XRS-FP Fundamental Parameters Tutoria

The following with associated files (spectra, *.mca and application, *.tfr) guides a new user of CrossRoads Scientific XRF Fundamental Parameters Application software through the setup and implementation of an analysis. This includes:

- 1. Qualitative inspection of the sample
- 2. Spectrum processing
- 3. Calibration
- 4. Analysis

It is most convenient to copy the supplied Tutorial Folder to your hard drive.

It is assumed that the x-ray spectrometer has been energy calibrated – see section 5.1, XRF Spectrometer Calibration and Monitoring of the XRS-FP Software Guide. And that spectrometer excitation parameters have been selected, i.e., incident beam collimation (if required), tube accelerating voltage, tube current, primary beam filter. The setup of these parameters will be spectrometer / application specific and are not within the scope of this tutorial other than to emphasize that in order to obtain accurate XRF analysis these must be defined and maintained in the XRS Application, tfr file.

Application: Bronze alloy (Cu-Sn alloy) – 3 approaches are demonstrated here: Standardless analysis, Calibration using pure bulk materials and Calibration using a single "type standard". A type standard is a standard of similar composition to that of the unknowns.

Procedure:

- 1. Launch XRS-FP Click anywhere on the splash screen to remove it from the display
- 2. From the Auto-Mode FP Analysis window, click Expert Mode

X Auto-Mode FP	Analysis		
Select Analy: Add New	sis Type Go Edit Auto Select	<u>A</u> uto Analyze <u>M</u> ode	<u>C</u> alibrate <u>E</u> xit
-Setup Autom ▼ Save Spec	ation Options trum □ Save Report ⊽ Update Spectra □	Show Statistics 🔲 Overla	ap Acquire/Proc.
Base File Na Seed #: 1	ne: C:\Program Files (x86)\CrossRoads Scientific\XRS # Measurements: 2 Delay Time	;FP\TEMP 2(s): 5	ng <u>G</u> et Path
Run #	Preset Livetime = 20		Value //

Figure 1

This will recall the Master.tfr file (see section 4.1, Loading the Software of the XRS-FP Software Guide).

- 3. From the XRS-FP Analyzer interface: Click **File>Open** (file type XRF report, *.tfr) **Bronze Bulk Analysis Tutorial.tfr** (this is the completed tfr / application)
 - 3.1. To start afresh, from the XRS-FP Analyzer interface click: File>New this will clear all of the application information, i.e., Component Table, Elements Table and Thickness information. The Measurement information (spectrometer configuration) is retained. There is now a "clean sheet" for set up of an application.

As noted above, it is not within the scope of this tutorial to go into the details of setting up specific spectrometer configurations. However, we will briefly review the excitation conditions used for the example presented here. Referring to the Measurement Conditions of the New XRS-FP Analyzer view on your display and presented below, Figure 2. The spectrometer is configured with a tungsten (W) target tube. A primary filter is used to remove the W L emissions from acquired spectra that would otherwise interfere with application analyte emissions, Cu from the Bronze. An accelerating potential is selected that is sufficient to fluoresce the desired x-ray emissions of the analytes. In this case, dictated by the Sn emissions – K critical potential is 29.190 keV, so, 47 kV tube potential was selected (~1.5 -2 X) the critical potential, if possible. This is also sufficient energy to fluoresce the Cu analyte line. A 240 μ A tube current was selected to provide count rates that would provide efficient analysis. This can be judged by %DT (dead time) – typically 45% ±10%.

	🔆 MTF-FP Analyzer 📃 🗶
	<u>File A</u> cquire <u>S</u> etup <u>C</u> alibrate <u>P</u> rocess <u>H</u> elp
	Acquire Set kV/uA kV: 27 [4->200] uA: 1000 (1->2000 Preset: 30 Time: 8.2 %DT: 0.0 X: 0 Y: 0 Z: 0
	Specimen Component Table: Thickness Information:
	# Lyr Component Type Conc. Error Units Mole% Error H
	Thick Type Error Units Density Fixed OK Total
	1 1.000 Caic 0.000 um 0.000 1 № 100.00] ×
	Threshold Settings
	Element Table: O Normal Coefficients In-sigma: 2.0 Clear Conc Method
	Element Cond Measurement Threshold Intensity Comp RDI (keV) Chi2 Quant Calibration
	Eint Line Code Intensity Error Backgr. Conc. Error MDL Atom% Sig Conc Method Ratio Low High Fit Method TCC Coeff
Measurement o	conditions /
spectrometer c	onfiguration
	Measurement & Processing Conditions: Generation Measurement Centre Processing
	Analy Source Detector Chamber Time (secs) Monitor
	Target Filter Thick(um) kV uA Type Filter Thick(um Atmos Preset Actual Intensity
	1 W Mo 50.00 27.01000.0 Sipin None 0.00 Air 30.0 8.2 0.0
	Status: Upened IFH file master.ttr 2 0n 0ff 2048 20 14 Tes 1
	Lomment: Matrix Beamindex 3 Filterindex 4

Figure 2

4. <u>Specimen / Application Components</u>: Add the application components (see section 5.2, XRF Elemental FP Calibration or Standardization of the XRS FP Software Guide). Components can be

elements or compounds. In this application we are working with alloying metals, elemental metals. In line 1 of the Components table enter Cu. To add another component, use the down arrow of your computer keyboard. Enter Sn and on line 2, # 2 component.

< x	RS	-FP		-								-								-	X
Eile	A	Acquire	<u>S</u> etup	<u>C</u> alibrate	Proces	s <u>H</u> elp					_			_							
A	cqu	uire		Set kV/u	A kV	47 (10->40)	uA: 240	<mark> </mark> (5->2	00) Pr	eset: <mark>1</mark>	00	Time: [0	%DT:	0.0	X: 0		Y: 0	Z: 0	
Spe	cir	nen Con	nponent	Table:								Thick	ness Ir	oformati	ion:						
#		Compo	onent	Туре	Conc	. Err	or	Units	Mole%	Erro	r				Laye	er				Normalize	
1	Cu	i i		Calc	0.00	00 0.0	0000 wt.2	۲ ۲	0.0000	0.00	00	Thic	sk.	Туре	Error	Unit	s D	ensity	Fixed C	IK Total	
2	Sr	1		Laic	1 0.00	001 0.0	1000 J WC 2	6	0.0000	1 0.00	<u></u>		0.000	Bulk	0.000	mg/cr	m2	0.000	F	100	.00
												,									
												Glob	al Thr	eshold	Settings						
le	me	nt Table	. (Normal	0	Coeffici	ents					n-sig	jma 🔤		00 Cle	ar C	Conc Me	thod			
#		Element	Cond			Mea	surement				Thre	shold	Inten	sity	Ratio	ROL	(keV)	Chi2	Quant	Calibration	
#	El	mt Line	Code	Intensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value	Conc	Meth	od	Method	Low	High	Fit	Method	TCC Coeff	
1	C	u Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000		Gaus	sian	None	0.000	0.000	0.00	FP	0.0	10
4.0.1			t Press	ering Com	litioner	6			C P			1									_
	120	inement i					T	Datast			''y				Manhar						
Coc	le -	T	X	Hay Source	e al az		T	Detect	or Theory		hamber	Durat	me (sec:	SJ	Monitor						
1	-	arget	Mo	75.00	J KV 47.0	240.0	i ype Si pie	None		umj A	Aunos	Preset	10 -	iciual 0.0	intensity						
			MO	13.00	47.0	290.0		Rioffie	0.0					0.0	0.0	- -					
S	tat	us: Unti	tled													1	On	Off 4	096 10	8 No	1
C) IN I	nent: F	P Softw	are for <u>Bu</u>	Ik XRF A	\nalys <u>is</u>										, .	,		,	, , , , , , , , , , , , , , , , , , , ,	
_	_																				

Sample Components

<u>F</u>igure 3

- 5. <u>Element Table</u>: As components are defined, the Element Table is filled in defaulting to what would nominally be the most intense analyte line available. In this case, the Cu Kα and Sn Kα. These are appropriate selections for this application.
- 6. <u>Thickness Table</u>: Accurate XRF analysis requires definition of the thickness of the sample material. In the case of this tutorial, the bronze is infinitely thick, which means that it has greater thickness than the escape depth of the highest energy line, the Sn Kα. This is defined as bulk and is the default **Type** setting in the Thickness Table. The default thickness for bulk analysis is zero (0). XRS-FP facilitates the analysis of less than infinitely thick samples by calculating the thickness; the **Type** field is set using the pull down to and selecting **Calculate**. Thickness of less than infinitely thick samples can also be **Fixed** (thickness and units must then be defined in the fields provided), or calculated by absorption (Absn) from the absorption of an emission from material below the layer being analyzed. Density and Unit fields only apply to less than infinitely thick samples.
 - 6.1. The Normalize field of the thickness table refers to component concentration. In thin film work layer concentration needs to be normalized to 100%. Normalizing to 100% is not required for bulk analysis, but is often employed. If not already done, this is a very good point to save the tfr that you are creating by clicking **File>Save As** (file type, XRF report, *.tfr) Enter the File Name

Bronze Bulk Analysis.tfr. At this point the application is defined. The next steps are to extract analyte intensities from the standard spectrum acquired under the excitation conditions defined in the Measurement and Processing Conditions Table and derive Calibration coefficients (sensitivities for each analyte emission).

7. <u>Spectrum Processing / Extracting Net Intensities</u> (see Section 14.3, Process Spectrum of the XRS Software Guide): Spectra supplied for this tutorial have been energy adjusted (see section 12.11, Setup Spectrum Adjust of the XRS Software Guide). To avoid doing a double adjust, from the XRS-FP Interface – Setup>Process> and make certain that the Auto Adjust Spectrum Gain & Offset on Load is unchecked, Figure 4, following.



- 7.1. Recall the Bronze spectrum: From the XRS-FP Analyzer interface File>Open (the Tutorial File
 - type is Amptek Spectrum (*.mca), Bronze Spectrum_Adjusted.mca Figure 5.



Figure 5

It is always a good idea to qualitatively inspect the spectrum prior processing. The spectrum, Bronze Spectrum_Adjusted that has been recalled below (Figure 6) is presented in Log mode, which can be very useful for qualitative inspection. Cu and Sn analyte peaks are identified, as well as, the processed escape peaks (black dotted line spectrum), trace of Pb (not uncommon to bronzes) and a small Zr system peak (coming from the spectrometer, not the sample). The Pb and Zr are very small peaks and will not interfere with the application calibration setup or analysis.



Figure 6

7.2. Spectrum Smooth, Escape Peak Removal Background Removal and Deconvolute: Click the Processing Radio Button above the Measurement & Processing Conditions Table to obtain the view of the XRS-FP Analyzer interface below – Figure 7, re section 3.1 and 3.2, Spectrum Processing of the XRS-FP Software Guide. We have chosen to apply one smooth function, remove escape peaks, and apply the Auto Background removal. Background low pass filter width parameter is set in **Setup>Processing** – see Figure 4 above. To apply these three functions and extract intensities from the XRS-FP Analyzer Interface Click: Process>Spectrum>All (Smooth-Escape Peak Removal-Background Removal-Deconvolution). There are several peak intensity extraction options. By clicking on the Intensity Method fields for the analyte lines of the Element Table these are displayed – Intensity, Gaussian and Reference. The tutorial uses the Gaussian fit of which there a 2, linear and nonlinear. Nonlinear is used here and is set as a processing parameter **Setup>Processing** (see Figure 4 above). Each Processing Function can also be applied manually (individually). Manual selection is very useful when selecting functions and associated parameters. Net peak intensities are extracted, integrated and displayed in the Intensity field of the Element Table of the XRS-FP Analyzer Interface. Intensities are expressed as count rates - counts/second - see Figure 8 below. Note that the intensities that you obtain may be slightly different from those displayed in Figure 8.

Eile Acquire Set kV/uA kV: 47 (10->40) uA: 240 (5->200) Preset: 10 Time: 0 2D T: 0.0 X: 0 Y: 0 Z: 0 Specimen Component Table: Thickness Information: Thickness Information: Thickness Information: Thick. Type Error Units Density Fixed OK Total 1 Cu Calc 0.0000 0.0000 w.% 0.0000 0.0000 momalize 2 Sn Calc 0.0000 0.0000 w.% 0.0000 0.0000 momalize Flement Table: C Normal C Coefficients Global Threshold Settings
Acquire Set kV/uA kV: 47 (10->40) uA: 240 (5->200) Preset: 10 Time: 0 2DT: 0.0 X: 0 Y: 0 Z: 0 Specimen Component Table: Thickness Information: Thickness Information: Thick. Type Error Layer Normalize 1 Calc 0.0000 w.% 0.0000 0.0000 Thick. Type Error Thick. Type Error Thick. Total 0.000 MK Total 0.000 Bulk v 0.000 mg/cm2 0.000 V 100.00 Image: 0.000 Fixed OK Total 0.000 Bulk v 0.000 mg/cm2 0.000 V 100.00 V Figurent Table: C Coefficients C Coefficients V 2000 Clear Conc Method Total
Specimen Component Table: Thickness Information: # Component Type Conc. Error Units Mole% Error I Layer Normalize 1 Cu Calc 0.0000 wt% 0.0000 0.0000 Thick. Type Error Units Density Fixed OK Total 2 Sn Calc 0.0000 wt% 0.0000 0.0000 mg/cm2 0.000 V 100.00 Image: Concefficients Image: Conce
Component Type Conc. Error Units Mole% Error Layer Normalize 1 Cu Calc 0.0000 0.0000 wt% 0.0000 0.0000 Thick. Type Error Units Density Fixed OK Total 2 Sn Calc 0.0000 wt% 0.0000 0.0000 Thick. Type Error Units Density Fixed OK Total 0.000 Bulk 0.000 mg/cm2 0.000 Total 0.000 mg/cm2 0.000 Total 6lobal Threshold Settings
1 Cu Calc 0.0000 wt.% 0.0000 0.0000 mt.% Thick. Type Error Units Density Fixed OK Total 2 Sn Calc 0.0000 wt.% 0.0000 0.0000 mt.% 0.0000 mt.% 0.000 0.000 mt.% 0.000 0.000 0.000 mt.% 0.000 0.000 mt.% 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.
2 3n Calc 0.0000 0.0000 0.0000 0.0000 mg/cm2 0.000 mg/cm2 100.000 Global Threshold Settings n-sigma ▼ 2.000 Clear Conc Method Conc Method
Global Threshold Settings
Global Threshold Settings
Element Table: Coefficients
Liement Lable: (Normal C Coefficients
H Element Cond Measurement Threshold Intensity Ratio R01 (keV) Chi2 Quant Calibration
Telmt Line Code Intensity Error Backgr. Conc. Error MDL Atom% Value Conc Method Method Low High Fit Method TCCCoeff
1 Cu Ka 1 0.00 0.00 0.00 0.000 0.000 0.000 Co00 0.000 CGaussian None 0.000 0.000 FP 0.00 ▲
Processing Radio Button
Measurement & Processing Conditions: C Measurement © Processing
Read No. Escape Sum Back- Background Remove Blank Spectrum C/R
Smths Peak Peak ground File Blank File Ratio
Status: Opened file C:\Users\Jim Bogert\Documents\Matrix Metrologies\Vendor Stuff\Crossroads\XRS Manual\Tutoria 1 Off Off 4096 10 8 No 1
Comment: FP Software for Bulk XRF Analysis

Figure 7

< XR	S-FP							-			1.00									ж
<u>F</u> ile	<u>A</u> cquire	<u>S</u> etup	<u>C</u> alib	orate <u>P</u> ro	cess <u>H</u>	elp														
Ac	quire		Set k	⟨V/uA	kV: 47	(10->4)) uA: <mark>240</mark>	[5->2	:00) P r	eset:	30	Time: 11	B.3	%DT	: <mark>0.0</mark>	X: 0		Y: 0	Z: 0	
Spec	imen Co	nponer	nt Table	:							_ Thicl	iness Info	ormatio	on:						
#	Comp	ionent	T	ype C	onc.	Error	Units	Mole%	Erro	r				Lay	ver				Normalize	
1	Cu			alc	0.0000	0.0000 w	.%	0.0000	0.00	000	🖞 Th	ick. T	уре	Error	Unit	s D	ensity	Fixed C	K Tot	al
2	Sn		14	alc	0.0000	0.0000 w	.%	0.0000	J U.UL			0.000 Bu	<mark>uk 📼</mark>	0.000) mg/cr	n2	0.000		10	0.00
Elem	ient Tabli	e:	• Nor	mal	C Coeff	icients]				Glo n-si	bal Thres gma 💌	hold S	ettings 10 Cl	ear C	onc Me	ethod			
	Element	Cond			M	leasureme	nt			Thr	eshold	Intensiț	у	Ratio	ROI (keV)	Chi2	Quant	Calibratio	n
# [Elmt Line	Code	Intens	ity Erro	r Backg	gr. Conc.	Error	MDL	Atom%	Value	Conc	Method	1	Method	Low	High	Fit	Method	TCC Coe	ff
1	Cu Ka	1	5321	.08 34	39 52.	.05 0.00	0 0.000	0.0000	0.000	0.00		Gaussia	n	None	7.865	8.210	0.01	FP	0	.00
2	Sn Ka	11	854	.24 14	01 23.	.38 0.00	0 0.0001	0.0000	0.000	0.00		liaussia	n	None	24.839	25.477	0.01	+P	<u> </u>	
Mea	surement	& Proc	essing	Condition	IS:	Net Int Decon	ensitie volutio	s froi n/Int	m Ga egrat	ussi tion	an									
	No.	Escape	Sum	Back-	Backgrou	und Remo	/e Blank Sp	ectrum	C/R											
Code	Smths	Peak	Peak	around	File	Blank	File		Ratio											
1	1	V		Auto									_							
																	-			
Sta	atus: Spe	ctrum I	ntensit	y Calcula	tions Co	mpleted									1	Off	Off 4	096 10	8 No	1
Co	nment: F	P Soft	ware fo	r Bulk XF	F Analys	sis														
_						_							_							

Figure 8

8. <u>Calibrate – unique case</u>: Most instrumental analysis requires calibration to a standard material. XRF is somewhat unique. Because X-ray physics are very well defined there are analysis circumstances where analysis can be performed without standards – truly standardless analysis. Standardless

analysis requires X-ray fundamental parameters algorithms be employed – XRS-FP is a fundamental parameters analysis program, that all the components in the sample material be defined either by the XRF analysis or input by the user and that the sample material be infinitely thick. The tutorial application meets these criteria.

8.1.So, having defined the elements in the bronze and extracted the net intensities a Standardless analysis can be made. Click Process>Analyze and results of the standardless analysis of the bronze are displayed – Wt% (Conc. in the Component Table) and Mole% (see Figure 9). Note that standardless results are always normalized to 100% - the total sample matrix must be defined.

X XR	S-FP										1.00	×	1								x
<u>F</u> ile	<u>A</u> cquire	<u>S</u> etup	<u>C</u> alibrat	e <u>P</u> roc	ess <u>H</u> elp																
Ac	quire		Set kV/	/uA	:V: <mark>47</mark> (1	10->40)	uA: 240	(5->2	00) Pre	eset: 3	0	Time: 18	.3	%DT:	0.0	X: 0		Y: 0		Z: <mark>0</mark>	
Spec	cimen Com	ponent	Table:								Thic	kness Info	rmatio	n:							
#	Compo	nent	Туре	; <u>Co</u>	nc. Erro	or l	Jnits	Mole%	Error					Lay	er				No	ormalize	Т
1 (Cu Sn		Calc Calc	73. 26.	8040 \ 0.4 1960 / 0.4	770 wt.% 298 wt.%	((84.0336 15.9664	0.54	31 19	Tł	nick. T. 0.000 B	ype ulk	Error 0.000	Unit: ma/cn	s D	ensity 0.000	Fixed	OK V	Total 100.0	
Elem	ent Table:	•	Norma		Coefficie	ents					Gla n-s	bal Thresl igma _▼	hold So 2.00	ettings	ear C	onc Me	ethod				
	Element	Cond			Meas	surement				Thre	shold	Intensity	, [Ratio	ROL	keV)	Chi2	Qua	nt C	alibration	Г
#	Elmt Line	Code	Intensity	Error	Backgr.	Conc.	Error	MDL .	Atom%	Value	Conc	Method		Method	Low	High	Fit	Meth	od T	CC Coeff	1
1	Cu Ka	1	5321.08	34.3	9 52.05	73.804	0.477 (0.0506	84.034	0.000		Gaussia	n	None	7.865	8.210	0.01	FP		0.00	
2	Sn Ka	1	854.24	14.0	1 23.38	26.196	0.430 (0.0749	15.966	0.000	Г	Gaussia	n	None	24.839	25.477	0.01	FP		0.00]_
Mea	surement &	Proce	ssing Co	nditions	: ON	leasure	ment	• Pro	ocessin	ıg]										[
Code	No. E	scape	Sum E	Back-	Background	Remove	Blank Spe	ectrum	C/R												
COUE	Smths	Peak	Peak g	round	File	Blank	File	F	Ratio												
1	1			Auto													 ▼				
Sta	atus: Comp	leted F	P Quant	itative i	Analysis										1	Off	Off	4096	10 8	No	1
Cor	nment: FF	Softw	are for B	ulk XRI	- Analysis																

Figure 9 Standardless Analysis

- 9. <u>Calibration with Pure Elemental or Compound Standards</u>: Standardless Analysis is convenient and provides a good semi-quantitative analysis. Another quantitative approach is using pure elemental bulk materials or compounds to establish Calibration Coefficients. The tutorial application provides a good example for this approach pure bulk Sn and pure bulk Cu are easily obtained. To implement this approach create a new tfr from the Bronze Bulk Analysis.tfr.
 - 9.1. File>Open (file type tfr) Bronze Bulk Analysis that was created in step 6.1 above. Then perform a File>New command and enter Cu in the component table (Cu Kα) is the default. A pure bulk Cu spectrum was acquired under the same excitation conditions that were defined for the Bronze application. Recall this file from the tutorial disk/folder Open>File (file type MCA spectra, *.mca) Cu Bulk_adjusted. Process this spectrum as described previously Process>Spectrum>All

9.1.1. Now Setup Quantification to determine the Calibration Coefficient (TCC) for Cu Kα for these excitation conditions – input the Concentration of the Cu in the Component Table to 100% and click Setup>Quant- Fundamental Parameters Calibration Method and click on the Multiple Standard radio button (we will be using 2 pure metals standards) and OK -Figure 10

	Quant Analysis Method	FP Calibration Mode
	Fundamental Parameters	C Standardless
	O FP with Scatter Ratios	One Standard
	O Simple Least-Square Fitting	Multiple Standards
18-68	File Name:	
111-111		

9.2. Generate the Cu Calibration Coefficient – **Calibrate>FP** a TCC calibration coefficient for Cu is generated – Figure 11

X	XRS	-FP									-									
E	le	<u>A</u> cquire	<u>S</u> etup	<u>C</u> alibi	Enter	100%	, for													
	Acq	uire	S	Set k	the pu	ure me	etal	240) (5->2	00) P r	eset:	10	Time: 14,	.5	%DT:[<mark>0.0</mark> X:	0	Y: 0		Z: 0
S	peci	men Com	ponent 1	Fable:								Thick	ness Info	rmatic	on:					
	#	Compo	onent	Туре	Conc	Erro	or L	Jnits	Mole%	Error					Layer	r			N	ormalize
		u		Calc	100.00	0.0 0.0	000 wt.%		0.0000	0.00		Th	ck. Tj	/pe	Error	Units	Density	Fixed	OK	Total
													0.000 Bi	ulk	0.000	mg/cm2	0.000			100.00
												Glo	oal Thresh	nold S	ettings	-		_		
E	leme	ent Table:		Normal	0	Coefficie	ents					n-si	gma 🔻	2.00	00 Clea	ar Con	: Method			
Г	Т	Flement				Mea	surement				Thre	shold	Intensitu		Batio	BOL(ke)	п Гры		nt (alibration
	#┢	Imt Line	Code I	ntensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value	Conc	Method	+	Method	Low H	iah Fit	Meth	od 1	CC Coeff
	1 (Cu Ka	1	9470.08	51.50	87.31	100.000	0.000	0.0000	0.000	0.000		Gaussian	۱.	None	7.865 8	.210 1.4	46 FF	'	42615.58
																u calib	ration	coeff	icier	nt 🔰
	امعد	uromont	t Proces	eina Cor	ditione	G	loseuro	mont	C Pr	000000	.a	1								
	ICas		a TTOCCS		luidons.						'y		()							
l la	ode	Target	X- Filter	Hay Sour	ce ni IV		Тире	Filter	Thick	(um) A	hamber troop	Prese	me (secs)		Monitor					
	1	W	Mo	75.00	47.0	240.0	Sipin	None	e 0.0	0	Air	11636	0.0	14.5	0.0	*				
																-				
1	Sta	tus: Com	nleted FF	^P calibra	tion									_			HI DH	4096	10 8	No 1
lli	Com	ment: FI	P Softwa	re for B	ulk XRF /	Analysis								_		, = , •				
Ľ							_			_	_			-						

Figure 11

- 9.3. To generate the Sn Kα TCC, edit the tfr replacing Cu in the Component Table with Sn and recall the previously collected pure bulk Sn spectrum File>Open (file type MCA spectrum) Sn bulk_adjusted and process the spectrum to extract the net Sn Kα Intensity Process>Spectrum>All
- 9.4.Generate the Sn Calibration Coefficient **Calibrate>FP** a TCC calibration coefficient for Sn is generated Figure 12

X	XRS	-FP						-					1.1	10						
Ei	e /	<u>A</u> cquire	<u>S</u> etup	<u>C</u> alibrate	<u>P</u> roce	ss <u>H</u> elp														
	Acq	uire	S	Set kV/i	IA k	/: <mark>47</mark> (10->40)	uA: 240	0 (5->2	00) Pre	eset:	60	_ Time	e: 46.6	%DT:	0.0 X:	0	Y: 0	2	Z: 0
S	peci	men Com	ponent 1	Table:								Т	ickness	: Informati	on:					
	ŧ	Compo	onent	Туре	Con	c. Err	or L	Jnits	Mole%	Error					Lay	er			No	rmalize
	1 <u>S</u>	1		Calc	100.0	000 0.0)000 wt.%	;	0.0000	0.00	00		Thick.	Туре	Error	Units	Density	Fixed	OK	Total
			`								7		0.000) Bulk	0.000	mg/cm2	0.000			100.00
		Re	place	Cu wi	th Sn	in the	Com	pone	nt Tab	le			ilobal T	hreshold S	Gettings					
ᄂ												<u>∼</u> [-sigma	▼ 2.0	00 Cle	ear Conc	Method			
E	eme	nt Table	•	Normal	0	Coefficie	ents						-							
ΙL	٠L	Element	Cond			Mea	surement				Th	reshold	In	tensity	Ratio	ROI (keV)	Chi2	Qua	nt C	alibration
Ľ	* EI	mt Line	Code	ntensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value	e Co	ic M	ethod	Method	Low Hig	gh Fit	Meth	iod T	CC Coeff
	1 5	n Ka	1	2914.65	16.47	122.48	100.000	0.000	0.0000	0.000	0.00		Ga	aussian	None	24.839 25.	477 0.2	:9 FF		56032.52
															S	n Calibra	ation (Coeff	icient	:
M	eası	irement t	& Proces	sing Con	ditions:	•	Measure	ment	O Pr	ocessin	g									
			X-	Ray Sourc	e:			Detec	tor	Ch	amber		Time (s	ecs)	Monitor					
۱Ľ	ode	Target	Filter	Thick(ur	n) kV	uA	Туре	Filter	r Thick(um) A	tmos	P	eset	Actual	Intensity					
ΙF	1	W	Mo	75.00	47.	0 240.0	Sipin	None	e 0.0	0	Air		60.0	46.6	0.0					
L																-				
ſ	Stat	us: Com	pleted FI	P calibra	tion											2 0	ff Off	4096	10 8	No 1
	Com	ment: Fl	P Softwa	re for Bu	ilk XRF	Analysis														

Figure 12

9.5. These TCC coefficients are easily transferred to the Bronze application by opening the Bronze application –File>Open (file type XRF reports, *.tfr) Bronze Bulk Analysis Enter Cu and Sn intensities in the Intensity fields of the Element Table – any intensities will do for this process – see the example below, Figure 13. Now click Process>Analyze the TCCs calculated from the bulk Cu and bulk Sn spectra (residing in memory) are written to the TCC field of the Bronze Analysis application. The composition reflects the analysis based on the intensities that were manually entered. We now have a Bronze application calibrated to pure bulk Cu and pure bulk Sn. Save this tfr - File>Save As (XRF reports, *.tfr) Bronze Analysis Pure Element Cal.

XRS-FP	
<u>File A</u> cquire <u>S</u> etup <u>C</u> alibrate <u>P</u> rocess <u>H</u> elp	
Acquire Set kV/uA kV: 47 (10->40) uA: 240 (5->200)	Preset: 10 Time: 0 %DT: 0.0 X: 0 Y: 0 Z: 0
Specimen Component Table:	Thickness Information:
# Component Type Conc. Error Units Mole%	Error Layer Normalize
1 Cu Calc 95.9379 0.0000 wt.% 97.7837 2 Sn Calc 4.0621 0.0000 wt.% 2.2163	0.0000 Thick. Type Error Units Density Fixed OK Total
	Global Threshold Settings
Element Table: • Normal C Coefficients	
LEIEment Cond Measurement	Threshold Intensity Ratio ROI(keV) Chi2 Quant Calibration
* Elmt Line Code Intensity Error Backgr. Conc. Error MDL Ato	m% Value Conc Method Method Low High Fit Method TCCCoeff
1 Cu Ka 1 1000.00 0.00 0.00 95.938 0.000 0.0000 97. 2 Sp Ka 1 20.00 0.00 0.00 4.062 0.000 0.0000 2	.784 0.000 Gaussian None 0.000 0.000 FP 42615.58 -
2	
Enter arbitrary intensities to enable auto	
Measureme writing of Cu and Sn pure element TCCs	ıg
on Process>Analyze command	amber Time (secs) Monitor
Targ	tmos Preset Actual Intensity
Status: Completed FP Quantitative Analysis	1 Off Off 4096 10 8 No 1
Comment. IFF Software for Bulk ARF Analysis	

Figure 13

9.5.1.Let's use this new pure elemental metal calibrated tfr to analyze the bronze spectrum.

- Recall the bronze spectrum File>Open (file type MCA spectra, *.mca) Bronze Spectrum_adjusted
- 2. Process the spectrum to extract net intensities Process>Spectrum>All
- Quantify Process>Analyze Figure 14 below. Compare these results to the standardless results – Figure 9. Cu values are within 6% relative and Sn values are within 16% relative.

imes XF	RS-FP			1							10.	н.									×
<u>F</u> ile	<u>A</u> cquire	<u>S</u> etup	<u>C</u> alibrate	<u>P</u> roce	ss <u>H</u> elp																
Ac	quire	ę	Set kV/i	uA kV	: <mark>47</mark> (1	0->40) (JA: 240	(5->20	D) Pres	set: 3	0	Time:	18.3	%DT:	0.0	X: 0		Y: 0		Z: 0	
Spe	cimen Com	ponent	Table:								Thick	ness l	nformati	D n :							
#	Compa	onent	Туре	£on	. 🔪 Erro	r U	nits I	Mole%	Error					Lay	er				N	ormalize	
1	Cu		Calc	/ 78.00	699 0.5	046 wt.%		86.9287	0.561	8 🔺	Th	ick.	Туре	Error	Unit	s D	ensity	Fixed	OK	Total	יך
2	Sn		Calc	21.9	301 0.3	598 wt.%		13.0713	0.214	5		0.000	Bulk	0.000	mg/cr	n2	0.000		~	100.0	0
				-	-						,										
											Glo	bal Thi	eshold S	Settings -							
Ш										Ŧ	n-si	ama	▼ 2.0	00 Cle	ar C	onc M	ethod				
Elen	nent Table:	•	Normal	0	Coefficie	nts						_						~			
[]	Element	Cond			Meas	urement				Thre:	shold	Inter	nsity	Ratio	ROL	(keV)	Chi2	Qua	nt (Calibration	Γ
# [Elmt Line	Code I	Intensity	Error	Backgr.	Conc.	Error	MDL A	tom% ۱	/alue	Conc	Met	hod	Method	Low	High	Fit	Meth	od '	CC Coeff	1
1	Cu Ka	1	5321.08	34.39	52.05	78.070	0.505 0	.0535 8	36.929	0.000		Gau	sian	None	7.865	8.210	0.01	FP		42615.58	<u></u>
2	Sn Ka	1	854.24	14.01	23.38	21.930	0.360 0	.0627 1	3.071	0.000		Gau	sian	None	24.839	25.477	0.01	FP		56032.52	J
																					-
Mea	surement a	& Proces	sing Con	ditions:	• •	leasuren	nent	O Pro	cessing	1											
		X	-Ray Sourc	ce			Detecto	r	Cha	mber	T	ime (sec	s)	Monitor							
Code	Target	Filter	Thick(ur	n) kV	uA	Туре	Filter	Thick(u	m) Atr	nos	Prese	t [.	Actual	Intensity	1						
1	W	Mo	75.00	47.0	0 240.0	Sipin	None	0.00	A	vir	3	0.0	18.3	0.0							
															-						
St	atus: Com	nleted Fl	P Quanti	tative Ar	nalusis										1	Dff	Off .	4096	10 8	No No	1
	mment: Ef	P Softwa	tre for BL	ik XRE.	Analysis	_						_		_	, ,		2				-
Director of					- mary sis				_				_	_							

Figure 14

- 10. <u>Calibration with "Type" Standard</u>: A Type Standard is a standard material having composition similar to the materials that will be analyzed with the system calibration. This is often the preferable standardization method, particularly if the standard is derived from the same process as the unknowns in a routine analysis regime. For the tutorial we will use the bronze spectrum that we have been employing as the Type Standard spectrum and the composition determined from the pure element calibration rounded values.
 - 10.1. From the XRS-FP Analyzer interface, recall the newly created, calibrated tfr, Bronze Bulk Analysis Pure Element Cal: File>Open (type file XRF report) Bronze Bulk Analysis Pure Element Cal
 - 10.2. The intensities in this tfr file are those from the Bronze Spectrum_adjusted.mca, so, it is not necessary to reprocess the spectrum, but we will round the composition to 78 wt% Cu and 22 wt% Sn. Enter **these values in the Conc.** column of the Component Table. So, we have the net intensities and composition of the Type Standard defined.
 - To Calibrate, determine Calibration Coefficients from the Bronze Type Standard click
 Setup>Quant click on the Single Standard radio button and OK
 - 10.4. Generate Calibration Coefficients click Calibrate>FP you will note a small change in the TCC values due to the rounding of the standard composition Figure 15 below. At this point you would want to save the Type Standard Calibration to a new name File>Save As (file type, XRF report, *.tfr) Bronze Bulk Analysis Type Std

🗙 XRS-FP		(A. R. R.)										
Eile Acquire Enter Standard Compo	osition 240 (5->200) Preset:	30 Time: 18.34865 %DT:	0.0 X: 0 Y: 0 Z: 0									
Specimen Component Table: # Component Type Conc. Err 1 Cu Calc 78.0000 0.5 2 Sn Calc 22.0000 0.3	or Units Mole% Error 1046 wt.% 86.9287 0.0000 1598 wt.% 13.0713 0.0000	Thickness Information:	er Normalize Units Density Fixed OK Total									
		Global Threshold Setting	Note changed TCCs following									
Element Table: (* Normal C Coefficie # Element Cond Mea # Element Line Code Intensity Error Backgr. 1 Cu Ka 1 5321.08 34.39 52.05 2 Sn Ka 1 854.24 14.01 23.38	Ints Th surement Th Conc. Error MDL Atom% Value 78.000 0.000 0.0000 0.000 0.000 22.000 0.000 0.0000 0.000 0.000	rreshold Intensity Ratio e Conc Method Method 00 Gaussian None 00 Gaussian None	ROI (keV) Chi2 Quant Calibration Low High Fit Method TCC Coeff 7.865 8.210 0.01 FP 43890.28 24.839 25.477 0.01 FP 57330.75									
Measurement & Processing Conditions:	easurement C Processing											
Code X-Ray Source	Detector Chamber	r Time (secs) Monitor										
Larget Filter Thick[um] kV uA 1 W Mo 75.00 47.0 240.0	Iype Filter Thick(um) Atmos Sipin None 0.00 Air	Preset Actual Intensity 30.0 18.3 0.0										
Status: Completed FP calibration 1 Off 4096 10 8 No 1 Comment: FP Software for Bulk XRF Analysis												

Figure 15