# SIR-FP Tutorial

Note: This tutorial describes the use of the Scattered-Intensity Ratio method (SIR-FP).



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# **DOCUMENT CHANGE LOG**

Date	Person	Pages	Description
20-Jun-13	Sarah Cross	All	Created document for SIR-FP Tutorial
01-Jul-13	Sarah Cross	Most	Updated document
23-Jul-13	Sarah Cross	Most	Updated document
02-Sep-13	Sarah Cross	Most	Updated document
10-Sep -13	Sarah Cross / Brian Cross	Most	Updated document



### **1 SIR-FP OVERVIEW**

What is SIR-FP (Scattered-Intensity Ratio with FP)? The SIR-FP method uses information from the Rayleigh and Compton scatter peaks to provide additional information about elements in a sample (typically elements with low atomic numbers) that cannot be analyzed using the FP method, because their x-ray lines are not detectable. The SIR-FP method can estimate the low atomic number fraction in sample analysis. Knowledge of these low Z elements is important as it permits one to better correct and account for FP matrix effects, thereby improving the accuracy of the elements that <u>are</u> detectable.

The SIR-FP option allows the user to select a series of TFR files that have been created from deliberately low-Z (atomic number) standards. Calibration of these standard files calculates a least-squares fit of the C/R (Compton-to-Rayleigh) ratios as a function of the mean Z of the material. Using this calibration one can then go on to do an FP calibration using single or multiple standards.

The complete SIR-FP method calibration requires both the SIR calibration as well as an FP calibration. The FP calibration can either be single or multi-standard (MLSQ). SIR **cannot** be used with standardless FP.

Note: The SIR-FP method should <u>not</u> be used in conjunction with the Peak-to-Compton method otherwise these two methods would be in direct conflict.

#### 2 SIR-FP APPLICATION

The following procedure along with associated spectra (\*.mca) and application (\*.tfr) files guides an XRS-FP software user through the SIR-FP calibration and subsequent analysis. This includes:

- 1. SIR calibration using low-Z standards
- 2. Integrating the SIR calibration with a single standard FP calibration
- 3. Integrating the SIR calibration with a MLSQ FP calibration



4. Analysis of an unknown using the complete SIR-FP method

The same SIR-FP method is also available for the multilayer FP software, XRS-MTFFP.

Please note that spectra collected for the SIR and the FP calibrations must be obtained under the same conditions. The same is true for the analysis of unknowns using the SIR-FP calibrations.

This tutorial was created using the analysis of rocks as an example. Secondary standards with varying atomic number (from low Z, such as carbon, to medium Z, such as Ti) will form the basis of the SIR calibration. This calibration will construct a least-squares fit of C/R ratios vs. Z for all the standards. It is recommended that at least 6 standards are used for this method. Following the SIR calibration, an FP calibration will be described for all measured elements. Combining the SIR and FP calibrations will then allow analysis of "unknown" samples.

\*It is recommended that you keep two full copies of the "SIR-FP Tutorial" folder on your computer. One will serve as the "working" folder and the other will be the "backup" folder, as some files will be overwritten during the tutorial.

#### **3 PROCEDURE**

- 1. Launch XRS-FP Click anywhere on the splash screen to remove it from the display.
- From the Auto-Mode FP Analysis window, click <u>Expert Mode</u> (Fig. 1 below). This will show the contents of the "Master.tfr" file (see section 4.1 of the "XRS-FP Software Guide" for additional information on loading the software).



X Auto-Mode FP Analysis	
Select Analysis Type           Add New         Go         Edit         Auto Select	Auto Analyze Mode Exit
Setup Automation Options Save Spectrum I Save Report I Update Spectra	Show Statistics 🗌 Overlap Acquire/Proc.
Base File Name:  C:\TEMP Seed #: 1 # Measurements: 3 Delay Time	ɛ(s): <mark>2 □ □ Create Log <u>G</u>et Path</mark>
Run # Preset Livetime = 20	Value

Figure 1. Auto-Mode FP Analysis Panel. Select the "Expert Mode" button.



 From the XRS-FP Expert Panel: Select File -> Open -> "C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\Initial.tfr" (or equivalent file location). See Figure 2 below.

📉 Open				x
CrossRoads Sc	ienti	fic	✓ Search SIR Files	٩
Organize 🔻 New folder			!≡ ▼ 🚺	0
🔆 Favorites	-	Name	Date modified Type	
🧮 Desktop		Al2O3Binder10 .tfr	8/28/2013 3:46 PM   TFR File	
🗼 Downloads		B2O3Binder05.tfr	8/28/2013 3:55 PM   TFR File	
💝 Dropbox		CaCO3.tfr	8/28/2013 3:56 PM   TFR File	
📃 Recent Places		📄 Initial.tfr	9/6/2013 5:35 PM   TFR File	
	=	K2SO4.tfr	8/28/2013 3:56 PM   TFR File	
\sub Libraries		NaCl.tfr	8/28/2013 3:57 PM TFR File	
Documents		Teflon.tfr	8/28/2013 3:57 PM TFR File	
J Music		TiO2.tfr	8/28/2013 3:57 PM TFR File	
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Videos				
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is Computer	Ŧ	•		•
File name:	Init	ial.tfr	✓ XRF Reports (*.tfr)	-
			Open 🛛	

**Figure 2. File Open Menu.** Open the "Initial.tfr" file under the "SIR Files" folder. This file acts as a template for this application.

This TFR file acts as a template for this application. Although the Component Table, Elements Table and Thickness information have no data at this point, the Measurement & Processing information (spectrometer configuration) is already pre-defined and loaded for this application. Note: if there is data in the "Measurement & Processing Conditions" Table in the Compton and



Rayleigh columns under the "Processing" radio button, **un-check and then re-check the "C/R Ratio" box**. This will clear the Compton and Rayleigh data in this table and create a "clean sheet" to begin the application (see Fig. 3).

Note that since the Compton and Rayleigh regions of interest (ROIs) are zero, the Gaussian deconvolution for the spectrum processing will automatically assign the regions for the first sample analyzed. For more information on setting and using ROIs see the section "Process Spectrum – Compton Peak" in the "XRS-FP Software Guide."

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XR!	S-FP																
File Acquire Setup Calibrate Process Help																	
Acc	Acquire         Set kV/uA         kV:         40         (10->50)         uA:         25         (5->200)         Preset:         0         Time:         34.259         %DT:         0.0         ICR:         0.0         OCR:         0.0         0.0         OCR:         0.0																
Spec	Specimen Component Table: Thickness Information:																
#	Comp	onent	Τy	pe Co	onc. Error	Un	its Mole%	Error				La	ver			Norma	lize
1			Ca	alc 0.	.0000 0.00	00 wt.%	0.0000	0.000	0 🔺	Thick	Type	Error	Unit	s D	ensity Fixe	d OK .	Total
										0.000	Bulk	0.00	0 ma/cr	m2	0.000		100.00
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Flem	ent Tabl	e 🗌	Nor	mal	C Coefficie	onte				n-sigma	<u> </u>	.000	Clear	Conc M	lethod		
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EI	m Line	Code	Intensity	Error	Backgr. Co	nc. Ei	ror MDL A	.tom% Va	lue Conc	Method	Metho	d Low	High	Fit	Method	TCC Coeff	
Ľ–	Ka	1	0.00	J U.UU	I U.UU L	.0001 0.	00010.00001	0.000  0.1		Liaussian	None	e   U.UL	0  0.000	0.00	FP	0.00	J
Measurement & Processing Conditions: C Measurement © Processing																	
<u> </u>	No. Escape Sum Back- Background Remove Blank Spectrum C/R Compton ROI (keV) Rayleigh ROI (keV)																
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p					and an and a second second												

**Figure 3. XRS- FP Expert Panel.** The "Initial.tfr" file acts as a template for this application. Note that this file inputs the proper Measurement & Processing information for this application (i.e. spectrometer configuration information).

4. From the XRS-FP Expert Panel: Select Setup -> Processing and make sure all parameters are identical to those shown below in Figure 4. Select "OK" to exit the dialog and save the parameters.

Setup Processing Parameters
Gaussian Deconvolution Parameters
Maximum Allowed Deviations for Nonlinear Deconvolution
Maximum # Iterations: 5
Line Ratio Factor: 2.0
Spectrometer Offset (eV): 100.0
Spectrometer Gain (%): 1.00
Spectrometer Peak Width (%): 20.0
Channel Weighting Factor: 1
Use Net Spectrum Weighting 🔽
Peak Width (FWHM) at Mn-Ka (eV): 130.0
Auto Calibration from Nonlinear Deconvolution
Use Auto Calibration Mn FWHM (eV): 0.0
Gain Factor: 0.0000 Offset (eV): 0.0
Spectrum Smoothing Parameters
Filter Type
🔿 Savitsky-Golay 💿 Gaussian 🔿 Tophat 🔿 Average
Number of Points
<b>• 3 • 5 • 7 • 9 • 11</b>
Auto Background Removal Parameters
Low-Pass Filter Width: 250 Max # Iterations: 30
Pile-Up (Sum Peak) Removal Parameters
Pulse-Pair Resolution (uS): 0.4 Time Constant (uS): 0.8
Spectrum Low-Energy Start (keV): 0.50 Lowest Z: 12 (Mg) Escape
Auto Adjust Spectrum Gain & Offset on Load
OK Cancel Defaults

Figure 4. Setup Processing Parameters Dialog. Check that all parameters are as shown here.

Now from the XRS-FP Expert Panel: Select File -> Open -> "...SIR-FP Tutorial\SIR Files\Al2O3Binder10.mca" (this is the MCA spectrum file for our 1<sup>st</sup> low-Z standard). See Figure 5 below. Note that the spectra for this tutorial are already adjusted and in calibration.

🗙 Open			,	X
CrossRoads	Scient	ific → SIR-FP Tutorial → SIR Files	✓ ✓ Search SIR Files	م
Organize 🔻 New folder			:== •	
Desktop	*	Name	Date modified Typ	e
Downloads		Al2O3Binder10.mca	8/22/2012 11:28 AM MC	A File
Uropbox		B2O3Binder05.mca	8/22/2012 11:28 AM MC	A File
Recent Places		CaCO3.mca	8/22/2012 11:28 AM MC	A File
4 🚍 Libraries		K2SO4.mca	8/22/2012 11:28 AM MC	A File
		NaCl.mca	8/22/2012 11:28 AM MC	A File
Music	Ε	Teflon.mca	8/22/2012 11:28 AM MC	A File
Pictures		TiO2.mca	8/22/2012 11:28 AM MC	A File
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🛛 🔣 Homegroup				
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	-	•	III	Þ
File name	e: Al2	2O3Binder10.mca	✓ Amptek Spectra (*.mca	.) 🔻
			Open 🔽	Cancel

Figure 5. File Open Menu. Open the first low-Z standard \*.mca file (e.g. Al2O3Binder10.mca) under the "SIR Files" folder.

6. Enter the component information in the "Specimen Component Table" (see Fig. 6). For this first low-Z standard ("Al2O3Binder10") enter the following components: "H74C37ON" then click "enter" (which will fill the individual elements in the "Element Table"), then "Al2O3" and "enter". Set the "Concentration" to 10 and 90 wt.% respectively.

Note that the Layer "Type" is set to "Bulk" in the "Thickness Information" table (which is mandatory for use with an SIR-FP calibration) and it is "Normalized" to a "Total" of 100% (see Fig. 6 below).

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File	File Acquire Setup Calibrate Process Help																	
Ac	Acquire         Set kV/uA         kV: 40 (10->50) uA: 25 (5->200)         Preset: 0         Time: 34.259         %DT: 0.0         ICR: 0.0         OCR: 0.0																	
Spee	cimen C	omponer	t Table:							Thickn	ess Info	ormation:						0
#	# Component Type Conc. Error Units Mole% Error Layer Normalize																	
11	1 H74C370N Calc 10.0000 0.0000 wt.% 0.0000 0.0000 Thick. Type Error Units Density Five OK Total																	
24	2 A203 Calc 90.0000 0.0000 wt.% 0.00000 0.000000																	
	Chiel Threshold Cations																	
	Global Threshold Settings																	
Elen	Lear Conc Method □																	
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	Imt Lin	e Lode	Intensity	Error	Backgr. L	onc. Erro		Atom%	Value Lo	nc Metr	bo	Method	LOW	High	Fit	Method	TLL Loeff	
2			0.00	0.00	0.00	B 095 0.0		0.000		Gaus	sian	None	0.000	0.000	0.00	None	0.00	<u> </u>
3	N Ka	0	0.00	0.00	0.00	0.255 0.0	00 0.0000	0.000	0.000	Gaus	sian	None	0.000	0.000	0.00	None	0.00	
4	O Ka	1 0	0.00	0.00	0.00 4	2.658 0.0	00 0.0000	0.000	0.000	Gaus	sian	None	0.000	0.000	0.00	None	0.00	
5	Al   Ka	1	0.00	0.00	0.00 4	7.634 0.0	00   0.0000	0.000	0.000	Gaus	sian	None	0.000	0.000	0.00	FP	0.00	
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Mea	Measurement & Processing Conditions: 6 Measurement C Processing																	
			X-Ray Sou	rce			Detector		Chamber	Tim	e (secs)		Monitor					
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1	1 Age None 0.000 40.0 25.0 Strift None 0.000 Air 0.0 34.55 0.0 A																	
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**Figure 6. XRS- FP Expert Panel.** Note the component information of the low-Z standard is entered in the "Specimen Component Table" and the thickness is set to "Bulk" and "Normalized" to 100% in the "Thickness Information" table.

Also note that the "C/R Ratio" checkbox is selected under the "Processing" conditions set in the "Measurement & Processing Conditions" Table (see Fig. 7). This must be selected for use with the SIR-FP calibration.

Meas	leasurement & Processing Conditions: C Measurement © Processing																
Carda	No.	Escape	Sum	Back-	Background	Remove	Blank Spectry	1	C/R	N	Compton	Compton	ROI (keV)	Rayleigh	Rayleigh f	ROI (keV)	$\square$
Loge	Smths	Peak	Peak	ground	File	Blank	File		Ratio	D	(c/s)	Low	High	(c/s)	Low	High	
1	2	•	N	Auto				1			0.00	0.000	0.000	0.00	0.000	0.000	-
									-								-

Figure 7. Measurement & Processing Conditions Table. Note that the "C/R Ratio" box is selected under the "Processing" conditions.

Note: All processing conditions must be the **SAME** for all MCA files used in the SIR-FP calibration.

7. From the XRS-FP Expert Panel: Select Process -> Spectrum -> All. Notice that there is now data for the Compton (c/s), Compton ROI (keV), Rayleigh (c/s) and Rayleigh ROI (keV) columns in the "Processing Conditions" table (see Fig. 8). Note that the Compton (c/s) and Rayleigh (c/s) values may vary due to the background removal during processing.

Meas	Measurement & Processing Conditions: C Measurement © Processing														
	No.	Escape	Sum	Back-	Background	Remove	Blank Spectrum	C/R	Compton	Compton	ROI (keV)	Rayleigh	Rayleigh f	ROI (keV)	
Loge	Smths	Peak	Peak	ground	File	Blank	File	Ratio	(c/s)	Low	High	(c/s)	Low	High	
1	2	V	~	Auto				N	562.92	20.220	21.720	120.63	21.720	22.500	-
															-

Figure 8. Measurement & Processing Conditions Table. Data is shown under the Compton and Rayleigh columns after spectrum processing.

- Now save the TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be saved as "Al2O3Binder10.tfr" or as an alternate filename of choice.
- 9. <u>REPEAT steps 5 8 above for ALL the low-Z standards</u> within the SIR folder. Remember to enter the components that correspond to the loaded MCA file for each standard. Also, check that the layer information is normalized to 100% and the C/R Ratio in the Processing Conditions table is checked. <u>Do not clear</u> the C/R information between standards, because we want to use the same Compton and Rayleigh ROIs. After processing the spectrum, remember to save the TFR file before moving on to the next standard! The following figures (Fig. 9-14) show screen shots of the XRS-FP Expert Panel for each of the remaining 6 SIR low-Z standards (data shown is after completion of step 8 above for each standard):

XRS-FP													
File Acquire Setup Calibrate Process Help													
Acquire Set kV/uA kV: 40 (10->50) uA: 25 (5->200	0) Preset: 0 Time: 27.581 %DT: 0.0 ICR: 0.0 OCR: 0.0												
Specimen Component Table:	Thickness Information:												
#         Component         Type         Conc.         Error         Units         Mole%         E           1         8203         Calc         95,0000         0.0000         wt.%         0.0000         0.           2         H74C370N         Calc         5.0000         0.0000         wt.%         0.0000         0.	irror         Layer         Normalize           10000												
	Global Threshold Settings												
Element Table: 🕜 Normal C Coefficients	lement Table:												
LElement Conc Measurement	Threshold Intensity Ratio RDI (keV) Chi2 Quant Calibration												
** Elmi Line Code Intensity Error Backgr. Conc. Error MDL Atom%	SValue Conc Method Method Low High Fit Method TCC Coeff												
1 H Ka 0 0.00 0.00 0.00 0.679 0.000 0.000 0.000	0.000 Gaussian None 0.000 0.000 None 0.00												
	0.000 Gaussian None 0.000 0.000 None 0.00												
4 N Ka 0 0.00 0.00 0.00 0.128 0.000 0.000 0.000	0 0.000 Gaussian None 0.000 0.000 None 0.00												
5 0 Ka 0 0.00 0.00 0.00 65.641 0.000 0.0000 0.000	0 0.000 🗖 Gaussian None 0.000 0.000 0.00 None 0.00												
Measurement & Processing Conditions: O Measurement • Proc	cessing												
No. Escape Sum Back- Background Remove Blank Spectrum C/	/R Compton Compton ROI (keV) Rayleigh Rayleigh ROI (keV)												
Smths Peak Peak ground File Blank File Ra	atio (c/s) Low High (c/s) Low High												
1 2 🔽 🗹 Auto	1267.86 20.220 21.720 151.43 21.720 22.500												
Status: Opened file C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files	s\B203Binder05.tfr 0 0ff 0n 2048 20 0.59 No 1												
Comment: FP Software for Bulk XRF Analysis													

Figure 9. XRS- FP Expert Panel. Data after processing B2O3Binder05.mca.

XRS-FP	X											
File Acquire Setup Calibrate Process Help												
Acquire Set kV/uA kV: 40 (10->50) uA: 25 (5->200) Preset: 0 Time: 25.515 2DT: 0.0 ICR: 0.0 OCR: 0.0												
Specimen Component Table: Thickness Information:												
#         Component         Type         Conc.         Error         Units         Mole%         Error         Layer         N	ormalize											
1 CaC 03 Cale 100.0000 0.0000 wt 2 0.0000 0.0000 Thick. Type Error Units Density Fixed 0K	Total											
0.000 Bulk 0.000 mg/cm2 0.000 F	100.00											
Global Threshold Settings												
n-sigma v 2.000 Clear Conc Method												
Liement lable: (* Normal (* Loefficients												
Element Conc Measurement Threshold Intensity Ratio R01 (keV) Chi2 Quant Calibrat	ion											
Telm Line Code Intensity Error Backgr. Conc. Error MDL Atom% Value Conc Method Method Low High Fit Method TCC Co	eff											
1 C Ka 0 0.00 0.00 0.00 12.000 0.000 0.000 0.000 Gaussian None 0.000 0.000 None	0.00											
2 U Ka U U.UU U.UU U.UU 0.00 47.555 U.UUU U.UUU U.UUU U.UUU L Gaussian None U.UUU U.UU U.UU None												
	0.00											
Measurement & Processing Conditions:												
No. Escape Sum Back- Background Remove Blank Spectrum C/R Compton Compton RDI (keV) Rayleigh Rayleigh RDI (keV)												
Code Smiths Peak Peak ground File Blank File Ratio (c/s) Low High (c/s) Low High												
1 2 V Auto 1 181.42 20.220 21.720 95.88 21.720 22.500												
Status: Opened file C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\CaCO3.tfr 0 Off On 2048 20 0.59 No 1												
Comment: FP Software for Bulk XRF Analysis	,,,											

**Figure 10. XRS- FP Expert Panel.** Data after processing CaCO3.mca. Note that in order for XRS-FP to process the carbon and oxygen elements in this low-Z standard, the compound MUST be entered as "CaC O3" in the "Component Table", i.e. with a space between the C and the O. Also be sure to enter "O" for oxygen, as the number "O" will not be recognized as the element oxygen!

🗸 XRS-FP										
File Acquire Setup Calibrate Process Help										
Acquire         Set kV/uA         kV:         40         (10->50)         uA:         25         (5->200)         Preset:         0         Time:         28.620         2DT:         0.0         ICR:         0.0         0CR:         0.0 </th										
Specimen Component Table: Thickness Information:										
#       Component       Type       Conc.       Error       Units       Mole%       Error       Normalize         1       K2S04       Cale       100.0000       0.0000       wt %       0.0000       0.0000       mt %       Trick.       Type       Error       Units       Density       Fixed       OK       Total         0       0000       Bulk       0.0000       mg/cm2       0.000       IV       100.000         Element Table:       ©       Normal       C Coefficients       Fixed       Conc Method       Image: Conc Method										
H         Element         Zonc         Measurement         Threshold         Intensity         Ratio         RDI (keV)         Chi2         Quant         Calibration           1         0         Ka         0         0.00         0.00         38.724         0.000 <td< th=""></td<>										
Measurement & Processing Conditions: C Measurement © Processing										
No. Escape Sum Back- Background Remove Blank Spectrum C/R Compton Compton ROI (keV) Rayleigh Rayleigh RoI (keV)										
Smths         Peak         ground         File         Blank         File         Ratio         (c/s)         Low         High         High           1         2         Image: Auto         Image: A										
Status:         Opened file C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\K2SO4.tfr         0         Off         0         2048         20         0.59         No         1           Comment:         FP Software for Bulk XRF Analysis										

Figure 11. XRS- FP Expert Panel. Data after processing K2SO4.mca.

$\times x$	XRS-FP																	
File	File Acquire Setup Calibrate Process Help																	
A	Acquire Set kV/uA kV: 40 (10->50) uA: 25 (5>200) Preset: 0 Time: 26.447 2DT: 0.0 ICR: 0.0 OCR: 0.0																	
Spe	Specimen Component Table: Thickness Information:																	
#	Comp	onent	Тур	e Cor	nc. Error	Unit	s Mole%	Error				Laye	si.			Norr	nalize	
1	NaCl		Cal	100.	0000 0.000	0 wt.%	0.0000	0.000	미스	Thick.	Туре	Error	Units	; [C	Density Fix	ed OK	Total	
										0.00	0 Bulk	0.000	mg/cm	n2	0.000		100.00	
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Eler	nent Tabl	e:	Norm	ial (	C Coefficie	nts				J' argina					, iourou			
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1	Na Ka	1	23.77	4.31	17.54 39.	339 0.0	000 0.0000	0.000 0.0	00	Gaussian	None	1.000	1.092	0.04	FP	0.1	0	*
2	CI Ka	1	13103.19	77.61	64.85 60.	661 0.0	000 0.0000	0.000 0.0	00 🔽	Gaussian	None	2.565	2.679	0.58	FP	0.1	00	
L L																		
																		-
Mea	surement	& Proc	essing (	ondition	is: O H	leasuren	nent 📀	Process	ing									
	No	Escape	Sum	Back.	Background	Bemove	Blank Spectrum	C/B	Compton	Compton	BULIKAVI	Baulaidh	Rauleich I	BULK	av III.			
Cod	E Smthe	Peak	Peak	around	File	Blank	File	Batio	(c/s)	Low	High	(c/e)	Low	Hia	<u>b</u>			
	2			Auto	1.10	Dialk	110	- Haub	162.3	1 20.220	21.720	87.31	21.720	22.5	500			
			010						<u></u>							0.10		
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	mment:	-P Soft	ware for	Bulk XF	IF Analysis													

Figure 12. XRS- FP Expert Panel. Data after processing NaCl.mca.

XRS-FP										
ile Acquire Setup Calibrate Process Help										
Acquire         Set kV/uA         kV:         40         (10->50)         uA:         25         (5->200)         Preset:         0         Time:         29.030         2DT:         0.0         ICR:         0.0         0CR:         0.0         0										
Specimen Component Table: Thickness Information:										
#         Component         Type         Conc.         Error         Units         Mole%         Error         Layer         Normalize										
1 C2F4 Calc 100.0000	0.0000 wt.% 0.0000 0.0	0000 🔺 Thick.	Type Error Units	Density Fixed OK Total						
		0.000	) Bulk 0.000 mg/cm2	0.000						
		- Global 1	hreshold Settings							
		n-sigma	▼ 2.000 Clear Con	c Method 🔲						
Element Table:       Normal      Co	pefficients	, -								
+ Element Conc M	Measurement	Threshold Intensity	Ratio ROI (keV) Ch	2 Quant Calibration						
<sup>#</sup> ElmI Line Code Intensity Error Backs	gr. Conc. Error MDL Atom%	Value Conc Method	Method Low High Fi	t Method TCC Coeff						
1 C Ka 0 0.00 0.00 0.1	.00 24.019 0.000 0.0000 0.000	0.000 Gaussian	None 0.000 0.000 0.1	00 None 0.00						
		U.UUU Gaussian	None U.000 0.000 0.							
				· · · · · · · · · · · · · · · · · · ·						
Measurement & Processing Conditions:	○ Measurement	essing								
No. Escape Sum Back- Backg	ground Remove Blank Spectrum C/F	R Compton Compton F	ROI (keV) Rayleigh ROI	(keV)						
Smths Peak Peak ground Fi	iile Blank File Rati	tio (c/s) Low	High (c/s) Low I	ligh						
1 2 🔽 🗹 Auto		1252.45 20.220	21.720 177.65 21.720 3	22.500						
				-						
Status: Opened file C:\CrossRoads Scie	entific\SIR-FP Tutorial\SIR Files\	\Teflon.tfr	0	Dff On 2048 20 0.59 No 1						
Comment: FP Software for Bulk XRF Ana	alysis									

Figure 13. XRS- FP Expert Panel. Data after processing Teflon.mca.

XRS-FP										
File Acquire Setup Calibrate Process Help										
Acquire Set kV/uA kV: 40 (10->50) uA: 25 (5->200) Preset: 0 Time: 19.359 2DT: 0.0 ICR: 0.0 OCR: 0.0										
Specimen Component Table: Thickness Information:										
# Component Type Conc. Error Units Mole% Error Layer Normalize										
1 1702 Calc 100.0000 0.0000 wt 2 0.0000 0.0000 Thick. Type Error Units Density Fixed OK Total										
0.000 Bulk 0.000 mg/cm2 0.000 T F 100.00										
Element Table: © Normal © Coefficients										
# Element Zonc Measurement Threshold Intensity Ratio R0I (keV) Chi2 Quant Calibration										
Elmi Line Zode Intensity Error Backgr. Conc. Error MDL Atom% Value Conc Method Low High Fit Method TCC Coeff										
1 0 Ka 0 0.00 0.00 0.00 0.00 0.000 0.000 0.000 0.000 Γ Gaussian None 0.000 0.000 0.000 0.00 A										
Weasurement & Processing Conditions:     C     Measurement     Processing										
No. Escape Sum Back- Background Remove Blank Spectrum C/R Compton Compton ROI (keV) Rayleigh Rayleigh ROI (keV)										
- <sup>ODE</sup> Smiths Peak Peak ground File Blank File Ratio (c/s) Low High (c/s) Low High										
1 2 V Auto V 110.64 20.220 21.720 102.17 21.720 22.500										
Status:  Opened file C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\TiO2.tfr 0   0   0ff   0n   2048   20   0.59   No   1										
Comment: FP Software for Bulk XRF Analysis										

Figure 14. XRS- FP Expert Panel. Data after processing TiO2.mca.

10. Now go to the XRS-FP Expert Panel: Select Calibrate -> SIR-FP. This will display the "SIRFP Files for Calibration of C/R Ratios vs. Mean-Z" dialog. Double click in the "TFR Filename" cell to select the TFR filenames to be used for calibration (i.e. the \*tfr files created above for all the low-Z standards). See Figure 15 below. To add additional TFR files (standards) simply use the down-arrow key to add a row. After each TFR file is loaded the Mean Z and C/R Ratio for that standard is displayed in appropriate columns (Fig 15). Note: a previously created SIR calibration file can also be loaded instead of loading each TFR file in turn.

$\times$	SI	RFP Files for Calibration of	of C/R Ratios vs. Mean-Z			x
Г	_				5	
	#		TFR Filename	Mean Z	C/R Ratio	
	1	C:\CrossRoads Scientific\S	IR-FP Tutorial\SIR Files\Al203Binder10.tfr	10.120	4.830	
	2	C:\CrossRoads Scientific\S	8.620			
	3	C:\CrossRoads Scientific\9	SIR-FP Tutorial/SIR Files/CaCO3.tfr	12.570	1.940	
	4	C:\CrossRoads Scientific\S	SIR-FP Tutorial\SIR Files\K2S04.tfr	14.410	1.660	
	5	U:\UrossRoads Scientific\S	IR-FP Tutorial/SIR Files/NaUlttr	14.640	1.960	
	븟	U: \UrossHoads Scientific\3 C:\CrossBaads Scientific\3	DR-FPT Lutorial/STR Files/Terion.ttr	16 290	7.060	
			1	⊂ Linear Fit Param	eters	<b>•</b>
		Clear		Classes In		
		Save	Calibrate	Slope: ().	0 0	
		Load				
			Exit			

Figure 15. SIRFP Files for Calibration of C/R Ratios vs. Mean-Z Dialog. TFR files created from the low-Z standards are entered. The associated Mean Z and C/R Ratio are displayed for each file.

11. Once <u>all</u> the TFR files have been loaded (see above), click on the "<u>Calibrate</u>" button to do the least-squares fit of the two variables (C/R Ratio vs. Mean Z). Note: each of the variables is actually converted to a log function so that the scope can cover a wider range in detail. It was found that log-log plots produced better linear fits that the straight linear fitting.

At this point there should be a plot that looks like the following (see Fig. 16).



**Figure 16. Least Squares Fit of C/R Ratios vs. Mean-Z of Sample**. The resulting calibration curve is displayed Ln(C/R) vs. Ln(Mean-Z).

12. Click on the "Exit" button in the least-squares plot above (Fig. 16) and then click on the "<u>Save</u>" button (Fig. 17 below) to save the full SIR-FP calibration as an \*.sir file (i.e. "Tutorial.sir"). Then click on the "Exit" button.

🔀 si	RFP Files for Calibration of C/R Ratios vs. Mean-Z			×
# 1 2 3 4 5 6 7	TFR Filename           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\Al203Binder10.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\B203Binder05.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\CaC03.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\K2S04.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\NaCl.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\NaCl.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\Teflon.tfr           C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\TiO2.tfr	Mean Z 10.120 6.990 12.570 14.410 14.640 8.280 16.390	C/R Ratio 4.830 8.620 1.940 1.660 1.960 7.060 1.180	<u> </u>
	Clear Calibrate Int	Fit Parame Slope: <mark>-2.</mark> ercept: <u>6.5</u>	eters 3974 3391	•
	Exit			

Figure 17. Saving the SIR-FP Calibration file. The SIR-FP calibration is saved as an \*.sir file using the "Save" button.

Note: For practical applications, if the tube or any parameter is changed, then the entire calibration <u>must</u> be done again using the actual standards and live acquisition.

# Single Standard FP Calibration:

- 13. Having completed the calibration of the low-Z standards and obtained an SIR calibration file (\*.sir), we will now make a <u>single standard FP calibration</u> as the next step. Select File -> Open -> "C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\RockStd1.tfr" (or equivalent file location).
- 14. Now open the corresponding spectrum file from the XRS-FP Expert Panel: Select File -> Open -> "...SIR-FP Tutorial\FP Files\RockStd1.mca"

- 15. Select: Process -> Spectrum -> All from the XRS-FP Expert Panel.
- 16. Then from the XRS-FP Expert Panel: Select Setup -> Quant. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 18. Select the radio buttons for "Fundamental Parameters" with "One Standard". Then click OK.

Setup FP Calibration Method	
Quant Analysis Method • Fundamental Parameters	FP Calibration Mode
C FP with Scatter Ratios C Simple Least-Square Fitting	© One Standard © Multiple Standards
SIR-FP File Name:	
<u>OK</u>	Cancel

**Figure 18. Setup FP Calibration Dialog.** For the single standard FP calibration select the radio buttons for "Fundamental Parameters" with "One Standard." Then select "OK" to exit.

Now select: Calibrate -> FP from the XRS-FP Expert Panel. This generates TCC's which are populated under the "Calibration TCC Coefficients" column in the "Element Table" (see Fig. 19 below).

XRS-FP										
File Acquire Setup Calibrate Process Help										
Acquire         Set kV/uA         kV: 40 (10->50) uA: 25 (5->200)         Preset: 300         Time: 198.840         2DT: 0.0         ICR: 0.0         OCR: 0.0										
Specimen Component Table: Thickness Information:										
# Component Type Conc. Error Un	its Mole% Error	Layer	Normalize							
1 C Fixed 2.0800 0.0000 wt %	9.5608 0.0000  Thick.	Type Error Units Density Fit	xed OK Total							
3 Na20 Fixed 0.1400 0.0000 wt %		Bulk 0.000 mg/cm2 0.000 [	100.00							
4 Ba Calc 788.000 0.000 ppm	0.0000 0.0000									
5 Cu Calc 31.000 0.000 ppm 6 Ni Calc 82.800 0.000 ppm		reshold Settings								
	n-sigma	▼ 2.000 Clear Conc Method								
Element Table: © Normal C Coefficients	, _									
+ Element Conc Measurement	Threshold Intensity	Ratio ROI(keV) Chi2 Quant	Calibration							
Elml Line Code Intensity Error Backgr. Conc. Er	rror MDL Atom% Value Conc Method	Method Low High Fit Method	TCC Coeff							
1C K Ka 1 507.71 5.75 25.66 2.864 0.	.000 0.0000 0.000 0.000 Gaussian	None 3.250 3.375 0.05 FP	56506.68							
12 Ti Ka 1 209.19 3.21 24.79 0.513 0.	.000 0.0000 0.000 0.000 Gaussian	None 4.418 4.604 0.01 FP	36405.97							
13 V Ka 1 18.38 1.55 25.10 0.022 0.	.000 0.0000 0.000 0.000 Gaussian	None 4.872 5.025 0.02 FP	51971.4							
14 Mn Ka 1 99.34 2.70 44.43 0.116 0.	.000 0.0000 0.000 0.000 Gaussian	None 5.799 5.998 0.07 FP	32470							
		None 6.302 6.306 0.34 FF								
Measurement & Processing Conditions: O Measure	ement · Processing									
No. Escape Sum Back- Background Remove	Blank Spectrum C/R Compton Compton RC	)I (keV) Rayleigh Rayleigh ROI (keV)								
Smths Peak Peak ground File Blank	File Ratio (c/s) Low	High (c/s) Low High								
1 2 🔽 🗹 Auto	263.25 20.220	21.720 96.45 21.720 22.500								
Status: Opened file C:\CrossRoads Scientific\SIR-FP	Tutorial\FP Files\RockStd1.tfr	1 Off On 2	2048 20 0.59 No 1							
Comment: FP Software for Bulk XRF Analysis										

Figure 19. XRS- FP Expert Panel. Calibration coefficients (TCCs) are generated after selecting "Calibrate -> FP."

- **18.** Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be resaved as "RockStd1.tfr" or as an alternate filename of choice.
- 19. Having obtained the TFR file above, select Setup -> Quant. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 20. Now we want to combine the single standard FP calibration with the previously obtained SIR calibration. To do this, select the radio buttons for "FP with Scatter Ratios" with "One Standard." In the "SIR-FP File Name" text box double click to add the SIR file saved from the SIR calibration in step 12 above (e.g. Tutorial.sir). Then click "OK".

Setup FP Calibration Method	×								
Quant Analysis Method       FP Calibration Mode         O Fundamental Parameters       O Standardless         Image: FP with Scatter Ratios       Image: O One Standard         Image: Simple Least-Square Fitting       O Multiple Standards									
SIR-FP File Name: C:\CrossRoads Scientific\SIR-FP 1	Tutorial\SIR Files\Tutorial.sir								
ОК	Cancel								

**Figure 20. Setup FP Calibration Dialog.** To combine the single standard FP calibration with the previously obtained SIR calibration, select the radio buttons for "**FP with Scatter Ratios**" with "One Standard." Then select "OK" to exit.

**20.** This will bring up the dialog shown in Figure 21. Select **"Yes"** to "Reset All Elements to the SIRFP method?"

Leaving Quant XRF Method Setup
Reset All Elements to SIRFP method?
Yes No

Figure 21. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to the SIRFP method.

- 21. Now save the full FP and SIR calibration TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be re-saved as "FP\_Cal\_File\_SIRFP.tfr" or as an alternate filename of choice. This TFR file contains a link to the SIR file created previously (i.e., Tutorial.sir).
- 22. At this point we are ready to define a sample for analysis. From the XRS-FP Expert Panel set-up the "Component Table" for an "unknown". Clear the 3 "fixed" element lines at top (i.e. C, H2O and Na2O). Add 2 lines at the bottom of the "Component Table". These are "fictional elements" at this point. The Component name is left blank (see Fig. 22 below). Set the "Type" for these two lines as "SIR-FP" (all other "Components" are set to "Calc"). Check that the "Thickness Information"



Table is "Normalized" (check box selected) to <u>100%</u>. Note that oxygen is determined by stoichiometry.

< XRS	S-FP		_	-			-		-								
<u>F</u> ile	<u>A</u> cquire	Setup	<u>C</u> alibra	te <u>P</u> ro	cess <u>H</u> elp												
Acq	Acquire Set kV/uA kV: 40 (10->50) uA: 25 (5->200) Preset: 300 Time: 198,840 %DT: 0.0 ICR: 0.0 OCR: 0.0																
Specimen Component Table: Thickness Information:																	
#	Compa	nent	Туре	Con	nc. Error	Un	its Mole%	Error				Lay	er			Normal	ze
14 M	g0		Calc	2.6	6000 0.00	)0 wt.%	3.56	14 0.0000	<u> </u>	Thick.	Туре	Error	Units	: De	ensity Fix	ed OK T	otal
15 K2	20		Calc	3.4	1500 0.29	58 wt.%	1.09	41 0.0000	김	0.000	Bulk	0.000	) mg/cm	12	0.000		100.00
17 S	nu		Calc	0.1		02 Wt.% 10 wt %	0.05				•	•					
18			SIRFF	P 1 0.0	0.00 0.00	00 wt.%	0.00										
15			SIRFF	P 0.0	0.00	00 wt.%	0.00	0.000		Global T	hreshold	Settings					
Eler	ant Tatt	. [	C N		·····					n-sigma	▼ 2.0	000 C	lear C	Conc M	ethod 🛛		
cieme	ent rable		• Norma	) IE	Loeffici	ents				L							
#L	Element	Conc			Measur	ement		T	hreshold	Intensity	Ratio	RO	l (keV)	Chi2	Quant	Calibration	
# Eli	ml Line	Code	Intensity	Error	Backgr. C	onc. E	rror MDL	Atom% Va	lue Conc	Method	Metho	d Low	High	Fit	Method	TCC Coeff	
1 0	I Ka	0	0.000	0.00	0.00 4	3.520 0	0.000 0.0000	0.000 0.0	000	Gaussian	None	0.00	0 0.000	0.00	None	0.00	<b>^</b>
2 M	g Ka	1	1.764	0.85	9.31	1.568 0	0.000 0.0000	0.000 0.0		Gaussian	None	1.21	0 1.307	0.02	SIRFP	103165.62	
3 A	i Ka G Ka	1	252 441	2.54	12.18 1	1.114 U				Gaussian	None	1.44	1 1.533	0.10	CIDED	110895.93 51502.76	
5 P	P Ka	1	1.196	1.12	13.69	2.203 0	0.000 0.0000	0.000 0.0		Gaussian	None	1.96	2 2.065	0.04	SIREP	11425.76	
6 S	Ka	1	43.529	1.81	15.10	0.715 (	0.000 0.0000	0.000 0.0	00	Gaussian	None	2.25	3 2.361	0.01	SIRFP	36835.94	-
Mana	woment	t Proc		 andition	n [ C ]		mont G	Proposi			1						
meas	urement		Jessing Co	unuuun	s. 0	reasure		Flucess	ny								
Code	No.	Escape	Sum	Back-	Background	Remove	Blank Spectru	ım C/R	Compton	Compton R	IOI (keV)	Rayleigh	Rayleigh F	ROI (ke\	0		
	Smths	Peak	Peak g	ground	File	Blank	File	Ratio	(c/s)	Low	High	(c/s)	Low	High			
	2	V		Auto					263.25	20.220	21.720	96.45	21.720	22.50	0		
Sta	tus: C:\0	CrossR	oads Scie	entific\S	IR-FP Tute	orial\FP	Files\Cal_Fi	le_SIRFP.	tfr				1	Off	On 2	048 20 0.5	9 No 1
Соп	nment: F	P Soft	ware for l	Bulk XR	F Analysis												

**Figure 22. XRS- FP Expert Panel.** Add two blank rows at the bottom of the "component Table" to be used for the SIR-FP elements in the analysis of the "unknown" sample.

- 23. From the XRS-FP Expert Panel open an "unknown" spectrum. For the purpose of this tutorial select File -> Open -> "...SIR-FP Tutorial\FP Files\UnknownRock.mca."
- 24. Now select: Process -> Spectrum -> All from the XRS-FP Expert Panel.
- 25. Then select: Process -> Analyze.
- 26. Now save the TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be saved as "C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\UnknownRock\_FP-SIR\_AutoZ.tfr" or as an alternate filename of choice. See figure 23 below to compare the data

obtained from the analysis of the "unknown" sample.

Layer	Tabl	le									
# Thi	.ck	туре	Err	or U	nits	Den	sity N	Jorm. Tot	al		
1 0.0	00	Bulk	0.0	00 mq	g/cm2	0.	00	On 100	0.00		
Sampl	e Tal	ole									
Layer	COL	nponer	nt	Type	Conc	n.	Error	Units	Mole%	Error	
i	Ba	-		Calc	795.	11	116.85	58 ppm	0.030	0.004	
1	Cu			Calc	189.	61	4.765	ppm	0.016	0.000	
1	N1			Calc	83.4	69	10.919	) ppm	0.007	0.001	
1	Rb			Calc	148.	32	8.630	ppm	0.009	0.001	
1	Sr			Calc	179.	60	9.133	ppm	0.011	0.001	
1	V			Calc	221.	74	26.440	) ppm	0.023	0.003	
1	Zr			Calc	135.	21	8.487	ppm	0.008	0.000	
1	P20	25		Calc	40.3	13	0.492	WL.8	42.057	0.182	
1	710	12		Calc	40.0	62	0.019	wt 2-	0.569	0.001	
1	A10	202		Calc	21 1	74	0.729	wt 2-	10.925	0.012	
i	Fe	203		Calc	9.7	87	0.037	wt. %	3.224	0.012	
1	Cat	5		Calc	2.9	74	0.049	wt. %	2.790	0.046	
1	Mat	5		Calc	2.6	22	1.789	wt. %	3,422	2.335	
1	K20	5		Calc	3.4	78	0.056	wt.%	1.942	0.031	
1	MnO	0		Calc	0.1	51	0.006	wt.%	0.112	0.004	
1	S			Calc	0.7	21	0.042	wt.%	1.183	0.070	
1	N			SIRFP	3.8	51	0.000	wt.%	14.466	0.000	
1	0			SIRFP	5.7	99	0.000	wt.%	19.069	0.000	
Flore	ant m	blo									
Eleme	IIL Ia	Cond	Pot 10	Toto	petty		rror	Intonetti	Cong	Cong	Calibration
ETHIC	Code	Code	Mothe	od (a	21151Uy	-	C/S)	Method	conc.	Mothod	Coofficient
0	Ka	0000	None	0.00	0	0.	0000	Gaussian	41.558	None	0.000
Ma	Ka	1	None	1.76	54	0.	8510	Gaussian	1.581	SIRFP	103165.600
Al	Ka	1	None	104	382	2.	5362	Gaussian	11,207	SIRFP	110895,900
S1	Ka	1	None	352	441	з.	9165	Gaussian	22.453	SIRFP	51502.760
Р	Ka	1	None	1.19	96	1.	1151	Gaussian	0.163	SIRFP	11425.760
S	Ka	1	None	43.5	529	1.	8118	Gaussian	0.721	SIRFP	36835.940
K	Ka	1	None	507.	.708	5.	7542	Gaussian	2.887	SIRFP	56506.680
Ca	Ka	1	None	452.	.836	5.	2860	Gaussian	2.125	SIRFP	43951.510
T1	Ka	1	None	209.	.188	з.	2137	Gaussian	0.517	SIRFP	36405.970
v	Ka	1	None	18.3	382	1.	5499	Gaussian	0.022	SIRFP	51971.480
Mn	Ka	1	None	99.3	339	2.	7048	Gaussian	0.117	SIRFP	32470.720
Fe	Ka	1	None	6733	3.831	17	.7701	Gaussian	6.845	SIRFP	30515.300
N1	Ka	1	None	24.8	385	2.	3018	Gaussian	0.008	SIRFP	83404.870
CU	Ka	1	None	93.3	548	2.	3460	Gaussian	0.019	SIRFP	45075 000
RD	Ka	1	None	51.	10/	2.	2210	Gaussian	0.015	SIRFP	402/0.890
31	Ka	1	None	02.0	571	2.	0121	Gaussian	0.018	SIRPP	4/0010 100
BD	Ka	1	None	45.3	754	1	8450	Caussian	0.014	SIRFP	3552374 000
Dd	nd	1	None	1/.	104	±.	0400	Gaussidli	0.000	SINCE	3332374.000

**Figure 23. Data from Unknown Sample (FP/SIR/AutoZ)**. Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the single standard FP calibration, the SIR calibration and "Auto Z," where the software estimates the two low-Z matrix elements.

27. Here is an example using the same single standard FP calibration as described above; however, rather than allowing the software to estimate the 2 low-Z elements they are entered by the user (i.e. fixed). This method is designed to be used if you know something about the unknown sample. For the tutorial we will use H and N as our "preferred elements" in "Component Table". Enter these elements into the last two rows of the "Component Table." Set the concentration ("Conc.") to zero and select "Type -> SIR-FP" (Fig. 24). Also check that the thickness information is still normalized to a total of 100% (Fig. 24).

Sp	Specimen Component Table: Thickness Information:																	
#	# Component Type Conc. Error Units Mole% Error											Layer	r			Normalize		
14	MgO	Calc	2.5450	1.7366	wt.%	2.4630	0.0000	<b></b>	•	Thick.	Туре	Error	Units	Density	Fixed	ок/	Total	
15	K20	Calc	3.3718	0.0540	wt.%	1.3962	0.0000			0.000	Pulk	0.000	malom?	0.000			100.001	
16	Mn0	Calc	0.1466	0.0056	wt.%	0.0806	0.0000			0.000	DUIK	0.000	mg/cmz	0.000		1	100.00	
17	8	Calc	0.6992	0.0412	wt.%	0.8505	0.0000											
KE.	н) 🥢	SIRFP	0.0000	0000	wt.%	19.1803	0.0000											
19	SIRFP 0.0000 wt.% 33.0062 0.0000 _ Global Threshold Settings																	
1	Presigna V 2000 Clear Conc Method																	

Figure 24. XRS- FP Expert Panel. Enter H and N as the two "fixed" elements in the "component Table."

- **28.** Now select **Process** -> **Analyze** (again). This time to get the concentration for the two "fixed" elements, H and N.
- 29. Save the TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be saved as "C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\UnknownRock\_FP-SIR\_FixedZ.tfr" or as an alternate filename of choice. See figure 25 below to compare the data obtained from the analysis of the "unknown" sample.



Layer # Thic	Tabl k	Type	Err	or Un	its	Den	sity	Norm.	Tot	al		
1 0.00		Bulk	0.0	)0 mg	/cm2	0.	00	On	100	.00		
Sample	Tab	ole										
Layer	Соп	ponei	nt	туре	Conc	n.	Error	U	nits	Mole%	Error	
1	Ba			Calc	770.	60	113.2	55 p	pm	0.022	0.003	
1	Cu			Calc	183.	80	4.619	р	pm	0.011	0.000	
1	N1			Calc	80.9	14	10.58	5 p	pm	0.005	0.001	
1	Rb			Calc	143.	77	8.365	p	pm	0.007	0.000	
1	sr			Calc	174.	08	8.852	p	pm	0.008	0.000	
1	V			Calc	214.	97	25.63	3 p	pm	0.016	0.002	
1	Zr			Calc	131.	05	8.226	p	pm	0.006	0.000	
1	P20	5		Calc	0.3	62	0.477	W	t.%	0.099	0.131	
1	S10	02		Calc	46.6	17	0.733	W	t.%	30.264	0.476	
1	T10	02		Calc	0.8	35	0.018	W	t.%	0.408	0.009	
1	A12	203		Calc	20.5	35	0.706	W	t.%	7.856	0.270	
1	Fe2	203		Calc	9.4	87	0.035	W	t.%	2.317	0.009	
1	Cac	)		Calc	2.8	83	0.048	W	t.%	2.005	0.033	
1	Mgc	)		Calc	2.5	45	1.737	W	t.%	2.463	1.681	
1	K2C	)		Calc	3.3	72	0.054	W	t.%	1.396	0.022	
1	Mnc	)		Calc	0.1	41	0.006	W	t.%	0.081	0.003	
1	S			Calc	0.6	99	0.041	W	t.%	0.851	0.050	
1	н			SIRFP	0.4	96	0.000	W	t.%	19.177	0.000	
1	N			SIRFP	11.8	53	0.000	W	C.8	33.008	0.000	
Elemen	t Ta	able -										
Elmt L	1ne	Cond	Ratic	Inte	nsitv	E	rror	Inte	nsitv	Conc.	Conc	Calibration
C	ode	Code	Metho	d (c	/s)	(	c/s)	Me	thod		Method	Coefficient
С	Ka	0	None	0.00	0	0.	0000	Gaus	sian	0.000	None	0.000
N	Ka	0	None	0.00	0	0.	0000	Gaus	sian	11.853	None	0.000
0	Ka	0	None	0.00	0	0.	0000	Gaus	sian	40.321	None	0.000
Mg	Ka	1	None	1.76	4	0.	8510	Gaus	sian	1.535	SIRFP	103165.600
Al	Ka	1	None	104.	382	2.	5362	Gaus	sian	10.868	SIRFP	110895.900
S1	Ka	1	None	352.	441	3.	9165	Gaus	sian	21.791	SIRFP	51502.760
P	Ka	1	None	1.19	6	1.	1151	Gaus	sian	0.158	SIRFP	11425.760
S	Ka	1	None	43.5	29	1.	8118	Gaus	sian	0.699	SIRFP	36835.940
K	Ka	1	None	507.	708	5.	7542	Gaus	sian	2.799	SIRFP	56506.680
Ca	Ka	1	None	452.	836	5.	2860	Gaus	sian	2.060	SIRFP	43951.510
T1	Ka	1	None	209.	188	3.	2137	Gaus	sian	0.501	SIRFP	36405.970
V	Ka	1	None	18.3	82	1.	5499	Gaus	sian	0.021	SIRFP	51971.480
Mn	Ka	1	None	99.3	39	2.	7048	Gaus	sian	0.114	SIRFP	32470.720
Fe	Ka	1	None	6733	.831	17	.7701	Gaus	sian	6.636	SIRFP	30515.300
N1	Ka	1	None	24.8	85	2.	3018	Gaus	sian	0.008	SIRFP	83404.870
Cu	Ka	1	None	93.3	48	2.	3460	Gaus	sian	0.018	SIRFP	0.000
Rb	Ka	1	None	51.7	6/	2.	1297	Gaus	sian	0.014	SIRFP	45275.890
sr	Ka	1	None	62.0	/1	2.	2318	Gaus	sian	0.017	SIRFP	4/553.230
Zr	Ka	1	None	45.3	56	2.	0131	Gaus	sian	0.013	SIRFP	49012.100
Ba	Ka	1	None	17.7	54	1.	8450	Gaus	sian	0.077	SIRFP	3552374.000

**Figure 25. Data from Unknown Sample (FP/SIR/FixedZ)**. Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the single standard FP calibration, the SIR calibration and "Fixed Z," where the user enters the two preferred ("fixed") low-Z matrix elements.



**30.** Having completed the analysis of an "unknown" sample using a single standard FP calibration combined with the SIR calibration, we will now go on to use the MLSQ method to obtain an FP calibration from all non-low-Z elements. First, from the XRS-FP Expert Panel: Select **File** ->



**Open** -> "C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\RockStd1.tfr" (or equivalent file location). See Figure 26 below.

📉 Open					x
😋 🕞 🗸 🕌 « CrossRoads Sc	ienti	fic 🔸 SIR-FP Tutorial 🕨 MLSQ Files 🛛 👻	✓ Search MLSQ Fill	es	P
Organize 🔻 New folder			:==	•	0
No. 100 Desktop	*	Name	Date modified	Туре	
Downloads		MLSQ_Cal_File.tfr	8/28/2013 4:38 PM	TFR File	
Recent Places		MLSQ_Cal_File_SIRFP.tfr	8/28/2013 5:31 PM	TFR File	
		RockStd1.tfr	8/28/2013 4:36 PM	TFR File	
词 Libraries		RockStd1-with SIRFP.tfr	8/28/2013 5:33 PM	TFR File	
Documents	-	RockStd1-with-SIKFP-fixed-eimts-C-F.ttr	8/28/2013 5:30 PIVI 8/28/2013 4:35 PM	TER File	
J Music	=	RockStd3.tfr	8/28/2013 4:36 PM	TFR File	
Pictures		RockStd4.tfr	8/28/2013 4:37 PM	TFR File	
Videos					
🔣 Homegroup					
🖳 Computer					
	Ŧ	•			•
File name:	Roo	kStd1.tfr	✓ XRF Reports (*.tfr)		-
			Open	Cancel	

Figure 26. File Open Menu. Open the first MLSQ TFR file, e.g. "RockStd1.tfr".

31. Now from the XRS-FP Expert Panel: Select File -> Open -> "...SIR-FP Tutorial\MLSQ Files\RockStd1.mca" (this is the MCA spectrum file for our 1<sup>st</sup> MLSQ standard). A spectrum similar to that below in Figure 27 will be displayed. Note that the spectra for this tutorial are already adjusted and in calibration



Figure 27. MLSQ Standard Spectrum. Spectrum for the first MLSQ standard, "RockStd1.mca".

- 32. Select: Process -> Spectrum -> All from the XRS-FP Expert Panel.
- 33. Then from the XRS-FP Expert Panel: Select Setup -> Quant. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 28. Select the radial buttons for "Fundamental Parameters" with "One Standard". Then click OK. Note it is important to select single standard as the "FP Calibration Mode" as each standard used for the MLSQ calibration will first be processed as a single standard and only later will these files be merged.

Setup FP Calibration Method	×
Quant Analysis Method Fundamental Parameters FP with Scatter Ratios Simple Least-Square Fitting	FP Calibration Mode C Standardless C One Standard C Multiple Standards
SIR-FP File Name:	
OK	Cancel

**Figure 28. Setup FP Calibration Method.** Select "Fundamental Parameters" for the "Quant Analysis Method" and "**One Standard**" for the "FP Calibration Mode".

- **34.** Now select: **Calibrate** -> **FP** from the XRS-FP Expert Panel. This generates TCC's which are populated under the "Calibration TCC Coefficients" column in the "Element Table".
- **35.** Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be resaved as "RockStd1.tfr" or as an alternate filename of choice.
- 36. <u>REPEAT steps 30-35</u> above for <u>ALL</u> the individual <u>MLSQ</u> standards within the "MLSQ Files" folder. Remember to select "Fundamental Parameters" with "One Standard" under the "Setup -> Quant" Dialog for each of the four MLSQ standards (i.e. "RockStd1", "RockStd2", "RockStd3", "RockStd4").
- 37. Having obtained the 4 TFR files above for the 4 MLSQ standards, select Setup -> Quant. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 29. Now select the radio buttons for "Fundamental Parameters" with "Multiple Standards". Click "OK" to exit the dialog.

Setup FP Calibration Method	
Quant Analysis Method Fundamental Parameters FP with Scatter Ratios Simple Least-Square Fitting	FP Calibration Mode Standardless One Standard Multiple Standards
SIR-FP File Name:	
ОК	Cancel

Figure 29. Setup FP Calibration Method. Select "Fundamental Parameters" for the "Quant Analysis Method" and "Multiple Standards" for the "FP Calibration Mode".

**38.** If you have just finished an SIR-FP analysis from the previous step above it will prompt the following dialog (see Fig. 30 below). Select "Yes".



Figure 30. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to the FP method.

**39.** Now Select: **Calibrate** -> **MLSQ** from the XRS-FP Expert Panel. This will bring up the dialog, "TFR Files for Multi-Standard XRF Calibration", shown below in Figure 31.

ζT	FR	Files	for I	Multi-S	tandard	XRF Cali	bration		i he									×
Γ					Lis	t of TFR Fi	les						D	ata				
Ľ					TFR S	tandard Fil	ename			Elmt	Lin	e Conc	Intens	ity MT (	[mg/cm2	2) TCI	С	
1	D	oubl	e-Clicl	k here ti	o load th	e TFR Sta	ndard file	e				0.000	0.0	000	0.00	0	0.00	<b>A</b>
	Cle	ar		St Calib	ive ration	Ca	Load librati	on	Choos Mode	se <sup>1</sup>	MLSQ I	Model	Calib	prate	Ce	librate All		▼ Plot
Г	Т								Calibratio	n Coeffic	ionte							
#	ᅣᇛ	Int	Line	Code	Avera			00		rr2		003		Low M	т	High h	AT.	
		ante	LINC	0	ATOID	0.00000		0.000	00	0.000	000	0.0	0000	0.	00000	0	.00000	<b>_</b>
																		•
М	eas	urem	ent &	Proces:	sing Con	ditions:												
-	ode		X-R	ay Sour	ce	Chambei	Time	(secs)	No.	Escape	Sum	Back-	Remove	2				
Ľ	Juc	Ta	rget	Filter	kV	Atmos	Preset	Actual	Smooths	Peak	Peak	ground	Blank					
F	1				0.0		0.0	0.0	0						*	E	Exit	

Figure 31. TFR Files for Multi-Standard XRF Calibration. Dialog displayed from the "Calibrate -> MLSQ" menu item.

**40.** Double click in the "TFR Standard Filename" cell to load the TFR filenames to be used for the MLSQ calibration (eg. "RockStd1.tfr"). To add additional TFR files (standards) simply use the down-arrow key to add a row. Then load "RockStd2.tfr" and subsequently use the same method for the other two standards, "RockStd3.tfr" and "RockStd4.tfr". See Figure 34 below.

41. Now click the "Choose Model" button in the "TFR Files for Multi-Standard XRF Calibration" dialog (Fig 34). This will bring up another dialog called, "Define Model for MLSQ Fitting" (see Fig. 32 below). Select the type of model to be used by clicking on the "Ordinate (Y)" drop-down menu button (Fig. 32). Select the "Intensity" model (model #9) in the "Ordinate (Y)" column for this method (Fig. 33).



Figure 32. Define Model for MLSQ Fitting Dialog. Under the "Ordinate (Y)" column select the drop-down menu button to select the type of model to be used with this method.

The fitting "Polynomial" can either be "Linear" (Slope & intercept) or quadratic, which has an additional quadratic term. Use "Linear" for this tutorial.



**Figure 33. Define Model for MLSQ Fitting Dialog.** Under the "Ordinate (Y)" column select the drop-down menu button to select the "Intensity" model (model #9). Note this is the ideal model for use with this method.

Then click the "Exit" button to go back to the main "Calibrate -> MLSQ" dialog.

**42.** In the "TFR Files for Multi-Standard XRF Calibration" dialog click on the "**Calibrate**" button. See figure 34 below. Note: The "Calibrate" button is used if each standard has ALREADY been calibrated individually, as if each one were a single standard (as done in this tutorial).

#### **Recommended Method for MLSQ Calibration:**

- A. Calibrate each standard for the MLSQ calibration as if it were a single standard (individually). Then load these TFR files into the MLSQ calibration (as done in this tutorial). Now select the "Calibrate" button.
- B. Alternatively, the "Calibrate All" button can be used which does the spectrum processing and single standard calibration for each standard listed in the "List of TFR Files". We recommend the user follow the method described in (A) above, as it allows for a better understanding of the process and is more controllable.

$\times$	TFR	Files	for I	Multi-	Standa	rd XRF Ca	libration			-0	×Ι						23
					-												
[	۰L					ist of TFR.	Files						0	)ata			
Ľ	"[				TFR	Standard F	ilename			Elmt	Lir	ie Conc	Inten	sity MT (n	ng/cm2)	TCC	
	10	:\Cro	ssRo	ads Sc	cientific	SIR-FP Tu	orial\ML9	Q Files\F	RockStd	. Na	Ka	a 0.00	0 0.	.000	0.000	0.00	<u>_</u>
	21	2\Ure 2\Ure	ssHo ssBo	ads So ado So	cientific'	SIR-FP Tu SIR-FP Tu	orial\ML9	ių Files\ł O Files\I	RockStd RockStd	Na Na	K K	a 2.21;	8 U. 8 O	.070	0.000	62801.76	
	4 0	:\Cro	ssRo	ads Sc ads Sc	cientific <sup>4</sup>	SIR-FP Tu	orial\MLS	0 Files (Files )	RockStd	. Na		a 0.034 a 0.694		.019	0.000	58479.09	
	Cle	ear		S Cali	ave bratic	in Ci	Load alibrati	on 📢	Choo		MLSQ	Model (	Calil	brate	Cali	ibrate All	, Plot
	Т								Calibratio	on Coeffic	cients						
‡	ּון	Elmt	Line	Code	Ave	rage TCC	Т	CC		CC2	Т	CC3		Low MT	·	High MT	
	1	Va	Ka	1		0.0000	0	0.000	00	0.00	000	0.0	0000	0.0	00000	0.00000	
	2 1	/lg	Ka	1		0.0000	0	0.000	00	0.00	000	0.0	0000	0.0	00000	0.00000	
l H	3 4	AI Si	Ka	1		0.0000		0.000		0.00	000	0.0		0.0		0.00000	
	5	P	Ka	1		0.0000	0	0.000	00	0.00	000	0.0	0000	0.0	00000	0.00000	
	6	S	Ka	1		0.0000	0	0.000	00	0.00	000	0.0	0000	0.0	00000	0.00000	-
M	lea:	urem	ent %	Proce	ssina D	nditions:											
	ica.	I	X.B	au Soi	irce	Chambe	Time	(secs)	No	Escape	Sum	Back	Berrow		_		
	Code	HT.	rnet	Gy 300		Atmos	Preset	Actual	Smooths	Paak	Poak	around	Blank				1
⊢⊢	1		iget In	Non	e 40	Aunos 0 Air	nn		2			Auto		·		Exit	
			.9		+0	*  1W		0.0			<u>, , , , , , , , , , , , , , , , , , , </u>	- 100			¥		

**Figure 34. TFR Files for Multi-Standard XRF Calibration Dialog.** All four MLSQ standards saved from step 36 above (i.e. "RockStd1.tfr", "RockStd2.tfr", "RockStd3.tfr" and "RockStd4.tfr") have been loaded. The "Choose Model" button brings up the dialog called "Define Model for MLSQ Fitting", where the type of model is selected. Ideally this is the "Intensity" model (model #9). Select the "Calibrate" button to perform the full MLSQ calibration.

**43.** The "Plot" button displays the least squares plot for each element (see Figs. 35-36). The "Pervious" and "Next" buttons display plots for all the elements. Click the "Next" button to scroll through all the plots and observe the quality of the fit for each element. Having scrolled through all elements the dialog will automatically close, or you can use the "Exit" button.



Figure 35. MLSQ Least Squares Plot for Al. Least squares plot for Al.



Figure 36. MLSQ Least Squares Plot for Fe. Least squares plot for Fe.

44. Now click the "Save Calibration" button (see Fig. 37 below) to save the full MLSQ calibration file. This will save 2 files for the MLSQ calibration (an \*.lsq file and a \*.tfr file). For example, the two files saved in this tutorial are the default names: "MLSQ\_Cal\_File.lsq" and "MLSQ\_Cal\_File.tfr." Save these files in this location: C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files.



**Figure 37. TFR Files for Multi-Standard XRF Calibration Dialog.** Save the full MLSQ calibration (an \*.lsq file and a \*.tfr file) using the "Save Calibration" button.

- 45. We now have a complete MLSQ calibration in addition to our SIR calibration. At this point the two methods can be combined and used for analysis of an unknown sample. From the XRS-FP Expert Panel open the TFR saved from the MLSQ calibration (step 44 above). For example, select File -> Open -> "MLSQ\_Cal\_File.tfr".
- 46. Now from the XRS-FP Expert Panel: Select Setup -> Quant. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 38. Select the radio buttons for "FP with Scatter Ratios" with "Multiple Standards". In the "SIR-FP File Name" text box double click to

add the TFR file saved from the SIR calibration in step 12 above (e.g. Tutorial.sir). Then click "OK".

Setup FP Calibration Method	
Quant Analysis Method C Fundamental Parameters FP with Scatter Ratios C Simple Least-Square Fitting	FP Calibration Mode C Standardless C One Standard Multiple Standards
SIR-FP File Name: C:\CrossRoads Scientific\SI	R-FP Tutorial\SIR Files\Tutorial.sir
OK	Cancel

**Figure 38. Setup FP Calibration Method Dialog.** Select "**FP with Scatter Ratios**" for the "Quant Analysis Method" and "**Multiple Standards**" for the "FP Calibration Mode". Load the SIR-FP File name saved from the SIR calibration (e.g. Tutorial.sir).

**47.** This will bring up the dialog shown in Figure 39. Select **"Yes"** to "Reset All Elements to SIRFP method?"



Figure 39. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to SIRFP method?"

**48.** At this point we are ready to define a sample for analysis. From the XRS-FP Expert Panel set-up the "Component Table" for an "unknown". Clear the 3 "fixed" element lines at top. Add 2 lines at the bottom of the "Component Table". These are "fictional elements" at this point. The Component name is left blank. Set the "Type" for these two lines as "SIR-FP" (all other

"Components" are set to "Calc"). Check that the "Thickness Information" Table is "Normalized" (check box selected) to <u>100%</u>. See Figure 40 below.



**Figure 40. XRS- FP Expert Panel – Define a Sample for Analysis.** Delete the first 3 "fixed" elements in the "Component Table" and add 2 lines at the bottom of the "Component Table" for analysis of the "unknown". Leave the "Component" field blank and set their "Type" to "SIRFP" (all other "Components" are set to "Calc"). Check that the "Thickness Information" Table is "Normalized" to 100%.

Note: For analysis using the SIR-FP method two elements must be designated as type "SIR-FP" in the "Component Table". There are two ways to do this:

- A. Either specify the 2 elements in the "Component Table". For example, if the low-Z unanalyzed material might be a hydrocarbon then H and F could be defined.
- B. Or leave the 2 components blank in the "Component Table" (as described above). If the components are left blank the software will find two elements that estimate what the low-Z unanalyzed material is.
- 49. Now save the full MLSQ and SIR calibration TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be re-saved as ""C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\MLSQ\_Cal\_File\_SIRFP.tfr" or as an alternate filename of choice

- **50.** Now from the XRS-FP Expert Panel open an "unknown" spectrum for analysis. For the purpose of this tutorial select **File** -> **Open** -> "...**SIR-FP Tutorial\MLSQ Files\UnknownRock.mca.**"
- **51.** Select: **Process -> Spectrum -> All** from the XRS-FP Expert Panel.

Layer Table -----

**52.** Finally select: **Process** -> **Analyze** from the XRS-FP Expert Panel. This will perform the full analysis of the "unknown" using the combined SIR-FP and MLSQ methods, thus yielding elements with concentrations that estimate the 2 "blank elements" for low-Z unanalyzed material, as well as concentrations for the other elements analyzed in the unknown sample. See figure 41 below to compare the data obtained from the analysis of the "unknown" sample

# Th 1 0.	1ck 00	Type Bulk	Err(	or Uni 0 mg/	lts Der /cm2 0.	nsity 1 .00	Norm. Tot On 100	al .00		
Samp	le Tal	ble -								
Laye	r Coi Ba	mpone	nt :	Type Calc	Concn. 1087.89	Error 155.5	Units 03 ppm	Mole% 0.047	Error 0.007	
1	Cu		(	Calc	253.43	24.30	5 ppm	0.024	0.002	
1	N1		(	Calc	111.49	12.09	7 ppm	0.011	0.001	
1	Rb		(	Calc	149.23	11.58	2 ppm	0.010	0.001	
1	Sr		(	Calc	182.34	15.13	3 ppm	0.012	0.001	
1	V		(	Calc	270.80	40.10	1 ppm	0.031	0.005	
1	Zr		(	Calc	130.84	7.362	ppm	0.008	0.000	
1	P20	05	(	Calc	0.307	0.287	wt.%	0.128	0.119	
1	S10	02	(	Calc	48.848	0.717	wt.%	48.111	0.706	
1	T10	02	(	Calc	0.933	0.022	wt.%	0.691	0.016	
1	Al	203	(	Calc	20.522	0.761	wt.%	11.911	0.442	
1	Fe.	203	(	Calc	9.823	0.044	wt.%	3.640	0.016	
1	Ca	0	(	Calc	2.722	0.051	wt.%	2.872	0.053	
1	Mg	0	(	Calc	2.681	1.364	wt.%	3.936	2.003	
1	K2	0	(	Calc	3.318	0.068	wt.%	2.084	0.042	
1	Mn	0	(	Calc	0.141	0.007	wt.%	0.117	0.006	
1	S		(	Calc	0.534	0.055	wt.%	0.985	0.102	
1	N		:	SIRFP	1.821	0.000	wt.%	7.694	0.000	
1	0		:	SIRFP	3.540	0.000	wt.%	13.093	0.000	
Elem	ent T	able								
Elmt	Line	Cond	Rat10	Inter	nsity H	Error	Intensity	Conc.	Conc	Calibration
	Code	Code	Metho	i (c,	(s)	(c/s)	Method		Method	Coefficient
0	Ka	0	None	0.000	) 0.	.0000	Gaussian	46.202	None	0.000
Mg	Ka	1	None	1.764	40.	8510	Gaussian	1.617	SIRFP	113387.100
Al	Ka	1	None	104.3	382 2.	5362	Gaussian	10.861	SIRFP	118246.900
S1	Ka	1	None	352.4	441 3.	9165	Gaussian	22.834	SIRFP	50925.790
P	Ka	1	None	1.196	51.	1151	Gaussian	0.134	SIRFP	18444.560
S	Ka	1	None	43.52	29 1.	8118	Gaussian	0.534	SIRFP	70962.540
K	Ka	1	None	507.1	708 5.	7542	Gaussian	2.754	SIRFP	57676.940
Ca	Ka	1	None	452.8	336 5.	2860	Gaussian	1.945	SIRFP	49934.990
T1	Ka	1	None	209.1	188 3.	2137	Gaussian	0.559	SIRFP	33556.480
v	Ka	1	None	18.38	32 1.	5499	Gaussian	0.027	SIRFP	47622.900
Mn	Ka	1	None	99.33	39 2.	7048	Gaussian	0.109	SIRFP	39846.670
Fe	Ka	1	None	6733.	.831 1	7.7701	Gaussian	6.871	SIRFP	29381.590
N1	Ka	1	None	24.88	35 2.	.3018	Gaussian	0.011	SIRFP	68170.730
Cu	Ka	1	None	93.34	48 2.	3460	Gaussian	0.025	SIRFP	231839.300
Rb	Ka	1	None	51.70	57 2.	1297	Gaussian	0.015	SIRFP	44298.390
Sr	Ka	1	None	62.0	/1 2.	2318	Gaussian	0.018	SIRFP	47402.430
Zr	Ka	1	None	45.35	6 2.	0131	Gaussian	0.013	SIRFP	50522.960
Ba	Ka	1	None	17.75	54 1.	8450	Gaussian	0.109	SIRFP	2504930.000

**Figure 41. Data from Unknown Sample (MLSQ/SIR/AutoZ)**. Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the MLSQ calibration, the SIR calibration and "Auto Z," where the software estimates the two low-Z matrix elements.



- 53. Save the TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be saved as "C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\UnknownRock\_MLSQ-SIR\_AutoZ.tfr" or as an alternate filename of choice.
- 54. Here is an example using the same MLSQ calibration as described above; however, rather than allowing the software to estimate the 2 low-Z elements they are entered by the user (i.e. fixed). This method is designed to be used if you know something about the unknown sample. For the tutorial we will use H and O as our "preferred elements" in "Component Table". Enter these elements into the last two rows of the "Component Table." Set the concentration ("Conc.") to zero and select "Type -> SIR-FP" (Fig. 42). Also check that the thickness information is normalized to a total of 100% (Fig. 42).

Sp	Specimen Component Table: Thickness Information:																
#	Component	Туре	Conc.	Error	Units	Mole%	Error					Laye	r			No	ormalize
14	1 MgO	Calc	2.6811	1.3642	wt.%	3.9365	0.0000		•	Thick.	Туре	Error	Units	Density	Fixed	ок /	Total
15	K20	Calc	3.3179	0.0676	wt.%	2.0844	0.0000			0.000	Bulk	0.000	ma/cm2	0.000			100.00
16	MnO	Calc	0.1407	0.0073	wt.%	0.1174	0.0000			0.0001	Dank	0.000	ingrome.	0.000		1.	100.00
1	S.	Calc	0.5335	0.0550	wt.%	0.9846	0.0000										
18	H)	SIRFP	0.0000	1000	wt.%	7.6940	0.0000	1 1									
19	SIRFP 0.0000 wt.% 13.0931 0.0000 Gibbal Threshold Settings																
	n-sigma V 2000 Clear Conc Method																

Figure 42. XRS- FP Expert Panel. Enter H and O as the two "fixed" elements in the "component Table."

- **55.** Now select **Process** -> **Analyze** (again). This time to get the concentration for the two "fixed" elements, H and O.
- 56. Save the TFR file by selecting File -> Save As from the XRS-FP Expert Panel. This can be saved as C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\UnknownRock\_MLSQ-SIR\_FixedZ.tfr" or as an alternate filename of choice. See figure 43 below to compare the data obtained from the analysis of the "unknown" sample.

Layen # Thi 1 0.(	r Tabl Lck )0	le Type Bulk	Erro 0.00	r Un mg	its /cm2	Dens 0.0	sity N 00	Norm. Tot On 100	al .00		
Sampl Layei	le Tak c Con	ble	nt T	ype	Conc	n.	Error	Units	Mole%	Error	
1	Ba	-	С	alc	1090	.20	155.83	33 ppm	0.023	0.003	
1	Cu		C	alc	253.	95	24.355	5 ppm	0.012	0.001	
1	N1		C	alc	111.	72	12.123	3 ppm	0.006	0.001	
1	Rb		C	alc	149.	54	11.600	5 ppm	0.005	0.000	
1	Sr		C	alc	182.	73	15.165	5 ppm	0.006	0.001	
1	V		C	alc	271.	34	40.182	2 ppm	0.016	0.002	
1	ZI D20	DE.	0	alc	131.	12	1.3//	ppm	0.004	0.000	
1	P20	22	2	alc	48.9	37	0.287	wt.s	23 917	0.059	
1	T10	22	č	alc	0.9	35	0.022	wt. %	0.344	0.008	
1	Al	203	č	alc	20.5	63	0.762	wt.%	5,922	0.220	
1	Fe2	203	C	alc	9.8	43	0.044	wt.%	1.810	0.008	
1	Cat	C	C	alc	2.7	27	0.051	wt.%	1.428	0.027	
1	MgC	D	C	alc	2.6	86	1.367	wt.%	1.957	0.996	
1	K20	D	C	alc	3.3	25	0.068	wt.%	1.036	0.021	
1	MnO	D	C	alc	0.1	41	0.007	wt.%	0.058	0.003	
1	S		C	alc	0.5	35	0.055	wt.%	0.489	0.050	
1	Н		S	IRFP	0.3	71	0.000	Wt.8	10.805	0.000	
T	0		S	TREP	51.0	99	0.000	WC.8	93.786	0.000	
Eleme	ont Ta	able .									
Elmt	Line	Cond	Rat1o	Inte	nsity	Er	ror	Intensity	Conc.	Conc	Calibration
	Code	Code	Method	(0	:/s)	(0	c/s)	Method		Method	Coefficient
Н	Ka	0	None	0.00	0	0.0	0000	Gaussian	0.370	None	0.000
0	Ka	0	None	0.00	0	0.0	0000	Gaussian	92.790	None	0.000
Mg	Ka	1	None	1.76	4	0.8	3510	Gaussian	1.620	SIRFP	113387.100
Al	Ka	1	None	104.	382	2.5	5362	Gaussian	10.883	SIRFP	118246.900
S1	Ka	1	None	352.	441	3.9	9165	Gaussian	22.875	SIRFP	50925.790
P	Ka	1	None	1.19	6	1.1	151	Gaussian	0.134	SIRFP	18444.560
S	Ka	1	None	43.5	29	1.8	3118	Gaussian	0.535	SIRFP	70962.540
K CD	Ka	1	None	1507.	108	5.	060	Gaussian	2.760	SIRPP	J/6/6.940
Cal Tri	Ka	1	None	452.	100	3.4	2860	Gaussian	1.949	SIRPP	49934.990 33556 A00
v	Ka	1	None	19 3	92	1 0	5499	Caussian	0.027	GIDED	47622 900
Mn	Ka	1	None	99.3	39	2.	7048	Gaussian	0.109	SIRFP	39846.670
Fe	Ka	1	None	6733	.831	17.	7701	Gaussian	6.885	SIRFP	29381.590
N1	Ка	1	None	24.8	85	2.3	3018	Gaussian	0.011	SIRFP	68170.730
Cu	Ка	1	None	93.3	48	2.3	3460	Gaussian	0.025	SIRFP	231839.300
Rb	Ka	1	None	51.7	67	2.1	297	Gaussian	0.015	SIRFP	44298.390
Sr	Ka	1	None	62.0	71	2.2	2318	Gaussian	0.018	SIRFP	47402.430
Zr	Ka	1	None	45.3	56	2.0	0131	Gaussian	0.013	SIRFP	50522.960
Ba	Ka	1	None	17.7	54	1.8	3450	Gaussian	0.109	SIRFP	2504930.000

**Figure 43. Data from Unknown Sample (MLSQ/SIR/FixedZ)**. Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the MLSQ calibration, the SIR calibration and "Fixed Z," where the user enters the two preferred ("fixed") low-Z matrix elements.