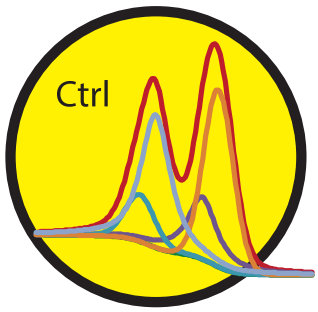
Technical note

Excel XPS & NEXAFS data analysis code



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Abstract

I have developed the XPS and XAS data analysis code for the synchrotron radiation (SR) soft x-ray beamline users to calibrate the energy and intensity in photons and electrons and analyze the peak composition and shape in the background subtracted profile. The code works in the Visual Basic Applications (VBA) on the Windows Microsoft Excel 2007 or later version utilizing the Solver Excel add-in for least square fit optimisation. Excel 2016 on Mac is also supported partly. Users easily handle and share the XPS and XAS data on their laptop computers for efficient usage of beamtime, and analyze it into the publications. According to the peak energy database specified in the code, users identify the atomic elements and its chemical shifts in the XPS and XAS spectra measured at the synchrotron beamline. The relative sensitivity factor and photo ionization cross section database are used to calibrate the peak intensity measured at the synchrotron-based XPS as well as standalone XPS system. The curve fit function sequentially evaluates the atomic or chemical ratios of the elements in your XPS data among the samples.

1 Background

I have developed the Excel visual basic applications (VBA) code to analyze the soft X-ray photoemission spectroscopy (XPS) and absorption spectroscopy (XAS or NEXAFS) spectra, because no software or code was available for SR-based XPS data analysis in public. Even though a number of commercial software have been developing such as CasaXPS (used in Kratos), MultiPak (ULVAC PHI), Avantage (Thermo Scientific), Spectral Data Processor (XPS International), they are basically optimized for the standalone XPS system utilized with the Mg or Al $K\alpha$ anode as a X-ray source, which generates a photon energy of 1486.6 eV. However, synchrotron radiation (SR) produces a wide spectrum of photon energy and the monochromator and mirror optics deliver SR to the spot on the sample surface in various energy resolution and spot size used for XPS. To process the number of SR-based spectral data, the professional analytical software such as Igor Pro (WaveMetrics), Origin (OriginLab), MATLAB, Mathmatica (WOLFRAM) etc. has been used to inspect the photoelectron energy and intensity at the beamline prior to the chemical analysis detailed. However, these software are relatively expensive for XPS beginners and further required for scripting to streamline spectral analyses in their own macro language.

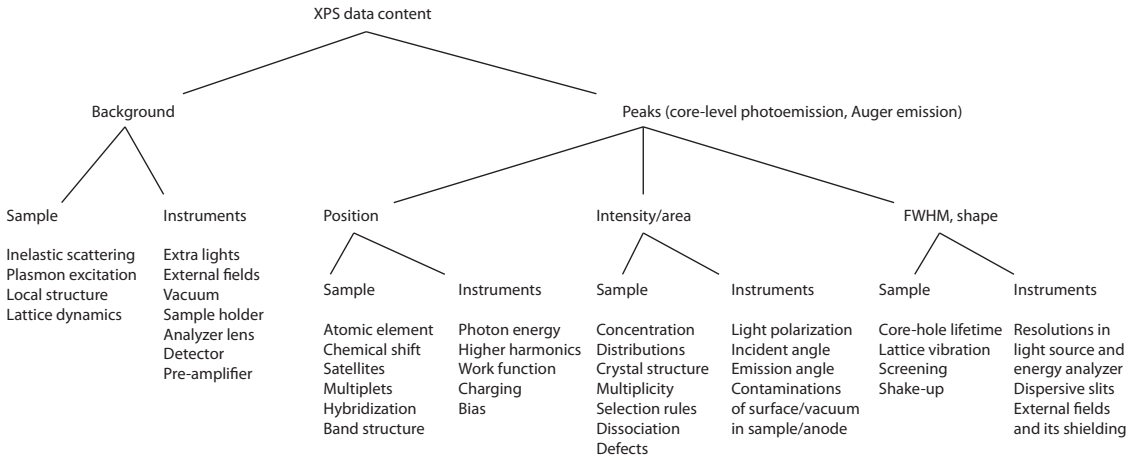

Figure 1: A schematic diagram of XPS data content taken into account in analysis.

Microsoft Excel is a default standard spreadsheet-based software to inspect and visualise the numerical data in various fields of daily jobs, because relational formulation among cells in spreadsheet and Solver non-linear optimisation function in Excel add-in robustly handle scientific and engineering data as well as financial and accounting data. In addition, the VBA code streamlines the standard data analysis process without elaborated copy and paste actions on the spreadsheet, and instantly plots the charts in the worksheet. Even though the optimisation performance and numerical accuracy are quite limited in the big data analysis, the Excel VBA code makes your spectral data analysis simple and comprehensive on your own laptop PC. Python and R are scientific scripting languages included with robust analytical and statistical libraries, and sophisticated integrated development environment (IDE) for each language is freely available. Advanced and licensed XPS data analysis software such as Unifit and AAnalyzer has been greatly developed in

terms of Peak and BG fitting functions deep into "Art" or "Black Magic" of curve fitting. However, to promote the academic and industrial research projects, the data have to be shared with users and collaborators during or after the experiment to discuss the data quality and necessity for the further additional experiment. Excel workbooks analyzed in this code are easily distributed without any script code attached in the workbook, because all relational formulations are stored in the worksheets. Charts in Excel worksheet can also be placed in the Word document or PowerPoint slide as objects for your brief experimental report. In this report, we present the detailed function of our Excel VBA code optimised for soft X-ray based XPS and XAS.

2 Introduction

Ctrl+Q is a powerful code for XPS and XAS data analyses based on the Microsoft Excel VBA and solver function. Ctrl+Q has useful functions for energy and intensity calibration, spectral normalisation, peak identification, spectral comparison, background subtraction, peak fitting, and export the summary of fitting results as illustrated in Fig. 2. The code has been developed and optimized for user service at the BL3.2Ua in the Siam Photon Laboratory (Synchrotron Light Research Institute). Any spectral data imported and formatted in the Excel spreadsheet, which consist at least of spectral intensity and its corresponded energy in two columns, can be analysed by using the code. Various peak shapes can be decomposed in the fitting with a number of background functions. The SR-based XPS used to vary the photon energy to increase the spectral intensity in a way that the photoionisation cross section increases as the photon energy decreases or increases at the resonance energy. The Excel VBA code works well together with the database of core level binding energy, chemical shifts for main peaks, and atomic or relative sensitivity factor (RSF) for each level based on the XPS standard reference used with Al Kα anode. The photon energy dependent atomic sensitivity factor is evaluated with photoionisation cross section database, which is available online. Auger electron peaks appear in the XPS spectra at the constant kinetic energy, and their binding energies are varied with the photon energy used to measure XPS. The VBA code distinguishes between the XPS and Auger peaks instantly, so we can easily tune the photon energy appropriate for your measurement without overlap among them. For XAS data analysis, XPS database are used for XAS analysis limited in the soft x-ray energy range.

3 Installation

The code is based on the VBA and installed in the VBE as a Personal Workbook Macro with a shortcut key assignment at "CLAM2" listed in the top of Sub procedures. Solver function also needs to be installed in Excel as a default add-in and referenced in the VBE for curve fit procedure. Any data analysis process starts from the Option of Macro menu "CLAM2" or the shortcut key "Ctrl" & "q" assigned even in the blank workbook. In the workbook, the code analyzes the data depending on either what worksheet is active or what syntax is specified in active worksheet. See details in attached tutorials (How_to_use_Excel_XPS_macro_pub.pdf) or YouTube Video: https://youtu.be/tWpcnDjkHzo.

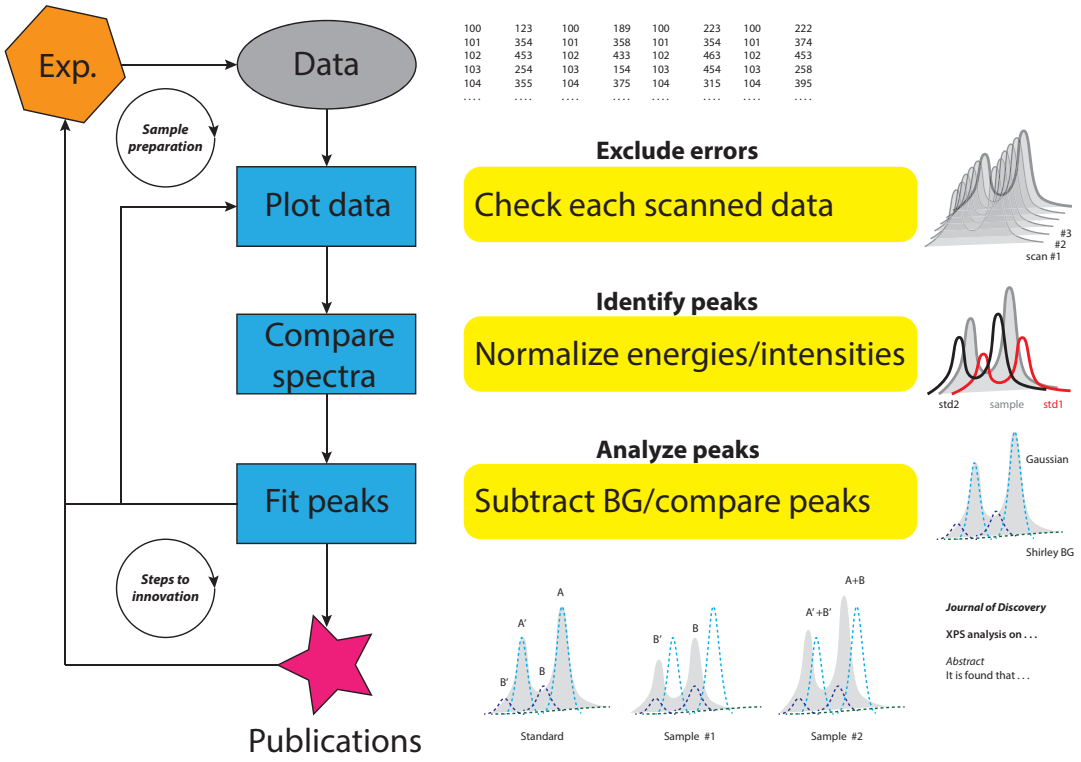

Figure 2: A schematic diagram of XPS data analysis processes up to the publications.

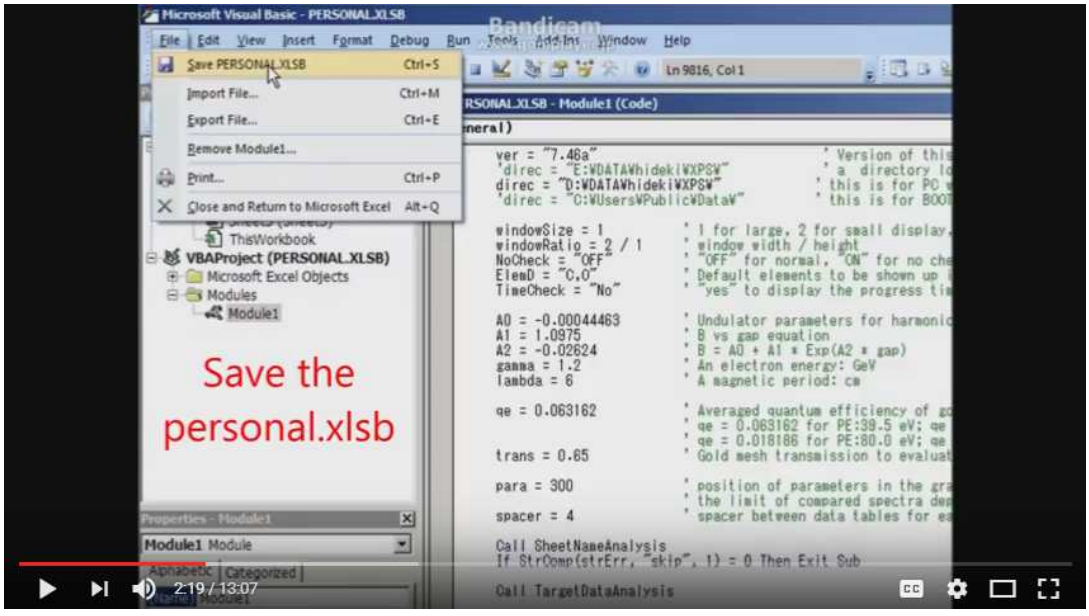

Figure 3: Instruction video on VBA code installation.

A1 syntax	Data below A2 column	Data below B2 column
KE/eV	Kinetic energy	XPS
BE/eV	Binding energy	XPS
PE/eV	Photon energy	XAS
GE/eV	Photon energy	Grating scan
AE/eV	Electron energy	Auger scan
QE/eV	Molecular mass	Q-mass scan
ME/eV	Position	Mechanial scan

Table 1: Two-cloumn data in the spreadsheet followed by syntax in A1 cellformat.

Worksheet	Function	Operational commands
Data	Original data	
Graph	Plot and compare charts	comp, exp, auto, etc.
Exp	Exported data	
Fit	Curve fitting	ana, debug
Ana	Atomic concentration	ana
Cmp	BG-subtracted charts	exp
Rto	Compare multiple samples	

Table 2: Name and function of each worksheet produced.

4 Data loading

Any data formatted in the Excel spreadsheet can be analysed in the code as follows. The energy and intensity data in the spreadsheet are prepared in the two columns below A2 & B2 cells, respectively. "KE/eV" at the A1 cell in the same sheet makes the first column data as the kinetic energy of spectrum. "BE/eV" at the A1 cell is recognized as the binding energy to the first column data, "PE/eV" at the A1 cell the photon energy, and "ME/eV" for any other purposes. The workbook must be saved as a worksheet name, which represents for a spectrum data, and then run the code in the worksheet called as the Data sheet. The code makes several sheets additional to the Data sheet named after the Data sheet or workbook name such as Graph_*filename* and Fit_*filename*.

What kind of sheet or data column set generated depends on the operation in the worksheet. In the Graph sheet of XPS data, one spectrum data consists of three columns. First column is used for kinetic energy, second binding energy, and third spectral intensity. In the bottom of first three-column set, the other three columns are followed to be further normalized. First and second columns of second set are the same as those in the first set, and third column the normalized spectral intensity by offset and multiple factors. First chart shown in the Graph sheet is based on the second and third columns in the second set, and second chart is on the first and third columns in the second set.

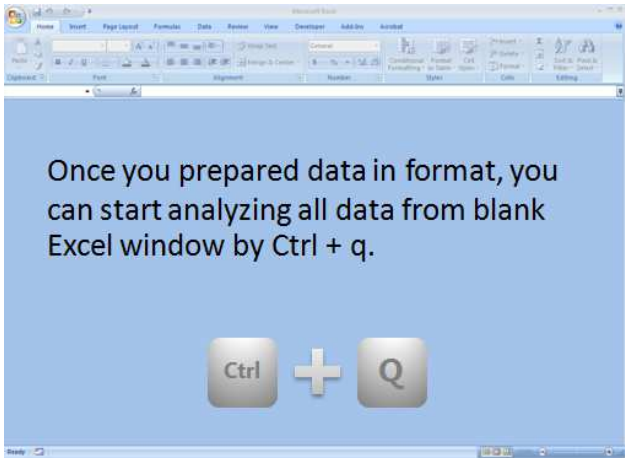

Figure 4: Batch processing on multiple files.

5 Comparing data

You can compare the spectral data with one after another in the Graph sheet. Open the Excel file analyzed in this code and type "comp" in the D1 cells of Graph sheet. Choose the Excel files including the Graph sheet in it to be compared. You can also add the data one after another to type "comp" in the every 3 columns after D1 like G1, J1, and so on. Compared data normalized and calibrated in that sheet is easily exported in the sets of two-column data for each spectrum by "exp" in A1 cell. The resulting data in the Exp sheet can be imported in the software you want to plot for further analysis or quality to journal submission.

6 Energy and intensity calibration

Standard sample data or database is used to calibrate the peak energy or spectral intensity. In the Graph sheet, the photon energy, work function, and charging factor are adjustable parameters for binding energy calibration. The offset and multiple factors are also available to scale spectral intensity for data comparison. To compare the multiple spectra at a glance, both ends of spectral intensity are automatically scaled in the syntax of "auto" at A1 cell in Graph sheet. To specify the energy ranges for spectral offset and multiple scaling, "auto[x0,x1:x2,x3]" can be used in a way that the spectral range between x0 and x1 is averaged to be 0 (offset) and the range between x2 and x3 is averaged to be 1 (multiple). If either x0/x2 or x1/x3 is null, nothing happens to be scaled in the corresponding range. The original data scales for offset and multiple are 0 and 1 respectively.

7 Spectral normalization

Spectral intensity is divided (normalized) by the other reference spectrum to compensate the noise or contamination happened during the measurement. Reference data can be

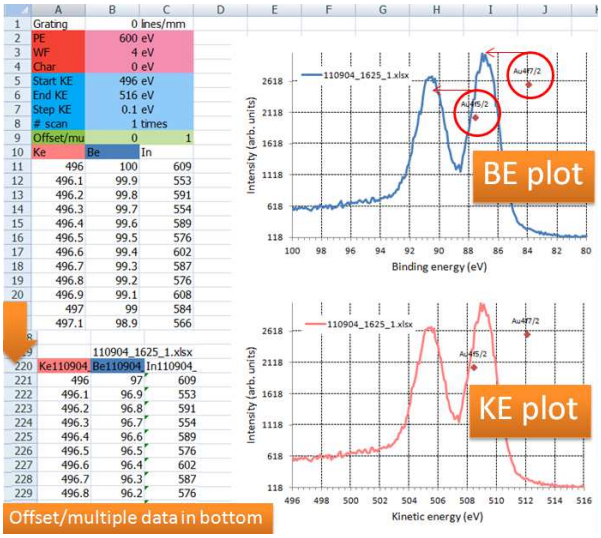

Figure 5: Graph sheet.

added as the second data set by "comp" in the Graph sheet prior to the normalization as mentioned above. The code started with "norm" at A1 cell in the Graph sheet continues normalizing the first data set by the second data set leading to the resultant third data set. According to the normalized data in the third data set in the Graph sheet, the Norm sheet is produced with normalized data set to be analyzed in the code further.

8 Curve fitting

The peaks calibrated and identified by the database in the Graph sheet are analyzed in the Fit sheet based on the least-square regression method. Peak area is evaluated with analytical and numerical ways together with the choice of background subtraction processes. The number of peaks can be chosen with parameters such as curve shape, energy, FWHM width, amplitude etc. All the parameters can be constrained or limited in a specific range. Amplitude ratios and peak energy differences among the peaks are also adjustable in the cells with specified syntax.

8.1 Type of background subtraction and peak fitting function

- Gaussian, Lorentzian, and its blended function with tail parameters for asymmetric peak ("G" to "TSGL")
- Shirley and Tougaard backgrounds blended with and without polynomial function
- Constant, linear, quadratic, and cubic for polynomial background
- Polynomial and its blended backgrounds optimized with peak fittings(active mode: "BG" to "ABG")
- Arctangent and Victoreen backgrounds for XAS pre-edge subtraction

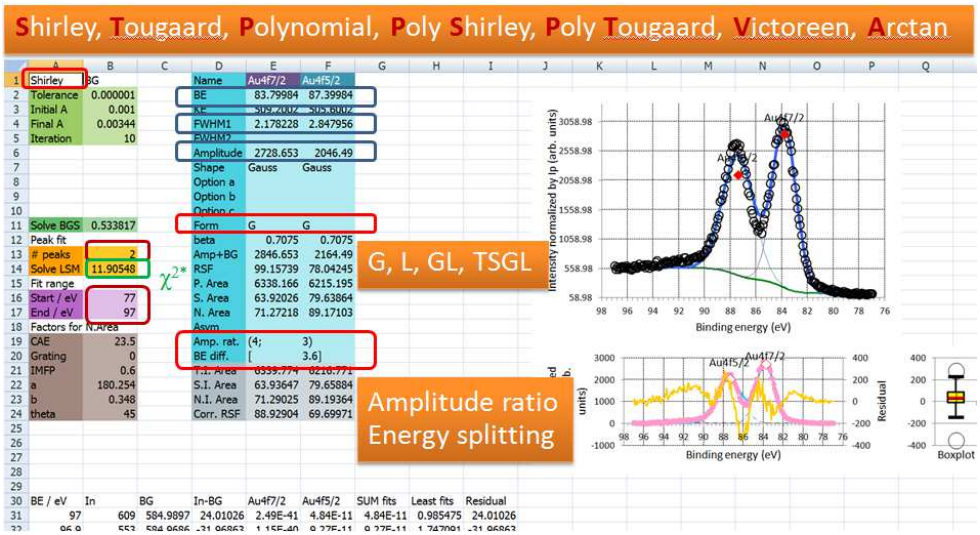

Figure 6: Fit sheet.

Syntax	Shape	Option a	Option b
G	Gaussian		
L	Lorentzian		
GL	Sum blend of G and L		
TSGL	Exponential blend of GL	Tail scale	Tail length

Table 3: Peak shape function available in Fit sheet.

- Trapezoidal (numerical) integration for peak areas normalized by various sensitivity factors including photoionization cross section, source angle correction, MFP, analyzer transmission function etc.
- User-defined function can be easily implemented in the Visual Basic programming.

9 Multiple data file analysis

Once a XPS data is analyzed in the Excel VBA code, you can apply its analysis in the another Excel files in terms of the energy and intensity calibration or fitting curve as initial parameters. Atomic concentration in each sample for each element is summarized in the Ana sheet based on the Fit sheets of all spectra. The trend of atomic concentrations in samples is summarized in the Rto sheet based on the Ana sheets for all samples.

10 References for database

On-line database links are also freely available for everyone to identify the database references. Electron energy and RSF for each element can be setup in UD.xlsx in the database directory for XPS and AES worksheets.

Syntax A1	Syntax B1	Syntax C1	Technique	Optimization
Shirley	BG		XPS	static
Tougaard	BG		XPS	static
Polynomial	BG		XPS/XAS	static
Polynomial	ABG		XPS/XAS	active
Polynomial	Shirley	ABG	XPS	active
Polynomial	Tougaard	ABG	XPS	active
Victoreen	BG		XAS	static
Arctanget	BG		XAS	active

Table 4: Background function available in Fit sheet.

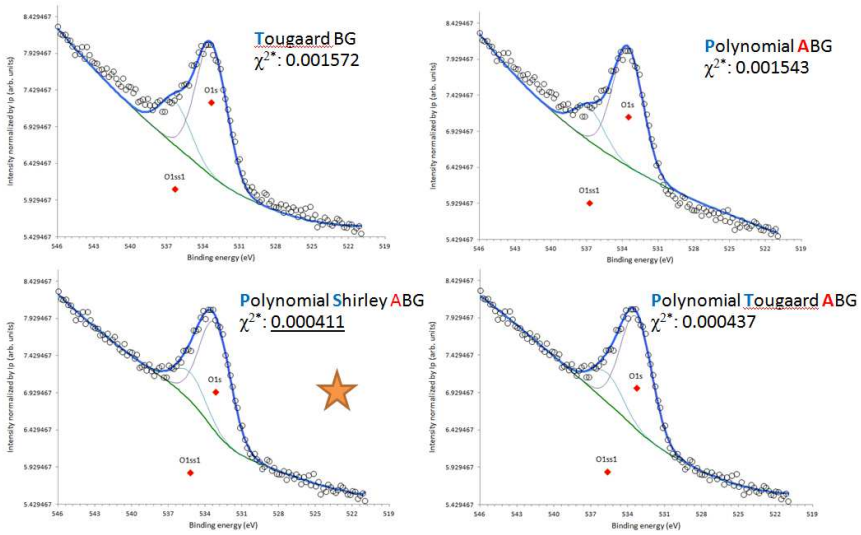

Figure 7: A comparison of background subtracted spectra.

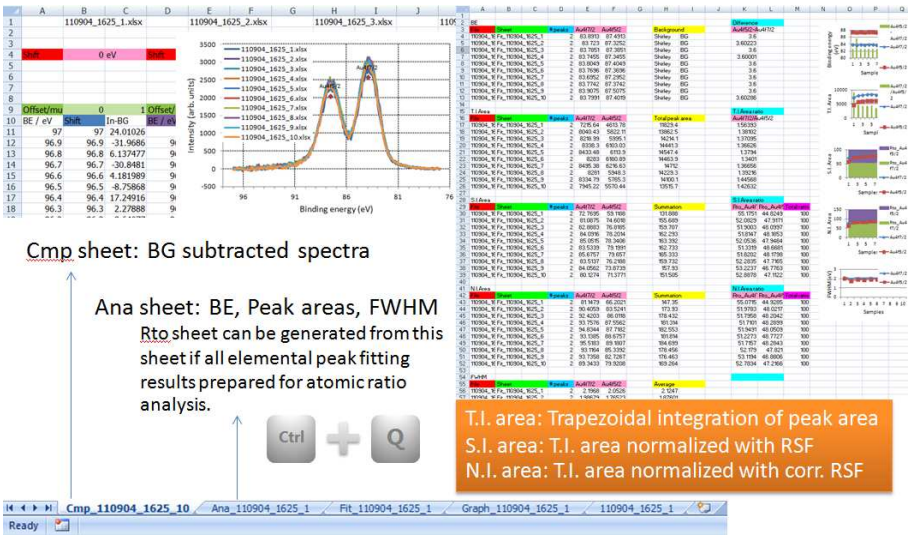

Figure 8: Cmp sheet.

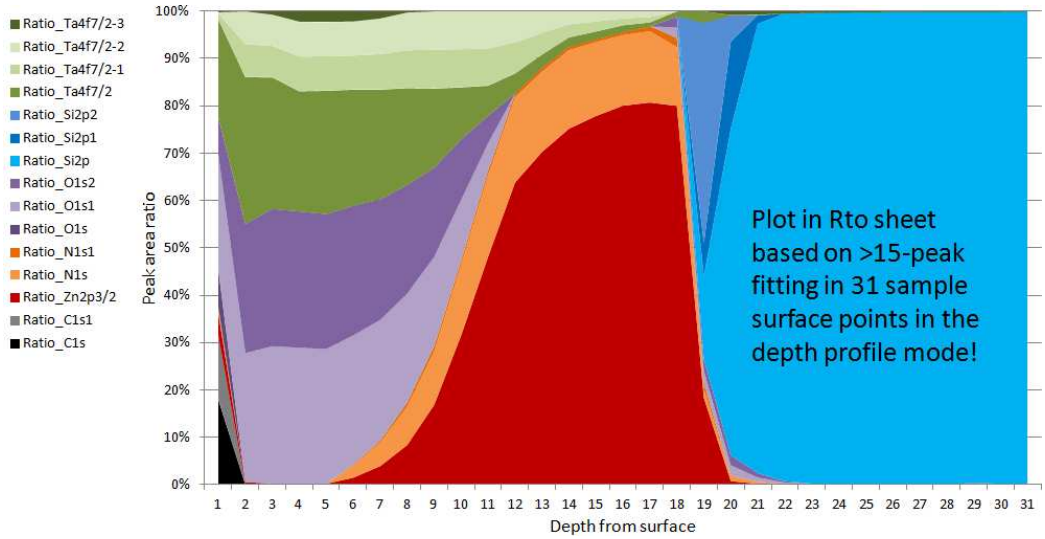

Figure 9: Rto sheet.

- http://www.uksaf.org/data.html

10.1 XPS

- X-ray data booklet

  http://xdb.lbl.gov/

- Values compiled by Gwyn P. Williams (updated Excel file and poster available)

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

- X-ray booklet binding energy database combined with Scofield photoionization cross-section database from "Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV" J. H. Scofield Journal of Electron Spectroscopy and Related Phenomena, 8129-137 (1976).

  DOI: 10.1016/0368-2048(76)80015-1

10.2 AES

- "Calculated Auger yields and sensitivity factors for KLL-NOO transitions with 1-10 kV primary beams" S. Mroczkowski and D. Lichtman, J. Vac. Sci. Technol. A 3, 1860 (1985).

  DOI: 10.1116/1.572933

- http://www.materialinterface.com/

  (Electron beam energy at 1, 3, 5, and 10 keV for relative cross section and derivative factors)

10.3 XAS folder

The Atomic Scattering Factor files are placed in this folder.

- "X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at E = 50-30,000 eV, Z = 1-92", B. L. Henke, E. M. Gullikson, and J. C. Davis, Atomic Data and Nuclear Data Tables 54, 181-342 (1993).

  DOI: 10.1006/adnd.1993.1013

- The Atomic Scattering Factor Files online.

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

10.4 WebCross folder

Photoionization cross section online database files should be downloaded and placed in this folder.

- https://vuo.elettra.eu/services/elements/WebElements.html

- "Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters" J. J. Yeh, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993.

- "Atomic subshell photoionization cross sections and asymmetry parameters: 1 <= Z <= 103" J. J. Yeh and I. Lindau, Atomic Data and Nuclear Data Tables, 32, 1-155 (1985).

  DOI: 10.1016/0092-640X(85)90016-6

Note that database are supposed to be revised and updated locally based on the experiment. All the database files are based on Al Kα source energy at 1486.6 eV, and webCross data normalize the RSF. You may also check spectral lines and profiles in the link below;

10.5 Other

- NIST X-ray Photoelectron Spectroscopy Database

  http://srdata.nist.gov/xps/

- "The NIST X-ray photoelectron spectroscopy (XPS) database" C. D. Wagner, NIST Technical Note 1289 (1991).

  https://archive.org/details/nistxrayphotoele1289wagn

- The Surface Analysis Society of Japan: Common Data Processing System

  http://www.sasj.jp/COMPRO/index.html

11 Selected publications

Ctrl+Q has been installed for many users during the experiment and post-data processing, and contributed to XPS and NEXAFS data analysis and a variety of publications included high-impact Tier-1 journals.

- ACS Appl. Mater. Interfaces: 10.1021/am505127g, IF: 7.504
- ACS Appl. Mater. Interfaces: 10.1021/acsami.7b02833, IF: 7.504
- Carbon: 10.1016/j.carbon.2015.01.018, IF: 6.337
- Catalysis Science & Technology: 10.1039/C5CY00464K, IF: 5.773
- Sensors and Actuators B: 10.1016/j.snb.2013.12.017, IF: 5.401
- Scientific Reports: 10.1038/srep11922, IF: 4.259
- Solar Energy: 10.1016/j.solener.2015.12.019, IF: 4.018
- Journal of Environmental Management: 10.1016/j.jenvman.2015.09.036, IF: 4.010
- Environmental Chemistry Letters: 10.1007/s10311-015-0538-y, IF: 3.594
- Applied Surface Science: 10.1016/j.apsusc.2016.01.180, IF: 3.387
- RSC Advances: 10.1039/C6RA09972F, IF: 3.108
- J. Phys.: Condes. Matter: 10.1088/0953-8984/28/36/365002, IF: 2.649
- J. Phys. D: Appl. Phys.: 10.1088/0022-3727/47/5/055109, IF: 2.588
- Current Applied Physics: 10.1016/j.cap.2014.01.003, IF: 1.971
- Australian Journal of Chemistry: 10.1071/CH17078, IF: 1.328
- Nucl. Instr. and Methods in Phys. Res. B: 10.1016/j.nimb.2017.01.061, IF: 1.109
- Sains Malaysiana: 10.17576/jsm-2017-4605-13, IF: 0.470

12 Excel limitations

Unlike the common scientific program, Excel is typically eligible for finantial and accounting businesses. You can find the detailed limitations online. For example, Number precision is limited at 15 digits, so the number data should be normalized in the appropriate range from pico to tera. It will also effect to Solver tolerance to judge the convergence point. Adjustable parameters in Solver are limited up to 200, so then the maximum number of peak for fitting is about 30. Excel cannot plot the surface contour beyond the 255 series, so it is not appropriate to plot the surface map in high resolution. Even though calculation and operational speeds are not obviously optimized for the big data, Excel takes a great advantage of accessibility and relational spread-sheet interface.

Excel handles 64 bit double precision floating point numbers based on IEEE 754, which is standard for decimal/binary floating-point arithmetic.

13 Latest information

The code and technical notes are available online for public reviewing. However, the code designed and optimized for beamline is given for beamline users or participants to the workshop. The code has been developing further with advanced function, which might conflict with the other function as the version advances. Any comments or suggestion are welcome. Hands-on tutorial course will be organized in ASEAN workshop of photoemission spectroscopy and microscopy (AWPESM) held in every two years at SLRI or any if requested. The schedule of AWPESM workshop included advanced functions will be announced online.

- https://github.com/heitler/xps-excel-macro
- DOI: 10.5281/zenodo.1320738