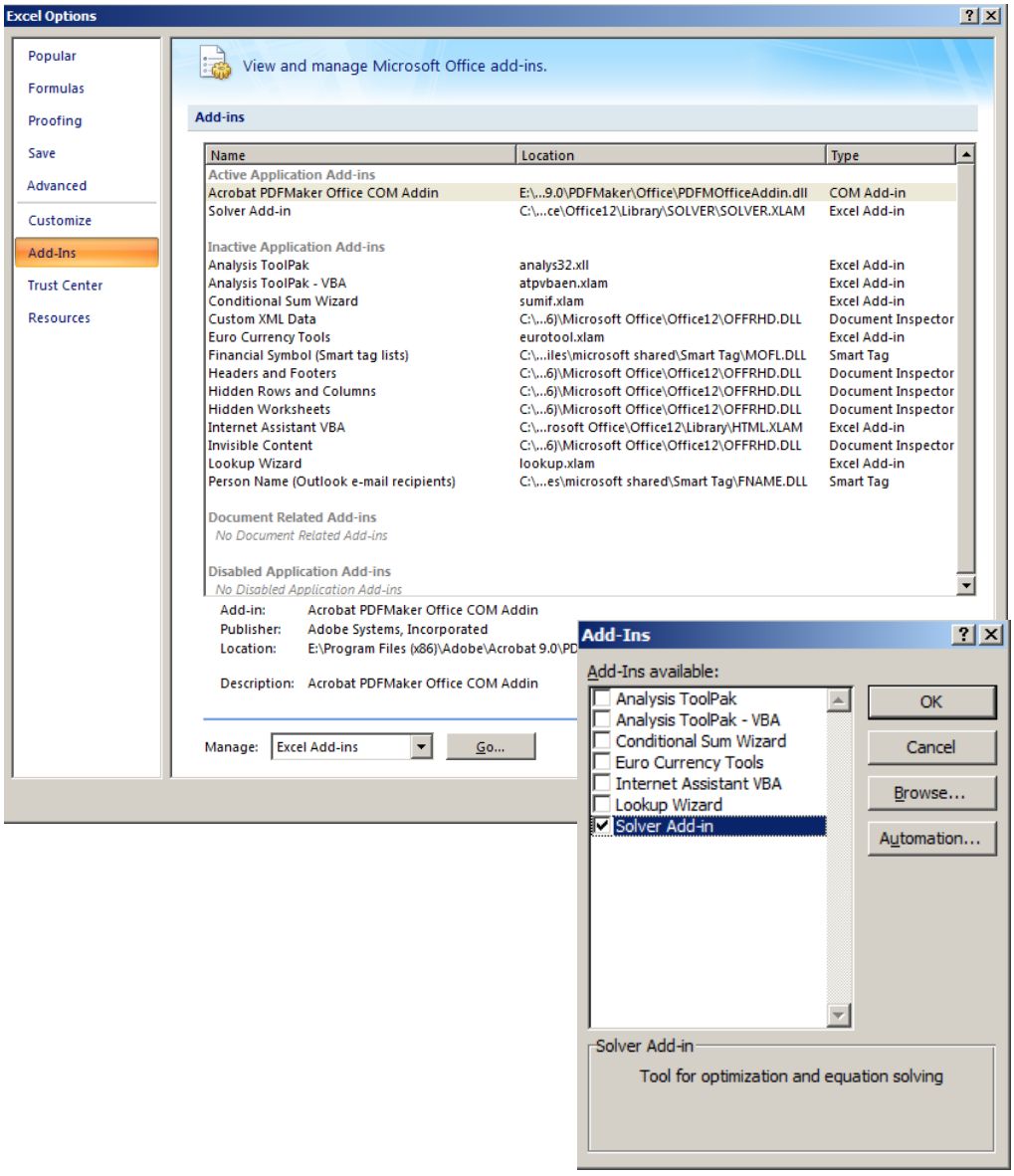
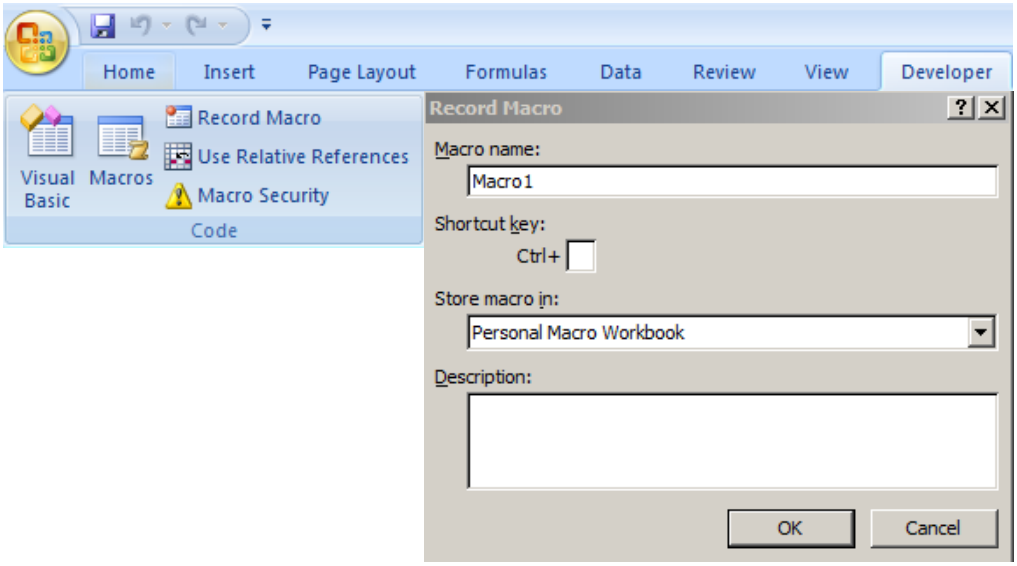
Peak-fitting procedures on XPS data by Excel *Hideki NAKAJIMA, rev. 20170317*

1. Unzip the package delivered or download it in the link below.
   https://github.com/heitler/xps-excel-macro
   You can also find the instruction and readme in it.

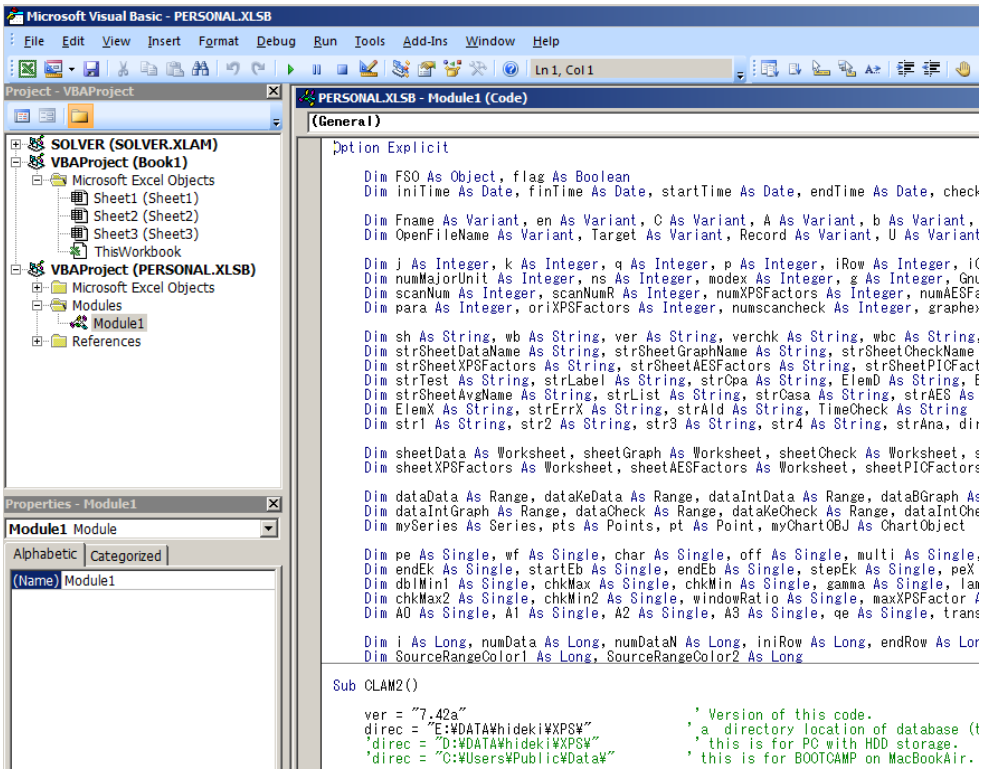
2. Install the Visual Basic for Applications (VBA) code and Solver add-ins in Excel.
   a. Install **Solver add-ins** from Excel Options - Add-Ins - Go... - Solver Add-in. Clicking OK automatically starts installation of Solver in Excel.



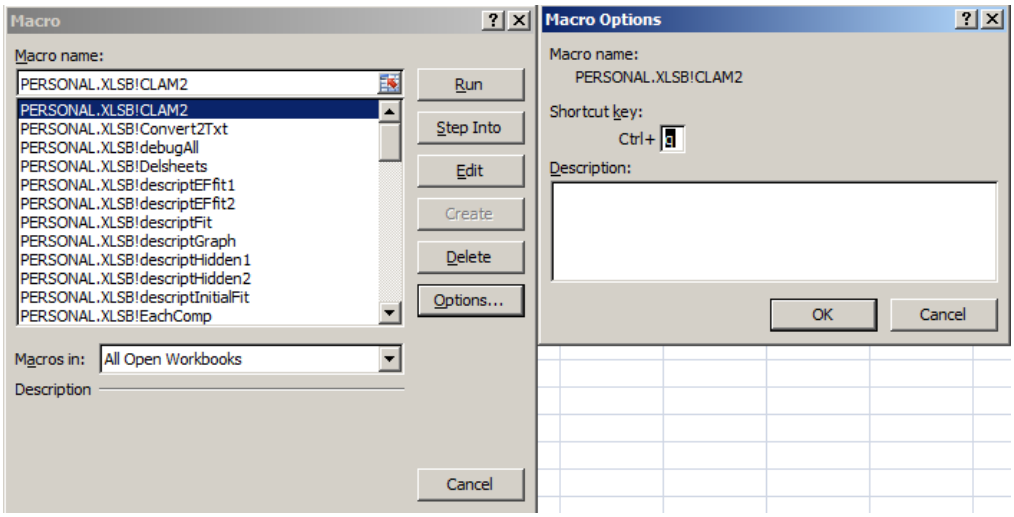
b. Create a Personal Macro Workbook (**personal.xlsb**).
   i. Show Developer tab in the Ribbon in Excel Options - Popular
   ii. Record Macro from Developer tab by any name.
   iii. Store macro in: "Personal Macro Workbook" and click OK.
   iv. Stop Recording from Developer tab in the same icon.



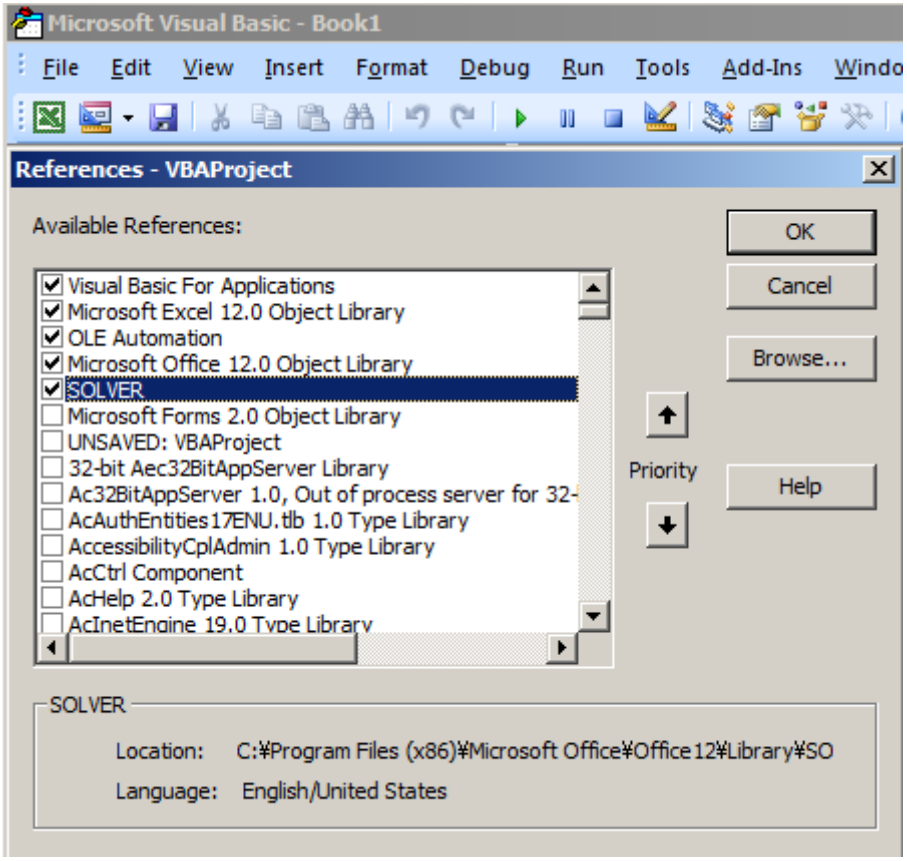
c. Copy the VBA code (personal_macro_workbook.vb or LoadCLAMxxx.vb) into your personal.xlsb (VBAProject - Modules - Module1) from VBA editor (Alt+F11 or Developer tab - Visual Basic).



d. Assign the shortcut keys (**Ctrl + q**) for the VBA code from Developer tab - Macros - Personal.xlsb!CLAM2 - Options... - Shortcut key: Ctrl + "q".



e. Check Solver add-ins library in the VBAProject references from VBA editor - Tools - Solver.



f. Create the folder specified in the code (for example, "D:\Data\hideki\XPS\") and place the files from the Data folder in it. If you have no database files or folders, the code generates user-defined database workbook in the first run of the VBA code as a filename “UD.xlsx”, and then you can modify or add your elements with binding energies and sensitivity factors for your light source such as MgKa, AlKa, and so on. The binding energy is available online, for example, from the link below.

https://userweb.jlab.org/~gwyn/

Data files for cross section in “webCross” folder is also required to normalize sensitivity factors at a photon energy given by the synchrotron beamline.

https://vuo.elettra.eu/services/elements/data/

Data files for atomic scattering factor in “XAS” folder is used to evaluate the absorption strength at the absorption edge in each element.

http://henke.lbl.gov/optical_constants/asf.html

3. Import data in Excel.
   a. Save tab-delimited texts or spreadsheet file with KE/BE scale in the first column and spectral intensity in the second column. The first line of the first column should be either “KE/eV” for kinetic energy or “BE/eV” for binding energy in XPS. XAS used to be “PE/eV”. The first line of the second column should be either “AlKa” for 1486.6 eV of photon energy or empty for dialog to be asked for photon energy used.

	A	B	C
1	BE/eV	AlKa	
2	382	19655	
3	381.9	19555	
4	381.8	19215	
5	381.7	20310	
6	381.6	19330	

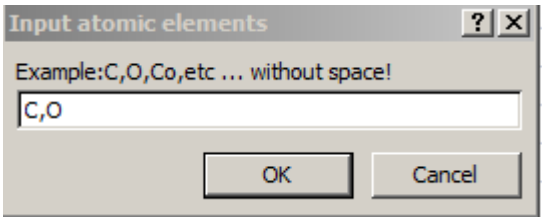
Note that, if you want to directly load text data in your format, modify *Sub FormatData* to specify the row and column positions.

   b. Open the text data file or workbook with Excel (right-click on text file).

   c. Run the VBA code by the shortcut key (Ctrl + q).
      i. Note that run the VBA code to update the analysis, plot or fitting after you revise any parameters in the following process.

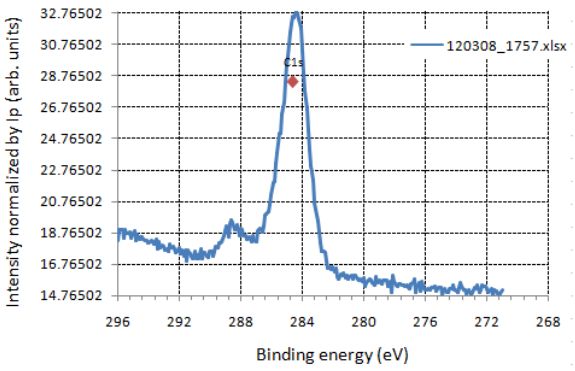
ii. Each sheet has a number of useful commands to be analyzed in details, but it can be learned afterwards.

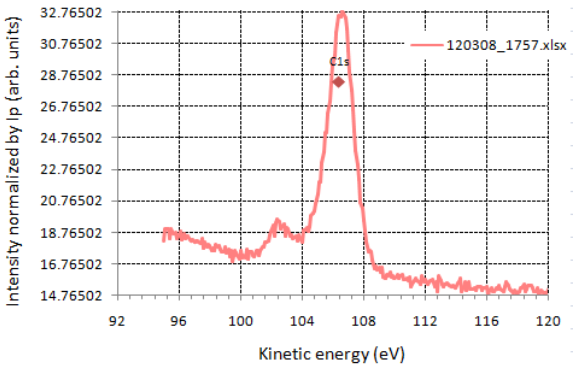
d. Input the atomic elements to be analyzed and shown up in graphs.



4. Calibrate the binding energy (BE) of spectrum by changing photon energy (PE), work function (WF), and charging factor (Char).
   a. Compare the standard data (XPS standard BE database given by **red marker**) or spectrum (C1s peak as *adventitious* carbon) to calibrate the binding energy.
   b. Change numbers to shift the spectrum in B2:B4 cells as specified.
   c. Spectra can be compared by typing "*comp*" with Ctrl + q (Select the Excel files to be compared after the shortcut key).
   d. Change Offset or Multiple factors in B9:C9 cells to scale the spectral intensity.
   e. Show the standard chemical shifts by "*chem*" in C10 cell with Ctrl + q.

	A	B	C
1	Grating	1200	lines/mm
2	PE	400	eV
3	WF	4	eV
4	Char	5	eV
5	Start KE	95	eV
6	End KE	120	eV
7	Step KE	0.1	eV
8	# scan	2	times
9	Offset/mu	0	1
10	Ke	Be	In
11	95	296	18.24582
12	95.1	295.9	18.98156
13	95.2	295.8	18.98809
14	95.3	295.7	18.95247
15	95.4	295.6	18.38897
16	95.5	295.5	18.98469
17	95.6	295.4	18.70909
18	95.7	295.3	18.69295
19	95.8	295.2	18.78642
20	95.9	295.1	18.38407
21	96	295	18.63752
22	96.1	294.9	18.86496
23	96.2	294.8	18.29049
24	96.3	294.7	18.65735
25	96.4	294.6	18.3639
26	96.5	294.5	18.52746
27	96.6	294.4	18.51605
28	96.7	294.3	18.31696
29	96.8	294.2	18.23294
30	96.9	294.1	18.2889
31	97	294	18.13778
32	97.1	293.9	18.19053
33	97.2	293.8	18.25074
34	97.3	293.7	18.17802
35	97.4	293.6	18.06134
36	97.5	293.5	18.35725





5. Fit peaks based on the element identified with binding energy calibrated in the Graph sheet.

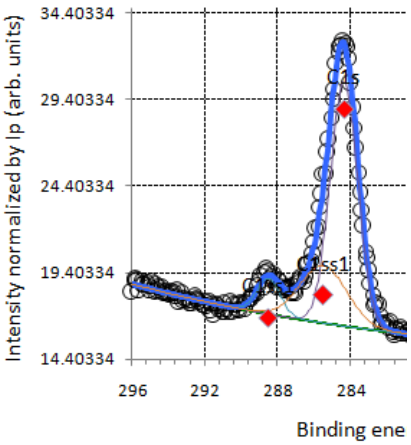
a. Set up the background shape by typing following in A1 and A2 cells.
    i. A1 for "s" to Shirley's BG (default)
    ii. A1 for "t" to Tougaard's BG
    iii. A1 for "p" to Polynomial BG (including constant and linear)
    iv. A1 for "p" and A2 for "s" to Polynomial Shirley BG
    v. A1 for "p" and A2 for "t" to Polynomial Tougaard BG
    vi. A1 for "v" to Victoreen BG used for XAS
    vii. A1 for "a" to Tangent Arc BG used for XAS
    viii. A1 for "e" to fit the Fermi edge.
b. Set up the fitting binding energy range in B11 and B12 cells.
c. Set up peak amplitude (E6,F6,...), FWHM (E4,...), BE (E2,...), and number of peaks (B8). Note that the parameters can be fixed as constraints with bold type face on each number.
d. Setup peak shape in E7, F7, ... cells as follows;
    i. "0" or "Gauss" for a normal distribution
    ii. "1" or "Lorentz" for a Cauchy distribution
    iii. Any value between 0 and 1 or "Voigt" for pseudo-Voigt function (italic type face on numbers for asymmetric function)
    iv. More peak shapes available from Form cells like G, L, GL, TSGL.
e. Setup amplitude ratios and BE differences if desired.

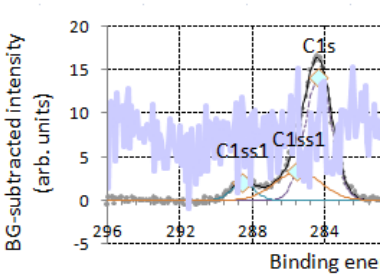
Name	C1	C2	C3
Amp. rat.	(2;	1)	
BE diff.	[	0.1;	0.2]

Table description above means that amplitude ratio between C1 and C2 peaks is 2:1 and the binding energy differences among C1, C2, and C3 are 0.1 and 0.2 eV, respectively.

f. The differences in three peak areas are summarized in the table below. The corresponding three numerical Trapezoidal integration areas are also shown.

	A	B	C	D	E	F	G
1	Polynomina	BG		Name	C1s	C1ss1	C1ss1
2	a0	16.18374		BE	284.3813	288.5255	285.5001
3	a1	-1.7401		KE	106.6187	102.4745	105.4999
4	a2	0.674588		FWHM1	1.779027	1.509679	3.020733
5	a3	-0.13876		FWHM2			
6	Solve LSM	3.93E-05		Amplitude	14.07587	2.05178	3.317964
7	Solver Fit			Shape	Gauss	Gauss	Gauss
8	# peaks	3		Amp+BG	28.84089	16.8168	18.08298
9	Solve LSM	0.002866		Sensitivity	33.92099	33.92099	33.92099
10	Fit range			P. Area	26.70359	3.303142	10.68799
11	Start / eV	271		S. Area	0.787229	0.097377	0.315085
12	End / eV	296		N. Area	7.406359	0.92	2.967545
13	Factors for N.Area			Asym			
14	CAE	50		Amp. rat.			
15	Grating	2		BE diff.			
16	MFP	0.6					
17	a	1.35					
18	b	0.35					
19							
20	BE / eV	In	BG	Int-BG	C1s	C1ss1	C1ss1
21	296	18.24582	18.73719	-0.49137	9.98E-51	8.25E-30	1.08E-14
22	295.9	18.98156	18.70922	0.272345	7.51E-50	4.98E-29	2.03E-14
23	295.8	18.98809	18.68138	0.30671	5.56E-49	2.94E-28	3.79E-14
24	295.7	18.95247	18.65368	0.298787	4.04E-48	1.69E-27	7.05E-14
25	295.6	18.38897	18.62612	-0.23715	2.89E-47	9.52E-27	1.3E-13
26	295.5	18.98469	18.5987	0.385986	2.03E-46	5.22E-26	2.39E-13
27	295.4	18.70909	18.57142	0.137669	1.4E-45	2.79E-25	4.37E-13
28	295.3	18.69295	18.54428	0.148675	9.48E-45	1.46E-24	7.93E-13

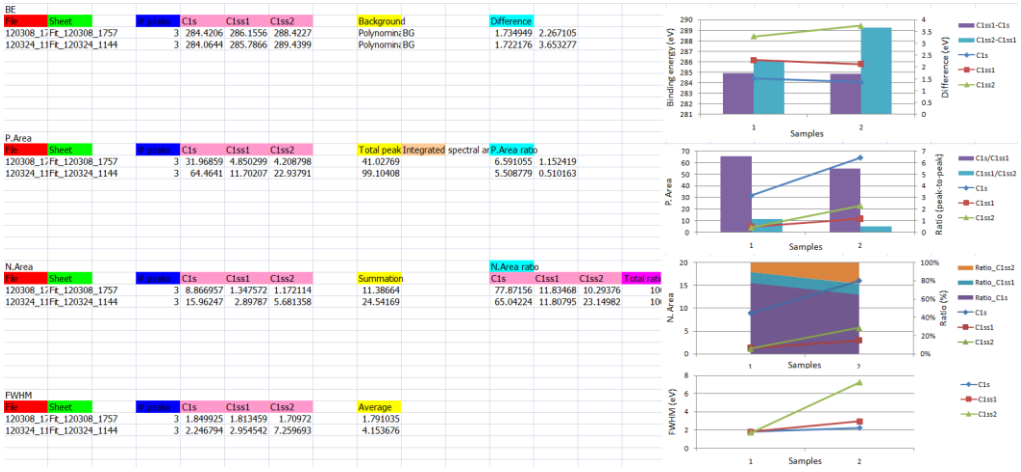




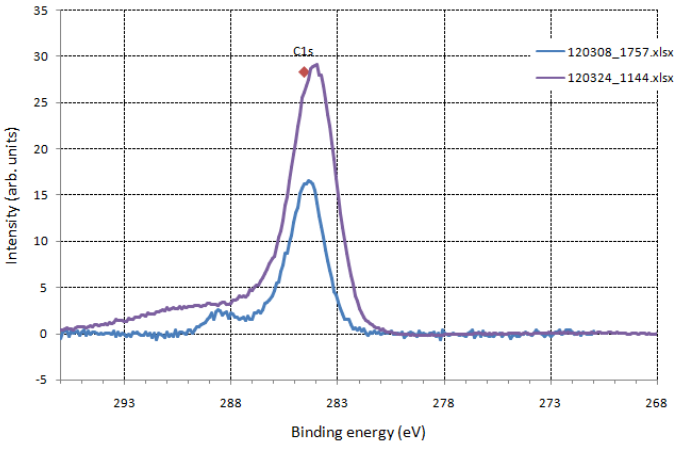
	Usages	Descriptions	Factors to be effective
P/T.I. Area	Single-element peak	Peak area calculated without any factors	Amplitude, FWHM
S. Area	Multiple-element peaks	Peak area calculated with atomic sensitivity factor based on photo-ionization cross-section	Amplitude, FWHM, PE, Sensitivity based on element specified in graph sheet
N. Area	Multiple-element peaks measured under different BL or analyzer conditions	Peak area calculated in "S. Area" plus normalized with empirically calculated factors at BL CLAM2 including XPS mean-free path of photoelectrons, transmission function of electron energy analyzer based on pass energy, grating efficiency	Amplitude, FWHM, PE, KE, Sensitivity, CAE, Grating, MFP factor, a & b based on formalism from CasaXPS

6. Sample analysis after the fitting on each spectrum.

a. Compare the peak areas and shifts based on the fitting results by typing "*ana*" in D1 cell with Ctrl + q at Fit sheet (Select Excel files to be compared).



	A	B	C	D	E	F
1		120308_1757.xlsx			120324_1144.xlsx	
2						
3						
4	Shift	0 eV		Shift		
5						
6						
7						
8						
9	Offset/mu	0		1	Offset/	
10	BE / eV	Shift	Int-BG		BE / eV	
11	296	296	-0.55923			
12	295.9	295.9	0.208652			
13	295.8	295.8	0.247106			
14	295.7	295.7	0.24319			
15	295.6	295.6	-0.28882			
16	295.5	295.5	0.338167			
17	295.4	295.4	0.09362			
18	295.3	295.3	0.108319			
19	295.2	295.2	0.232414			
20	295.1	295.1	-0.13952			
21	295	295	0.144126			
22	294.9	294.9	0.401555			
23	294.8	294.8	-0.14314			
24	294.7	294.7	0.253295			



7. The batch processing analyzes the number of data files sequentially.
   a. Close all workbooks by pressing ctrl + “w”, and show blank window in Excel.
   b. Shortcut key: ctrl + “q” to run the code.
   c. Choose the multiple files in the dialogue, and type the element.