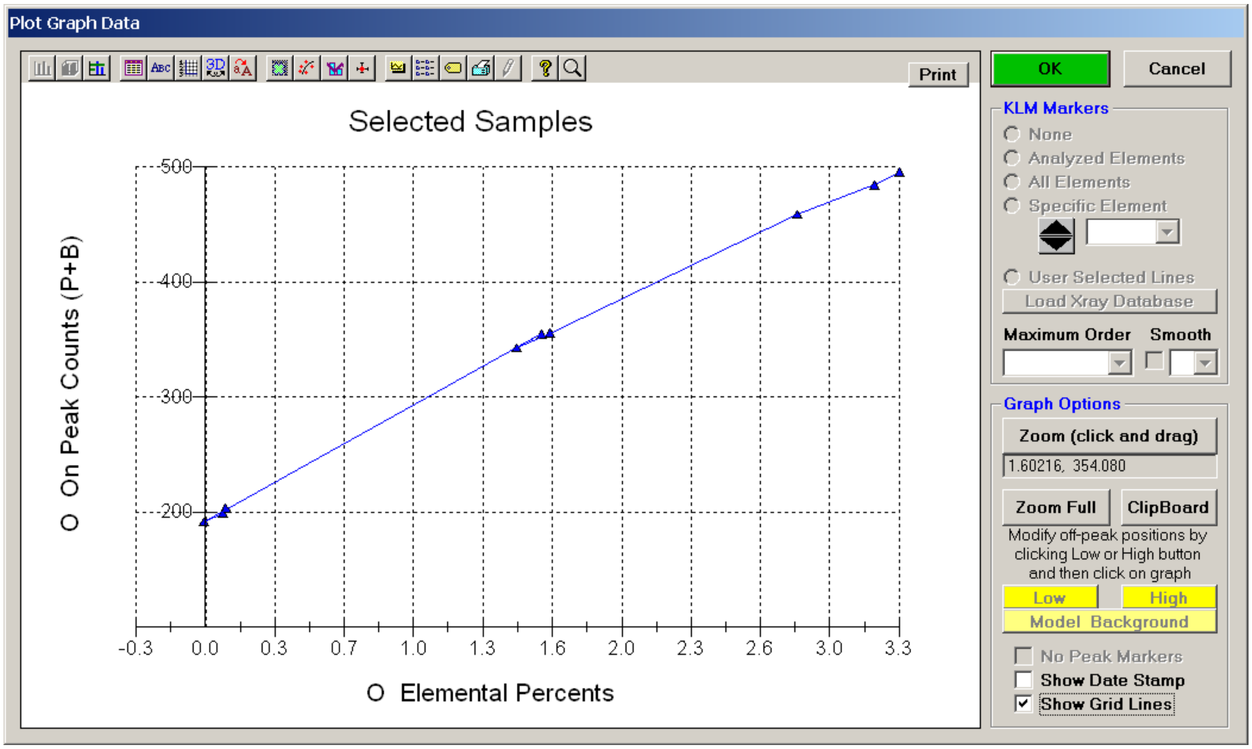
Intensity Error Bars

☐ Plot Error Bars
n Sigma 1
n Spacing 1

Click the **Output** button.

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

The **Plot Graph Data** window appears.



1.60216, 354.080

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

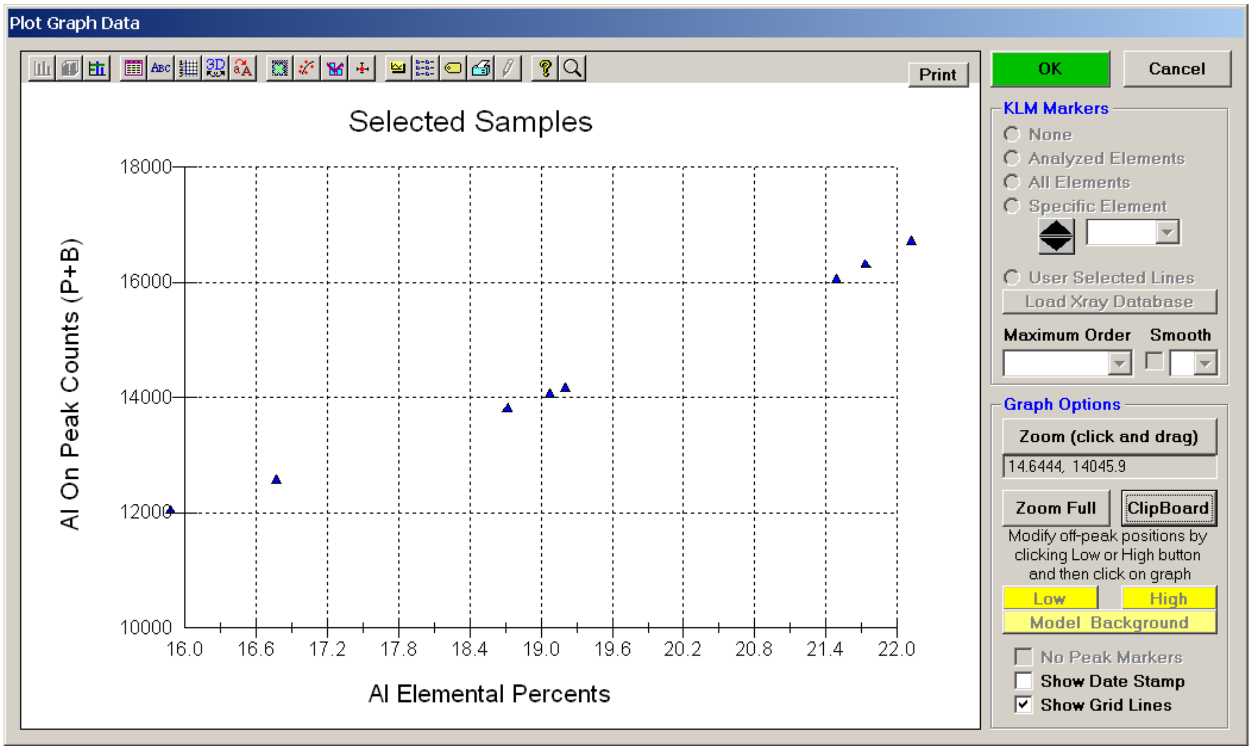
☐ No Peak Markers
☐ Show Date Stamp
☑ Show Grid Lines

The *Show Grid Lines* check box has been marked to facilitate reading the percent and count values. This calibration curve may be printed out by clicking the **Print** button next to the **OK** button. If the user selects the *Force Black and White Print* check box in the **Plot!** window, then the corresponding output will be a black and white print, if not, then the printer will output the above gray background.

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.



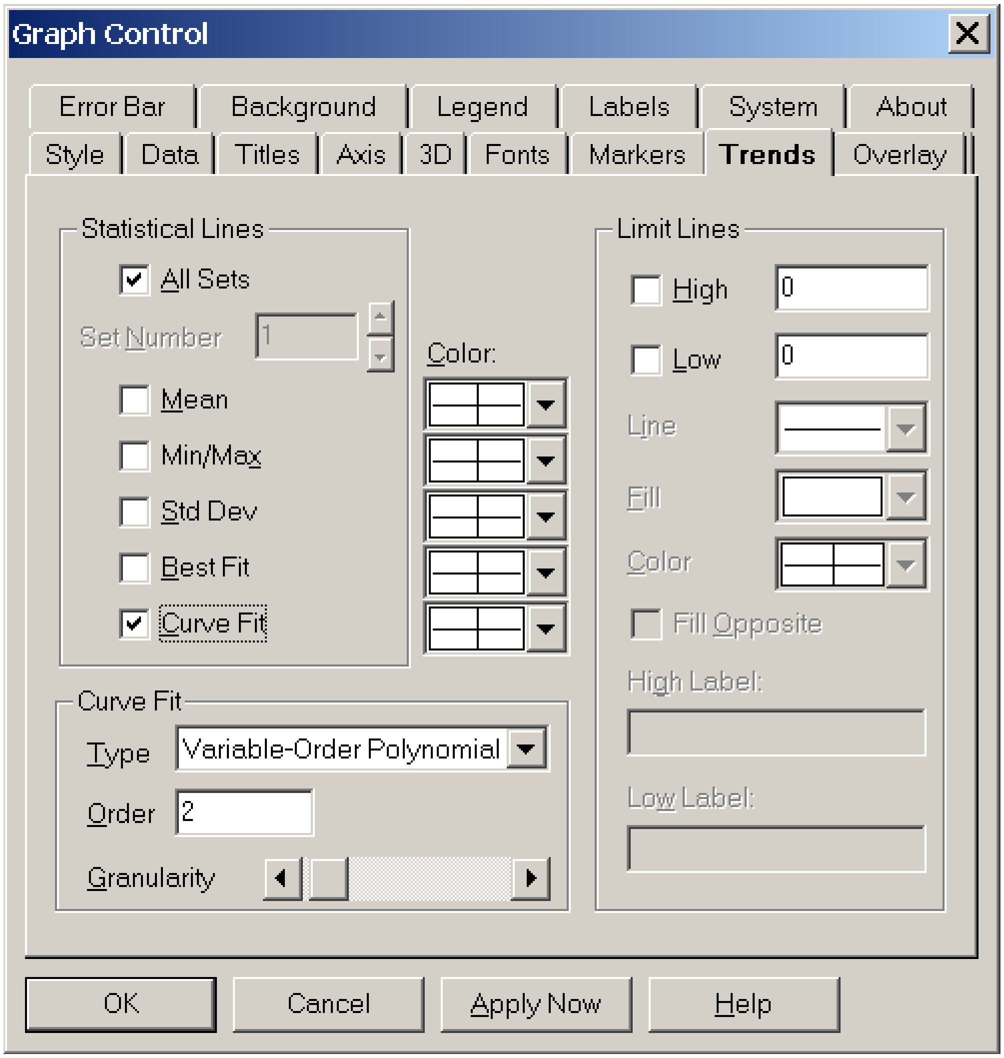
14.6444, 14045.9

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

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

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* as required.



Statistical Lines

☑ All Sets

Set Number 1

☐ Mean

☐ Min/Max

☐ Std Dev

☐ Best Fit

☑ Curve Fit

Color:

Curve Fit

Type Variable-Order Polynomial

Order 2

Granularity

Limit Lines

☐ High 0

☐ Low 0

Line

Fill

Color

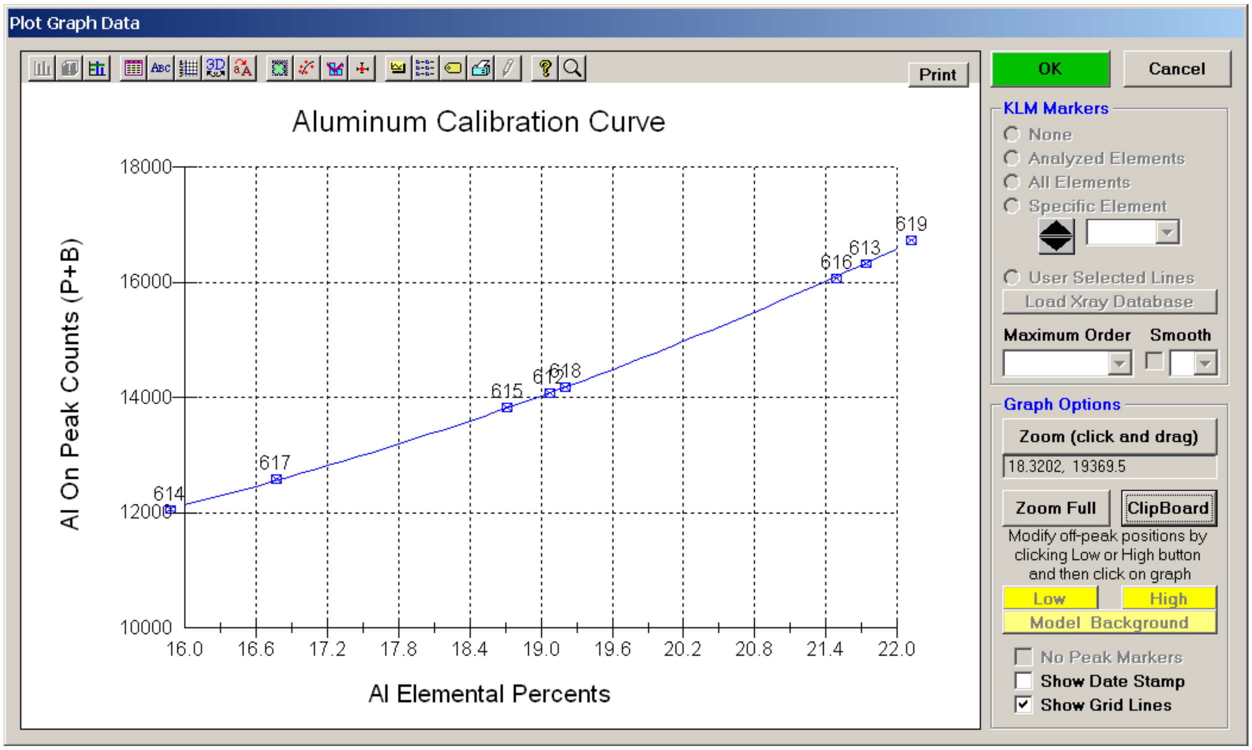
☐ Fill Opposite

High Label:

Low Label:

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.



○ None
○ Analyzed Elements
○ All Elements
○ Specific Element
○ User Selected Lines

18.3202, 19369.5

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

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
First/Last Date-Time: 12/11/2000 04:03:01 PM to 12/11/2000 04:06:28 PM
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**.

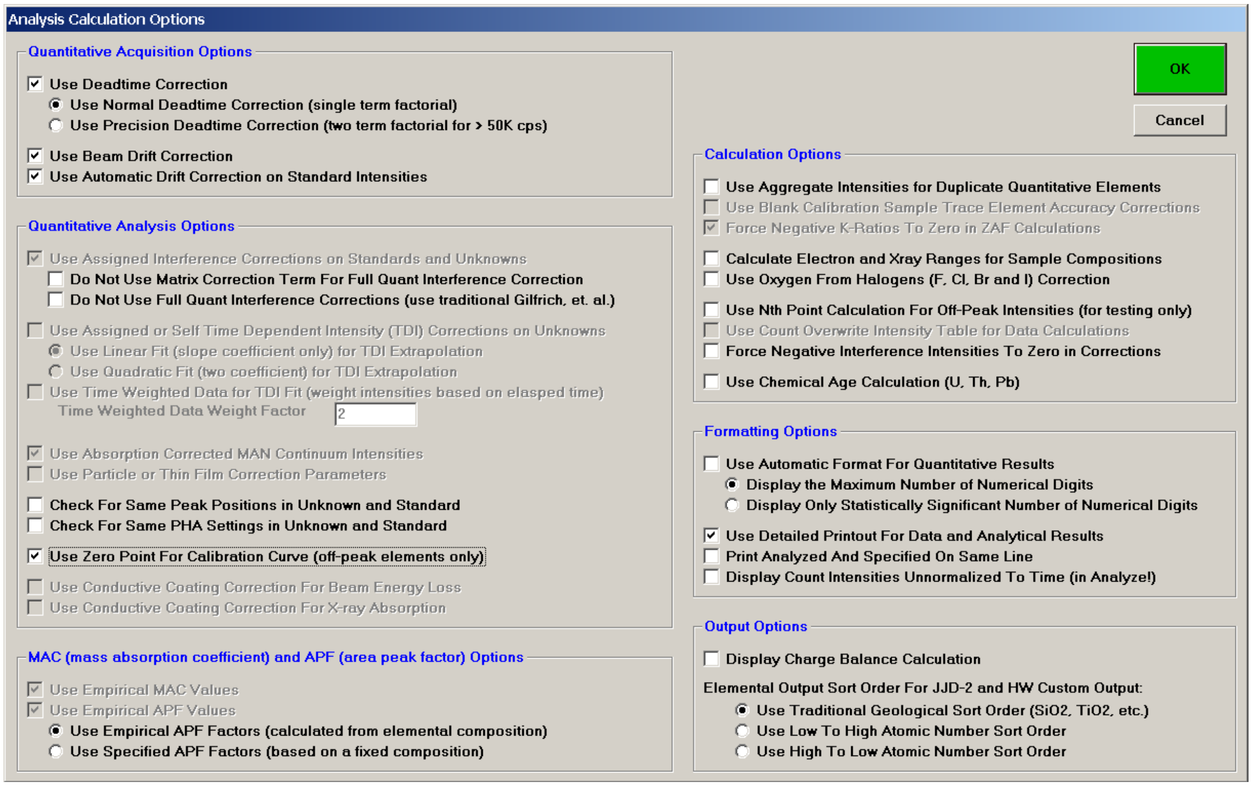
An example is printed next.

```
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
First/Last Date-Time: 12/11/2000 01:27:41 PM to 12/11/2000 01:40:41 PM
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.



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

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)

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!)

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

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.

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Time Dependent Intensity (TDI) Corrections

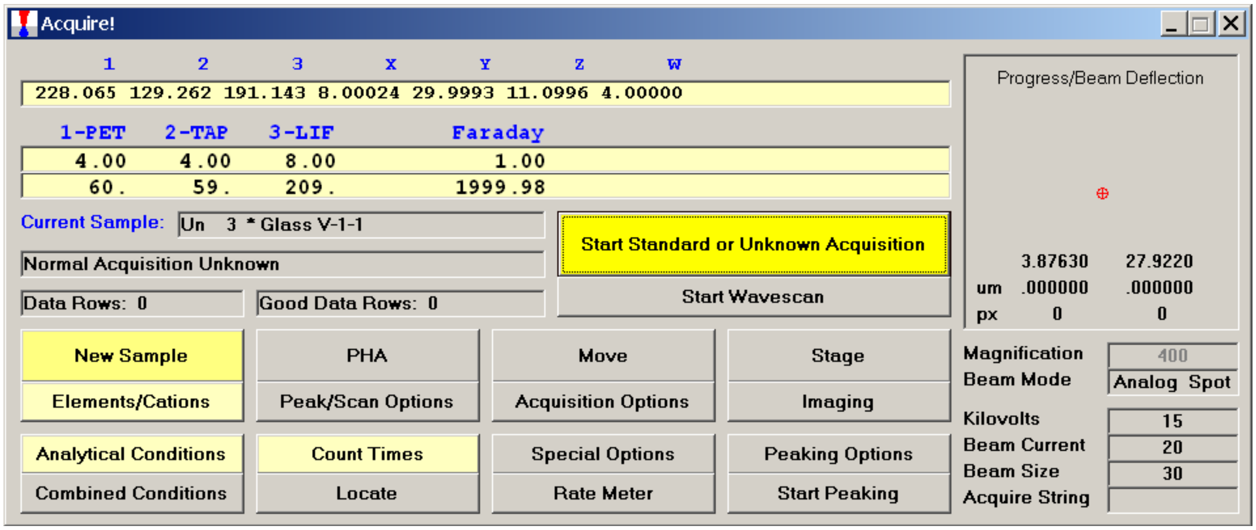
PROBE FOR EPMA gives the user two powerful methods for the correction of time dependent intensity element effects unknown samples. Each correction option provides a means to automatically correct data for the time dependent loss of x-ray intensity due to continuous electron bombardment (heating damage/charge 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, 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.



1	2	3	X	Y	Z	W
228.065	129.262	191.143	8.00024	29.9993	11.0996	4.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	8.00	1.00
60.	59.	209.	1999.98

Current Sample: Un 3 * Glass V-1-1

Normal Acquisition Unknown

Data Rows: 0

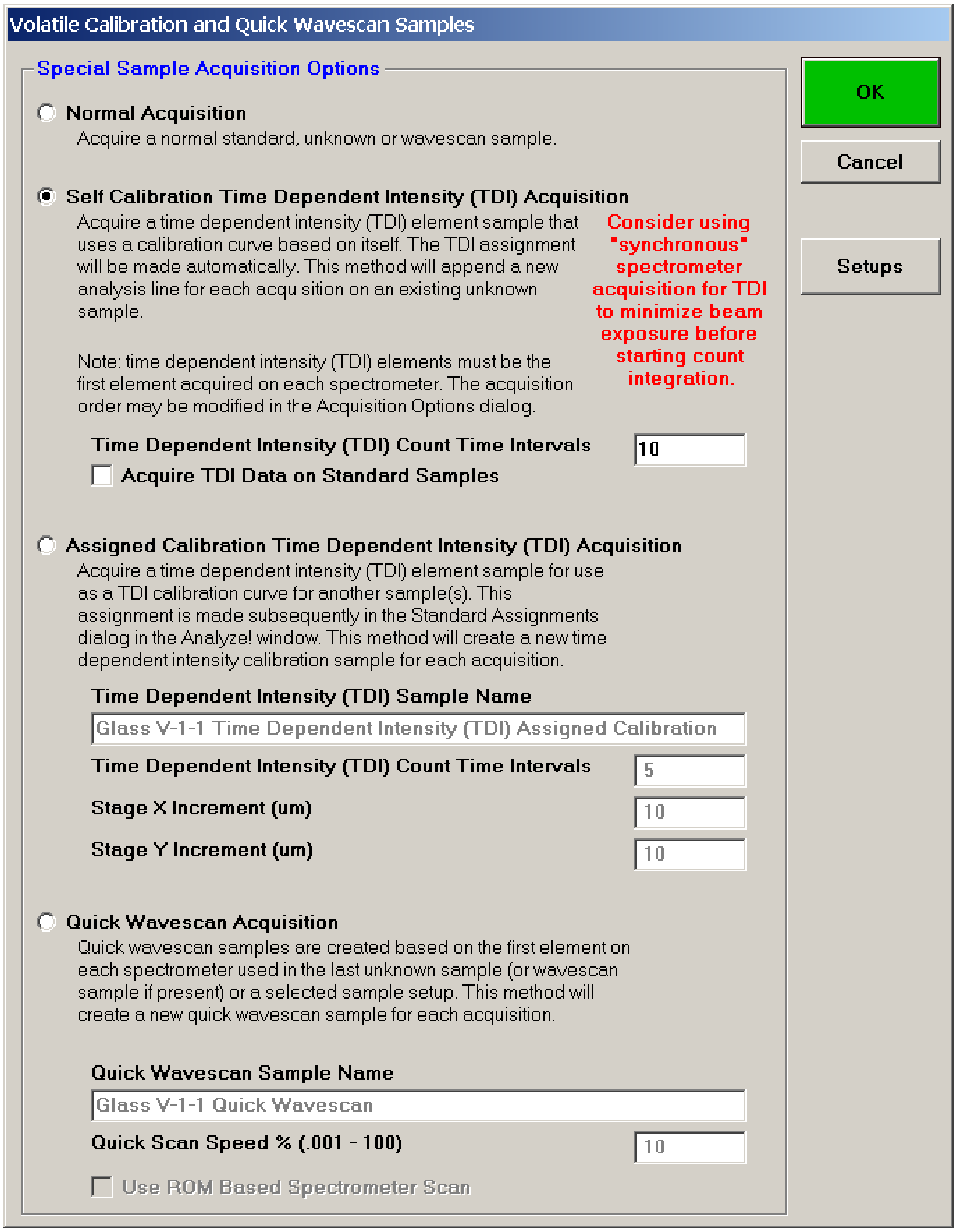
Good Data Rows: 0

	3.87630	27.9220
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	20
Beam Size	30
Acquire String	

Click the **Special Options** button in the **Acquire!** window.

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.



○ 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.

Consider using "synchronous" spectrometer acquisition for TDI to minimize beam exposure before starting count integration.

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.

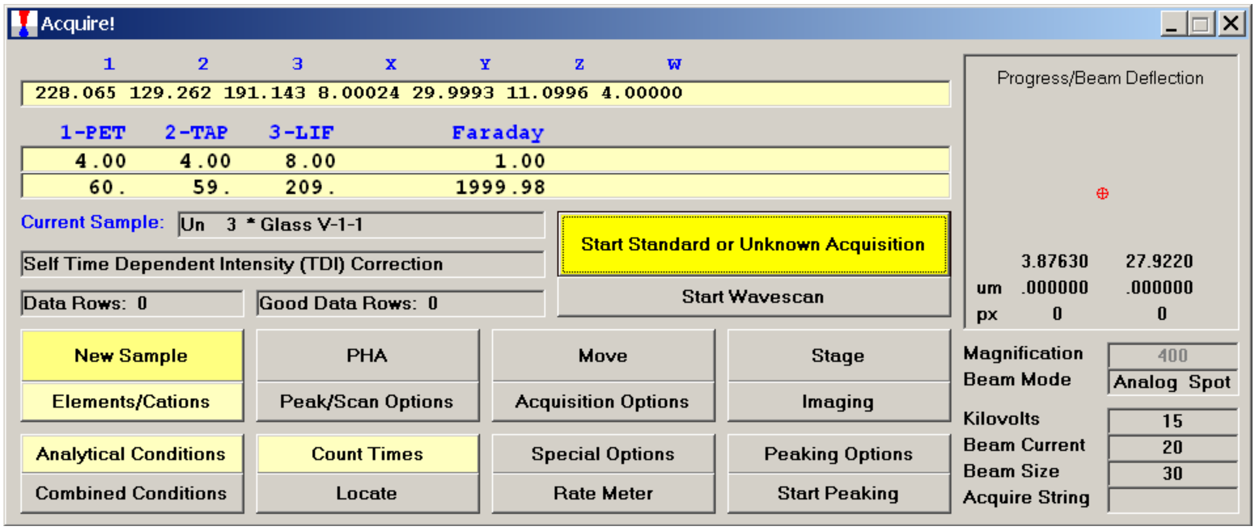
Time Dependent Intensity (TDI) Sample Name: Glass V-1-1 Time Dependent Intensity (TDI) Assigned Calibration
Time Dependent Intensity (TDI) Count Time Intervals: 5
Stage X Increment (um): 10
Stage Y Increment (um): 10

○ 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: Glass V-1-1 Quick Wavescan
Quick Scan Speed % (.001 - 100): 10
☐ Use ROM Based Spectrometer Scan

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

Click the **Start Standard or Unknown Acquisition** button to initiate count data collection on the unknown sample.



1	2	3	X	Y	Z	W
228.065	129.262	191.143	8.00024	29.9993	11.0996	4.00000

1-PET	2-TAP	3-LIF	Faraday
4.00	4.00	8.00	1.00
60.	59.	209.	1999.98

Current Sample: Un 3 * Glass V-1-1

Self Time Dependent Intensity (TDI) Correction

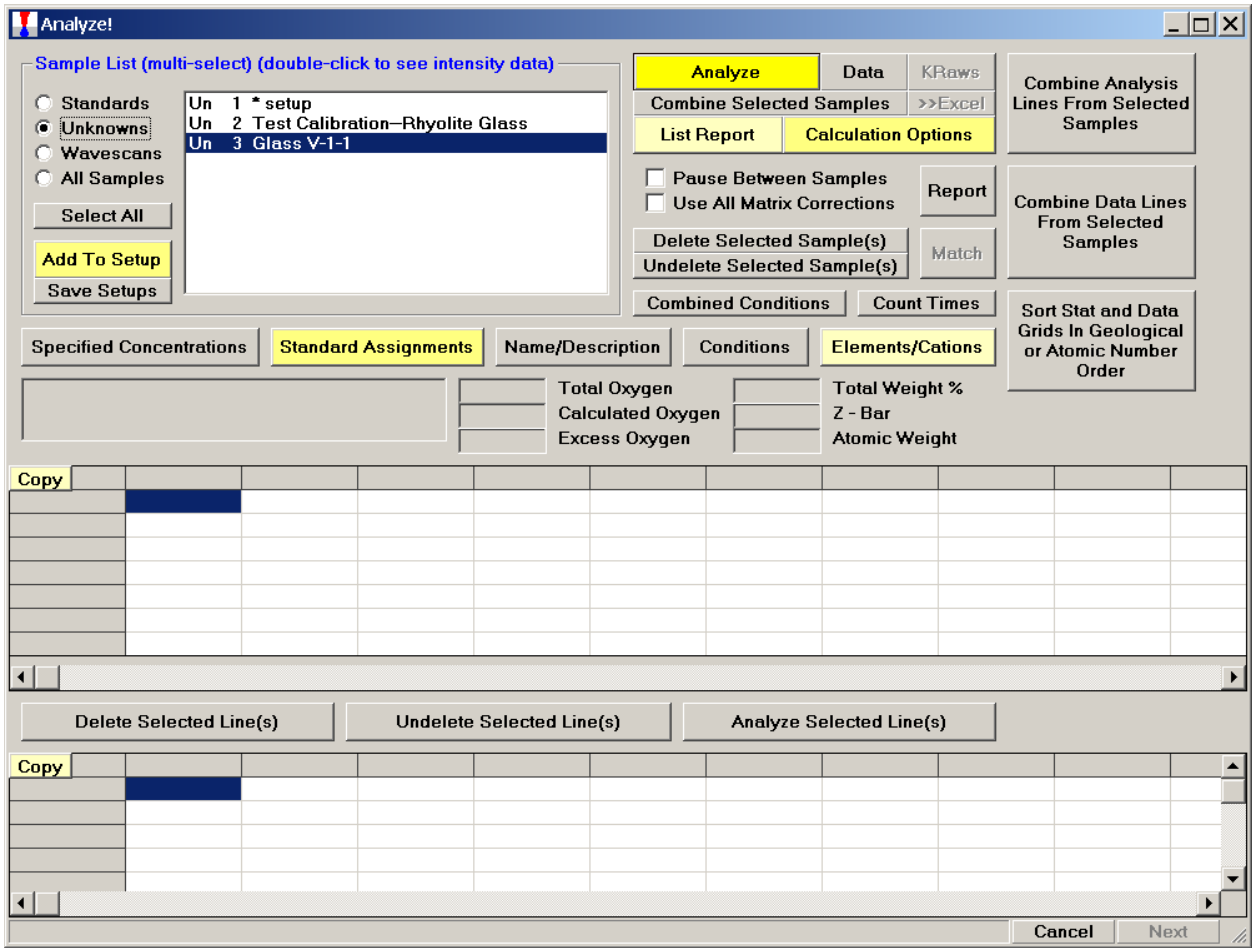
Data Rows: 0

Good Data Rows: 0

	3.87630	27.9220
um	.000000	.000000
px	0	0

Magnification	400
Beam Mode	Analog Spot
Kilovolts	15
Beam Current	20
Beam Size	30
Acquire String	

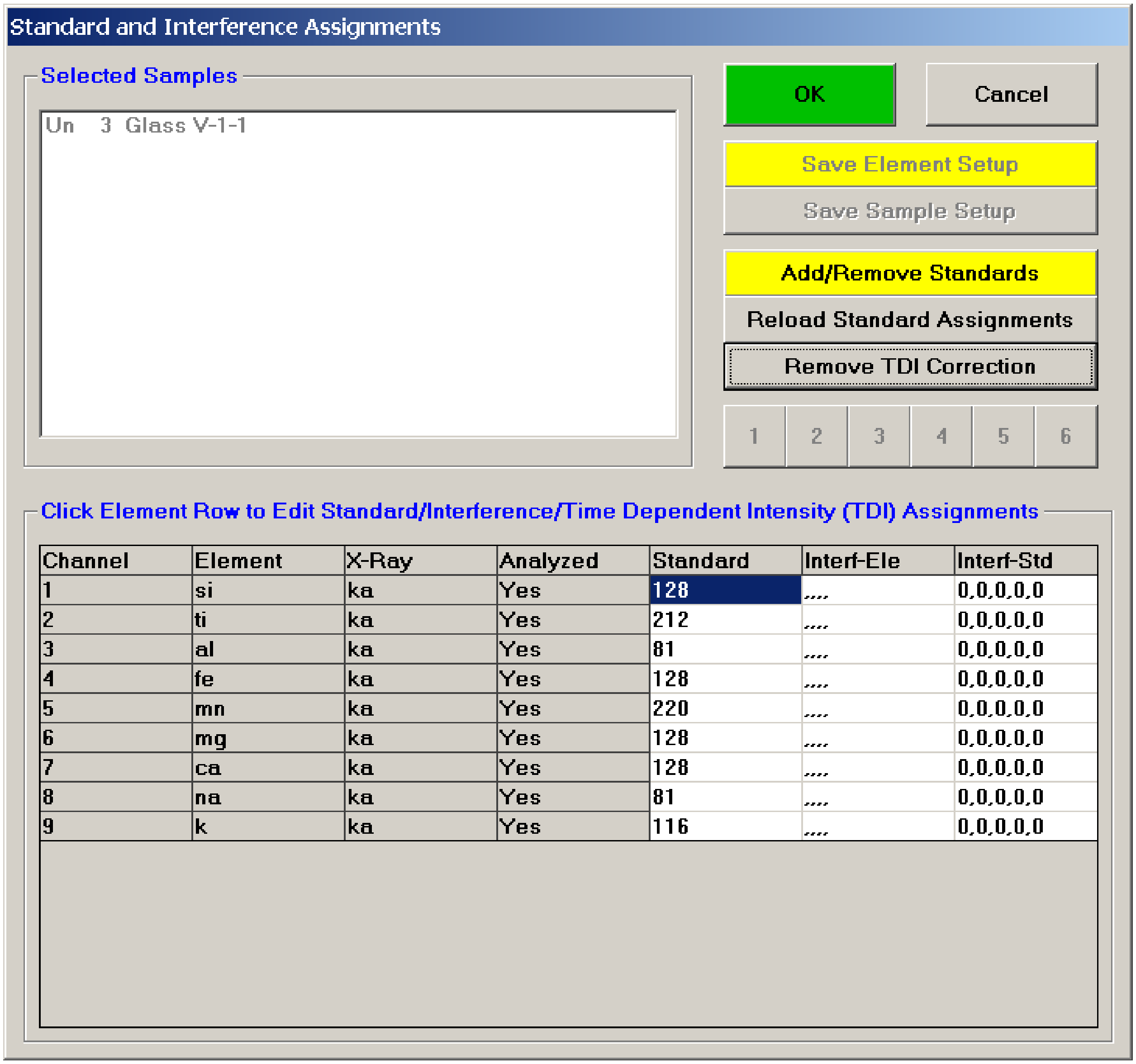
After collecting an unknown sample the user may display the volatile correction from the **Analyze!** window.



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

Click the **Standard Assignments** button.

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

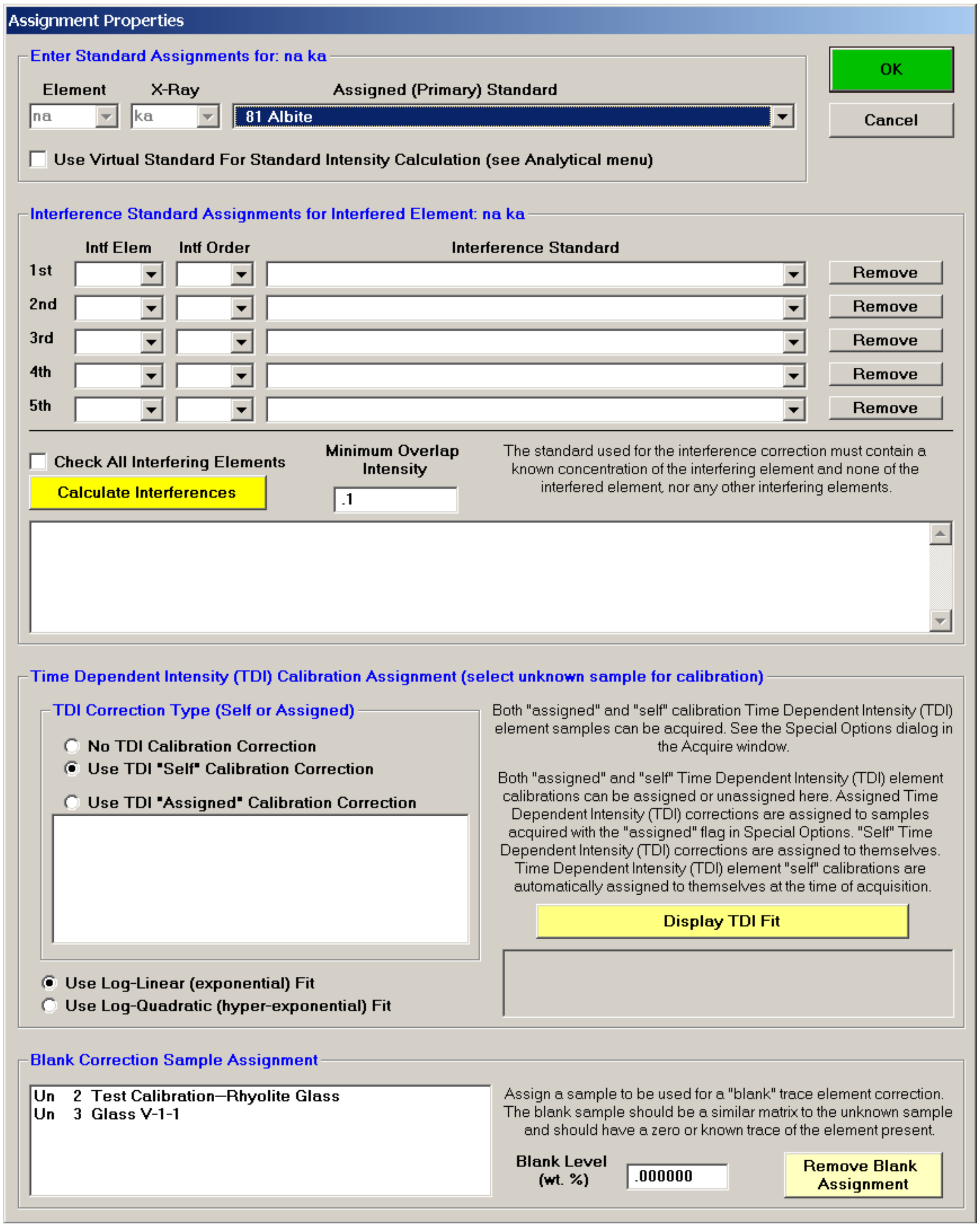


Un 3 Glass V-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	si	ka	Yes	128	,,,,,	0,0,0,0,0
2	ti	ka	Yes	212	,,,,,	0,0,0,0,0
3	al	ka	Yes	81	,,,,,	0,0,0,0,0
4	fe	ka	Yes	128	,,,,,	0,0,0,0,0
5	mn	ka	Yes	220	,,,,,	0,0,0,0,0
6	mg	ka	Yes	128	,,,,,	0,0,0,0,0
7	ca	ka	Yes	128	,,,,,	0,0,0,0,0
8	na	ka	Yes	81	,,,,,	0,0,0,0,0
9	k	ka	Yes	116	,,,,,	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.



Enter Standard Assignments for: na ka

Element: na
X-Ray: ka
Assigned (Primary) Standard: 81 Albite

☐ 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

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 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

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.

Blank Correction Sample Assignment

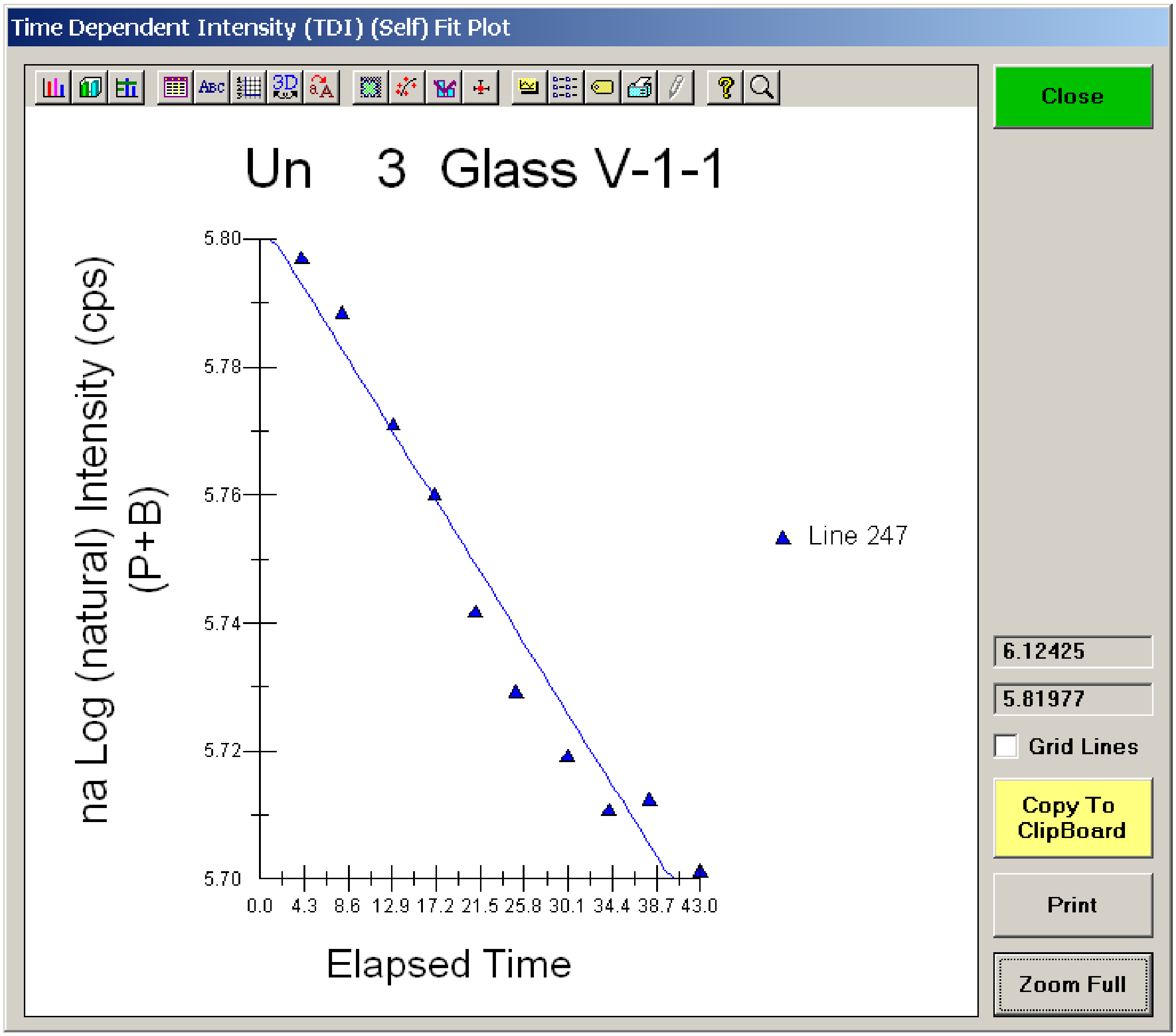
Un 2 Test Calibration--Rhyolite Glass
Un 3 Glass V-1-1

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

Highlight the appropriate *Time Dependent Intensity (TDI) Calibration Assignment* sample and click the **Display TDI Fit** button. Two types of fits are possible; Log-Linear or Log -Quadratic.

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



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.

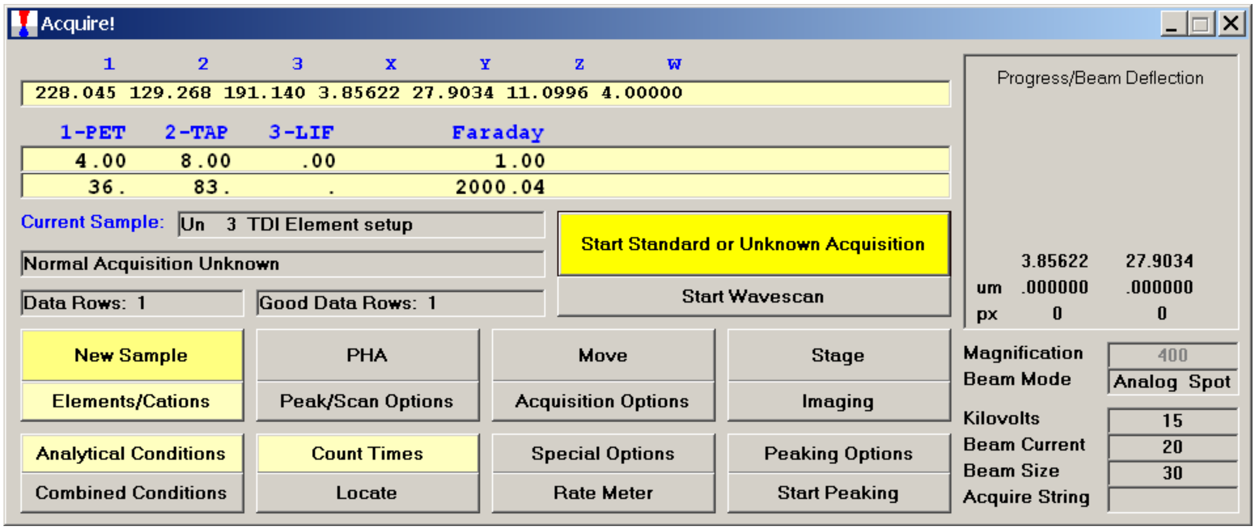
The extrapolation correction is quantitative in that the correction is based on a self calibration curve acquired during the run. The correction uses the actual elapsed time for all calculations. It is applied during the ZAF or Phi-Rho-Z iteration phase of the analysis to correct for changes in the matrix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

Click the **Special Options** button in the **Acquire!** window.



```
      1        2        3        X        Y        Z        W
 228.045  129.268  191.140  3.85622  27.9034  11.0996  4.00000

   1-PET    2-TAP    3-LIF              Faraday
    4.00     8.00      .00                 1.00
     36.      83.        .              2000.04
```

Current Sample: Un 3 TDI Element setup

Normal Acquisition Unknown

Data Rows: 1

Good Data Rows: 1

```
        3.85622    27.9034
um      .000000    .000000
px            0          0
```

Magnification: 400

Beam Mode: Analog Spot

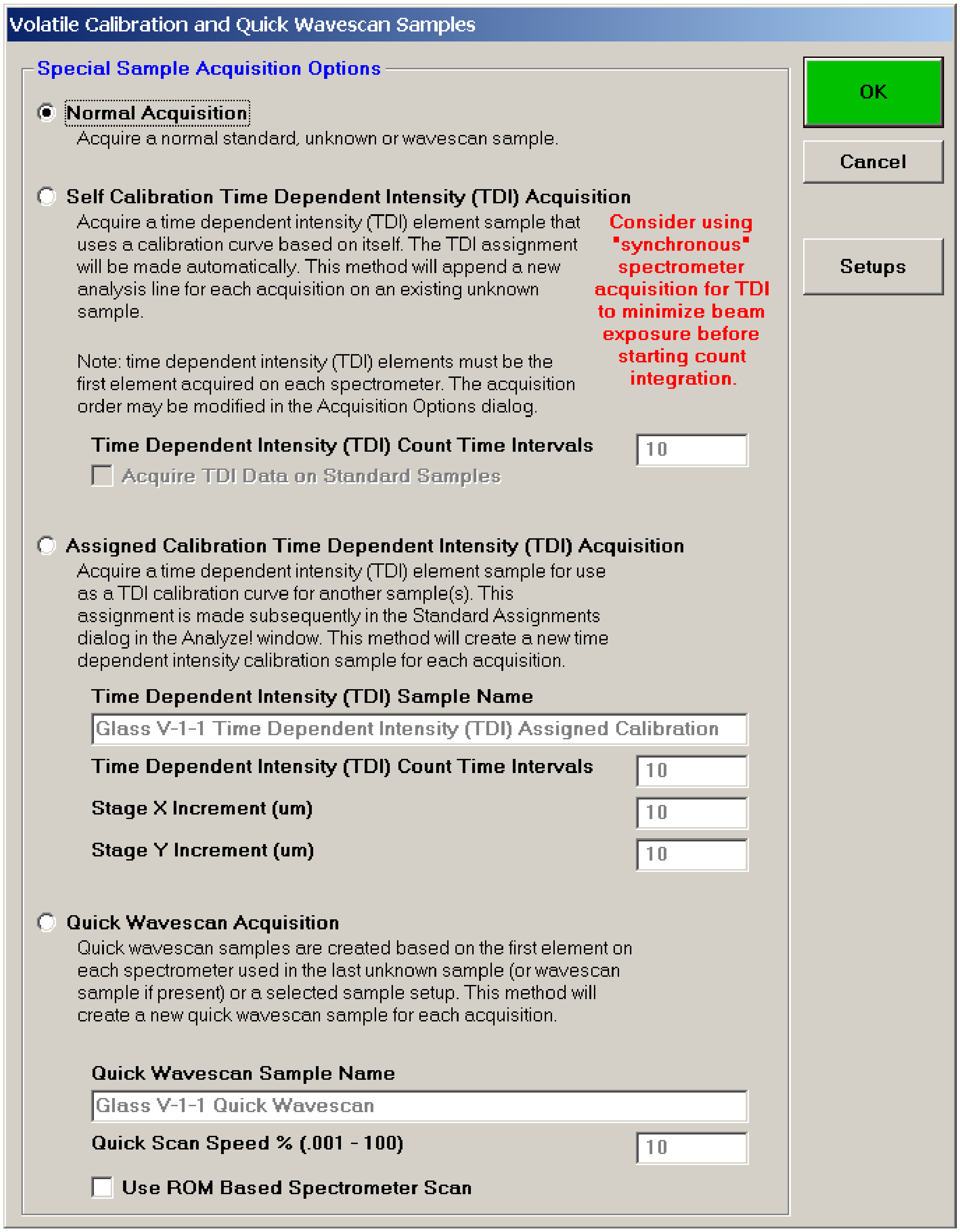
Kilovolts: 15

Beam Current: 20

Beam Size: 30

Acquire String:

The **Volatile Calibration and Quick Wavescan Samples** window opens. The default acquisition choice is *Normal Acquisition*.



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.

Consider using "synchronous" spectrometer acquisition for TDI to minimize beam exposure before starting count integration.

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: Glass V-1-1 Time Dependent Intensity (TDI) Assigned Calibration

Time Dependent Intensity (TDI) Count Time Intervals: 10

Stage X Increment (um): 10

Stage Y Increment (um): 10

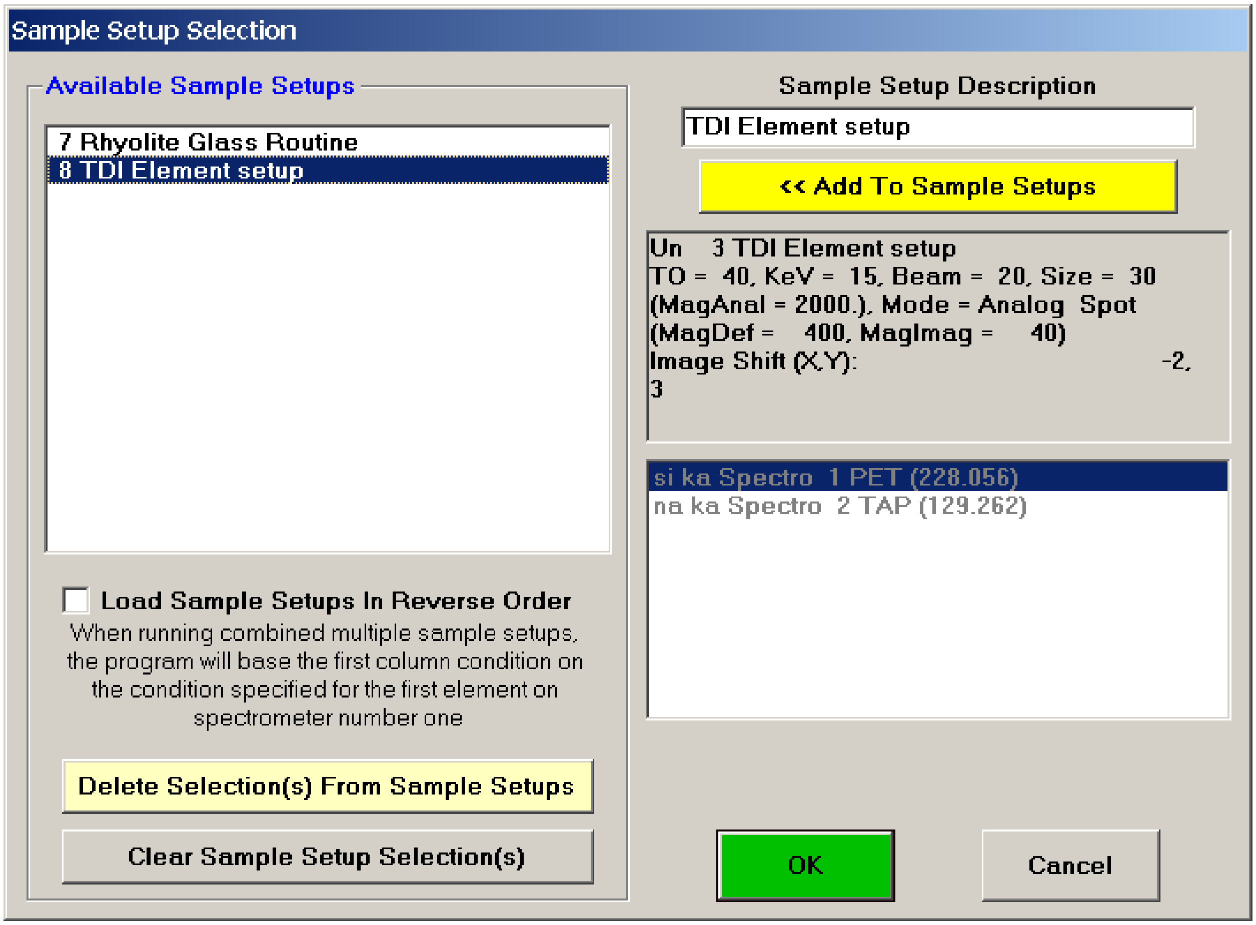
○ Quick Wavescan Acquisition
Quick wavescan samples are created based on the first element on each spectrometer used in the last unknown sample (or wavescan sample if present) or a selected sample setup. This method will create a new quick wavescan sample for each acquisition.

Quick Wavescan Sample Name: Glass V-1-1 Quick Wavescan

Quick Scan Speed % (.001 - 100): 10

☐ Use ROM Based Spectrometer Scan

Click the **Setups** button in the **Volatile Calibration and Quick Wavescan Samples** window, opening the **Sample Setup Selection** dialog box. Check that the appropriate volatile setup is active.



Sample Setup Selection

Available Sample Setups

7 Rhyolite Glass Routine
8 TDI Element 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

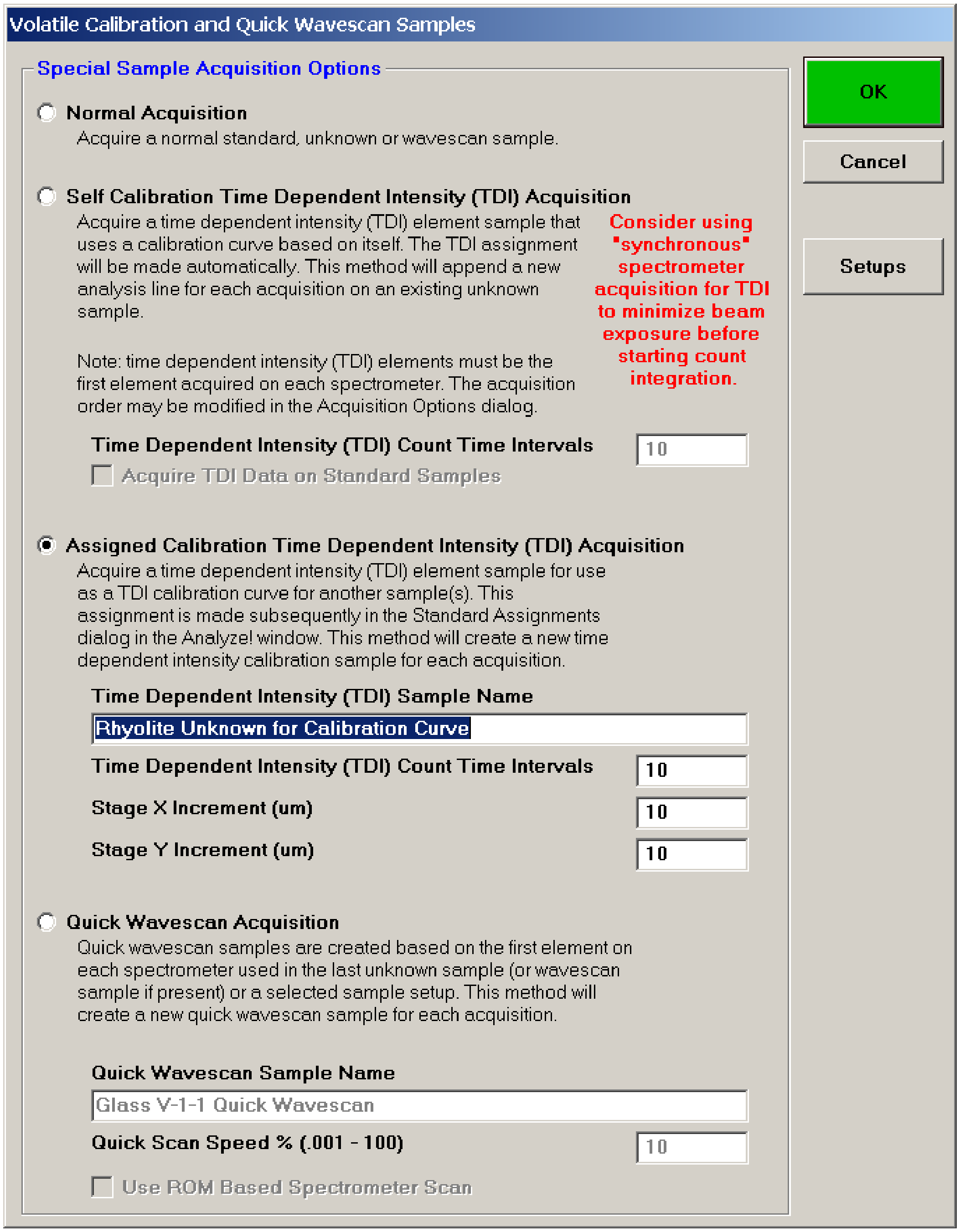
Sample Setup Description: TDI Element setup

```
Un    3 TDI Element setup
TO =  40, KeV =  15, Beam =  20, Size =  30
(MagAnal = 2000.), Mode = Analog  Spot
(MagDef =    400, MagImag =     40)
Image Shift (X,Y):                         -2,
3
```

```
si ka Spectro  1 PET (228.056)
na ka Spectro  2 TAP (129.262)
```

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.

Consider using "synchronous" spectrometer acquisition for TDI to minimize beam exposure before starting count integration.

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: Glass V-1-1 Quick Wavescan
Quick Scan Speed % (.001 - 100): 10
☐ Use ROM Based Spectrometer Scan

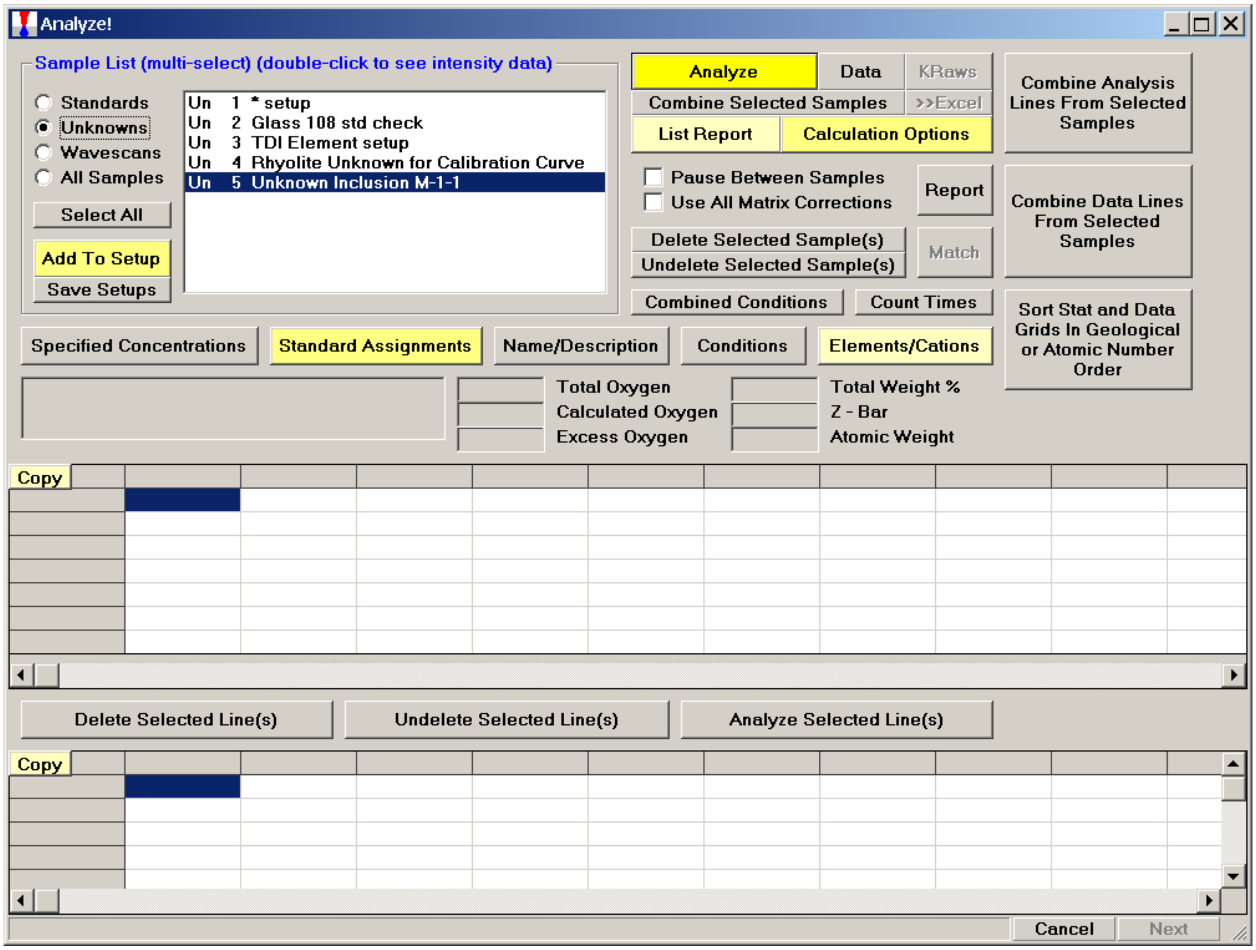
The TDI element effect will be calibrated precisely on the first unknown sample. One important assumption is that the TDI element behavior on the calibration sample is similar to all the unknowns to be analyzed. Therefore, because a consistent TDI correction is used, variation in composition represents 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.

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.



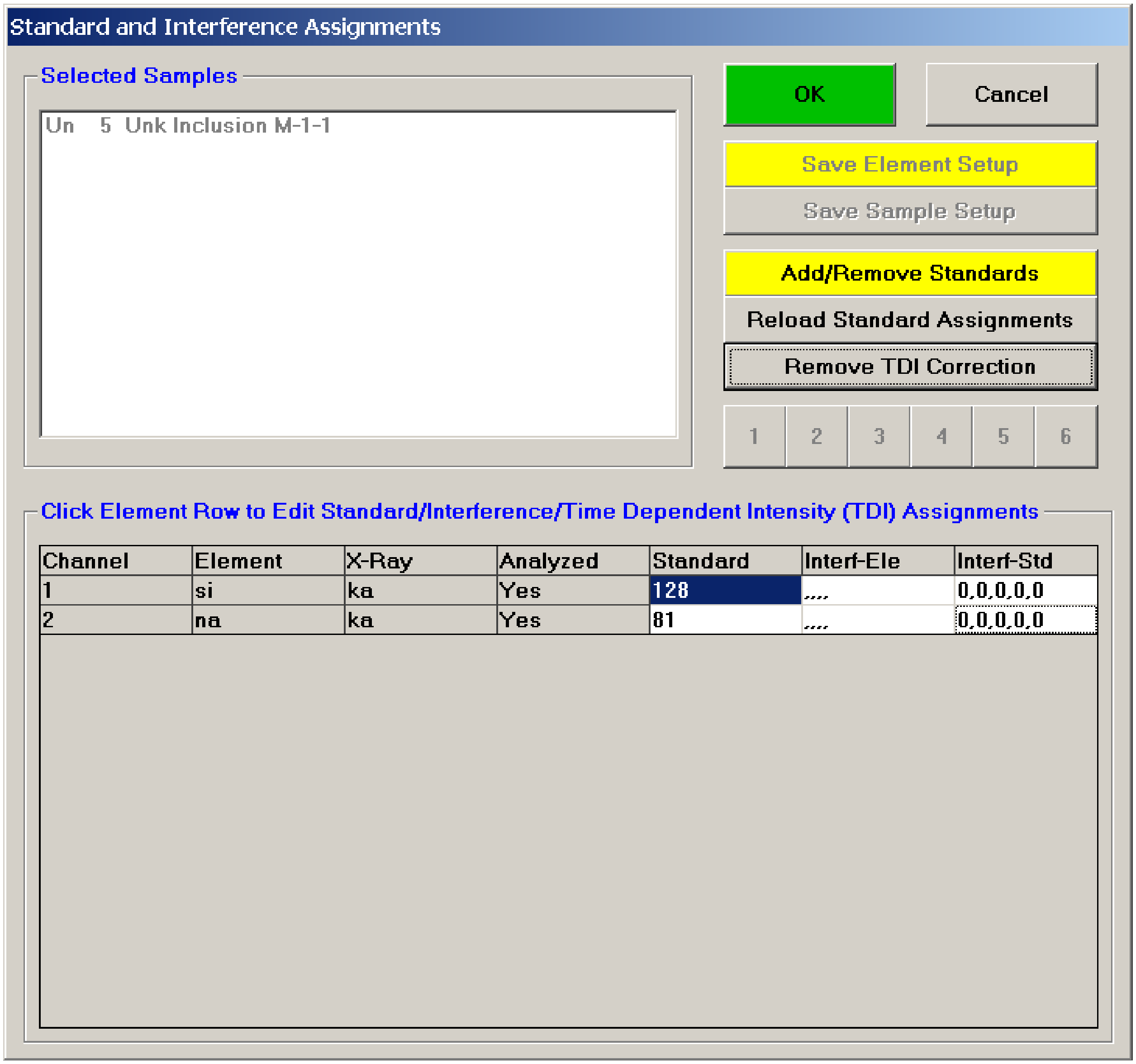
○ Standards
● Unknowns
○ Wavescans
○ All Samples

☐ Pause Between Samples
☐ Use All Matrix Corrections

Un 1 * setup
Un 2 Glass 108 std check
Un 3 TDI Element setup
Un 4 Rhyolite Unknown for Calibration Curve
Un 5 Unknown Inclusion M-1-1

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

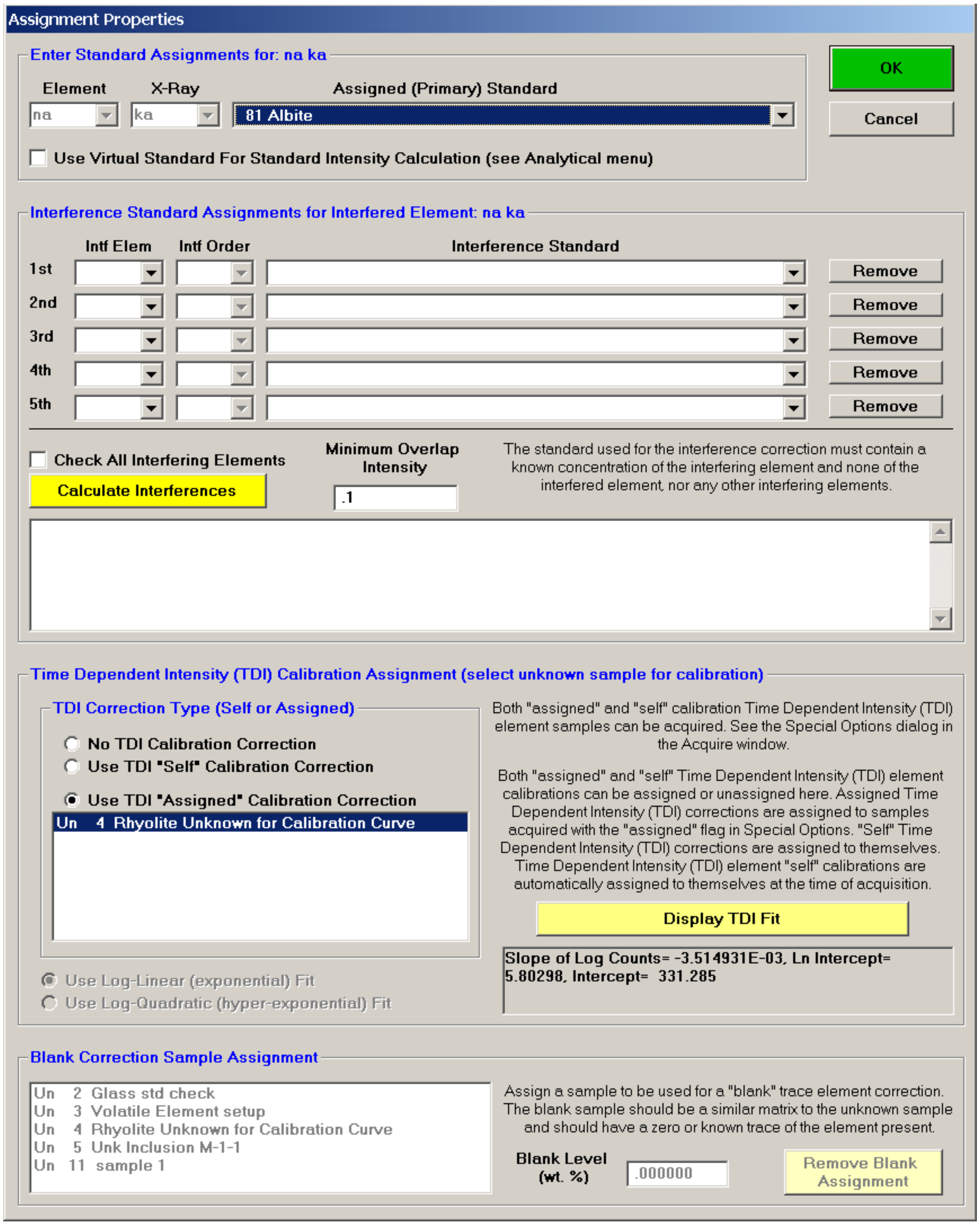


Un 5 Unk Inclusion M-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	si	ka	Yes	128	,,,,	0,0,0,0,0
2	na	ka	Yes	81	,,,,	0,0,0,0,0

To evaluate the correction effect on sodium, click that element's row to view and edit its' TDI assignment.

The **Assignment Properties** window opens and lists all possible volatile element calibration samples.



Element: na
X-Ray: ka
Assigned (Primary) Standard: 81 Albite

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

☐ Check All Interfering Elements

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.

○ No TDI Calibration Correction
○ Use TDI "Self" Calibration Correction
● Use TDI "Assigned" Calibration Correction

Un 4 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

Slope of Log Counts= -3.514931E-03, Ln Intercept= 5.80298, Intercept= 331.285

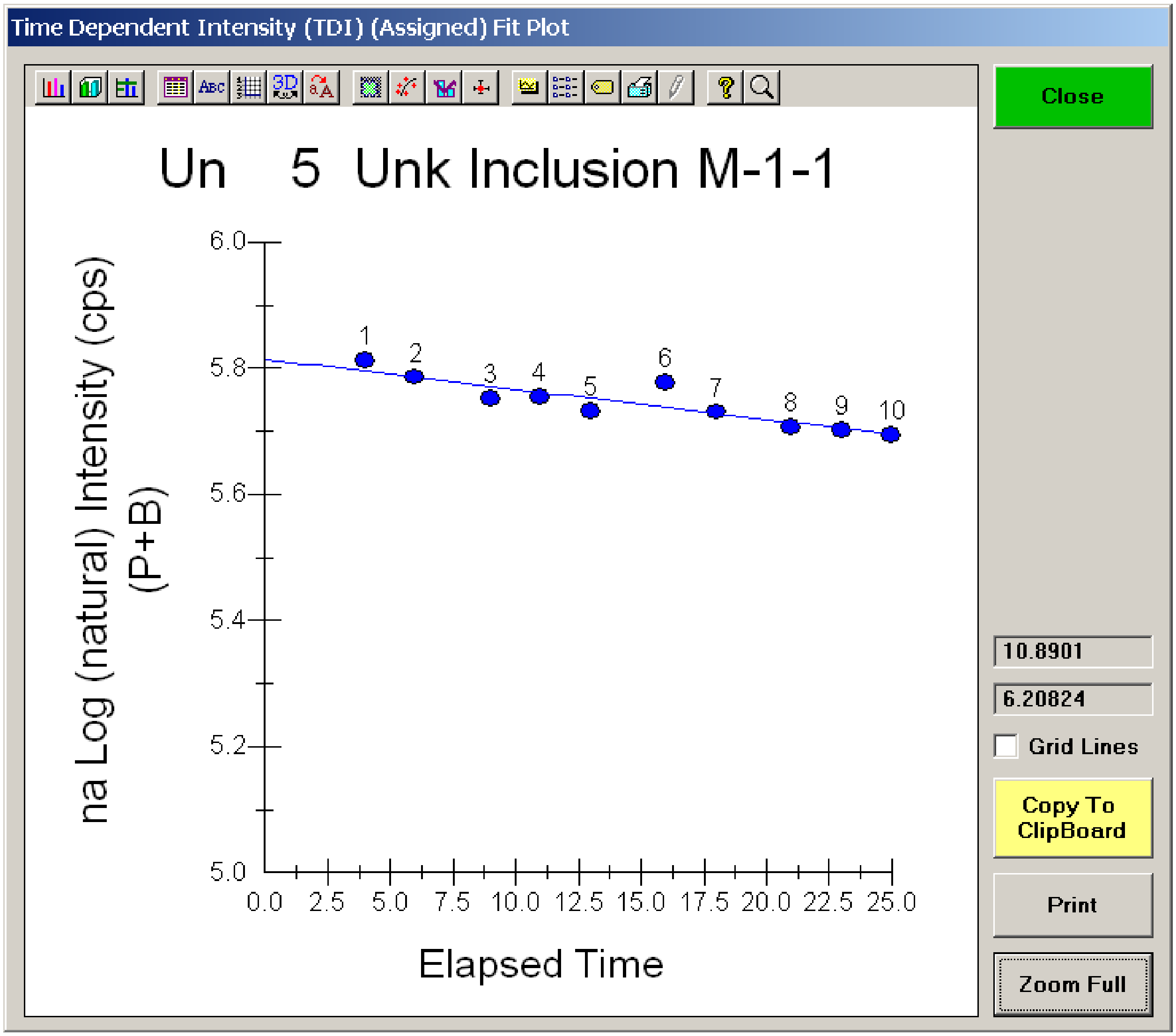
Un 2 Glass std check
Un 3 Volatile Element setup
Un 4 Rhyolite Unknown for Calibration Curve
Un 5 Unk Inclusion M-1-1
Un 11 sample 1

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

Highlight the appropriate *Time Dependent Intensity Calibration Assignment* sample and click the **Display TDI Fit** button.

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



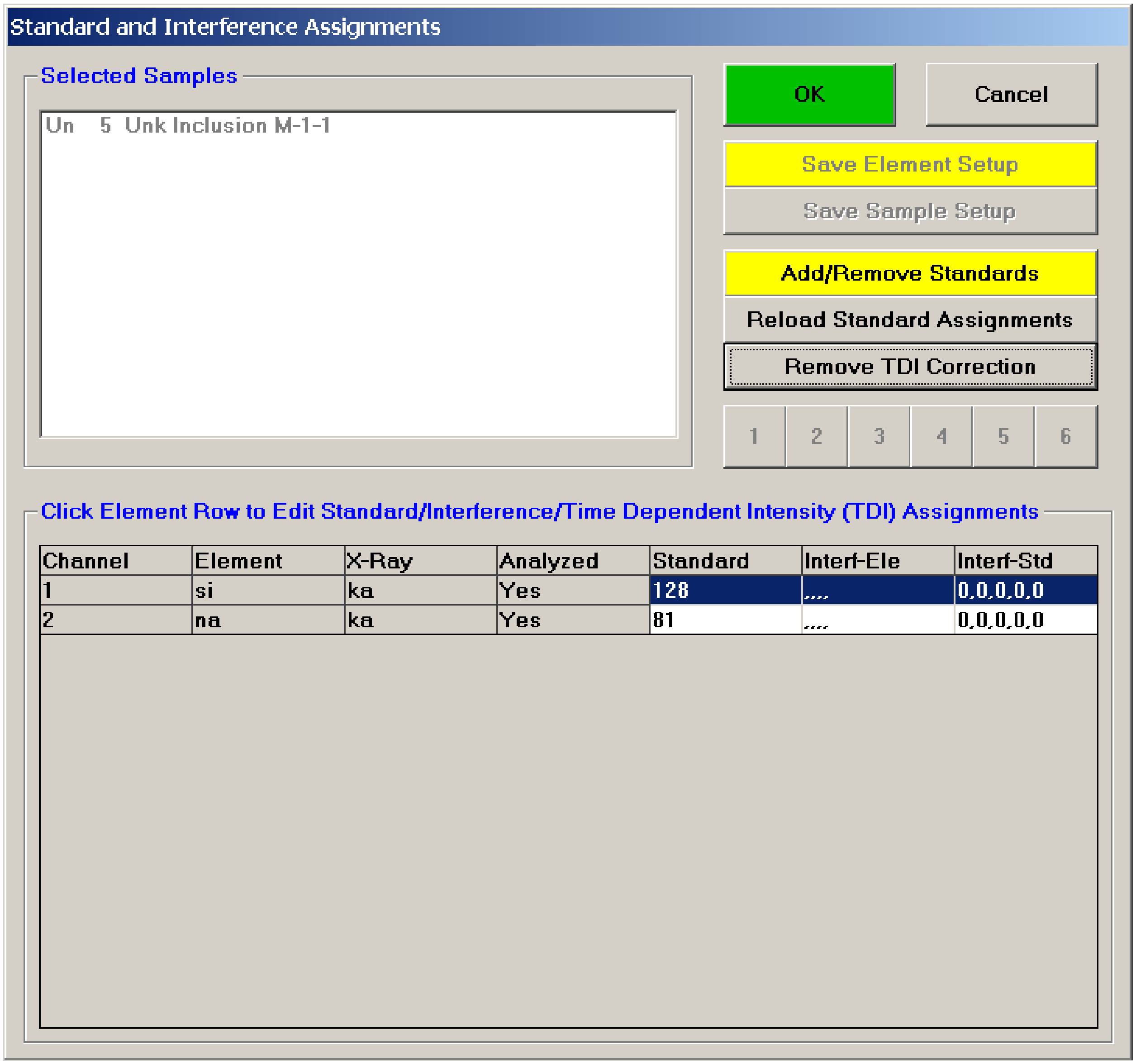
The drop in sodium count intensity with time appears to fit an exponential function (Nielson and Sigurdsson, 1981). A plot of the natural log of the intensity data versus time should yield a straight line relationship as seen above.

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.

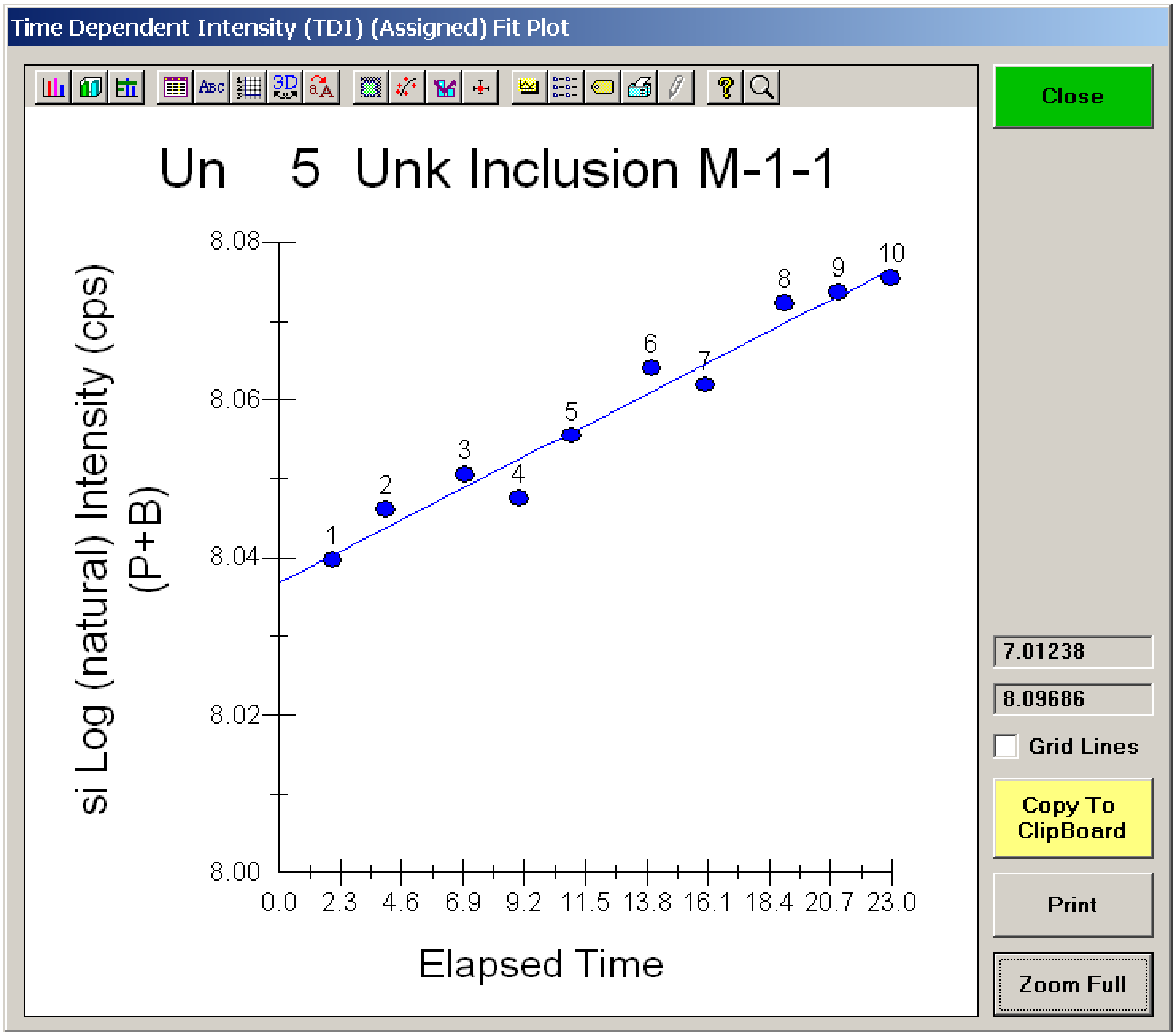


Un 5 Unk Inclusion M-1-1

Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	si	ka	Yes	128	,,,,	0,0,0,0,0
2	na	ka	Yes	81	,,,,	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).

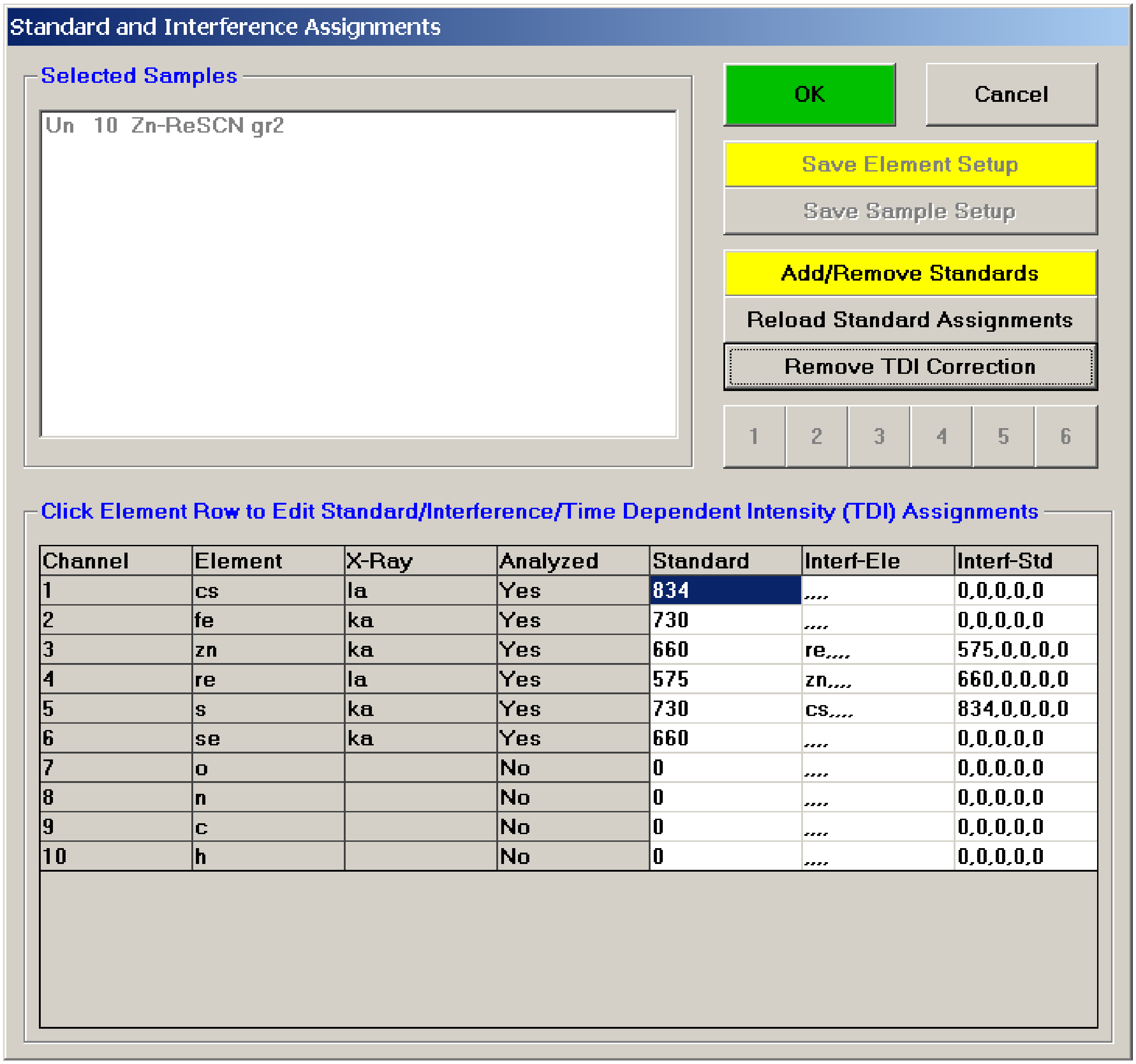
The following example (analyzed at U.C. Berkeley by John Donovan) involves the dual interference of zinc and rhenium in a natural organo-metallic phase. Both lines interfere with each other (Zn Kα and Re Lα) and both lines are used for quantitative analysis. Other elements analyzed for are cesium, iron, 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.



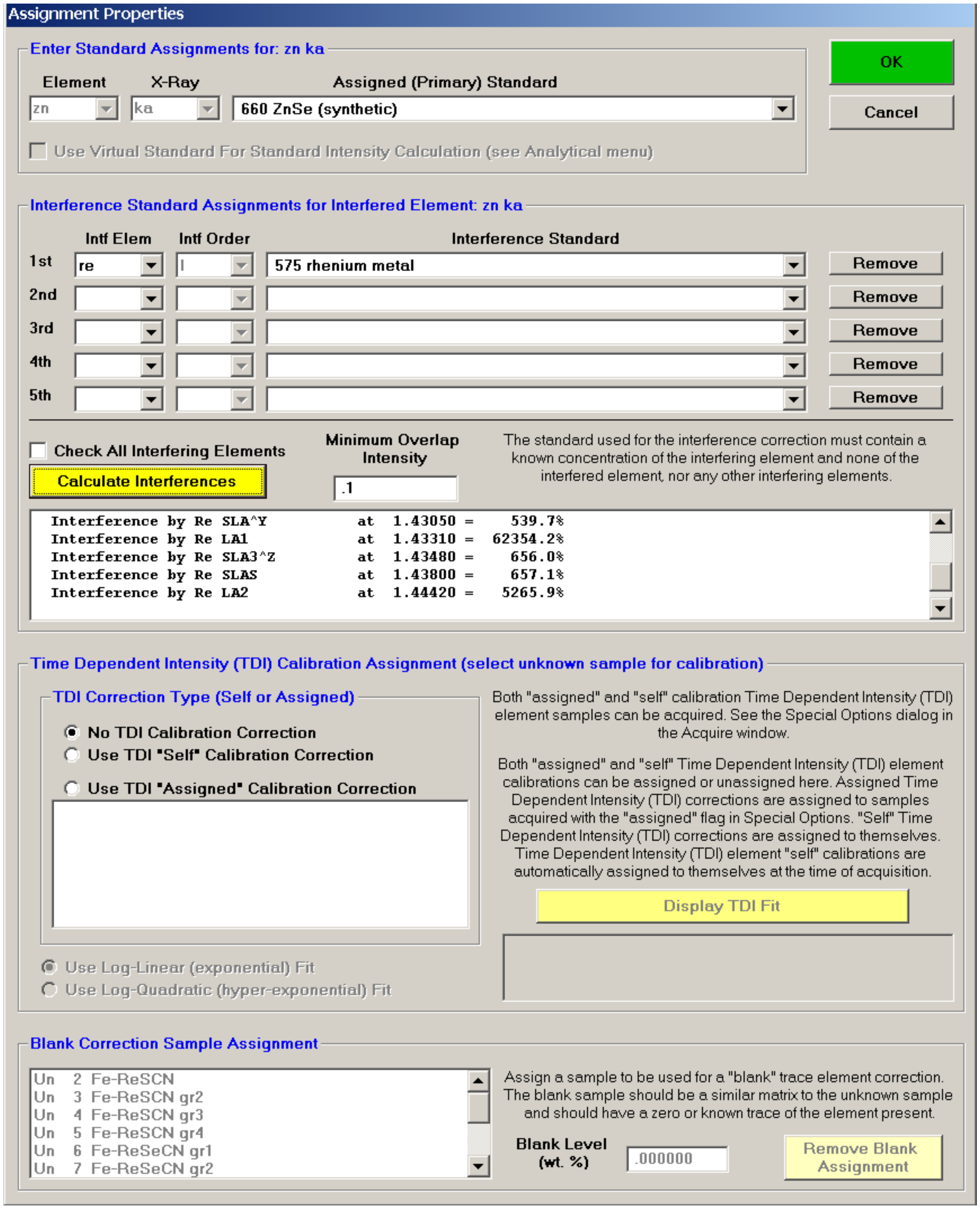
Channel	Element	X-Ray	Analyzed	Standard	Interf-Ele	Interf-Std
1	cs	la	Yes	834	,,,,	0,0,0,0,0
2	fe	ka	Yes	730	,,,,	0,0,0,0,0
3	zn	ka	Yes	660	re,,,,	575,0,0,0,0
4	re	la	Yes	575	zn,,,,	660,0,0,0,0
5	s	ka	Yes	730	cs,,,,	834,0,0,0,0
6	se	ka	Yes	660	,,,,	0,0,0,0,0
7	o		No	0	,,,,	0,0,0,0,0
8	n		No	0	,,,,	0,0,0,0,0
9	c		No	0	,,,,	0,0,0,0,0
10	h		No	0	,,,,	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.



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	l	575 rhenium metal
2nd			
3rd			
4th			
5th			

☐ Check All Interfering Elements

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.

```
Interference by Re SLA^Y         at  1.43050 =    539.7%
Interference by Re LA1           at  1.43310 =  62354.2%
Interference by Re SLA3^Z        at  1.43480 =    656.0%
Interference by Re SLAS          at  1.43800 =    657.1%
Interference by Re LA2           at  1.44420 =   5265.9%
```

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

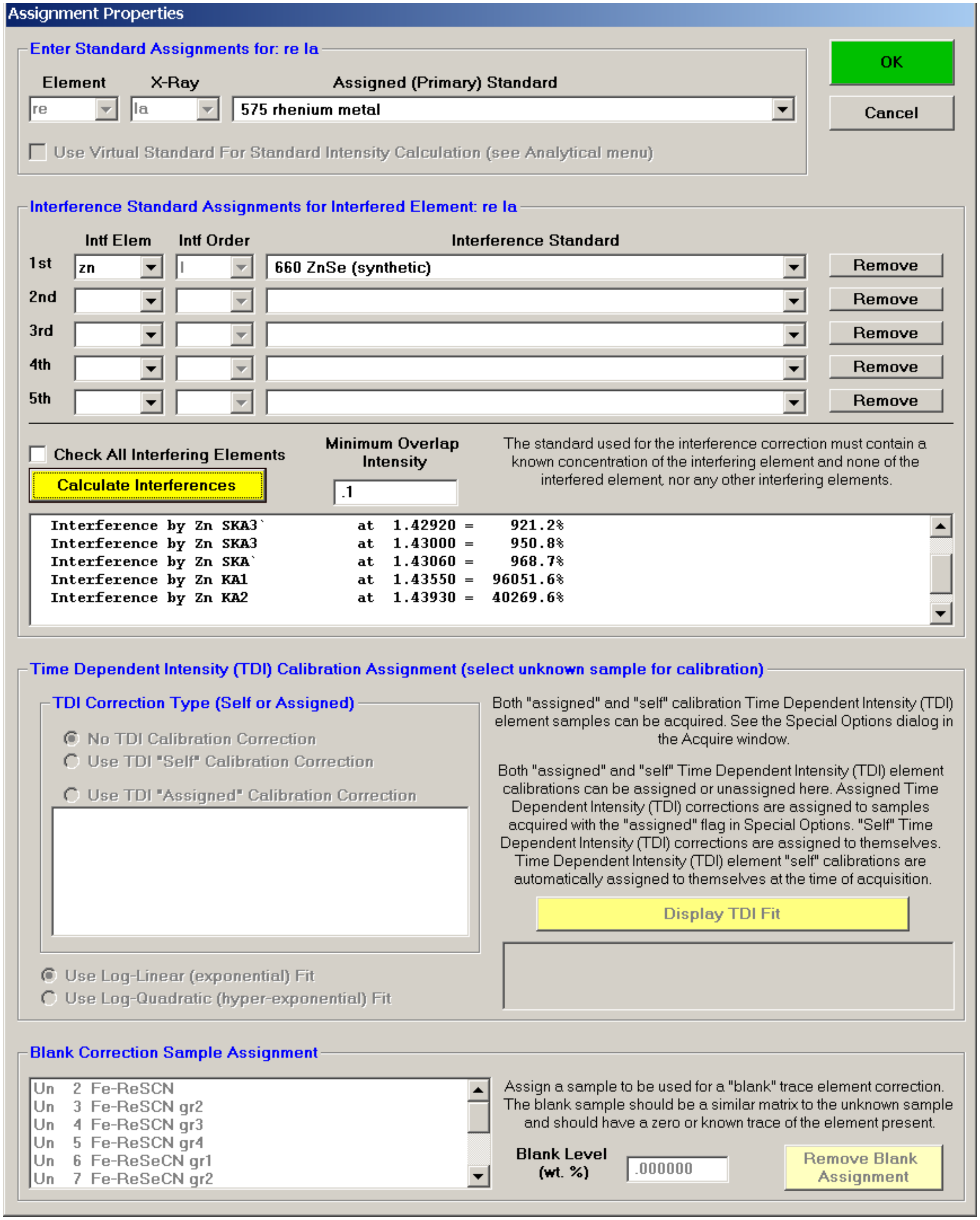
Blank Correction Sample Assignment

Un 2 Fe-ReSCN
Un 3 Fe-ReSCN gr2
Un 4 Fe-ReSCN gr3
Un 5 Fe-ReSCN gr4
Un 6 Fe-ReSeCN gr1
Un 7 Fe-ReSeCN gr2

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

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.

```
Interference by Zn SKA3`          at  1.42920 =    921.2%
Interference by Zn SKA3           at  1.43000 =    950.8%
Interference by Zn SKA`           at  1.43060 =    968.7%
Interference by Zn KA1            at  1.43550 =  96051.6%
Interference by Zn KA2            at  1.43930 =  40269.6%
```

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

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.

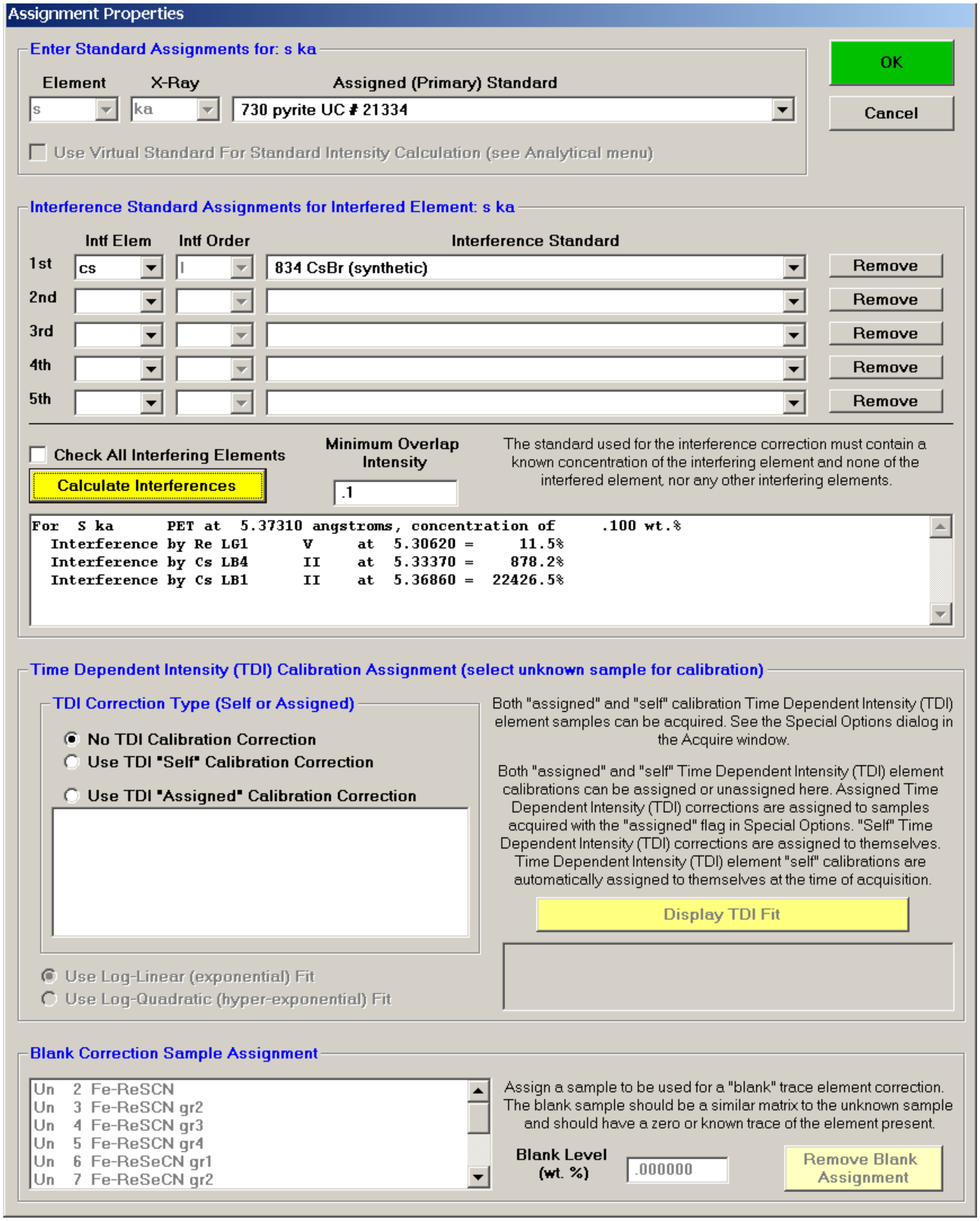
Blank Correction Sample Assignment

```
Un   2  Fe-ReSCN
Un   3  Fe-ReSCN gr2
Un   4  Fe-ReSCN gr3
Un   5  Fe-ReSCN gr4
Un   6  Fe-ReSeCN gr1
Un   7  Fe-ReSeCN gr2
```

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: s
X-Ray: ka
Assigned (Primary) Standard: 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

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  S ka      PET at  5.37310 angstroms, concentration of     .100 wt.%
  Interference by Re LG1      V    at  5.30620 =     11.5%
  Interference by Cs LB4      II   at  5.33370 =    878.2%
  Interference by Cs LB1      II   at  5.36860 =  22426.5%
```

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

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.

Blank Correction Sample Assignment

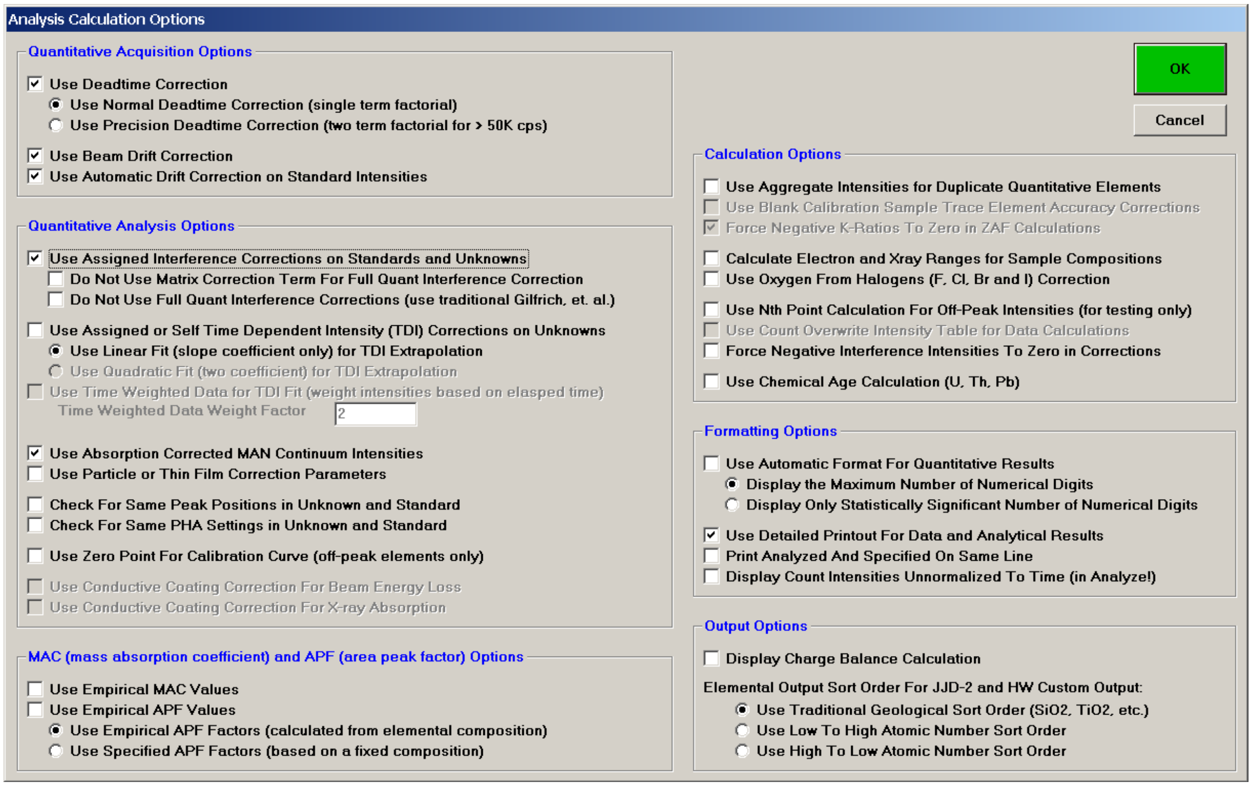
Un 2 Fe-ReSCN
Un 3 Fe-ReSCN gr2
Un 4 Fe-ReSCN gr3
Un 5 Fe-ReSCN gr4
Un 6 Fe-ReSeCN gr1
Un 7 Fe-ReSeCN gr2

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.



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

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)

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!)

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
First/Last Date-Time: 06/15/1998 04:39:29 PM to 06/15/1998 04:55:23 PM
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
First/Last Date-Time: 06/15/1998 04:39:29 PM to 06/15/1998 04:55:23 PM
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
First/Last Date-Time: 06/15/1998 01:40:14 PM to 06/15/1998 01:48:18 PM
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
First/Last Date-Time: 06/15/1998 01:50:41 PM to 06/15/1998 01:58:46 PM
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
First/Last Date-Time: 06/15/1998 01:40:14 PM to 06/15/1998 01:48:18 PM
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
First/Last Date-Time: 06/15/1998 01:50:41 PM to 06/15/1998 01:58:46 PM
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) 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 Heijliers (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:

$$\mathrm{APF} = \frac{I_U^I \cdot I_S^P}{I_U^P \cdot I_S^I}$$

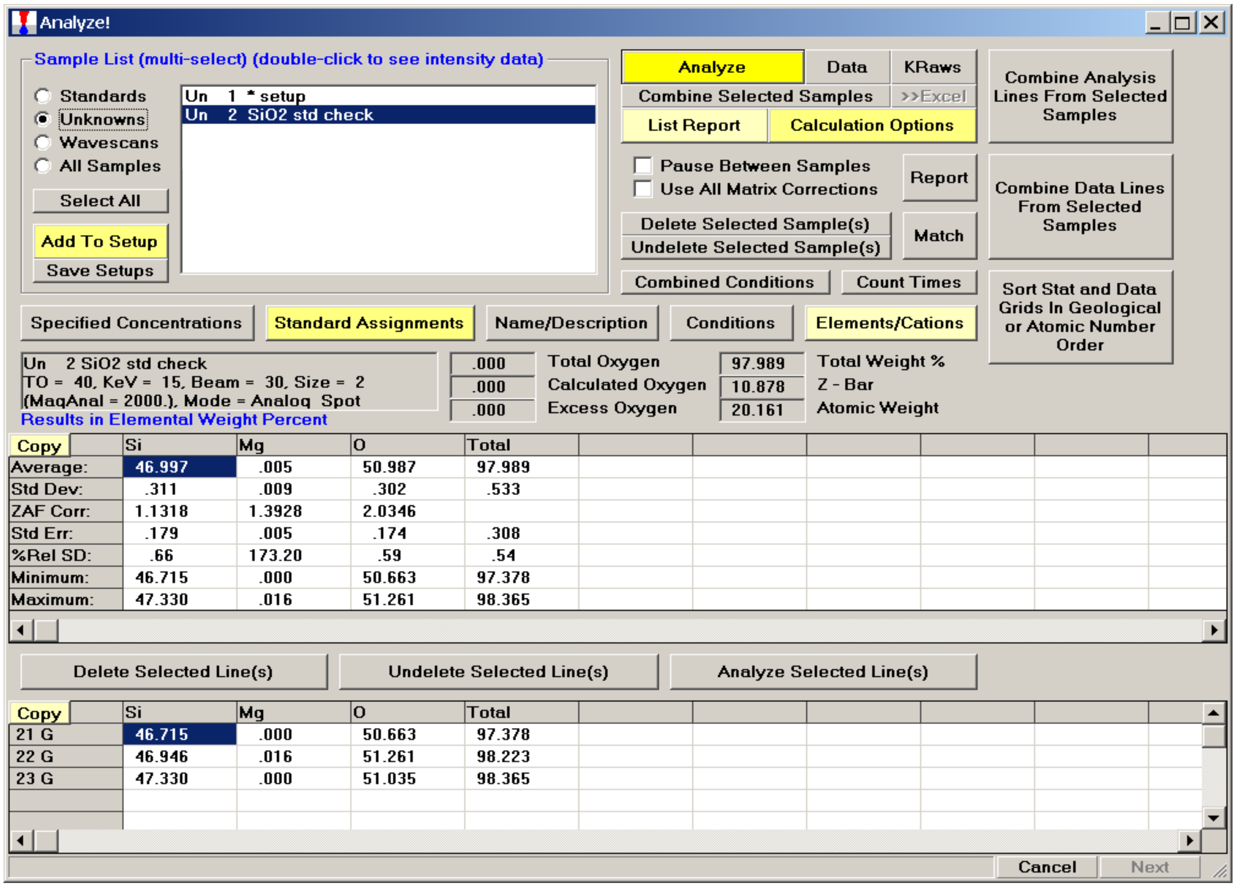
Where : I_U^I is the integrated intensity of the secondary standard
I_S^P is the peak intensity of the primary standard
I_U^P is the peak intensity of the secondary standard
I_S^I is the integrated intensity of the primary standard

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.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 * setup
Un 2 SiO2 std check

☐ Pause Between Samples
☐ Use All Matrix Corrections

Un 2 SiO2 std check
TO = 40, KeV = 15, Beam = 30, Size = 2
(MagAnal = 2000.), Mode = Analog Spot
Results in Elemental Weight Percent

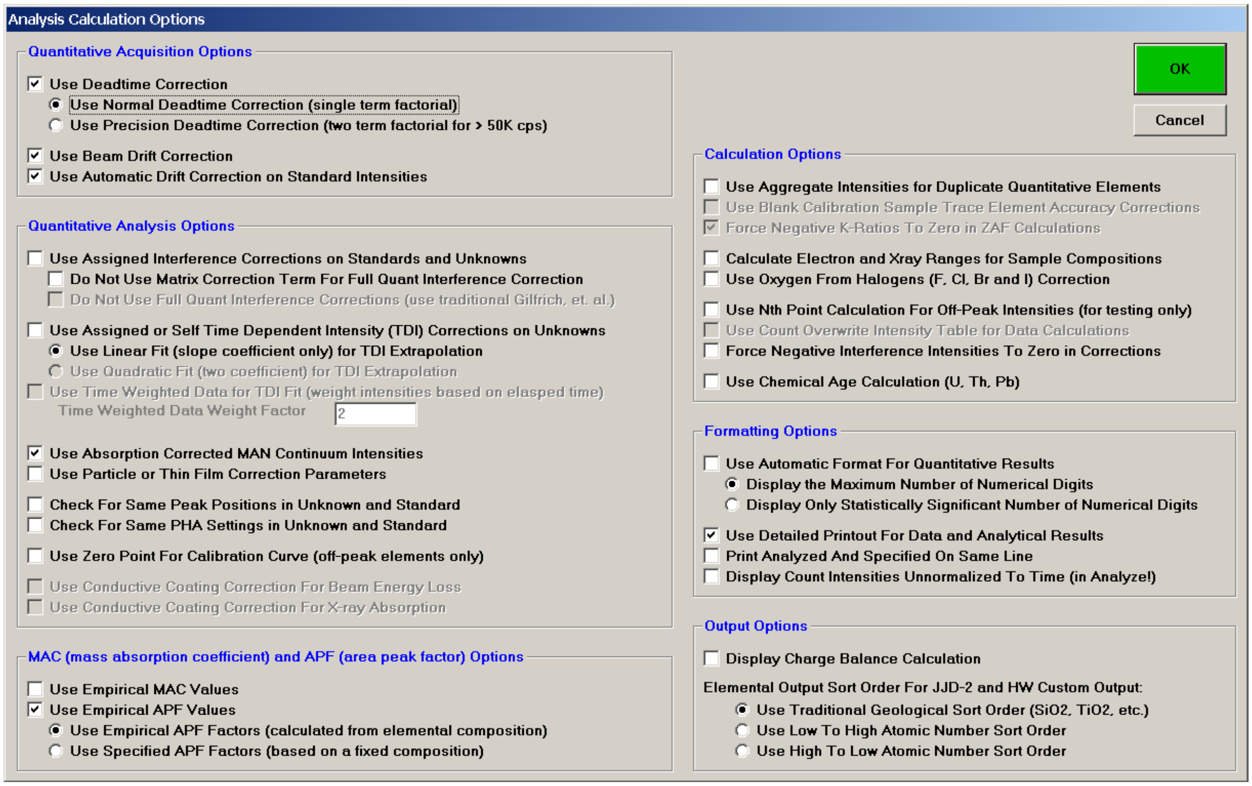
.000 Total Oxygen
.000 Calculated Oxygen
.000 Excess Oxygen
97.989 Total Weight %
10.878 Z - Bar
20.161 Atomic Weight

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
21 G	46.715	.000	50.663	97.378
22 G	46.946	.016	51.261	98.223
23 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.


Analysis Calculation Options

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

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)

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!)

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

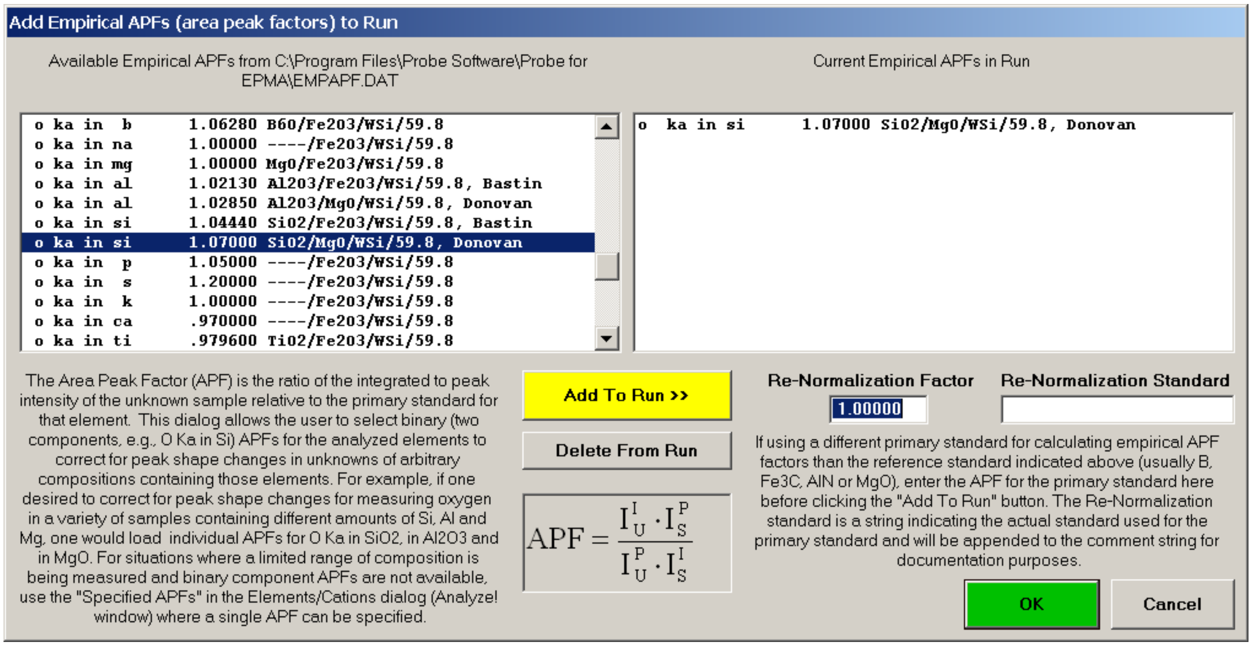
Click the **OK** button.

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.

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 **Add To Run** >> button to place the selected empirical APF into the run.



Add Empirical APFs (area peak factors) to Run

Available Empirical APFs from C:\Program Files\Probe Software\Probe for EPMA\EMPAPF.DAT

```
o ka in  b      1.06280 B60/Fe2O3/WSi/59.8
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      1.20000 ----/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
```

Current Empirical APFs in Run

```
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. 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.

$$APF = \frac{I_U^I \cdot I_S^P}{I_U^P \cdot I_S^I}$$

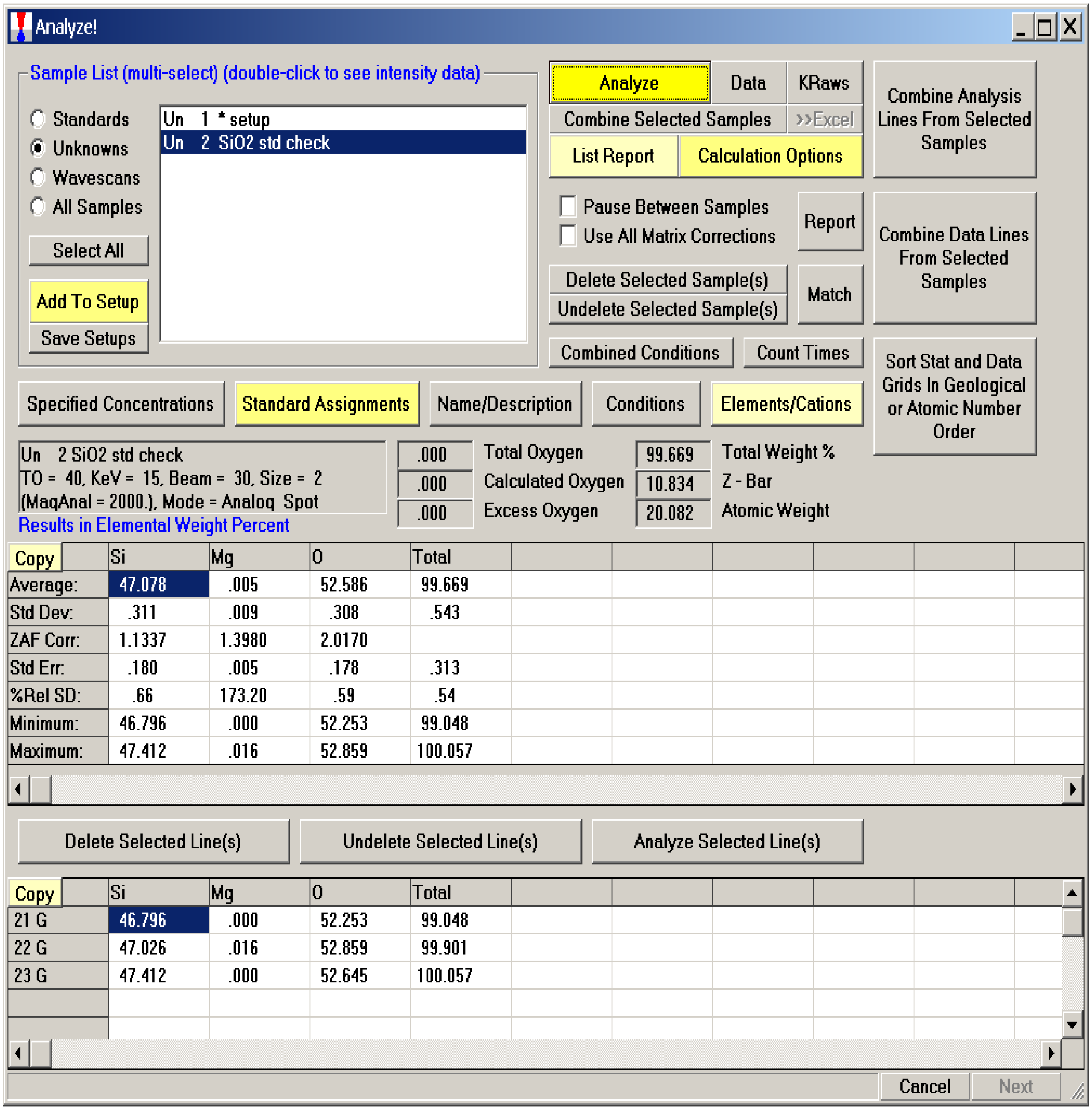
Re-Normalization Factor: 1.00000

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.

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.



○ Standards
● Unknowns
○ Wavescans
○ All Samples

Un 1 * setup
Un 2 SiO2 std check

☐ Pause Between Samples
☐ Use All Matrix Corrections

Un 2 SiO2 std check
TO = 40, KeV = 15, Beam = 30, Size = 2
(MagAnal = 2000.), Mode = Analog Spot
Results in Elemental Weight Percent

.000	Total Oxygen	99.669	Total Weight %
.000	Calculated Oxygen	10.834	Z - Bar
.000	Excess Oxygen	20.082	Atomic Weight

Copy	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

Copy	Si	Mg	O	Total
21 G	46.796	.000	52.253	99.048
22 G	47.026	.016	52.859	99.901
23 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 empirical APF values in each run. The user may enter one or more APF factors for each emitting element 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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References

Bastin G.F., and Heijliers H.J.M., (1984) Quantitative Electron-Probe Microanalysis of Carbon in Binary Carbides., *Microbeam Analysis* (Editors: A.D. Romig, Jr. and J.I. Goldstein) pp 291-294.

Bastin G.F., and Heijliers H.J.M., (1991) Quantitative Electron-Probe Microanalysis of Ultra-Light Elements (Boron-Oxygen)., *Electron Probe Quantitation* (Editors: K.F.J. Heinrich and D.E. Newbury), New York: Plenum Press pp 145-161.

Deer W.A., Howie R.A., and Zussman J., (1992) *An introduction to The Rock-Forming Minerals, Second Edition,* New York: Wiley.

Donovan J.J., Snyder D.A., and Rivers M.L., (1993) An Improved Interference Correction for Trace ElementAnalysis. Microbeam Analysis **2** 23-28.

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