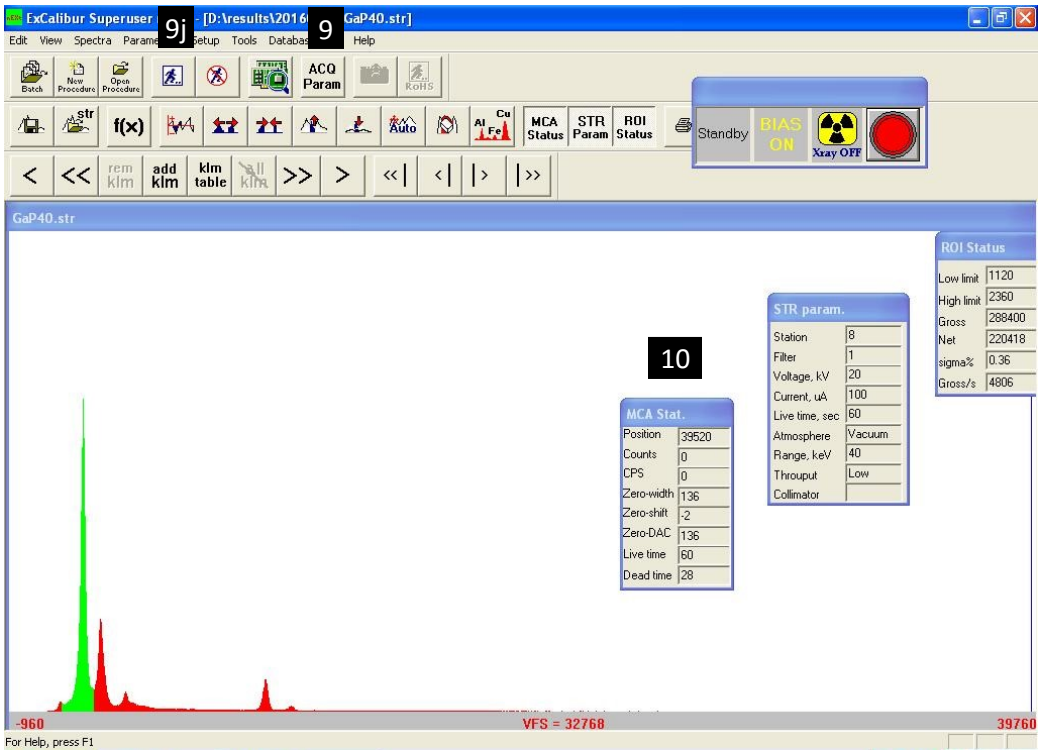
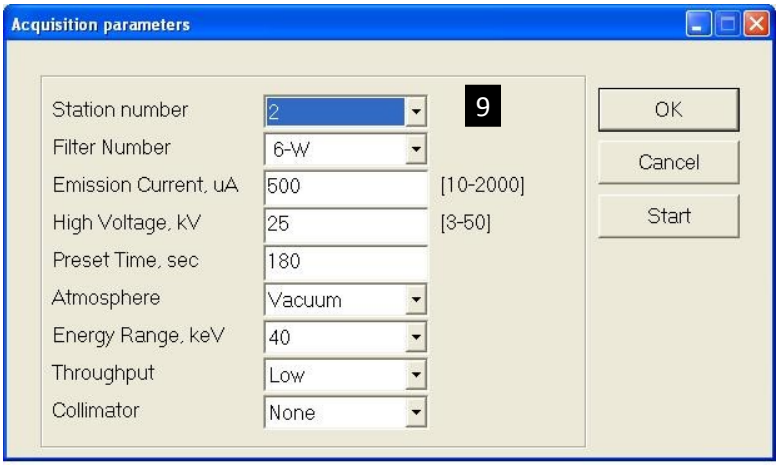
Standard Operating Procedure for XRF (Ex-Calibur)

1. Prepare the sample holder(s) for your measurement by installing a new Mylar film onto the plastic cups. Instrument can measure up to 8 samples per cycle
2. Put your sample(s) into the cup(s). Sample can be in any form (fine powder, solid pellet, thin film, liquid, etc.). If you have to prepare standards for quantitative analysis (semi-quantitative measurements do not require standards), make sure that the standards have the same form with your samples (X-ray absorption coefficient must be similar)
3. Make sure instrument is idle by checking that the X-ray safety red light is turned off. Login in NUCore to have the screen of the computer turned on
4. Start 'nEXt' software (icon on the desktop) and
    a. Provide a user name (e.g., your first name)
    b. Type the number seven (7) in the password field
    c. Under 'Initialization Mode' select 'Full Initialization' (default)
    d. Under 'Mode' select 'Superuser'
    e. Press on the 'Next>>' button
    f. Initialization will run for a few seconds, and 'MCA' and 'Controller' status should change to 'OK'
    g. Press on the 'Superuser' button, 'Spectra view' window opens up
5. Open the sample tray door and install your sample's cup(s) in the appropriate tray positions numbered from 1 to 8. If sample chamber is under vacuum and you cannot open the door, in 'Spectra view', go to 'Tools' menu and select 'Vacuum off'. System will purge the chamber and you should be able to open the door now



6. Close the Autosampler door. If the door is not completely closed the interlock system will not allow the X-ray tube to be energized. Use vacuum for any form of sample except liquids. If the vacuum pump is switched off, press the red ON/OFF switch on the power strip at the bottom right side of the instrument table

7. Move the X-ray Enable/Disable switch (on the top right corner of the instrument) to the 'Enable' position. Red light next to the switch turns on
8. When the instrument is not used for more than 24 hours it is necessary to gradually condition the X-ray tube before using very high voltage (>20 kV) acquisitions (for elements heavier then Rubidium). Warm up is not necessary for voltages below 20 kV (for Sodium to Bromine). Under 'Tools' menu, click on the 'Run Warmup batch' option if you want to operate above 20 kV
9. Set the acquisition parameters for your sample(s) by pressing on the 'ACQ Param' button on the icon bar. In the acquisition parameter window, you need to set:
   a. The position of your sample in the autosampler (1-8) under 'Station number'
   b. Filter in front of the X-ray beam. When a filter is placed between the tube and the sample, then X-rays below the K-edge of the filter will be absorbed, improving the signal to background ratio for elements of interest and hence improving precision and detection limit. The filter reduces the beam intensity by eliminating X-rays which are not producing a useful signal. Based on the elements you have in your material, select:
      i. '1-None' for all light elements (Cu and below) expect S and Cl
      ii. '2-Ti' for all light elements (Fe and below) except for Ti and Sc but including S and Cl
      iii. '3-Fe' for all light elements (V and below)
      iv. '4-Cu' for Fe and above (50 kV)
      v. '5-Rh' for Ca to Mo (25-40 kV)
      vi. '6-W' for As to Ru (50 kV)



   c. 'Emission Current, uA' must be set high enough to have >500 counts per second (CPS) but at the same time keeping the detector dead time between 25% and 35%. Set the current at 10 uA and use your highest concentration sample to find the optimum current
   d. 'High Voltage, kV' must be set approximately 1.5x to 2x the amount of energy required to excite the element of interest. Use the attached tables to look for the emission lines of your elements, e.g., Kβ1 line of Cobalt is ~ 7.65 kV which means you have to use a voltage value of at least 12 kV (1.5 x 7.6 kV) in order to excite Co efficiently

e. 'Preset time, sec' will vary depending on the concentration of the element of interest. If you are looking at high concentrations (%), use 60-180 s. If you are looking at ppm concentrations, 180-300 s would be used. For liquids, a good time would be 180-240 s due to sagging of the X-ray film in the cup, and evaporation

f. 'Atmosphere' can be set to 'Vacuum' for all forms of sample except for liquids which you need to select 'Helium'. Make sure the main valve on the Helium cylinder is opened

g. 'Energy Range, keV' can be either '10' or '40'. Depending on the emission energies of your elements choose the appropriate range

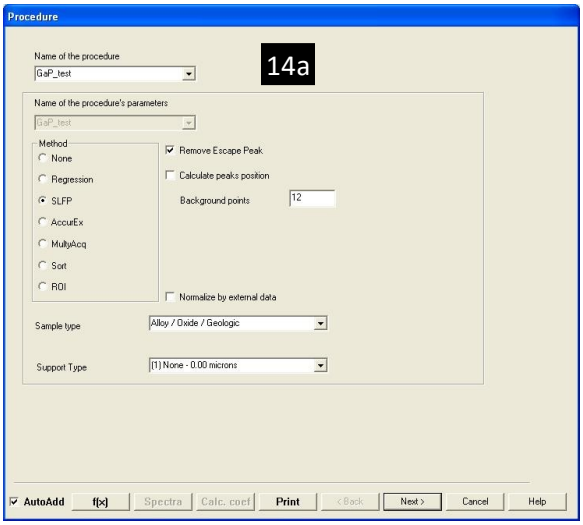
h. 'Throughput' at 'Low'

i. 'Collimator' at 'None'

j. Click on the 'Start' button and acquisition will start in a few seconds. Alternatively, you can press on 'OK' and click on the 'Run' button 

10. During acquisition, press on the 'MCA Status' button to see information such as CPS, dead time, etc. If dead time is too low (< 20) or too high (50>), or CPS is <500 you need to adjust the 'Emission Current, uA'. To stop the collection and change the acquisition parameter: Press on the 'Stop' button (icon with running person and a red line through) and set 'Emission Current, uA' to a higher value, e.g., 50 uA
11. A good spectrum should have enough counts (> 5,000) and a high signal-to-noise ratio
12. Collect spectra of your samples and standards using the same acquisition conditions
13. During or after a collection of a spectrum, you can identify all peaks by either right clicking on the spectrum and select 'Identify Peaks' or clicking on the Peak Identification icon 
14. Go to 'Edit' menu and select 'New procedure' to build a measurement procedure where you define the elements of interest to be quantified, acquisition parameter for the data collection, etc.

a. **For semi-quantitative analysis:**



i. Set the name of your procedure at 'Name of the procedure'

ii. Select 'SLFP' as a 'Method' (StandardLess Fundamental Parameters)

iii. Tick the 'Remove Escape Peak' option

iv. Untick the 'Calculate peaks position'

v. Set 'Background points' to '12'

vi. Select the appropriate sample type under 'Sample Type'

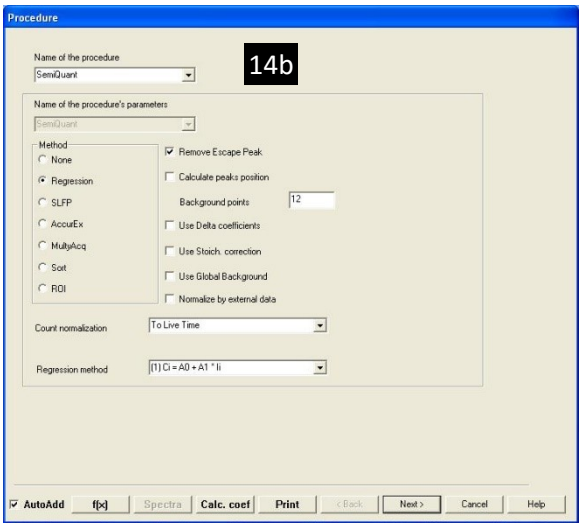
vii. 'Support type' is typically Mylar. Press on the 'Next' button

viii. Under 'Acquisition Parameter' tab, define all acquisition parameters using the optimum values determined in step 7 and press on the 'Next' button

ix. Select your 'Elements of Interest' from the periodic table on the tab and press on the 'Next' button

b. **For quantitative analysis (measured standards for creating a calibration curve are required):**

i. Set the name of your procedure at ‘Name of the procedure’
ii. Select ‘Regression’ as a ‘Method’
iii. Tick the ‘Remove Escape Peak’ option
iv. Untick the ‘Calculate peaks position’
v. Tick the ‘Use Stoich correction’ box and put ‘100’ if the concentration of all of your elements adds up to 100%
vi. Set ‘Count normalization’ to ‘To Live Time’
vii. Use linear equation (1) as a ‘Regression method’ and press on the ‘Next’ button
viii. Define all acquisition parameters using the optimum values determined in step 7 and press on the ‘Next’ button



ix. Select your ‘Elements of Interest’ from the periodic table on the tab and press on the ‘Next’ button
x. (Optional) Can you set concertation limits under the ‘Criterion’ tab
xi. On the ‘Standards’ tab press on the ‘Add standard’ button and load one by one all the files measured for your standards by starting with your Blank spectrum
xii. Enter the concentration next to each standard after you have added all files. After you have finished entering the standard concentration click on another ‘concentration box’ to register the last number into the database
xiii. Click on the ‘Calculate Coefficient’ tab. An asterisk in the field indicates for the computer to calculate that term. ‘A0’ is the intercept and ‘A1’ is the slope. If you have more than 3 standards put an asterisk on the ‘A0’ term
xiv. Click on the "Calc. coef" button at the bottom of the window. This will calculate the regression graph
xv. Click on the ‘Report’ tab
    - ‘Show Coefficient’ button will show you the value of each linear term, standard deviation, correlation, etc.
    - ‘Show Report’ button will show the calculated and actual concentration comparisons
    - ‘Show lines’ will show the graph of the regression
xvi. Click on the ‘Save’ button to save the procedure

15. Go to ‘New Batch’ under the ‘Edit’ menu to build the ‘Batch’ sequence where you can associate the sample position in the autosampler (1 thru 8) with a specific procedure you have created in step 7
16. When measurement is done:
    a. Remove the cup(s) with your sample(s), disassemble each cup and remove the Mylar film. Take the contaminated Mylar film back to your lab for disposal (do not leave it next to the instrument or though it in the trash can)
    b. Leave the chamber under vacuum and close the main valve on the LHe cylinder
    c. Move the X-ray Enable/Disable switch to the ‘Disable’ position. Red light next to the switch turns off
    d. Remove any vials, weighing paper, etc. you may have left in the room

e. Logoff from NUCore

X-Ray Data Booklet Table 1-2. *Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines.*

Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha_1$
3 Li	54.3								
4 Be	108.5								
5 B	183.3								
6 C	277								
7 N	392.4								
8 O	524.9								
9 F	676.8								
10 Ne	848.6	848.6							
11 Na	1,040.98	1,040.98	1,071.1						
12 Mg	1,253.60	1,253.60	1,302.2						
13 Al	1,486.70	1,486.27	1,557.45						
14 Si	1,739.98	1,739.38	1,835.94						
15 P	2,013.7	2,012.7	2,139.1						
16 S	2,307.84	2,306.64	2,464.04						
17 Cl	2,622.39	2,620.78	2,815.6						
18 Ar	2,957.70	2,955.63	3,190.5						
19 K	3,313.8	3,311.1	3,589.6						
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9			
21 Sc	4,090.6	4,086.1	4,460.5	395.4	395.4	399.6			

Table 1-2. *Energies of x-ray emission lines (continued).*

Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha_1$
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4			
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2			
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8			
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8			
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5			
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4			
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8			
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8			
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7			
31 Ga	9,251.74	9,224.82	10,264.2	1,097.92	1,097.92	1,124.8			
32 Ge	9,886.42	9,855.32	10,982.1	1,188.00	1,188.00	1,218.5			
33 As	10,543.72	10,507.99	11,726.2	1,282.0	1,282.0	1,317.0			
34 Se	11,222.4	11,181.4	12,495.9	1,379.10	1,379.10	1,419.23			
35 Br	11,924.2	11,877.6	13,291.4	1,480.43	1,480.43	1,525.90			
36 Kr	12,649	12,598	14,112	1,586.0	1,586.0	1,636.6			
37 Rb	13,395.3	13,335.8	14,961.3	1,694.13	1,692.56	1,752.17			
38 Sr	14,165	14,097.9	15,835.7	1,806.56	1,804.74	1,871.72			
39 Y	14,958.4	14,882.9	16,737.8	1,922.56	1,920.47	1,995.84			
40 Zr	15,775.1	15,690.9	17,667.8	2,042.36	2,039.9	2,124.4	2,219.4	2,302.7	

41	Nb	16,615.1	16,521.0	18,622.5	2,165.89	2,163.0	2,257.4	2,367.0	2,461.8	
42	Mo	17,479.34	17,374.3	19,608.3	2,293.16	2,289.85	2,394.81	2,518.3	2,623.5	
43	Tc	18,367.1	18,250.8	20,619	2,424	2,420	2,538	2,674	2,792	
44	Ru	19,279.2	19,150.4	21,656.8	2,558.55	2,554.31	2,683.23	2,836.0	2,964.5	
45	Rh	20,216.1	20,073.7	22,723.6	2,696.74	2,692.05	2,834.41	3,001.3	3,143.8	
46	Pd	21,177.1	21,020.1	23,818.7	2,838.61	2,833.29	2,990.22	3,171.79	3,328.7	
47	Ag	22,162.92	21,990.3	24,942.4	2,984.31	2,978.21	3,150.94	3,347.81	3,519.59	
48	Cd	23,173.6	22,984.1	26,095.5	3,133.73	3,126.91	3,316.57	3,528.12	3,716.86	
49	In	24,209.7	24,002.0	27,275.9	3,286.94	3,279.29	3,487.21	3,713.81	3,920.81	
50	Sn	25,271.3	25,044.0	28,486.0	3,443.98	3,435.42	3,662.80	3,904.86	4,131.12	
51	Sb	26,359.1	26,110.8	29,725.6	3,604.72	3,595.32	3,843.57	4,100.78	4,347.79	
52	Te	27,472.3	27,201.7	30,995.7	3,769.33	3,758.8	4,029.58	4,301.7	4,570.9	
53	I	28,612.0	28,317.2	32,294.7	3,937.65	3,926.04	4,220.72	4,507.5	4,800.9	
54	Xe	29,779	29,458	33,624	4,109.9	—	—	—	—	
55	Cs	30,972.8	30,625.1	34,986.9	4,286.5	4,272.2	4,619.8	4,935.9	5,280.4	
56	Ba	32,193.6	31,817.1	36,378.2	4,466.26	4,450.90	4,827.53	5,156.5	5,531.1	
57	La	33,441.8	33,034.1	37,801.0	4,650.97	4,634.23	5,042.1	5,383.5	5,788.5	833
58	Ce	34,719.7	34,278.9	39,257.3	4,840.2	4,823.0	5,262.2	5,613.4	6,052	883
59	Pr	36,026.3	35,550.2	40,748.2	5,033.7	5,013.5	5,488.9	5,850	6,322.1	929
60	Nd	37,361.0	36,847.4	42,271.3	5,230.4	5,207.7	5,721.6	6,089.4	6,602.1	978
61	Pm	38,724.7	38,171.2	43,826	5,432.5	5,407.8	5,961	6,339	6,892	—
62	Sm	40,118.1	39,522.4	45,413	5,636.1	5,609.0	6,205.1	6,586	7,178	1,081

Table 1-2. *Energies of x-ray emission lines (continued).*

Element	Kα_1	Kα_2	Kβ_1	Lα_1	Lα_2	Lβ_1	Lβ_2	Lγ_1	Mα_1
63 Eu	41,542.2	40,901.9	47,037.9	5,845.7	5,816.6	6,456.4	6,843.2	7,480.3	1,131
64 Gd	42,996.2	42,308.9	48,697	6,057.2	6,025.0	6,713.2	7,102.8	7,785.8	1,185
65 Tb	44,481.6	43,744.1	50,382	6,272.8	6,238.0	6,978	7,366.7	8,102	1,240
66 Dy	45,998.4	45,207.8	52,119	6,495.2	6,457.7	7,247.7	7,635.7	8,418.8	1,293
67 Ho	47,546.7	46,699.7	53,877	6,719.8	6,679.5	7,525.3	7,911	8,747	1,348
68 Er	49,127.7	48,221.1	55,681	6,948.7	6,905.0	7,810.9	8,189.0	9,089	1,406
69 Tm	50,741.6	49,772.6	57,517	7,179.9	7,133.1	8,101	8,468	9,426	1,462
70 Yb	52,388.9	51,354.0	59,370	7,415.6	7,367.3	8,401.8	8,758.8	9,780.1	1,521.4
71 Lu	54,069.8	52,965.0	61,283	7,655.5	7,604.9	8,709.0	9,048.9	10,143.4	1,581.3
72 Hf	55,790.2	54,611.4	63,234	7,899.0	7,844.6	9,022.7	9,347.3	10,515.8	1,644.6
73 Ta	57,532	56,277	65,223	8,146.1	8,087.9	9,343.1	9,651.8	10,895.2	1,710
74 W	59,318.24	57,981.7	67,244.3	8,397.6	8,335.2	9,672.35	9,961.5	11,285.9	1,775.4
75 Re	61,140.3	59,717.9	69,310	8,652.5	8,586.2	10,010.0	10,275.2	11,685.4	1,842.5
76 Os	63,000.5	61,486.7	71,413	8,911.7	8,841.0	10,355.3	10,598.5	12,095.3	1,910.2
77 Ir	64,895.6	63,286.7	73,560.8	9,175.1	9,099.5	10,708.3	10,920.3	12,512.6	1,979.9
78 Pt	66,832	65,112	75,748	9,442.3	9,361.8	11,070.7	11,250.5	12,942.0	2,050.5
79 Au	68,803.7	66,989.5	77,984	9,713.3	9,628.0	11,442.3	11,584.7	13,381.7	2,122.9
80 Hg	70,819	68,895	80,253	9,988.8	9,897.6	11,822.6	11,924.1	13,830.1	2,195.3
81 Tl	72,871.5	70,831.9	82,576	10,268.5	10,172.8	12,213.3	12,271.5	14,291.5	2,270.6

82	Pb	74,969.4	72,804.2	84,936	10,551.5	10,449.5	12,613.7	12,622.6	14,764.4	2,345.5
83	Bi	77,107.9	74,814.8	87,343	10,838.8	10,730.91	13,023.5	12,979.9	15,247.7	2,422.6
84	Po	79,290	76,862	89,800	11,130.8	11,015.8	13,447	13,340.4	15,744	—
85	At	81,520	78,950	92,300	11,426.8	11,304.8	13,876	—	16,251	—
86	Rn	83,780	81,070	94,870	11,727.0	11,597.9	14,316	—	16,770	—
87	Fr	86,100	83,230	97,470	12,031.3	11,895.0	14,770	14,450	17,303	—
88	Ra	88,470	85,430	100,130	12,339.7	12,196.2	15,235.8	14,841.4	17,849	—
89	Ac	90,884	87,670	102,850	12,652.0	12,500.8	15,713	—	18,408	—
90	Th	93,350	89,953	105,609	12,968.7	12,809.6	16,202.2	15,623.7	18,982.5	2,996.1
91	Pa	95,868	92,287	108,427	13,290.7	13,122.2	16,702	16,024	19,568	3,082.3
92	U	98,439	94,665	111,300	13,614.7	13,438.8	17,220.0	16,428.3	20,167.1	3,170.8
93	Np	—	—	—	13,944.1	13,759.7	17,750.2	16,840.0	20,784.8	—
94	Pu	—	—	—	14,278.6	14,084.2	18,293.7	17,255.3	21,417.3	—
95	Am	—	—	—	14,617.2	14,411.9	18,852.0	17,676.5	22,065.2	—