

Using

XPSPEAK

Version 4.1

November 2000

XPS Peak Fitting Program for WIN95/98 XPSPEAK Version 4.1	1
<i>Program Installation.....</i>	<i>1</i>
<i>Introduction.....</i>	<i>1</i>
First Version	1
Version 2.0	1
Version 3.0	1
Version 3.1	2
Version 4.0	2
Version 4.1	2
Future Versions	2
General Information (from R. Kwok).....	3
Using XPS Peak.....	3
<i>Overview of Processing</i>	<i>3</i>
<i>Appearance</i>	<i>4</i>
<i>Opening Files</i>	<i>4</i>
Opening a Kratos (*.des) text file	4
Opening Multiple Kratos (*.des) text files	5
<i>Saving Files</i>	<i>6</i>
<i>Region Parameters.....</i>	<i>6</i>
Loading Region Parameters.....	6
Saving Parameters	6
<i>Available Backgrounds</i>	<i>6</i>
Averaging.....	7
Shirley + Linear Background	7
Tougaard	8
<i>Adding/Adjusting the Background.....</i>	<i>8</i>
<i>Adding/Adjusting Peaks.....</i>	<i>9</i>
Peak Types: p, d and f.....	10
Peak Constraints	11
Peak Parameters.....	11
Peak Function.....	12
<i>Region Shift.....</i>	<i>13</i>
<i>Optimisation.....</i>	<i>14</i>
<i>Print/Export.....</i>	<i>15</i>
Export	15
<i>Program Options.....</i>	<i>15</i>
<i>Compatibility</i>	<i>16</i>
File I/O	16
Limitations	17
Cautions for Peak Fitting	17

Sample Files:	17
gaas.xps	17
Cu2p_bg.xps	18
Kratos.des.....	18
ASCII.prn	18
Other Files	18

XPS Peak Fitting Program for WIN95/98 XPSPEAK Version 4.1

Program Installation

XPS Peak is freeware. Please ask RCSMS lab staff for a copy of the zipped 3.3MB file, if you would like your own copy

Unzip the XPSPEA4.ZIP file and run Setup.exe in Win 95 or Win 98.

Note: I haven't successfully installed XPSPEAK on Win 95 machines unless they have been running Windows 95c – CMH.

Introduction

Raymond Kwok, the author of XPSPEAK had spent >1000 hours on XPS peak fitting when he was a graduate student. During that time, he dreamed of many features in the XPS peak fitting software that could help obtain more information from the XPS peaks and reduce processing time.

Most of the information in this users guide has come directly from the readme.doc file, automatically installed with XPSPEAK4.1

First Version

In 1994, Dr Kwok wrote a program that converted the Kratos XPS spectral files to ASCII data. Once this program was finished, he found that the program could be easily converted to a peak fitting program. Then he added the dreamed features into the program, e.g.

- A better way to locate a point at a noise baseline for the Shirley background calculations
- Combine the two peaks of $2p_{3/2}$ and $2p_{1/2}$
- Fit different XPS regions at the same time

Version 2.0

After the first version and Version 2.0, many people emailed Dr Kwok and gave additional suggestions. He also found other features that could be put into the program.

Version 3.0

The major change in Version 3.0 is the addition of **Newton's Method** for optimisation

- Newton's method can greatly reduce the optimisation time for multiple region peak fitting.

Version 3.1

1. Removed all the run-time errors that were reported
2. A **Shirley + Linear** background was added
3. The **Export to Clipboard** function was added as requested by a user
 - Some other minor graphical features were added

Version 4.0

Added:

1. The asymmetrical peak function. See note below
2. Three additional file formats for importing data
 - A few minor adjustments

The addition of the **Asymmetrical Peak Function** required the peak function to be changed from the Gaussian-Lorentzian **product** function to the Gaussian-Lorentzian **sum** function. Calculation of the asymmetrical function using the Gaussian-Lorentzian product function was too difficult to implement. The software of some instruments uses the sum function, while others use the product function, so **both** functions are available in XPSPEAK. See *Peak Function, (Page 12)* for details of how to set this up.

Note:

If the selection is the **sum** function, when the user opens a ***.xps** file that was optimised using the Gaussian-Lorentzian **product** function, you have to re-optimize the spectra using the Gaussian-Lorentzian **sum** function with a different %Gaussian-Lorentzian value.

Version 4.1

Version 4.1 has only two changes.

1. In version 4.0, the printed characters were inverted, a problem that was due to Visual Basic. After about half year, a patch was received from Microsoft, and the problem was solved by simply recompiling the program
2. The import of multiple region VAMAS file format was added

Future Versions

The author believes the program has some weakness in the background subtraction routines. Extensive literature examination will be required in order to revise them. Dr Kwok intends to do that for the next version.

General Information (from R. Kwok)

This version of the program was written in Visual Basic 6.0 and uses 32 bit processes. This is freeware. You may ask for the source program if you really want to. I hope this program will be useful for people without modern XPS software. I also hope that the new features in this program can be adopted by the XPS manufacturers in the later versions of their software.

If you have any questions/suggestions, please send an email to me.

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I would like to thank the comments and suggestions from many people. For the completion of Version 4.0, I would like to thank Dr. Bernard J. Flinn for the routine of reading Leybold ascii format, Prof. Igor Bello and Kelvin Dickinson for providing me the VAMAS files VG systems, and my graduate students for testing the program. I hope I will add other features into the program in the near future.

R Kwok.

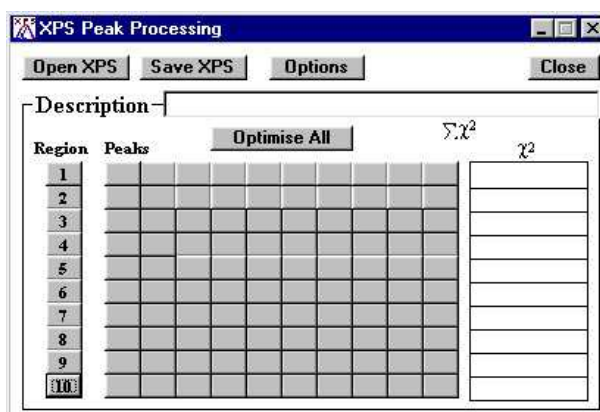
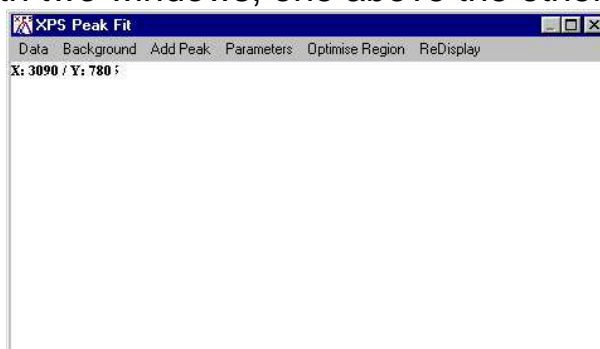
Using XPS Peak

Overview of Processing

1. Open Required Files
 - See *Opening Files (Page 4)*
2. Make sure background is there/suitable
 - See *Adding/Adjusting the Background, (Page 8)*
3. Add/adjust peaks as necessary
 - See *Adding/Adjusting Peaks, (Page 9)*, and *Peak Parameters, (Page 11)*
4. Save file
 - See *Saving Files, (Page 6)*
5. Export if necessary
 - See *Print/Export, (Page 15)*

Appearance

XPSPEAK opens with two windows, one above the other, which look like this:



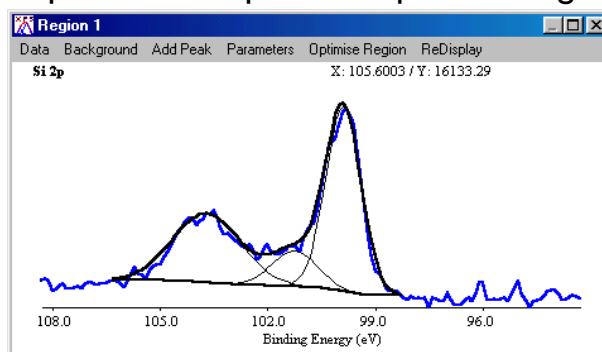
- The top window opens and displays the active scan, adds or adjusts a background, adds peaks, and loads and saves parameters.
- The lower window allows peak processing and re-opening and saving data

Opening Files

Opening a Kratos (*.des) text file

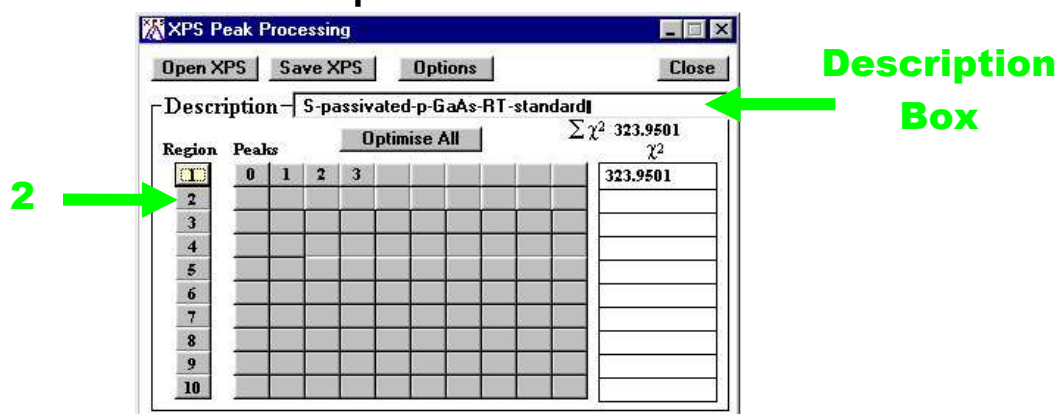
1. Make sure your data files have been converted to text files. See the back of the **Vision Software** manual for details of how to do this. Remember, from the original experiment files, each region of each file will now be a separate file.
2. From the **Data** menu of the upper window, choose **Import (Kratos)**
 - Choose directory
 - Double click on the file of interest

- The spectra open with all previous processing **INCLUDED**



Opening Multiple Kratos (*.des) text files

- You can open up a maximum of 10 files together.
- Open the first file as above
 - Opens in the first region (1)
 - In the XPS Peak Processing (lower) window, left click on **2** (second region), which makes this region active
 - Open the second file as in *Step 2, Opening a Kratos (*.des) text file, (Page 4)*
 - Opens in the second region (2)
 - You can only have one description for all the files that are open. Edit with a click in the **Description** box
 - Open further files by clicking on the next available region number then following the above step.
 - You can only have one description for all the files that are open. Edit with a click in the **Description** box



- To open a file that has already been processed and saved using XPSPEAK, click on the **Open XPS** button in the lower window. Choose directory and file as normal
- The program can store all the peak information into a ***.XPS** file for later use. See below.

Saving Files

1. To save a file click on the **Save XPS** button in the lower window
 2. Choose Directory
 3. Type in a suitable file name
 4. Click OK
- Everything that is open will be saved in this file
 - The program can also store/read the peak parameter files (*.RPA) so that you do not need to re-type all the parameters again for a similar spectrum.

Region Parameters

Region Parameters are the boundaries or limits you have used to set up the background and peaks for your files. These values can be saved as a file of the type *.rpa.

Note that these Region Parameters are completely different from the mathematical parameters described in *Peak Parameters, (Page 11)*

Loading Region Parameters

1. From the **Parameters** menu in the upper window, click on **Load Region Parameters**
2. Choose directory and file name
3. Click on **Open** button

Saving Parameters

1. From the **Parameters** menu in the **XPS Peak Fit** (Upper) window, click on **Save Region Parameters**
2. Choose directory and file name
3. Click on the **Save** button

Available Backgrounds

This program provides the background choices of

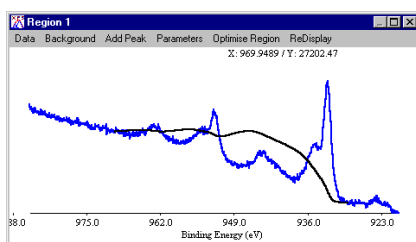
- Shirley
- Linear
- Tougaard

Averaging

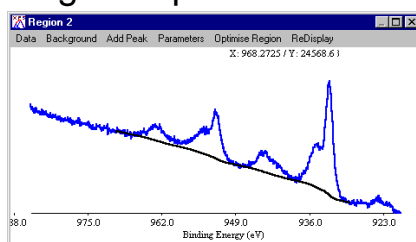
- Averaging at the end points of the background can reduce the time to find a point at the middle of a noisy baseline
 - The program includes the choices of None (1 point), 3, 5, 7, and 9 point average
 - This will average the intensities around the binding energy you select.

Shirley + Linear Background

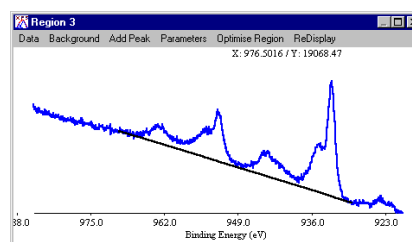
1. The **Shirley + Linear** background has been added for sloping backgrounds
 - The "Shirley + Linear" background is the Shirley background plus a straight line with starting point at the low BE end-point and with a slope value
 - If the slope value is **zero**, the original Shirley calculation is used
 - If the slope value is **positive**, the straight line has higher values at the high BE side, which can be used for spectra with higher background intensities at the high BE side
 - Similarly, a **negative** slope value can be used for a spectrum with lower background intensities at the high BE side
2. The **Optimization** button may be used when the Shirley background is **higher** at some point than the signal intensities
 - The program will increase the slope value until the Shirley background is below the signal intensities
 - Please see the example below - **Cu2p_bg.xps** - which shows background subtraction using the Shirley method (This spectrum was sent to Dr Kwok by Dr. Roland Schlesinger).
 - **A** shows the problematic background when the Shirley background is higher than the signal intensities. In the Shirley calculation routine, some negative values were generated and resulted in a non-monotonic increase background
 - **B** shows a "Shirley + Linear" background. The slope value was input by trial-and-error until the background was lower than the signal intensities
 - **C** was obtained using the optimisation routine



A slope = 0



B slope = 11



C slope = 15.17

Note: The background subtraction calculation cannot completely remove the background signals. For quantitative studies, the best procedure is "consistency". See *Future Versions, (Page 2)*.

Tougaard

For a Tougaard background, the program can optimise the B1 parameter by minimising the "square of the difference" of the intensities of ten data points in the high binding energy side of the range with the intensities of the calculated background.

Adding/Adjusting the Background

Note: The **Background** MUST be correct before **Peaks** can be added. As with all backgrounds, the range needs to include as much of your peak as possible and as little of anything else as possible.

1. Make sure the file of interest is open and the appropriate region is active
2. Click on **Background** in the upper window
 - The **Region 0** box comes up, which contains the information about the background

3. Adjust the following as necessary. See **Note**.
 - **High BE** (This value needs to be within the range of your data)
 - **Low BE** (This value needs to be within the range of your data)

NOTE: High and Low BE are not automatically within the range of your data. CHECK CAREFULLY THAT BOTH ENDS OF THE BACKGROUND ARE INSIDE THE EDGE OF YOUR DATA. Nothing will happen otherwise.

- **No. of Ave. Pts at end-points.** See *Averaging, (Page 7)*
- **Background Type**

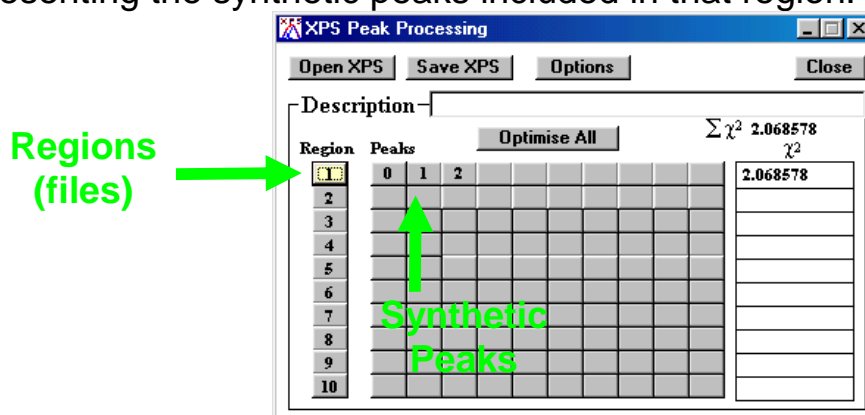
- **Note for Shirley + Linear:**
To perform the Shirley + Linear Optimisation routine:
 - a) Have the file of interest open
 - b) From the upper window, click on **Background**
 - c) In the resulting box, change or optimise the **Shirley + Linear Slope** as desired
 - Using **Optimize** in the **Shirley + Linear** window can cause problems. Adjust manually if necessary
3. Click on **Accept** when satisfied

Adding/Adjusting Peaks

Note: The Background MUST be correct before peaks can be added. Nothing will happen otherwise. See previous section.

- To add a peak, from the **Region** Window, click on **Add Peak**
 - The peak window appears
 - This may be adjusted as below using the Peak Window which will have opened automatically

In the **XPS Peak Processing** (lower) window, there will be a list of **Regions**, which are all the open files, and beside each of these will be numbers representing the synthetic peaks included in that region.



1. Click on a region number to activate that region
 - The active region will be displayed in the upper window
2. Click on a peak number to start adjusting the parameters for that peak.

- The Processing window for that peak will open

Peak 1

Peak Type S.O.S

Position
 Fix

FWHM
 Fix

Area
 Fix

% Lorentzian-Gaussian (0:G, 100:L)
 Fix

Asymmetry (TS=0 for symmetry)
0-1 0.01-200
 Actual FWHM: 2.212eV

3. Click off **Fix** to adjust the following using the maximum/minimum arrow keys provided:
 - **Peak Type.** (i.e. orbital – s, p, d, f)
 - **S.O.S** (Δ eV between the two halves of the peak)
 - **Position**
 - **FWHM**
 - **Area**
 - **%Lorentzian-Gaussian**
 - See the notes for explanations of how Asymmetry works.
4. Click on **Accept** when satisfied

Peak Types: p, d and f.

1. Each of these peaks combines the two splitting peaks
2. The FWHM is the same for both the splitting peaks, e.g. a p-type peak with FWHM=0.7eV is the combination of a $p_{3/2}$ with FWHM at 0.7eV and a $p_{1/2}$ with FWHM at 0.7eV, and with an area ratio of 2 to 1
3. If the theoretical area ratio is not true for the split peaks, the old way of setting two s-type peaks and adding the constraints should be used.
 - The **S.O.S.** stands for spin orbital splitting.

Note: The FWHM of the p, d or f peaks are the FWHM of the $p_{3/2}$, $d_{5/2}$ or $f_{7/2}$, respectively. The FWHM of the combined peaks (e.g. combination of $p_{3/2}$ and $p_{1/2}$) is shown in the **actual FWHM** in the Peak Parameter Window.

Peak Constraints

1. Each parameter can be referenced to the same type of parameter in other peaks. For example, for four peaks (Peak #0, 1, 2 and 3) with known relative peak positions (0.5eV between adjacent peaks), the following can be used
 - Position: Peak 1 = Peak 0 + 0.5eV
 - Position: Peak 2 = Peak 1 + 0.5eV
 - Position: Peak 3 = Peak 2 + 0.5eV
2. You may reference to any peak except with looped references.
3. The optimisation of the %GL value is allowed in this program.
 - A suggestion to use this feature is to find a nice peak for a certain setting of your instrument and optimise the %GL for this peak.
 - Fix the %GL in the later peak fitting process when the same instrument settings were used.
4. This version also includes the setting of the upper and lower bounds for each parameter.

Peak Parameters

This program uses the following **asymmetric Gaussian-Lorentzian sum function**

$$AGL(x, p, w, h, m, TS, TL) = h \left\{ (1-m) \cdot e^{-\ln(2) \cdot Q} + \frac{m}{1+Q} + TS \left[1 - e^{-\ln(2) \cdot Q} \right] \cdot e^{-\frac{6.9}{TL} Q} \right\}$$

Where:

- $Q = \left[\frac{2 \cdot (x - p)}{w} \right]^2$
- m=0 for 100% Gaussian
- m=1 for 100% Lorentzian
- TS and TL are the parameters for the asymmetric tail
- TS=0 for symmetric Gaussian-Lorentzian function

The program also uses the following **symmetrical Gaussian-Lorentzian product function**

$$GL(x, p, w, h, m) = h \left\{ \frac{e^{-(1-m)\ln(2)Q}}{1+m \cdot Q} \right\}$$

Where:

- $Q = \left[\frac{x-p}{w} \right]^2$
- $m=0$ for 100% Gaussian
- $m=1$ for 100% Lorentzian

Peak Function

Note:

If the selection is the sum function, when the user opens a *.xps file that was optimised using the Gaussian-Lorentzian **product** function, you have to re-optimize the spectra using the Gaussian-Lorentzian **sum** function with a different %Gaussian-Lorentzian value.

- You can choose the function type you want
1. From the lower window, click on the **Options** button
 - The peak parameters box comes up

The screenshot shows a dialog box titled "Option" with the following content:

Parameters for Search Method

	Position		Area		FWHM				
	Use	Step	Use	Step	Use	Step			
Level 1	<input checked="" type="checkbox"/>	±2	0.5	<input checked="" type="checkbox"/>	±50	10	<input checked="" type="checkbox"/>	±1	0.2
Level 2	<input checked="" type="checkbox"/>	±0.4	0.1	<input checked="" type="checkbox"/>	±9	1	<input checked="" type="checkbox"/>	±0.15	0.05
Level 3	<input checked="" type="checkbox"/>	±0.09	0.01	<input checked="" type="checkbox"/>	±0.9	0.1	<input checked="" type="checkbox"/>	±0.04	0.01
Level 4	<input type="checkbox"/>	±0.009	0.001	<input type="checkbox"/>	±0.09	0.01	<input type="checkbox"/>	±0.01	0.001

Parameters for Newton's Method

	Position	Area	FWHM	
	Use Delta	Use Delta	Use Delta	
Level 1	<input checked="" type="checkbox"/>	0.1	<input checked="" type="checkbox"/>	0.1
Level 2	<input type="checkbox"/>	0.05	<input type="checkbox"/>	0.05
Level 3	<input type="checkbox"/>	0.01	<input type="checkbox"/>	0.02
Level 4	<input type="checkbox"/>	0.005	<input type="checkbox"/>	0.01

Other fields: No. of trials: 5, Tolerance: 0.00001 %, GL Product (selected), GL Sum.

Buttons: Save Parameters, Load Parameters, OK.

- Select **GL sum** for the Gaussian-Lorentzian sum function
 - Select **GL product** for the Gaussian-Lorentzian product function.
2. For the Gaussian-Lorentzian sum function, each peak can have six parameters
 - Peak **Position**
 - **Area**
 - **FWHM**
 - %Gaussian-Lorentzian

- TS
- TL

If anyone knows what TS or TL might be, please let me know. Thanks, CMH

- Each peak in the Gaussian-Lorentzian product function can have four parameters
 - Peak *Position*
 - *Area*
 - *FWHM*
 - %Gaussian-Lorentzian

Since peak area relates to the atomic concentration directly, we use it as a peak parameter and the peak height will not be shown to the user.

Note: For asymmetric peaks, the FWHM only refers to the half of the peak that is symmetrical. The actual FWHM of the peak is calculated numerically and is shown after the actual FWHM in the Peak Parameter Window. If the asymmetric peak is a doublet (p, d or f type peak), the actual FWHM is the FWHM of the doublet.

Region Shift

A **Region Shift** parameter was added under the **Parameters** menu

- Use this parameter to compensate for the charging effect, the fermi level shift or any change in the system work function
- This value will be added to all the peak positions in the region for fitting purposes.

An example:

- A polymer surface is positively charged and all the peaks are shifted to the high binding energy by +0.5eV, e.g. aliphatic carbon at 285.0eV shifts to 285.5eV
- When the **Region Shift** parameter is set to +0.5eV, 0.5eV will be added to all the peak positions in the region during peak fitting, but the listed peak positions are not changed, e.g. 285.0eV for aliphatic carbon.

Note: I have tried this without any actual shift taking place. If someone finds out how to perform this operation, please let me know. Thanks, CMH.

In the meantime, I suggest you do the shift before converting your files from the Vision Software format.

- During any type of optimisation, you can press the "Stop Fitting" button and the program will stop the process in the next cycle.



Print/Export

In the **XPS Peak Fit** or **Region** window, From the **Data** menu, choose **Export** or **Print** options as desired

Export

- The program can export the ASCII file of spectrum (*.DAT) for making high quality figures using other software (e.g. SigmaPlot)
- It can export the parameters (*.PAR) for further calculations (e.g. use Excel for atomic ratio calculations)
- It can also copy the spectral image to the system clipboard so that the spectral image can be pasted into a document (e.g. MS WORD).

Program Options

1. The **%tolerance** allows the optimisation routine to stop if the change in the **difference** after one loop is less than the **%tolerance**
2. The default setting of the optimisation is Newton's method
 - This method requires a delta value for the optimisation calculations
 - You may need to change the value in some cases, but the existing setting is enough for most data.
3. For the binary search method, it searches the best fit for each parameter in up to four levels of value ranges
 - For example, for a peak position, in first level, it calculates the χ^2 when the peak position is changed by +2eV, +1.5eV, +1eV, +0.5eV, -0.5eV, -1eV, -1.5eV, and -2eV (range 2eV, step 0.5eV)
 - Then, it selects the position value that gives the lowest χ^2
 - In the second level, it searches the best values in the range +0.4eV, +0.3eV, +0.2eV, +0.1eV, -0.1eV, -0.2eV, -0.3eV, and -0.4eV (range 0.4eV, step 0.1eV)
 - In the third level, it selects the best value in +0.09eV, +0.08eV, ...+0.01eV, -0.01eV, ...-0.09eV
 - This will give the best value with two digits after decimal
 - Level 4 is not used in the default setting

- The range setting and the number of levels in the option window can be changed if needed.
4. The Newton's Method or Binary Search Method can be selected by clicking the "use" selection box of that method.
 5. The selection of the peak function is also in the Options window.
 6. The user can save/read the option parameters with the file extension *.opa
 - The program reads the default.opa file at start up. Therefore, the user can customize the program options by saving the selections into the default.opa file.

Compatibility

The program can read:

- Kratos text (*.des) files together with the peak fitting parameters in the file
- The ASCII files exported from Phi's Multiplex software
- The ASCII files of Leybold's software
- The VAMAS file format
- For the Phi, Leybold and VAMAS formats, multiple regions can be read
- For the Phi format, if the description contains a comma ",", the program will give an error. (If you get the error, you may use any text editor to remove the comma)

The program can also import ASCII files in the following format:

Binding Energy Value 1	Intensity Value 1
Binding Energy Value 2	Intensity Value 2
etc	etc

- The B.E. list must be in ascending or descending order, and the separation of adjacent B.E.s must be the same
- The file cannot have other lines before and after the data
- Sometimes, TAB may cause a reading error.

File I/O

The file format of XPSPEAK 4.1 is different from XPSPEAK 3.1, 3.0 and 2.0

- XPSPEAK 4.1 can read the file format of XPSPEAK 3.1, 3.0 and 2.0, but not the reverse
- File format of 4.1 is the same as that of 4.0.

Limitations

This program limits the:

- Maximum number of points for each spectrum to 5000
- Maximum of peaks for all the regions to 51
- For each region, the maximum number of peaks is 10.

Cautions for Peak Fitting

Some graduate students believe that the fitting parameters for the best fitted spectrum is the "final answer". This is definitely not true. Adding enough peaks can always fit a spectrum

- Peak fitting only assists the verification of a model
- The user must have a model in mind before adding peaks to the spectrum!

Sample Files:

gaas.xps

This file contains 10 spectra

1. Use **Open XPS** to retrieve the file. It includes ten regions
 - 1-4 for Ga 3d
 - 5-8 for As 3d
 - 9-10 for S 2p
2. For the Ga 3d and As 3d, the peaks are d-type with s.o.s. = 0.3 and 0.9 respectively
3. Regions 4 and 8 are the sample just after S-treatment
4. Other regions are after annealing
5. Peak width of Ga 3d and As 3d are constrained to those in regions 1 and 5
6. The fermi level shift of each region was determined using the As 3d_{5/2} peak and the value was put into the "Region Shift" of each region
7. Since the region shift takes into account the Fermi level shift, the peak positions can be easily referenced for the same chemical components in different regions, i.e.
 - Peak#1, 3, 5 of Ga 3d are set equal to Peak#0
 - Peak#8, 9, 10 of As 3d are set equal to Peak#7
8. Note that the %GL value of the peaks is 27% using the GL sum function in Version 4.0, while it is 80% using the GL product function in previous versions.

Cu2p_bg.xps

This spectrum was sent to me by Dr. Roland Schlesinger. It shows a background subtraction using the Shirley + Linear method

- See Shirley + Linear Background, (Page 7)

Kratos.des

- This file shows a Kratos *.des file
 - This is the format your files should be in if they have come from the Kratos instrument
 - Use import Kratos to retrieve the file. See *Opening Files, (Page 4)*
 - Note that the four peaks are all s-type
 - You may delete peak 2, 4 and change the peak 1,3 to d-type with s.o.s. = 0.7. You may also read in the parameter file: as3d.rpa.

ASCII.prn

- This shows an ASCII file
 - Use import ASCII to retrieve the file
 - It is a As 3d spectrum of GaAs
 - In order to fit the spectrum, you need to first add the background and then add two d-type peaks with s.o.s.=0.7
 - You may also read in the parameter file: as3d.rpa.

Other Files

(We don't have an instrument that produces these files at Auckland University., but you may wish to look at them anyway. See the readme.doc file for more info.)

1. Phi.asc
2. Leybold.asc
3. VAMAS.txt
4. VAMASmult.txt

Have Fun! July 1, 1999.