Standard Operating Procedure Rigaku ZSX Primus II XRF



Yale West Campus Materials Characterization Core *ywcmatsci.yale.edu* ESC II, Room A119C 810 West Campus Drive West Haven, CT 06516

Version 2.0, February 2024

- Please FOLLOW the SOP strictly to keep the facility in good condition. Any explorations are strongly prohibited unless permitted by lab manager.
- **Only** use the Core USB drive on the XRF computer.
- **NEVER** surf the web on the computer to minimize the risk of the computer being hacked
- Users should acknowledge MCC in their publications. The general acknowledgement for XRD should read:
 - "The XRF data was taken using the Rigaku ZSX Primus II at Yale West Campus Materials Characterization Core."
- The core reserves the right to use the data for core promotion.

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Rigaku ZSX Primus XRF Standard Operating Procedure

- 1 Introduction
 - 1) Instrument features:
 - > Wavelength Dispersive X-ray Fluorescence (WDXRF) systems with high resolution (typically 5 20 eV) and minimal spectral overlaps
 - > Analysis of elements from Be to U
 - > Tube above optics minimizes contamination issues
 - > Micro analysis to analyze samples as small as $500 \ \mu m$
 - > Mapping feature for elemental topography/distribution
 - > Helium seal means the optics are always under vacuum
 - 2) Location

Materials Characterization Core Room A119 810 West Campus Drive West Haven, CT 06516

3) Primary Staff Contact

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The Yale West Campus MCC Facilities are operated for the benefit of all researchers. If you encounter any problems with this facility, please contact the staff member listed above immediately. There is never a penalty for asking questions. If the equipment is not behaving exactly the way it should, contact a staff member.

Notice: Please **follow** strictly the **SOP** to keep the facility under good condition. Please **DO NOT** explore the operation program unless approved by core manager.

2 System status check

- 1) Sign in the logbook on the bench.
- 2) Check the **Spectrometer Status** below and make sure no warning messages appear. If not, contact the manager immediately.



3 System Startup

1) On the top menu, click on Startup/ Shutdown > Startup> to open the Spectrometer Startup window below:

٠	Initialize spectrometer
	Turn on x-ray
	Age x-ray tube
	Aging time:31min.
llı.	🗌 Adjust PHA
	🗌 Wait 🚺 🖃 min. and adjust
	Setting
	Position E - 1 -
	Detector PC SC

2) If a popup window below shows up



3) Click OK button above and check the small boxes in front of Initialize spectrometer, Turn on x-ray and Age x-ray below to finish the system startup/warmup. It could take from 31mins to 1 hour, depending on if the time since last use.

 Initialize spectrometer Turn on x-ray Age x-ray tube Aging time: 31 min. Adjust PHA Wait 1 min. and adjust Setting Position E 1 min. 	 Initialize spectrometer Turn on x-ray Age x-ray tube Aging time: 31 min. Adjust PHA Wait 1 min. and adjust Setting Position E - 1 Detector PC SC 	🗄 Spectr	ometer Startup 📃 🖃 🗾 💌
Aging time: 31 min.	Aging time: 31 min.		 Initialize spectrometer Turn on x-ray Age x-ray tube
Adjust PHA Vait 1 min. and adjust Setting Position E 1 Detector	Adjust PHA Wait 1 min. and adjust Setting Position E - 1 Detector PC SC		Aging time:31min.
Setting Position E - 1 - Detector ZPC ZSC	Setting Position E - 1 - Detector PC SC		Adjust PHA Wait min. and adjust
Position E - 1 - Detector VPC VSC	Position E - 1 - 1 - Detector PC SC		Setting
Detector VPC VSC	Detector V PC V SC		Position E - 1 -
			Detector 🔽 PC 💽 SC

- 4 Check PHA Analysis result
 - a) Once the measurement finishes, click the Maintenance > Maintenance Records > PHA Adjustment on the top menu.

b) In the PHA adjustment Record window below with PC (proportional counter) highlighted on the top, scroll down to the bottom and click the most recent time record. A red line will show up at the end of the Trend graph of Resolution curve as show below:



c) Move the mouse to the red line, right click and select PHA curve on the popup menu top open the PC Al-KA window below. Make sure the Gaussian shaped peak is centered at 200 and intensity between 4.0 and 6.0 kcps as highlighted. Contact the manager if not.



d) Close the window above and click SC (scintillator counter) button on the top of the PHA Adjustment Record window as shown below. Scroll down to the bottom and click the most recent time record. A red line will show up at the end of the Trend graph of Resolution curve as show below:



e) Move the mouse to the red line, right click and select **PHA curve** on the popup menu top open the **SC Al-KA** window below. Make sure the Gaussian shaped peak is centered at 200 as highlighted and intensity between 6.0 and 8.0 kcps. Contact the manager if not.



- 1) For solid samples, make sure the surface is flat and the sample is larger than chosen metal masks of the sample holder. Blow the surface with nitrogen inside the fume hood.
- 2) For powder samples, sandwich with prolene membranes provided by core. Maximize the surface area to increase the signal counts.
- 3) No liquid sample allowed.

6 Setting up Application File

1) Click **Qual Application** on the top menu to open the Application File setup window below:

Application File	Application File	
Ŷ		
Select Element Range		
Ŷ	Create a new application	
Sample Preparation	Modify an existing application	
	Rename and save the application	
	Delete an application	
Parameters	Print application information	
4	Output application information to Excel book	
Check Measuring Condition	This flow bar allows you to manage all aspects of qualitative analysis	
Ŷ		
Output Information	dialogs. It's also possible to save your application as a template [Rename and	
Ţ,	save application].	
Fuit	Press the [Next] button after making your choice.	
Con		
		Ŧ
	Back Next Cance	el

- 2) Select Create new application or Modify an existing application and click Next button.
 - a) Inside the Select an Application Template window, select Metal & Alloy.
 - b) Create the **Name of application** and choose/create a folder to save the application file. Click **Finished** button.

3) Ins the Select Element Range window below:

Heavu				D								_	1							Finad angle alam
Heavy(1)				D.	0						.0		J				TPO			Fixed angle elem.
Ca-KA K-KA		H					Q	ual e	leme	ents									He	Overlapped elem.
CI-KA S-KA		Li	Be				Fi	ked a	angl	e ele	eme	nts		в	с	N	0	F	Ne	
P-KA Si-KA		Na	Mg				0	/erla	ppe	d el	eme	nts		A1	Si	P	s	CI	Ar	
AI-KA Ma-KA		к	Са	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Na-KA		Rb	Sr	Y	Zr	Nb	мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe	
-ка) -ка		Cs	Ba	LA	Hf	Ta	w	Re	Os	Ir	Pt	Au	Hg	TI	Рb	Bi	Po	At	Rn	
		Fr	Ra	AC																
		I	.A	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Тb	Dy	Но	Er	Tm	Yb	Lu		
	-	4	١C	Ac	Th	Pa	υ	Np	Pu											
Delete al																				Delete all

- a) Click **Delete all** button on the bottom left corner to remove the elements already listed in the left space for Qualitative analysis.
- b) Select interested elements inside your sample by clicking on the periodic table which will appear yellow in the table and appear in the left side space as shown below:



c) Click the **Fixed angle elem.** button on the top right corner of the window above and click previously chosen elements which will appear cyan and listed in the right space for the **Fixed angle analysis** as show below:

Jualitative a	analysis					_													22	Fixed angle analysis		
3 -KA C -KA	~			B-	J					F	-U]		L		Ti-U			Fixed angle elem.		
N -KA) -KA		H					Qu	ial e	leme	ents									He	Overlapped elem.		
-KA		Li	Be				Fix	ed a	angl	e ele	emer	nts		в	с	N	0	F	Ne	B ·KA(FA) C ·KA(FA)		
		Na	Mg				0	/erla	ppe	d ele	eme	nts		A1	Si	р	S	CI	Ar	N -KA(FA) 0 -KA(FA)		
		к	Са	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	F-KA(FA)		
		Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
					Cs	Ba	L.A	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	Tİ	Pb	Bi	Po	At	Rn
				Fr	Ra	AC																
		I	A	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	УЪ	Lu				
		4	IC.	Ac	T'n	Pa	U	Np	Pu													
Delete	all																			Delete all		

a) Click Next button above top open the Sample Preparation for Metal & Alloy window below. **For powder sample** that has been sandwiched between prolene

P.Film	-				
					*
					-
	>	>	>	> Next	> Next Cance

films, check **Used** box and select **Prolene** in the dropdown menu. **For solid samples**, leave the **Used** box unchecked.

Sample Prepara	ation for Metal & Alloy	×
V Used	P.P.Film	
Memo	P.E.Film Prolene Kapton P.E.F-5u P.E.3.6u P.E.3.5u	^
Show op	ETNOM 3.0u	Next Cancel

4) Click the Next button above top open the Parameters window below:

•	
•	
•	
✓ Sealing	OUT 🔻
•	
•	
]	
]	
• Туре	-
Data	-
]	
	Sealing Sealing Type Data

- a) Memo: leave it blank.
- b) Measuring diameter: 20 mm if using 30mm metal mask on the sample holder;
 10 mm if using 20mm mask to avoid signals from the metal cover. Make sure your samples are larger than the metal mask openings.
- c) Atmosphere: Vacuum.
- d) **Sealing**: OUT (for solid samples).
- e) Component type: Metal.

- f) Balance: None. Unless there are possible impurities to choose from.
- g) Machine library: Do not use. Unless created before from standards.
- 5) Click Next button.
- 6) In the Check Measuring Condition window:
 - a) Double click each row top open the Scan Condition for specific element.
 - b) If an element has a small concentration/mass %, choose the **Step** of 0.010 degrees and change the **Speed** to 1-10 degrees/minute.
 - c) Click blue FA labeled row to open the Fixed Angle Condition for specific element. For small concentration elements, choose larger numbers for **Time Peak** and **Background**.
- 7) Click **Next** button.
- 8) In the **Output Information** window:
 - a) Chart output: Yes.
 - b) Peak list: Yes.
 - c) SQX result: Yes.
 - d) **Smoothing**: keep default values unless further smoothing of less smoothing is required on collected spectral peaks.
 - e) Check the box in front of the **Output detection limit for undetected element**.
 - f) Click Next and Exit buttons to finish the Application File Setup.

7 Survey Scan

1) Click EZ Analysis in the top menu and click EZ Scan button in the Sample ID Setting window below:



2) Double click the first row inside the table to open the EZ Scan - SEQ# window below:

5 ample pos	ition		Sample n	ame Operator	Comments
Position: A	• • 1	▼ Select		III.	,
Sample typ	e l	Meas. range	🔹 Diame	ter 🕴	Time
		F to U		▲ .	Long
Metal & A	Alloy		3	30mm	Standard
•		B to U		• I	Short
Advanced					
le name:	Plastic ref00	01]		
older	Common			- Browse	

a. **Position**: click the Select button and choose the right sample holder position from 2D array panel below:

5 ample posit	ion				Sample	e name	Operator	Comments
Position: A	▼ · 1	•	Select					
		(0	00	🔵 н	1	
Sample type	•	Meas.		00		🔵 G		Time
		- (00		🔵 F		Long
Motol 9 Al	leu	(0		e		Chandard
Metal & Al	iloy			0		🔵 D		Stanuaru
-		в		00		O C		Short
		(00		🔵 В		
Advanced	J	(0		O A		
le name:	Plastic ref00	1	1 2	3 4	4 5	6		
older:	Common		_			•	Browse	

- b. Sample type: leave Metal & Alloy unchanged.
- c. Meas. Range: choose F to U or B to U based on sample requirements.
- d. Diameter: choose 20mm for 30 mm metal mask and 10mm for 20 mm mask.
- e. **Time**: choose **Standard** (~15 mins) or **Long** (~30 mins) if survey scan is more interested than elemental scan for known matrix elements.

- f. File name: type in the filename specific to each sample.
- g. Folder: click Browse button and choose/create folder for data storage.
- h. Click **OK** to finish EZ Scan setup.
- 3) Repeat the steps above to finish rest of samples.
- 4) Click Analyze button on the bottom corner of the Sample ID Setting window to start scan.

8 Elemental Scan

1) Click sample ID button in the **Sample ID Setting** window below:

Sample po	osition		Sample informa	tion	
Position:	A ▼ · 3	▼ Select	Sample name	Operator	Comments
Analytical	condition				Mapping
		Sort by name	•		Ocenter
	Sample type	Memo			Mapping Select
	cvd films	TiO2			
	🗊 test				points
					Mapping file
					Setting
	Folder:	XRF users Vaso	nLi	•	
Result out	put				Manual input data
					Input Data
File name:	TiO2_opp001				
					Input Data

- a) Click **Qual** button on top of the window.
- b) **Position**: click the Select button and choose the right sample holder position from 2D array panel below:

Qual	Quant Control			•
Sample po	osition	Sample informat	tion	
Position: (A ▼ · 3 ▼ Select	Sample name	Operator	Comments
		ООО Н ООО Б		
Analytical	condition	F		Mapping
	Soi 🗢 🔵	E		Ocenter
				Mapping Select
	Sample type			
	Test			points
	1 2	3 4 5 6		Mapping file
				Create mapping file
	Folder: VPE upper VI	an li		Setting
Result out	tput	3001 EI		Manual input data
9				Input Data
ile name:				Sample size
older:	Common	▼ Bi	rowse	Data not entered

- c) Analytical condition: click on the Folder space highlight above and select the folder where the application file was created; choose the right file to use if more than one was listed.
- d) Mapping: choose Center to skip mapping.
- e) File name: type in the filename specific to each sample.
- f) Click **OK** to finish Elemental Scan setup.
- 2) Repeat the steps above to finish rest of samples.
- 3) Click **Analyze** button on the bottom corner of the **Sample ID Setting** window to start scan.

9 Check Mass% Results

- 1) Close the **Sample ID Setting** window.
- Click Data Processing on the top menu and choose Qual Result > SQX Calculation as shown below:

ZSX - Spectrometer Status		¥ g	7. II 💿 🕽			💬 Type a message h	ere
File Window Help					4		
0 🛱 🖬 🐰 🖬 🛍 🖨 🔘							
	N	1	8		C	Ø	
EZ Analysis Analysis	Data Processing	Qual Application	Quant Application	Utility	Maintenance	Startup / Shutdown	Micro Mapping
2128 days have passed since last data save. S	Qual Result	· <u>st</u>	Qual Data Handling	Save			
	Result Displ	ay 🔀	SQX Calculation				
	Quant Simu	lation					
	Mapping						

3) In the SQX Calculation window below:

SQX Calculation									
Plastic sample Browse Calc. Condition Calculate Print									
Sample : Date analyzed : 2024- 2-15 12:40									
Sample type : M	Sample type : Metal & Alloy Component type : Metal Matching library :								
Sample film corr. :	Sample film corr. : Impurity corr. :								
Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)		
С	62.5694	mass%	0.05277	C-KA	40.6397	59.4902			
0	37.4246	mass%	0.23343	0 -KA	2.7881	35.5829			
AI	0.0013	mass%	0.00045	AI-KA	0.0350	0.0013	0.0133		
Si	0.0033	mass%	0.00054	Si-KA	0.0986	0.0031	0.0197		
Mo	0.0014	mass%	0.00022	Mo-KA	6.9512	0.0013	14.2943		
Insert	Mo 0.0014 mass% 0.00022 Mo-KA 6.9512 0.0013 14.2943								

- a. Click **Browse** button above to locate the data folder and choose the **File name** in the popup **Data File Selection** window.
- b. Click **Calc. Condition** button to change the **Sample type**, **Comp. type** and other settings if needed in the **Calculation Condition** window. Click **OK** to quit the window.
- c. Click **Calculate** button to refresh the mass% result after modifying settings in the step above.
- d. Click **Insert**, **Delete**, **Change** or **Add** button to modify matrix elements for mass% calculation if needed, and click **Calculate** button to refresh the result.
- 4) Mass% result table export:
 - a. Click **File** > **Data Export...** on the top menu.
 - b. In the **Data Export** window, **Browse** to find the right folder. Change the **File name** if needed and click **OK** to finish.
- 5) Close the **SQX Calculation** window after finish. Click **Yes** on the popup **Confirmation** window.

10 Check spectra

 Click Data Processing on the top menu and choose Qual Result > Qual Data Handling as shown below:



 Choose the collected data file from the File Load window and click OK to open the Qual Data Handling: File Window as shown below:

stic sample 2024- 2-15 1 onditions Reference F	12:40 iles		Plastic	sample		•	Browse
Spectrum	Crystal	Start	End	Step	Unit	*	All
✓ Heavy	LiF(200)	5.000	90.000	0.020	deg		All Class
 Heavy(1) 	LiF(200)	13.000	19.000	0.020	deg	=	All Clear
🗹 Ca-KA	LiF(200)	110.000	116.000	0.050	deg		
🗹 K-KA	LiF(200)	133.000	140.000	0.050	deg		
🗹 CI-KA	Ge	89.930	95.930	0.050	deg		
S-KA	Ge	107.020	114.020	0.050	deg		
P-KA	Ge	136.870	143.870	0.050	deg		
Si-KA	PET	105.980	111.980	0.050	deg	-	

- 3) Select interested elements and click Open button to check spectra.
- 4) Spectra data export:
 - a. Click File > Transfer Qual Data... on the top menu to open the Qual Data Transmission window below:

File selection			1	
Demo-2016 🔺	File	Application	Sample name	Me
⊕ Training	✓ 110416_quar	. F-U_Solid_N_013	110416_quarter	2016-
🗄 🔒 XRF users	111116 penn	. COINS	1111116 penny 2	2016-
🕀 📕 Asa Car	111116_pen	F-U_Solid_N_015	TTTTT6 penny	2016-
Bingjun	2016 1028	F-U Solid N 002	penny 2 2n	2016-
enarre cdi Dequar ▼				
	•	m		•
Data tupe	Section and			
Element info	Text format	Spread sheet forma	t ▼ · CSV	
SQX result	Trans. method	Disk save	-	
🔘 Peak list	Send to		-	
2-theta - intensities	Folder			
Output w/o normal	C:WRF U	sers/Jason Li\2-19-24	Brows	e
	Eile name	File cev		

- b. Choose the interested data file from the window above.
- c. Data type: 2-theta-intensities.
- d. Text format: Spread sheet format and CSV.
- e. Trans. Method: Disk save.
- f. Folder: choose/create the output folder.
- g. File name: create output data filename.
- h. Click **OK** to finish.
- 5) Close the **Qual Data Handling: File Window** after finish.

11 Closing Steps

1) Click Startup / Shutdown on the top menu and click Shutdown.

File Window Help								
	B 🖨 🕖							E 6 6 2
EZ Analysis	Analysis	Data Processing	Qual Application	Quant Application	Utility	Maintenance	Startup / Shutdown Micro Mapping	
2128 days have passed since last data save. Save data to a external storage or other PC.				Data Save		Spectrometer Status		
							Startup	
							Tube / Atmosphere Change	
							Shutdown	

 In the Spectrometer Shutdown window below, select Manual shutdown, choose Turn off x-ray and click Start. If not planning to use the machine within a week, also choose Secure atmosphere (to stop vacuum pumping) and click Start.

🖺 Spectrometer Shutdown	
Manual shutdown	
Turn off x-ray	•
Secure atmospher	e
Automatic power-off	
Method Standby	
Unload	Stop Start

- 3) Wait for the x-ray power is turned off and the pump has stopped pumping.
- 4) Keep the ZSX software open.
- 5) Upload your data to the cloud drive such as Box or One Drive. DO NOT use personal USB drive.
- 6) Sign off the logbook.
- 7) Clean the bench sample preparation area, the sample holders and glass slides with clean wipes and isopropanol.
- 8) Put the sample holder and other tools back into the toolbox.