

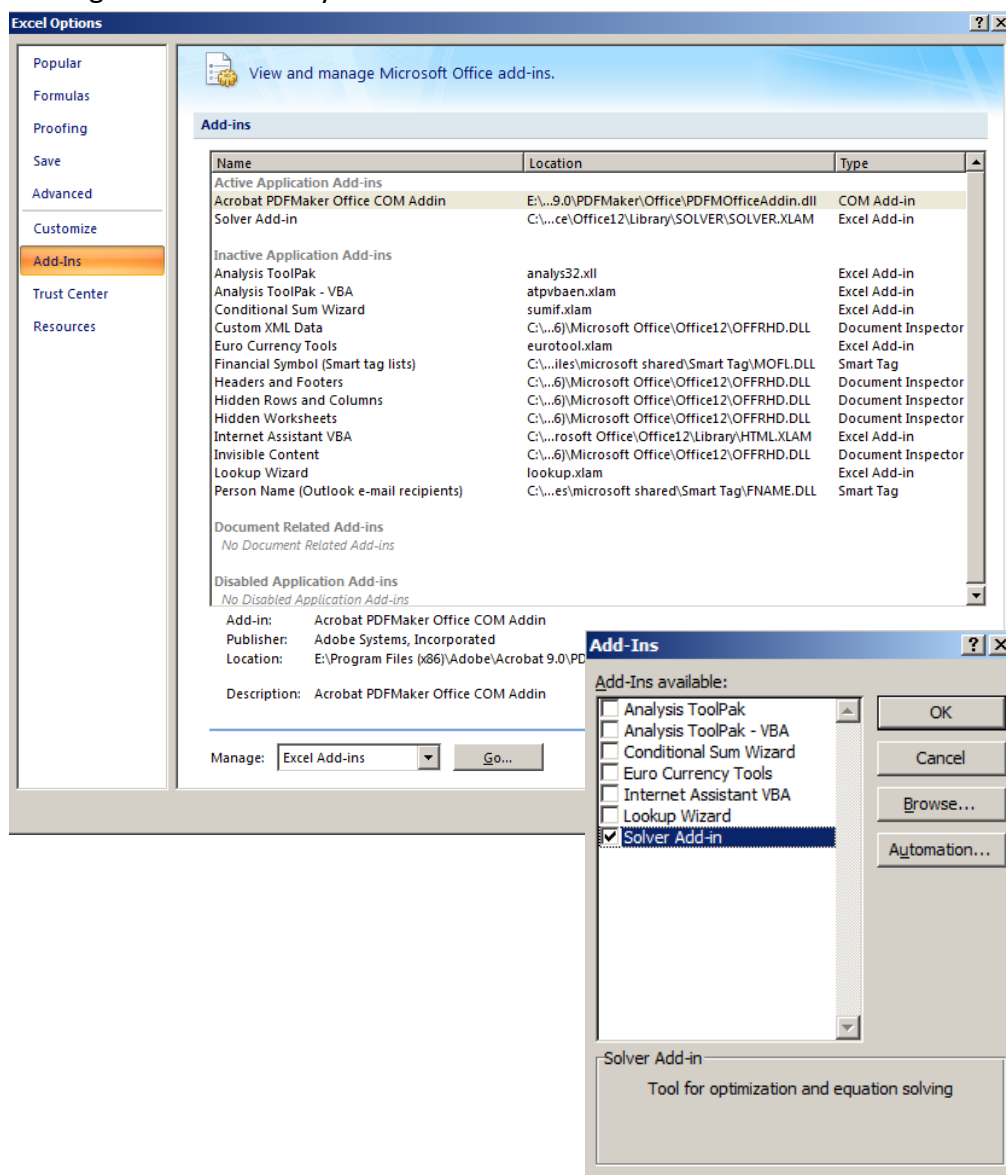
Peak-fitting procedures on XPS data by Excel

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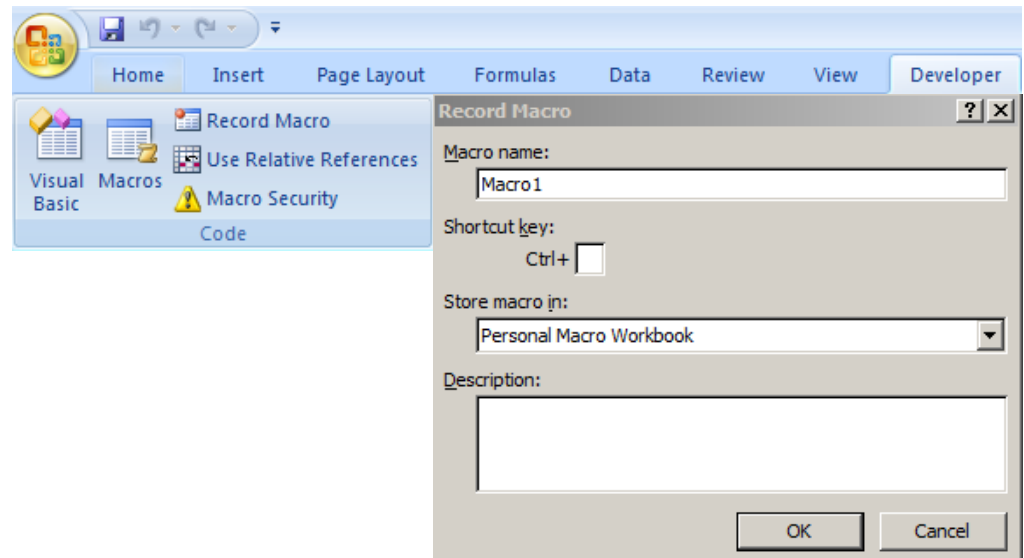
1. Unzip the package delivered in the workshop at SLRI. Trial package is also available from the link below.

<https://doi.org/10.5281/zenodo.1320738>

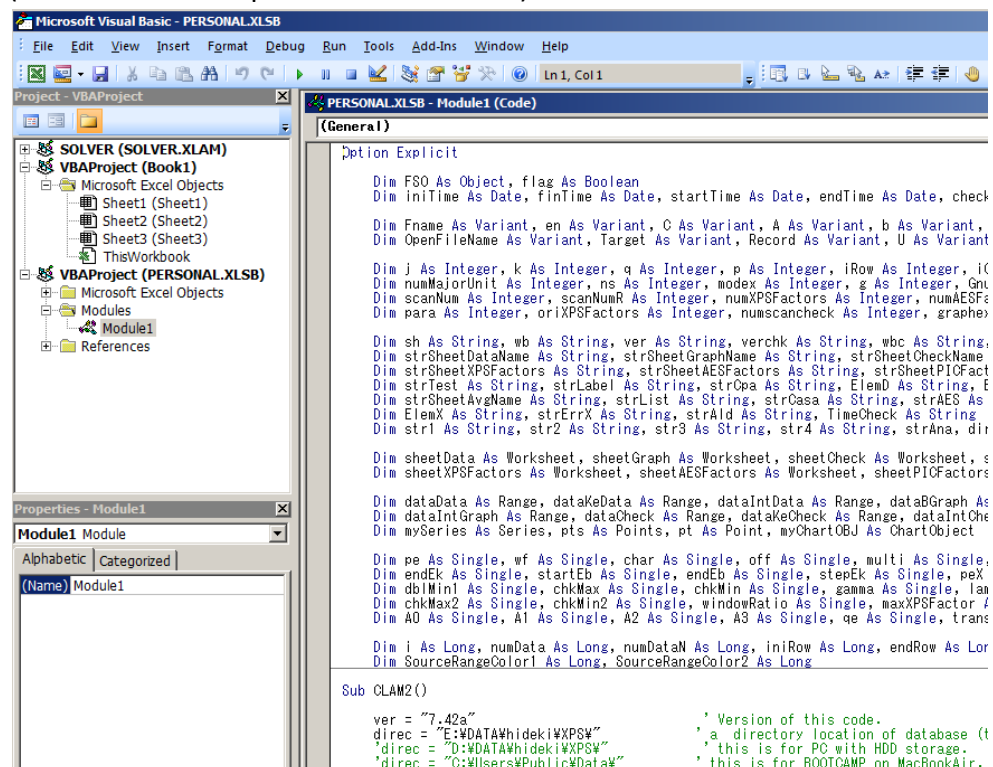
2. Activate Solver add-ins in Excel.
 - a. Install **Solver add-ins** from Excel Options - Add-Ins - Go... - Solver Add-in. Clicking OK automatically starts installation of Solver in Excel.



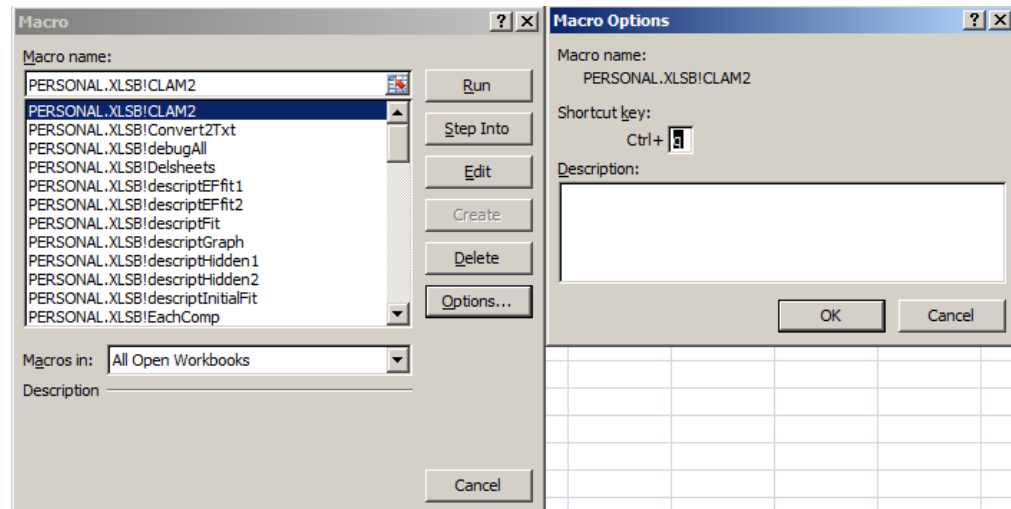
3. Install the Visual Basic Applications code in Personal Macro Workbook.
 - a. Create a Personal Macro Workbook (**personal.xlsb**).
 - i. Show Developer tab in the Ribbon in Excel Options - Popular
 - ii. Record Macro from Developer tab by any name.
 - iii. Store macro in: "Personal Macro Workbook"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



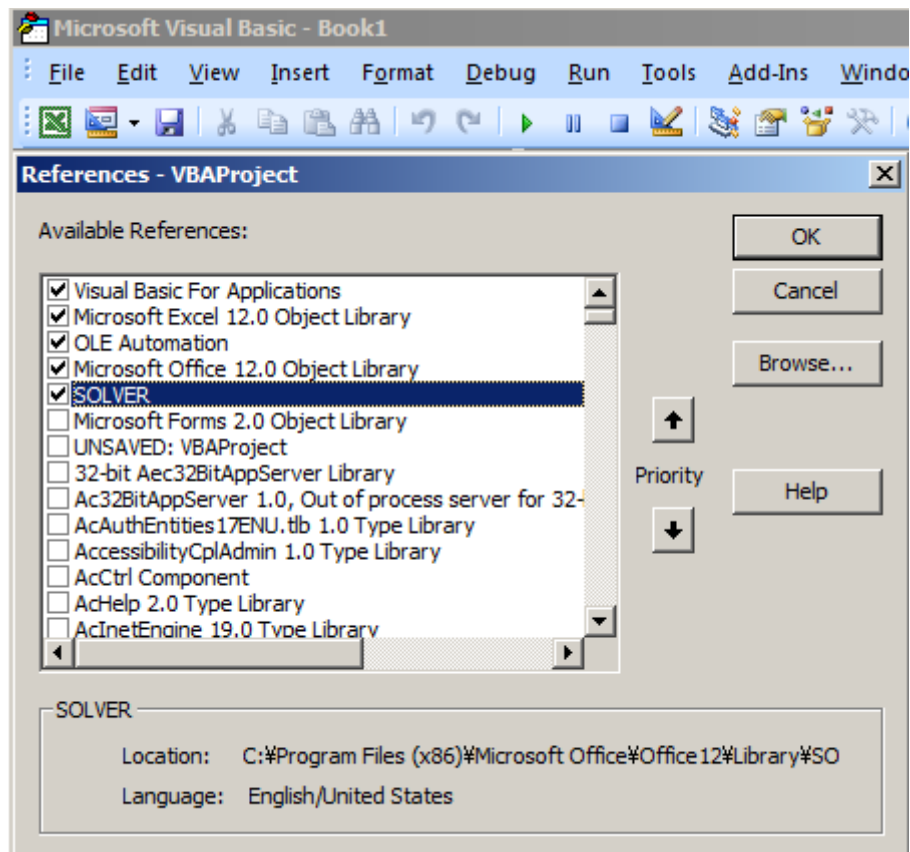
- b. Copy the VBA code (personal_macro_workbook.vb or LoadCLAMxxx.vb) into your personal.xlsb (VBAProject - Modules - Module1) from VBA editor (Alt+F11 or Developer tab - Visual Basic).



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



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



4. 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 MgK α , AlK α , 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

5. 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 "AlK α " for 1486.6 eV of photon energy or empty for dialog to be asked for photon energy used.

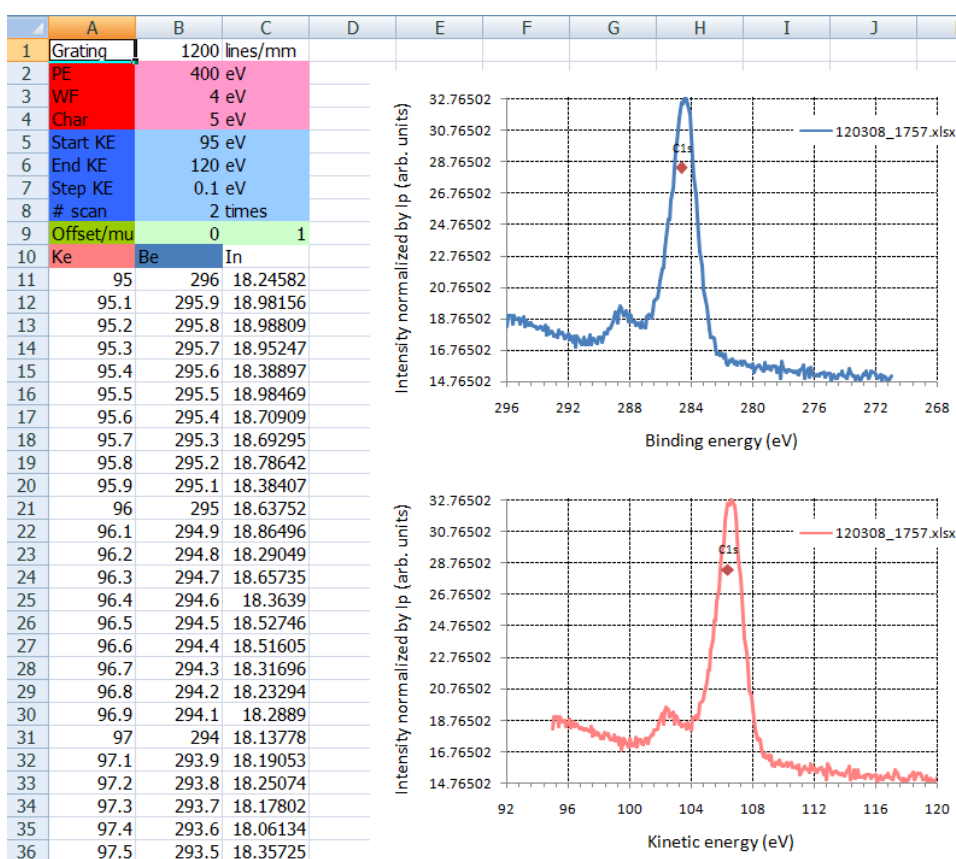
	A	B	C
1	BE/eV	AlK α	
2	382	19655	
3	381.9	19555	
4	381.8	19215	
5	381.7	20310	
6	381.6	19330	
7	381.5	18840	

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).
- Note that run the VBA code to update the analysis, plot or fitting after you revise any parameters in the following process.
 - 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.

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



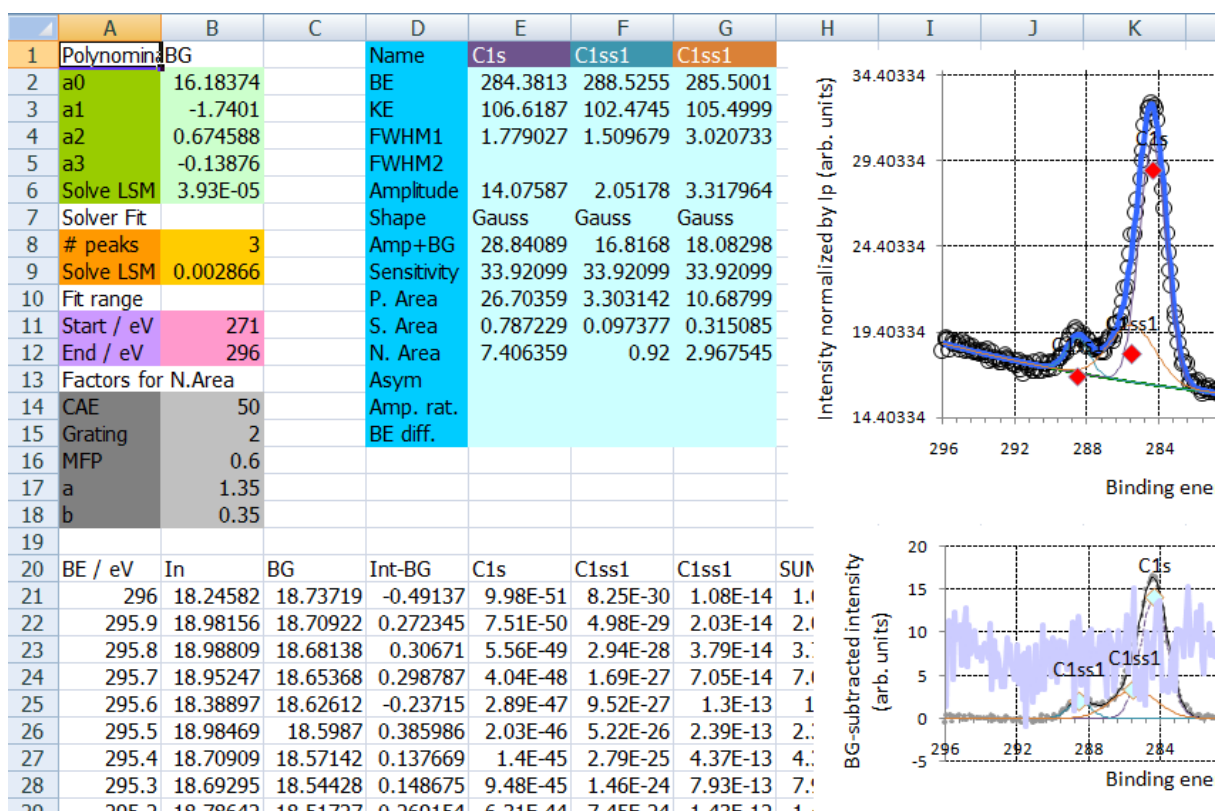
7. Fit peaks based on the element identified with binding energy calibrated in the Graph sheet.
- Set up the background shape by typing following in A1 and A2 cells.
 - A1 for "s" to Shirley's BG (default)

- 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.

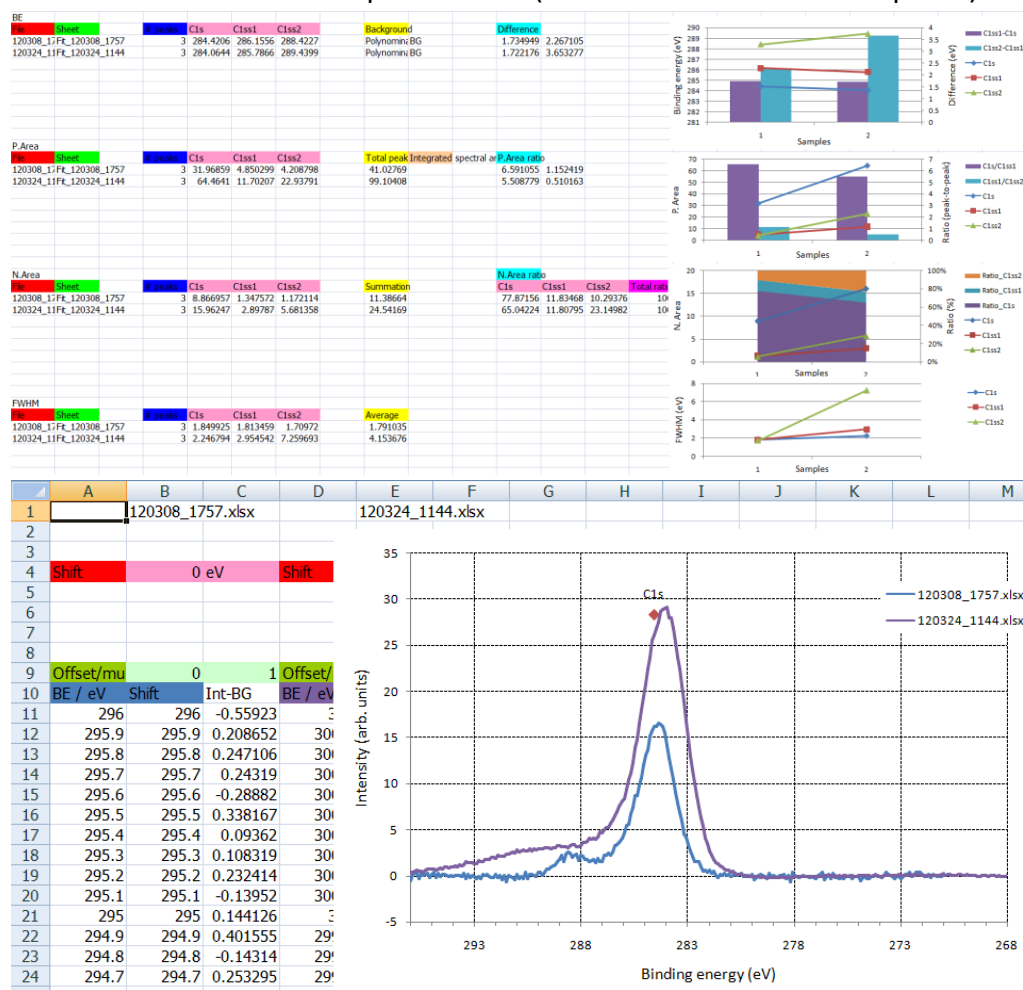
- f. The differences in three peak areas are summarized in the table below. The corresponding three numerical Trapezoidal integration areas are also shown.



	Usages	Descriptions	Factors to be effective
P. Area	Chemical state analysis	Peak area calculated with analytical formula and without any factors	Amplitude, FWHM
S. Area	Quantification of elements under the same condition	Peak area normalized with atomic sensitivity factor based on photo-ionization cross-section	Amplitude, FWHM, PE, Sensitivity based on element specified in the <i>Graph</i> sheet
N. Area	Quantification of elements under the various measurement 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 specified in the <i>Fit</i> sheet based on formalism from CasaXPS

Note: T.I./S.I./N.I. are numerically integrated areas with Trapezoidal rule applied to each corresponding area shown above.

8. 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).



9. 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.

