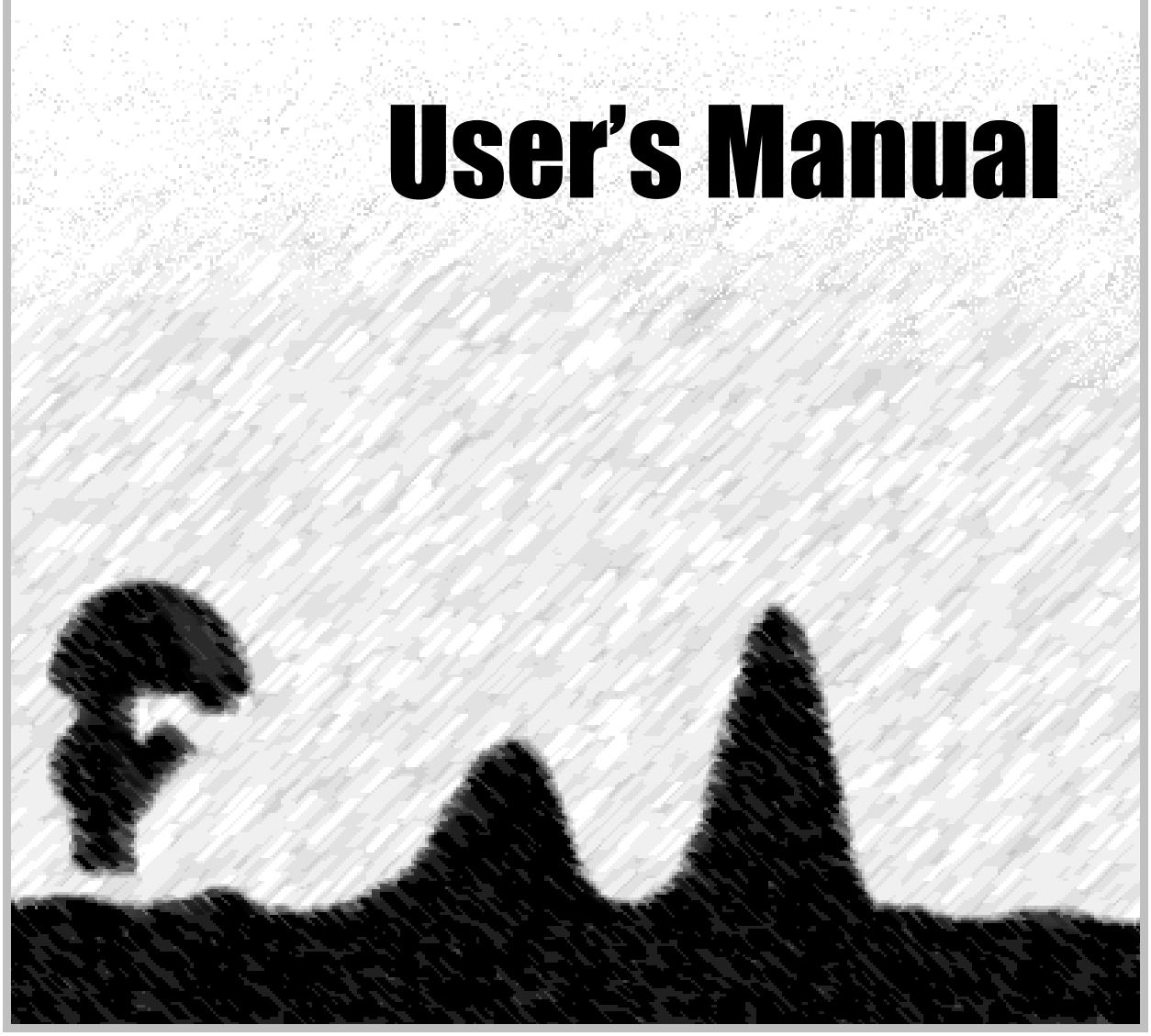
XPS MultiQuant
for Windows

Version 7.80

User's Manual



XPS MultiQuant

User's Manual

Budapest • 2018

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Revision: 7.80.02 (29-03-19)

Content

Introduction **6**

Legal Notes **7**

Installing XPS MultiQuant **8**
Uninstalling 8
Technical Notes 9

Using of the Program **12**
Starting XPS MultiQuant 12
Setting Parameters 13
Entering and Editing Input Data 13
Calculator in the Input Windows 15
Template Files 15
Importing Data 16
XPS Reduced Data Exchange Files 16
Converter Programs 16
Extracting Data from Various File Types 16
Managing Results and Charts 19
Managing Results and Charts 19
Saving and Printing 19
Exporting Results 20
Application of Structured Models 22
Intensity Simulation 24
Inelastic Mean Free Path 25
Carbonaceous Contamination 26
Miscellaneous Remarks 27

Step by Step **30**

Application Examples **38**

Applied Methods **46**
Homogeneous Model 46
Cross Sections 47
Angular Correction 48
Correction for Elastic Scattering 48
Inelastic Mean Free Path (IMFP) 48
Transmission Function 51
Contamination Correction 52
Multiline Approach 52
Normalisation of the Composition Results 53

Models for Structured Surfaces 55
Layers-on-Plane Model 57
Layers-on-Sphere Model 58
Layers-on-Cylinder Model 60
Layers-on-Polyhedron Model 61
Layers-on-Nanotube Model 63
Island Type Models 66
Oxide-Layer Model 67

Library Data 69
Chemical Elements 69
Photoelectron Lines 69
Cross Sections and Sensitivity Factors 69
Average Scale Factors 70
Asymmetry Parameters 70
Number of Valence Electrons 71
Geometry Correction Factors 71

Tips and Tricks 72
Transforming Angles 72
Layers Inside a Tube 73
Layers on Domes 75
Testing Layers 76
Transposing Cells 77
Exporting Comparison Chart 78
Relative Path for Transmission Files 78

Program References 79
Menu Commands 79
File Menu 79
Edit Menu 81
View Menu 82
Tools Menu 83
Windows Menu 85
Help Menu 85
File Menu (Notes window) 86
Edit Menu (Notes window) 86
Format Menu (Notes window) 87
Help Menu (Notes window) 87
Pop-up Menu (input windows) 88
Pop-up Menu (result windows) 89
Pop-up Menu (Chart window) 89
Pop-up Menu (Model Layout window) 90
Windows 91
Elements 91
Intensity 93
IMFP & Contamination 94
Composition 95
Chart 96
Model 97

Model Summary 99
IMFP & Contamination of Structured Models 99
Layer Thickness 100
Layer Calculation 101
Model Layout 102
Parameters 104
Parameter Summary 119
Polyhedron Editor 120
Notes 121
Intensity Simulation 122
Print 123
Print Options 124
Data Wizard 125
Open – Save As 126
Status Bar 126
Keyboard Commands 127
Shortcut Keys 127
Editing Keys 127
Menu Access Keys 127
Messages 128
Error collections 139
Pending Errors 140
Release Notes 141
Specifications 146
Literature 147
Contact 150
Index 151

Introduction

Quantitative evaluation of XP spectra is a major issue in surface characterisation. Numerous methods, models and data sets were developed and published but usually only the simplest ones are built into the commercial data systems used for the everyday work. The aim of developing the **XPS MultiQuant** program was to give a *practical* and *universal tool* to the surface chemists for obtaining the correct analytical results in most of the cases.

The program applies the 'classic' approach of the quantitative calculations, requiring the input of the integrated intensity of the measured XPS lines. All of the usual factors and correction methods, including calculated and experimental cross section values from several sources, asymmetry parameter, analyser transmission, IMFP, contamination of the adventitious carbon, can be applied and controlled independently. The necessary basic data for calculations (for elements, XPS lines, etc.) are integrated into the main library.
Calculation of several samples or experimental data sets (e.g., series of ion bombardments or heat treatments, etc.) can be done together. Results can be presented in various forms, like atomic %, atomic ratio, oxide molar ratio, etc., and can be printed and charted.
The sample geometry model can be selected from several options: beside the frequently applied 'infinitely thick homogeneous sample' model other ones for layered structures (both on flat and curved surfaces) are also available.

Legal Notes

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Installing XPS MultiQuant

XPS MultiQuant can be used under Windows 2000, XP, Vista, 7, 8 and 10 operating systems. Although it is not tested on Windows 98, ME and NT; it is expected to run on these systems as well.
You cannot simply copy the files from the distribution media to your hard disk. You must use the Setup program to decompress and install files into the correct folders. Before running setup, remove any previous installations of XPS MultiQuant.

To install XPS MultiQuant on your computer:

- Download the XPS MultiQuant distribution kit from the Internet
- Decompress the downloaded ZIP archive into an empty folder
- Run the *Setup.exe* program from this folder
- Follow the instructions of the setup program.
- If an appropriate *Service Update* is also available (with the same major version number), download and decompress the archive and follow the instructions of the attached *Read Me* file.

Uninstalling

If you, for any reason, do not want to use XPS MultiQuant any more, you can fully remove it easily.

To uninstall XPS MultiQuant from your computer:

- Press **Start** button
- Select **Settings \ Control Panel**
- Double click the **Add / Remove Programs** icon
- Select XPS MultiQuant from the list
- Press the **Add / Remove** button

Follow the instructions of the removal program. The names of the *Control Panel* items may vary in the different versions of the operating system.
If the program cannot be removed automatically, e.g., the *St6unst.log* file was accidentally deleted, remove the files and registry entries listed in the next chapter. If you are not familiar with the registry editing, do not tamper it; ask your system manager. After improper registry manipulation, your computer may become non-functional.
If you have programs using the same shared programming components (the files installed into the *\Windows\System* folder) do not remove them.

Technical Notes

Files Installed

File	Folder	Description
XMQ.exe	\Program Files\XMQ	XPS MultiQuant application
XMQ.lib	\Program Files\XMQ	XPS MultiQuant Library
XMQ.chm	\Program Files\XMQ	XPS MultiQuant Help
XMQ.mqw	\Program Files\XMQ	XPS MultiQuant Workspace
*.mtr	\Program Files\XMQ	Transmission files
St6unst.log	\Program Files\XMQ	Uninstall log file
Al-Layers.mqd	\Program Files\XMQ\Samples	Example data file
Al-Oxide.mqd	\Program Files\XMQ\Samples	Example data file
Cermet.mqd	\Program Files\XMQ\Samples	Example data file
C-nanotube.mqd	\Program Files\XMQ\Samples	Example data file
Contact.mqd	\Program Files\XMQ\Samples	Example data file
CuAgAu.mqd	\Program Files\XMQ\Samples	Example data file
LB-film.mqd	\Program Files\XMQ\Samples	Example data file
NaCl-multiline.mqd	\Program Files\XMQ\Samples	Example data file
NaCl-scaling.mqd	\Program Files\XMQ\Samples	Example data file
Si-ARXPS.mqd	\Program Files\XMQ\Samples	Example data file
SiN-powder.mqd	\Program Files\XMQ\Samples	Example data file
SiO2-contam.mqd	\Program Files\XMQ\Samples	Example data file
SiO2-simulation.mqd	\Program Files\XMQ\Samples	Example data file
Si-wafer.mqd	\Program Files\XMQ\Samples	Example data file
Cermet.mqt	\Program Files\XMQ\Samples	Example template file
Si-SiO2-CH.mqt	\Program Files\XMQ\Samples	Example template file
Cermet.mqx	\Program Files\XMQ\Samples	Reduced Data Exchange file
CuAgAu.mtr	\Program Files\XMQ\Samples	Transmission file
Exponential.mtr	\Program Files\XMQ\Samples	Transmission file
Polynom.mtr	\Program Files\XMQ\Samples	Transmission file
Rational.mtr	\Program Files\XMQ\Samples	Transmission file
Combined.mtr	\Program Files\XMQ\Samples	Transmission file
ContactProfile.xls	\Program Files\XMQ\Samples	Excel 2003 workbook
CermetDocument.doc	\Program Files\XMQ\Samples	Word 2003 document
ComCtl32.ocx	\Windows\System	Common Controls
Comdlg32.ocx	\Windows\System	Common Dialog Control
Graph32.ocx	\Windows\System	Graph Control
Gsw32.exe	\Windows\System	Graphic server
Gswag32.dll	\Windows\System	AutoGraph
Gswdll32.dll	\Windows\System	Graphic server library
MSflxgrd32.ocx	\Windows\System	FlexGrid Control
MSvbvm60.dll	\Windows\System	Visual Basic Virtual Machine
Sysinfo.ocx	\Windows\System	Sysinfo Control
Tabctl32.ocx	\Windows\System	Tabbed Dialog Control
St6unst.exe	\Windows	Uninstall program

Registry Entries

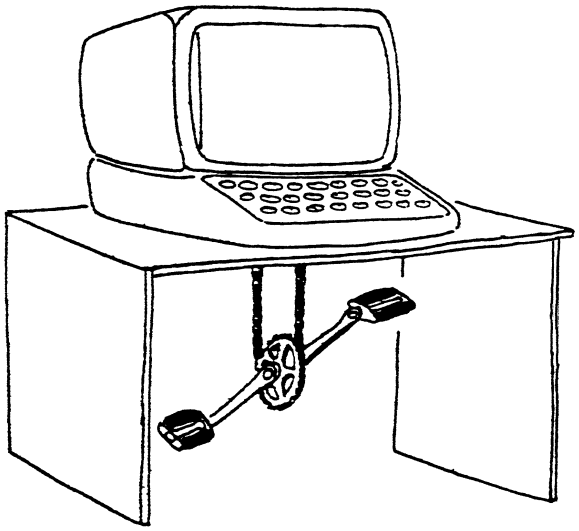
The first two entries store the default and initial settings of the program. The subsequent entries describe the XPS MultiQuant data, transmission and templates file types and also the XPS Reduced Exchange files (name, icon and associated program).

HKEY_CURRENT_USER\Software\VB and VBA Program Settings\XMQ\Defaults
HKEY_CURRENT_USER\Software\VB and VBA Program Settings\XMQ\Ini
HKEY_CLASSES_ROOT\.mqd
HKEY_CLASSES_ROOT\MQDfile
HKEY_CLASSES_ROOT\.mtr
HKEY_CLASSES_ROOT\MTRfile
HKEY_CLASSES_ROOT\.mqt
HKEY_CLASSES_ROOT\MQTfile
HKEY_CLASSES_ROOT\.mqx
HKEY_CLASSES_ROOT\MQXfile

Data, template and exchange files are associated with the XPS MultiQuant application while transmission files with Notepad.

Hardware Requirements

There is no special requirement; any computer [1] with x86-compatible processor is satisfactory. If the operating system can run with tolerable speed, XPS MultiQuant will run as well. The program occupies 2-8 Mbytes of hard disk space [2] (depending on components already installed). Printer is recommended.

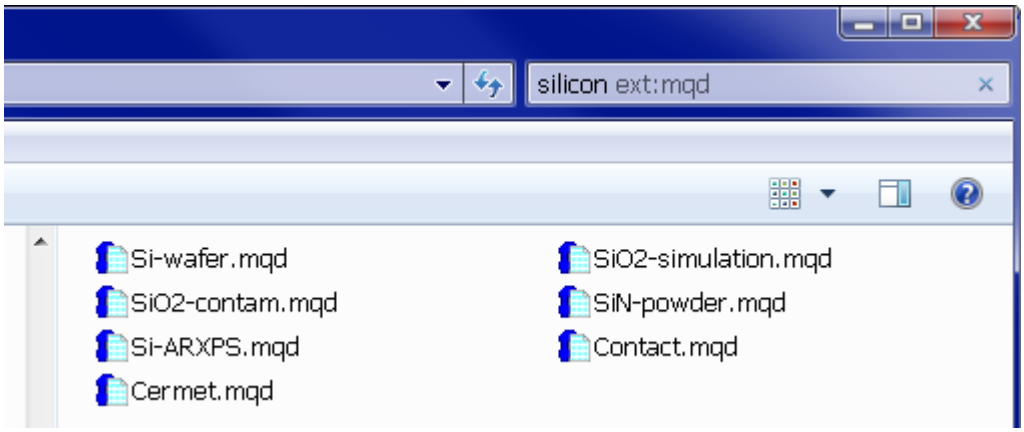


[1] Computers in the future may weigh no more than 1.5 tons. (*Popular Mechanics*, 1949)

[2] 640K ought to be enough for anybody. (*Bill Gates*, 1981)

Miscellaneous Remarks

- In Windows NT-based operating systems (NT, 2000, XP, Vista, 7, 8, 10) user may have to own administrative privileges to install some system components.
- The name of the *Windows* and *Windows\System* folders, where the shared components are located, may be slightly different (e.g., *WinNT*, and *WinNT\System32*) in the various versions of the operating system.
- In 64-bit operating systems the 32-bit applications, like XPS MultiQuant, are installed into the *Program Files (x86)* folder.
- From Windows Vista and above, the workspace file may be stored in the *C:\Users\[username]\AppData\Local\VirtualStore\Program Files\XMQ* folder, depending on the User Access Control (UAC) settings.
- XPS MultiQuant data files (*.mqd) can be stored on any drive in any folder.
- Although the language of XPS MultiQuant is always English, it applies the locale settings of your system (in the Control Panel *Regional Setting* or *Region and Language*), as different decimal and thousand separators, date formats, etc. (except in the analyser transmission files).
- XPS MultiQuant data are stored in binary files. Texts in the file (e.g., title, experiment labels, element symbols, notes) are stored in original forms thus the content of the file can be searched by the operating system or external programs.



Using of the Program

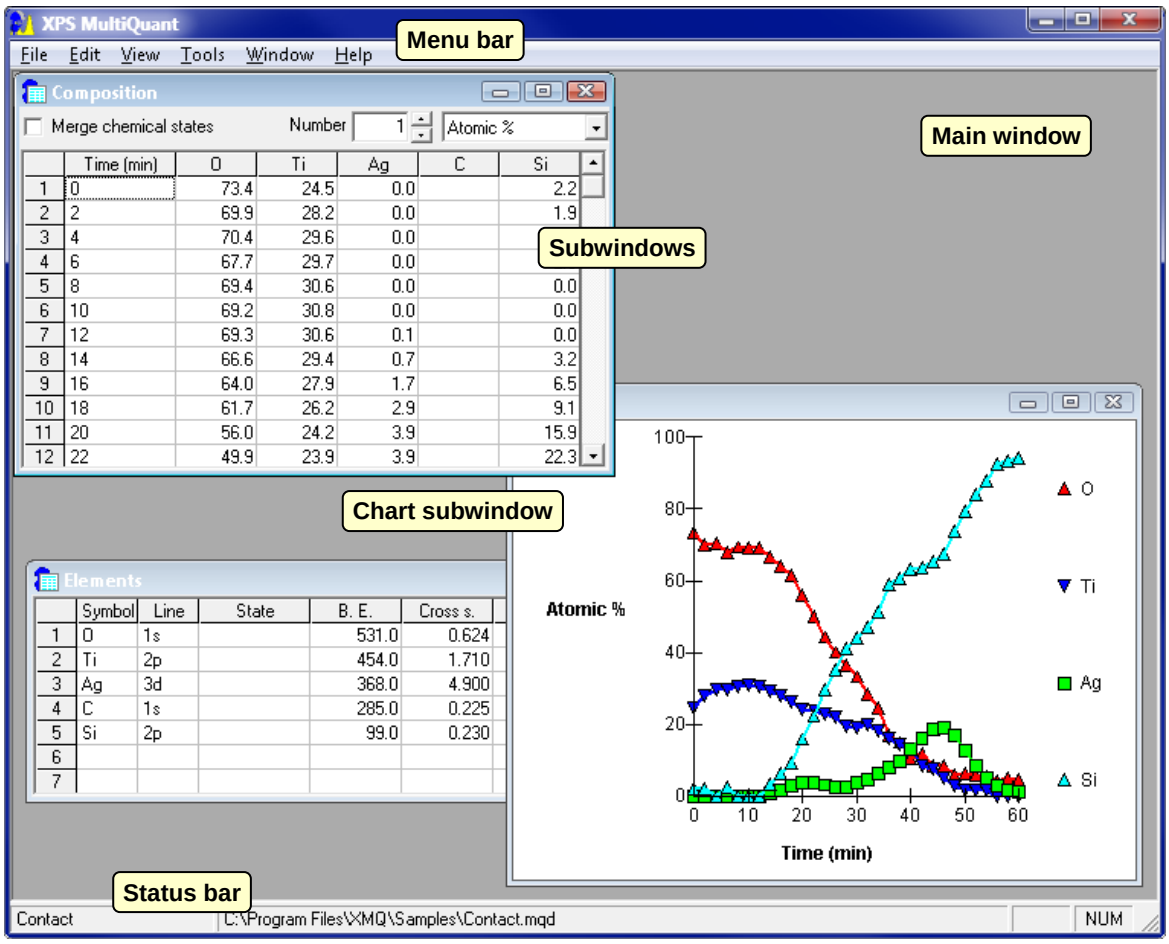
This chapter describes the first steps of using XPS MultiQuant. The basic knowledge of X-ray photoelectron spectroscopy and Microsoft Windows is assumed.

Starting XPS MultiQuant

The program can be started by several ways as usual in Windows.

- Press the **Start button** and select *XPS MultiQuant* from the *Programs* folder.
- Put a shortcut to the desktop and double click it.
- Double click the icon of any XPS MultiQuant data file (with *.mqd* extension).
- Previously processed XPS MultiQuant data files are also available in the list of the **Start button / Documents**.

When the program is running the main window may look like this:



When the program is started by clicking a data file or from the **Start button / Documents** the file is loaded and the results are calculated and displayed automatically.
The main window can be resized and repositioned as usual in Windows. At the top of the window, you can find the customary menu bar. At the bottom, the status bar shows the title of the calculation, the name of the current data file (if any), the pending page and the status of the NUMLOCK key.
If you are unfamiliar with XPS MultiQuant, invoke the *Data Wizard* (on the *Tools* menu). It gives you step-by-step instructions to setup a quantitative calculation.

Setting Parameters

It is a good practice before entering the input data for your quantitative calculations to set all of the parameters required, especially, when you start XPS MultiQuant at the first time. Most of the parameters have to be set only once unless you are lucky to have more than one spectrometer (or one with several operating modes). Perform the **View / Parameters** command and scan through the tabs and set or select the following items:

- Model type; usually *Homogeneous.*
- Excitation source.
- Cross section or sensitivity factor set. Usually let the *Enable library lookup* and *Splitting* features enabled.
- Method of inelastic mean free path correction. Try a simple exponential approach first.
- Angular correction and the excitation-analyser angle of the instrument.
- Method of contamination correction. For general use, selection of *Mohai* is suggested.
- Transmission function of the spectrometer.
- The typical labels you want to attach to the experiments

Every setting can be overwritten later as necessary. When all the parameters are set, select the **File / Save Defaults** command to store your preferred settings in the registry.

Entering and Editing Input Data

First of all, specify the elements you want to use in the calculation. Click the **File / New** or the **View / Elements** command to invoke the *Elements* window and fill the table. You can navigate in the table with the arrow keys or mouse clicks (see chapter "Keyboard Commands"). Type the symbol of the elements and the name of the selected lines. The "2p", "4f", etc. notations mean the whole doublet lines, while the "2p3/2" or "4f7" the doublet components. The program corrects the improper capitalisation of the element symbols and transition names. The "/2" tag is optional for the components. You can type either decimal point or decimal comma; always the current one is entered, as set in Windows. It is practical if you use two languages applying different symbols (e.g., English and German). You can enter the line notations simply by double clicking the cells. The program inserts the notations of the lines actually available for the selected cross section data set, and rotates them in increasing binding energy order.
After selecting the elements, click the **Tool / Library Lookup** command to fill all the fields left of the table from the library of XPS MultiQuant. Of course, you can type in your own data manually or you can overwrite any particular fields filled from the library. Use the *State*

column to distinguish between different chemical states of the same element; e.g., your sample contains carbon in carbonate form and has hydrocarbon contaminant on it. If the automatic contamination control (*Mohai*) is selected, the *State* of the contaminant C1s line must be left empty.

To improve the reliability of the calculations, you can apply more than one spectral line to quantify the same element. To switch on the *Multiline approach* feature, select the *Average* (simple average) or the *Ebel* (weighted average) method on the *Model* tab of the *Parameters* window. If the element calculated by multiple lines is present in more than one chemical states, you must provide data for all lines and all states for this element. E.g., if you measure the Si2s and Si2p lines of oxidised silicon, either you can calculate the total Si concentration (by the Si2s(total) and Si2p(total) lines) or both lines must be decomposed into Si^0 and Si^{4+} chemical sates (by the Si2s(0), Si2p(0), Si2s(4+) and Si2p(4+) lines).

The binding energy values of the library, used for calculating the analyser transmission and IMFP correction, are approximate values (usually for elemental state). However, you can enter the exact value to emphasise the chemical state. The number of the elements is counted automatically so do not leave empty lines between them.

Finishing with the *Element* window, close it by clicking the close button or by the **View / Elements** command. The values entered to the table are checked and you will get an error message if some of them are unrealistic.

When all element data are typed in, invoke the *Intensity* window by the **View / Intensity** command. Get the integral peak intensity data from your XPS data processing software after the usual pre-processing (correction for acquisition time, number of sweeps, background removal, etc.) and enter them into the table of *Intensity* window. In case of your data are also corrected for analyser transmission, set this feature to *None* in the *Parameter* window. The program distinguishes the empty and zero cells so you can use zero value to emphasise the absence of an element while an empty cell may simply mean ‘not measured’. If your data system is able to provide intensity data in tabulated form, as specified in chapter “Program References, Edit Menu”, you can enter all of the data in one step, using the **Edit / Paste Table** command.

Type the labels for your experiments. Labels hold auxiliary data, like sample name, tilt angle, temperature, time, etc.

If you apply more sophisticated IMFP or contamination correction, you have to fill the corresponding fields in the *IMFP & Contamination* window as well.

The content of any input window can be changed later at any time. To edit a cell, double click it. To insert or remove an element use the **Edit / Insert Row** or **Edit / Delete Rows** commands in the *Elements* window; to insert or remove experiments use the same commands in the *Intensity* window. The deleted rows can be recovered only once by the **Undo Delete Rows** command. If you want to add elements or experiments to the end of the tables, simply fill the last empty line.

Content of the cells can be simply copied and pasted within XPS MultiQuant or between external programs by the pop-up menu commands invoked by right mouse click.

The order of elements or experiments can be easily rearranged. Just drag and drop by the right mouse button the sequence number of the desired element (in the *Elements* window) or experiment (in the *Intensity* window) into the required new position. During the drag and drop operation, the mouse cursor is changing, indicating the action in progress.

Calculator in the Input Windows

Instead of numbers, simple arithmetic expressions may also be entered into the cells of the input windows (*Elements*, *Intensity*, *IMFP & Contamination*, *Model*). These may be used conveniently, e.g., for summing up the intensity of the components of a doublet line.
The expression consists of two numbers connected with an arithmetic operator. Valid operators are: addition (+), subtraction (–), multiplication (*) and division (/). Numbers may have sign, decimal separator (dot or comma, according to the locale settings of the operating system), exponent sign (e or E) and one or two-digit exponent with optional sign.
The expression is parsed and calculated immediately, when the ENTER or an ARROW key is pressed, and replaced with the result. If the expression is invalid, either syntactically or semantically (e.g., division by zero), the result is not shown and a warning tone is sounded.
The following table shows some examples for valid and invalid expressions.

Valid expressions			**Invalid expressions**	
123 + 123	=	*246*	123 + 12ee12	*Two exponent signs*
–123 + 456	=	*333*	–12e1.2 * 12	*Digit separator in exponent*
–12.3 + –123	=	*–135.3*	–12..34 + 12	*Two digit separators*
–456 / –12	=	*38*	12e–+12 * 12	*Two signs in exponent*
123.4 * 1.5	=	*185.1*	123 /	*Right hand operand missing*
12.3e+12 / 4e+10	=	*307.5*	12e+ /12	*Digit in exponent missing*
2.46E12 / 1.23E12	=	*2*	123 ** 123	*Two operators*
–1.2e–12 * –2e12	=	*2.4*	/ 123	*Left hand operand missing*

Template Files

XPS MultiQuant template files make the work easy if you frequently perform the same quantification on similar sample series. Template files, as data files, store all basic data, model definition, title and notes but do not save intensity values, labels and results (for the structured models). To save the current data set as template file, invoke the **File / Save as…** command and select the *XPS MultiQuant Template Files (*.mqt)* file type. You can open the template files as data files either by the **File / Open…** command or by drag and drop the file into the main window or by double click it. When a template file is loaded, the *Intensity* window appears immediately.
Template files can also be used to save various parameter sets beside the default one, stored in the registry. Select the required parameters in the *Parameters* window and create a template file without specifying elements.

Importing Data

Most time consuming task when using of XPS MultiQuant, is to type element and intensity data of the experiments. Transferring large amount of data by this way is tedious and may be the source of potential errors. The following chapter surveys the recommended methods of importing data.

XPS Reduced Data Exchange Files

XPS Reduced Data Exchange files are designed to transfer reduced data (peak position, FWHM, integral intensity, etc.) from spectral processing programs to other programs, e.g., for looking up line positions in a database, calculating IMFP for the determined energies, or performing advanced quantification.
The *XPS Reduced Data Exchange* files are unformatted character files with defined structure. They can be prepared on various computers under DOS, Windows, Unix, Linux and Macintosh operating systems and can be read without any previous conversion.
Interpreting of version 1.1 *XPS Reduced Data Exchange* files is fully implemented in XPS MultiQuant. Files can be opened like the standard data files by the **File / Open…** menu command or the source application can invoke XPS MultiQuant directly and pass the file as a parameter. Transferring of data can be routinely applied for simple quantification, ion etch depth profile, etc. and it gives immediate results. The advanced features (layer thickness calculation on flat or curved surfaces) cannot be addressed directly because these features require deeper user interaction anyway.

Converter Programs

Although using of XPS Reduced Data Exchange files is recommended for importing data, this format is not yet widely applied. Another possible solution may be, to interpret the quantification reports provided by most of the XPS data processing systems. These reports can usually be saved as simple text files. The files can be converted to XPS Reduced Data Exchange files, which can be read by XPS MultiQuant. Converter programs are available on the homepage of XPS MultiQuant. This way is convenient for regular use.

Extracting Data from Various File Types

The spectrum processing programs produce tabulated output in various file formats. To write a program to read of all file variants is unrealistic and not really necessary. Fortunately, the following procedure can help in most of the cases as follows. Open the file with its native (or similar) reader program, copy the required part of the file (row, column or matrix of numbers) and paste it into XPS MultiQuant.

The major cases are the followings:

- Cell-structured data files includes Excel workbooks (*.xls, *.xlsx), Data Interchange Format (*.dif) files, Origin (*.opj, *.opju) projects, tables in Word (*.doc, *.docx) and Rich Text Format (*.rtf) documents. Cells can be easily selected in any direction (row, column, matrix). When copied, cells are separated by TAB characters.

- The simple text (*.txt, *.csv) files does not contain real cell information. Tabulated items in these files are usually saved as delimiter separated text. Typical example is the comma-separated values (CSV) file, which can be generated by several programs. Text can be usually selected in rows only but some programs allows column selection as well.
- The items of tables in files prepared for human reading, e.g., printed to file (*.txt, *.prn, *.pdf, *.htm, *.html, etc.), are usually delimited by spaces.

XPS MultiQuant is ready to accept various types of delimited text for pasting without previous conversion. Delimiters includes comma, semicolon, tabulator, consecutive spaces or any other character selected in Windows. The line terminator characters can be carriage return (CR), line feed (LF) or both (CRLF) thus text can be pasted directly from files prepared on different computer systems.
The next table summarises the allowed combinations of various decimal symbols and list separators. As you see, most kinds of delimited text can be pasted, even when the number format is not changed in Windows. If you still had to alter the format settings, restart XPS MultiQuant.

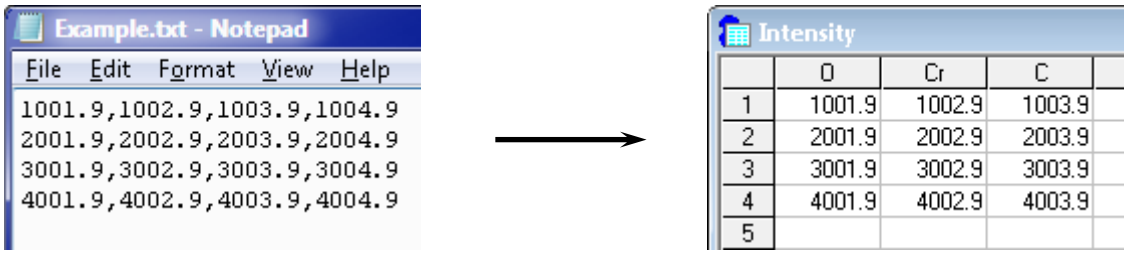
In the copied text		**Windows decimal symbol**	
List separator	**Decimal symbol**	**Point**	**Comma**
Tab	Point	OK	OK
	Comma	OK [1]	OK
	None	OK	OK
Comma	Point	OK	OK
	Comma	Not allowed	Not allowed
	None	OK	OK [2]
Semicolon	Point	OK	OK
	Comma	OK [1]	OK
	None	OK	OK
Spaces	Point	OK	OK
	Comma	OK [2]	OK
	None	OK	OK
Other [3]	Point	OK	OK
	Comma	OK [1]	OK
	None	OK	OK

[1] If column or single data item is copied, press SHIFT key during pasting.
[2] Press SHIFT key during pasting.
[3] Set the proper list separator character in Windows.

Spaces are normally served as item separators. If your data contain spaces (e.g., labels), they are split into two or more cells when pasted. To avoid it, press the SHIFT key during pasting. Space-containing data and space delimiters are usually cannot be combined. In that special case, copy your data column by column.
Depending on the actual combination of decimal symbol and list separator characters in the copied text, the SHIFT key either disables spaces as list separator or swaps the denotation of comma (e.g., list separator instead of decimal symbol or vice versa).

You need not memorize the above table; just use the **Paste** command. If the appearance of your pasted data differs from the expected, try the SHIFT + **Paste** variant.

The following examples illustrate that several decimal symbol and list separator combinations (→ represents TAB character) can produce the same result without customizing the number format in Windows (decimal symbol is set to point).




```
1001,9,1002,9,1003,9
2001,9,2002,9,2003,9
3001,9,3002,9,3003,9
4001,9,4002,9,4003,9
```

```
1002,1003,1004
2002,2003,2004
3002,3003,3004
4002,4003,4004
```

```
1001.9;1002.9;1003.9
2001.9;2002.9;2003.9
3001.9;3002.9;3003.9
4001.9;4002.9;4003.9
```

```
1001,9;1002,9;1003,9
2001,9;2002,9;2003,9
3001,9;3002,9;3003,9
4001,9;4002,9;4003,9
```

```
1002;1003;1004
2002;2003;2004
3002;3003;3004
4002;4003;4004
```

```
1001.9→1002.9→1003.9
2001.9→2002.9→2003.9
3001.9→3002.9→3003.9
4001.9→4002.9→4003.9
```

```
1001,9→1002,9→1003,9
2001,9→2002,9→2003,9
3001,9→3002,9→3003,9
4001,9→4002,9→4003,9
```

```
1002 → 1003 → 1004
2002 → 2003 → 2004
3002 → 3003 → 3004
4002 → 4003 → 4004
```

```
1001.9 1002.9 1003.9
2001.9 2002.9 2003.9
3001.9 3002.9 3003.9
4001.9 4002.9 4003.9
```

```
1001,9 1002,9 1003,9 ⇧
2001,9 2002,9 2003,9
3001,9 3002,9 3003,9
4001,9 4002,9 4003,9
```

```
1002    1003    1004
2002    2003    2004
3002    3003    3004
4002    4003    4004
```

Managing Results and Charts

Display the *Composition* window by the **View / Results** command. Results can be presented in eight different forms: Atomic %, Atomic ratio, Oxide molar %, Oxide molar ratio, Mass %, Mass ratio, Oxide mass % or Oxide mass ratio. If you select one of these forms from the dropdown list, the data in the table are recalculated immediately. When the percentage type results are selected, you can omit any element from the 100 % sum; just double click the element symbol. The omitted element can be brought back by double clicking again. When ratio type results are selected, the 'basis' element of the calculation can be set by double clicks as well. If the concentration of the selected basis element is zero for some experiments, the previous non-zero basis is kept for these experiments. The number of atoms of the basis element can be set in the *Number* textbox by clicking the arrow buttons. If you enter an element in more than one chemical state, the different states of the same element can be summed up by selecting the *Merge chemical states* check box. In this case the double clicks the element symbols will not work. This option is not available when oxide type results are selected because it makes no sense to add the quantity of different compounds. In these latter cases, the *Oxygen balance* is calculated and displayed in the last column of the window, which shows the ratio of measured and calculated (required by the applied chemical formula) oxygen. If it is less than 1, the surface is deficient in oxygen; if it is greater than 1, there is oxygen surplus.

Results can be demonstrated in graphical form in the *Chart* window (**View / Chart** command). It co-operates with the *Composition* window. Results are presented as line chart or as pie chart if only one experiment entered. When you change the *Composition* window, it is reflected in the *Chart* window (immediately or after clicking it). The X (category) axis of the line chart is taken from the *Labels* tab of the *Parameters* window. It can be altered easily by double clicking the label column headers. *Sequence number* as X-axis can be selected only in the *Parameters* window. Numeric labels (Time, Tilt, Temperature, etc.) are treated as numbers while text labels are simply enumerated. The Y (value) axis is chosen according to the result type in the *Composition* window. Elements omitted from percentage calculation are also omitted from the chart even if the result type is changed to ratio. If you have unnecessary data points, i.e., experiments in your series (e.g., a 60° tilt experiment in an ion etch series) you may omit them from the chart by double clicking the sequence number of the experiment. The number is changed to **X** showing that this experiment is switched off temporarily.

Feel free playing with different settings and find the best form of presentation, which suits your requirements. While you analyse your results, open the *Notes* window (**View / Notes** command), record your comments and store together with the respective data.

Saving and Printing

After entering data, you may want to save them for documentation, for further analysis or for extending later with new data. To save your work, select the **File / Save As** command. A standard Windows dialog box is shown to set or select the folder and file name. The default extension is .mqd. The file is binary thus do not tamper it with other programs. When you save the data for the first time, the file becomes the current file and its name is displayed in the status bar. Then you can save the data into the current file by the **File / Save** command or by the CTRL+S shortcut. Saved files can be loaded by the **File / Open** command. You can open files on mapped network drives as well but you must have writing permission to that

drive (full access type). Files can also be opened by drag and drop the data file from the Windows Explorer to the main window of XPS MultiQuant.
If you want to suspend your work and to continue it later, you can select the **File / Save Workspace** command. Once selected, the name of the current data file, the position, size and settings of the open windows are saved on exit. Next time, when you started the program without command line parameter (i.e., not by double clicking on a filename), the data file, registered in the workspace, is loaded and the layout of all windows are restored.
Results can be printed on any local or network printer connected to your computer. Perform the **File / Print** command. To start with, press the *Options* button and select the required printer, page orientation, font type and size. Return to the *Print* window, select items to be printed and press the *Print* button to print. Results are printed with the last selected settings (type, basis element, merging, etc.). Pages are spooled and printed only when physically full.
A small page icon is appearing in the status bar indicating the pending page. To print the pending, unfinished page, press the *Eject Page* button in the *Print* window or double click the page icon. Settings of the *Print* and *Print Options* windows are also stored in the registry when **File / Save Defaults** executed. You can also print the content of any window immediately. Just select the **File / Print Current** command or press CTRL+P to print the content of the active window. The logically connecting parts of the printout, like header and rows of a table, are kept together; take it into account when selecting the margin and font sizes. Large tables, which cannot be printed to one page, are tiled. A sample page of XPS MultiQuant output is illustrated on the next page. For printing the content of *Notes* and *Parameters*, use the **Print** command or button of these windows.

Exporting Results

Although the printed output of XPS MultiQuant is satisfactory in most of the cases, you may want to insert the results into your documents. The content of any window (except *Parameters* and *Chart*) can be copied to the clipboard by the **Edit / Copy Table** command and pasted into any Windows application. Two subcommands are available: apply the **Edit / Copy Table / ASCII** command to paste data into text files, Excel worksheets, etc. and the **Edit / Copy Table / MS Word** to paste into Word documents and create Word tables. Only whole tables with column headings can be exported. If you want to exchange data between two instances of XPS MultiQuant, press SHIFT key and use the **Edit / Copy Table / ASCII** and **Edit / Paste Table** commands to copy tables without headings.
To copy text from or paste into the *Notes* window, use the commands of the pop-up menu (right click). The graphics of the *Chart* and *Model Layout* windows can also be transferred to other applications by the **Copy** command of the pop-up menu of these windows.
To produce high quality graphs, e.g., depth profiles, export the results into Excel, Origin or any other charting program.

XPS MultiQuant 7.80 Thursday, 26 April, 2018

Cr-O-Si cermet film

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Parameters

Model:	Homogeneous	
Multiline approach:	None	
Excitation:	Mg K (1253 .6 eV)	
Cross sections:	Scofield	
IMFP correction:	method:	Exponential
	exponent:	0.5
Angular correction:	method:	Reilman
	analyser-excitation:	65.0 °
Transmission:	type:	FRR, CRR
Contamination correction:	method:	Mohai

Elements

Line	State	B. E.	Cross s.	Asymm.	At. w.	Val.	Ox.
O 1s		531.0	0.6240	2.0000	16.000	2	0
Cr 2p		574.0	2.3400	1.4590	52.000	3	3
C 1s		285.0	0.2250	2.0000	12.010	4	0
Si 2p		99.0	0.2300	1.1060	28.090	4	2

Intensity

	Time (min)	O	Cr	C	Si
1	0	837624	669910	41853	213533
2	10	467572	936964	20378	296118
3	20	436508	936100	21494	293938
4	30	422376	938868	15150	302254
5	40	424544	955776	16565	290347
6	50	417772	942724	13359	292522

Atomic %

	Time (min)	O	Cr	C	Si
1	0	64.8	14.5		20.6
2	10	42.5	23.9		33.6
3	20	41.0	24.6		34.4
4	30	39.7	24.8		35.5
5	40	40.2	25.4		34.4
6	50	39.9	25.2		34.9

Oxide molar %

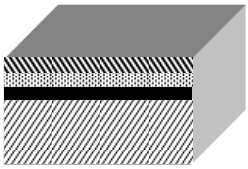
	Time (min)	O	Cr2O3	C	SiO2	O bal.
1	0		26.0		74.0	1.03
2	10		26.2		73.8	0.41
3	20		26.3		73.7	0.39
4	30		25.9		74.1	0.37
5	40		27.0		73.0	0.38
6	50		26.6		73.4	0.37

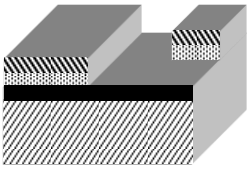
Notes

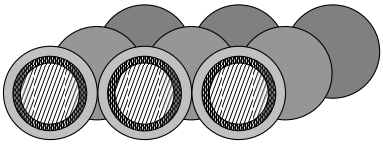
Cr-O-Si cermet film prepared by RF-sputtering of a Cr:O:Si target with a nominal atomic ratio of 1:1:1 onto thermally oxidised silicon wafers. Ion bombardments were performed by 2 keV Ar ions.

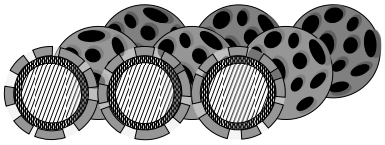
Application of Structured Models

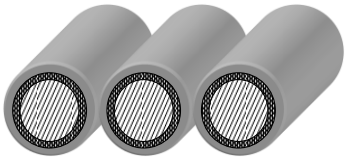
When the surface of the sample is covered by one or more overlayers and you know (or, at least, assume) the composition of the layers the thickness of the layers can be estimated from the photoelectron intensity ratios. The shape of the sample can be flat (e.g., thin layers, coatings, etc.), spherical (coated powder particles, e.g., paints, fillers, supported catalysts), cylindrical, including nanotubes (e.g., coated fibres for composites), or rough, modelled by polyhedrons (e.g., grooved, knurled surface, surface covered by individual crystallites). The program can handle as many as five layers; it is usually more than enough for the practice.

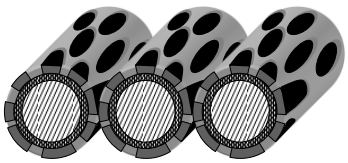

Layers-on-Plane

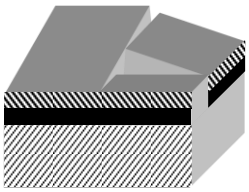

Islands-on-Plane

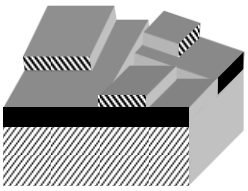

Layers-on-Sphere

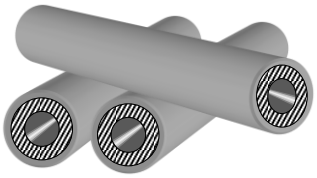

Islands-on-Sphere

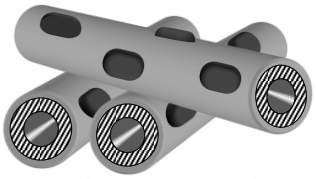

Layers-on-Cylinder


Islands-on-Cylinder


Layers-on-Polyhedron

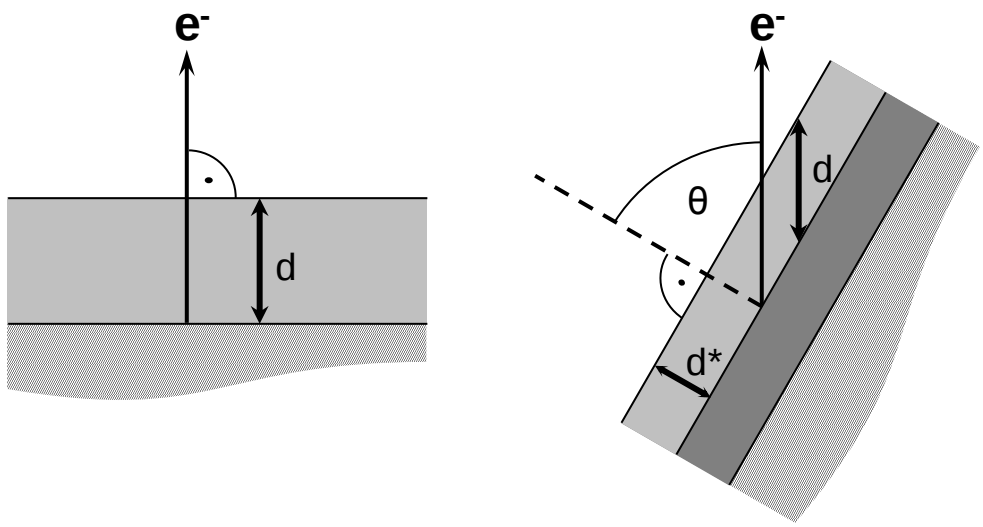

Islands-on- Polyhedron


Layers-on-Nanotube


Islands-on-Nanotube

First, enter the elements and intensity data as usual and select the model type in the *Model* tab of the *Parameters* window. Invoke the Model window by the **View / Model** command (available only when the model type is not *Homogeneous*). Give a descriptive name for each layer and the bulk material. You declare the presence of a layer by naming it thus the name is obligatory. Fill in the table, according to chapter “Model” in “Program References”.

Temporarily switch to *Homogeneous* model and study the overall composition of the underlying layers; this helps to estimate the layer thickness, and then switch back to the required structured model. Close the *Model* window and open the *Layer Thickness*. The *Layer Thickness* window shows the thickness of the overlayers for the experiments. The table is empty when first invoked, because the layer thickness values are not calculated automatically. For the same reason, the calculated thickness values are stored in XPS MultiQuant data files.
To calculate the layer thickness, double click the sequence number of the selected experiment. The *Layer Calculation* window is displayed. Select a basis element for the relative intensity comparison by double clicking the element symbol in the upper panel. Estimate and enter the thickness of each layer to the small table below and press ENTER. When the last number is entered the relative intensity is calculated and displayed. The *Diff %* column shows the percentage difference between the calculated and measured intensity; while the Q_{sum} row shows the sum of the squares of the differences. The *Chart* window let you compare the intensity values graphically (see chapter "Layer Calculation"). You can enter the next estimation immediately; intensity values are recalculated and displayed. The results of the previous calculations (the last two ones) are also displayed for comparison. If you do not enter thickness to a cell but press ENTER the previous value is retained. Vary the thickness of the layers until calculated intensity values are the closest to the measured ones, i.e., perform a manual least square fitting or press the *Autofit* button to calculate the parameters automatically. Then press the *OK* button or select the next or previous experiment by the small arrow buttons. The results of the calculation are summarised in the *Layer Thickness* window.
The geometric scheme of the applied model can be displayed in the *Model Layout* window.
There are some other characteristics to help defining more complex models. If you have some 'a priori' knowledge on the relation of the different layers, you may declare the thickness of different layers to be equal: double click the cells in the *Link to* row in the *Model* window until the number of the target layer appears. Furthermore, if you know that the layers are repeated on the sample, it is enough to define the 'unit' and to select the number of the repetitions in the *Multilayers* box in the Model tab of the *Parameters* window. The typical application of these features is the study of Langmuir-Blodgett type films.
If you record the spectra of a planar sample at several take-off angles (angle dependent XPS, 'ARXPS'), the thickness of the layers can be calculated using all of the experiments together with the *Layers-on-Plain* and *Islands-on-Plain models*.



This technique increases the number of independent variables (i.e., the “elements”) and you may calculate systems, which is ill defined when measured at one take-off angle only (typical example is single element islands on a single element substrate).
To use this feature select the *Angle dependent experiment set* check box in the *Model* tab and select the *Tilt* labels in the *Label* tab of the *Parameters* window. The calculation set (and also the data file) must contain the related angle dependent experiments only.
In the simplest case, when a metal is covered with its (native) oxide and the two chemical states of the metal can be resolved, the *Oxide-Layer* model can be applied. The thickness of the overlayer is calculated directly, based on the intensity of the metal lines originated from the bulk and from the oxide layer. The layer must be defined in the *Model* window, as described previously (composition, molecular weight, density, IMFP). The two chemical states of the main element must be denoted as ***Me*** (metal) and ***Ox*** (oxide) in the *Elements* window. For inserting the special state information quickly (rotating text in the Me – Ox – empty order), you can double click the appropriate cells of the *State* column.

Intensity Simulation

For several reasons (theoretical studies, test purposes, etc.) it is useful if the usual quantitative calculations can be done “backwards”, i.e., from the layout and the predicted composition of the sample the integrated photoelectron intensity values can be obtained. Actually, the program always solves this inverse task (i.e., intensity from layer thickness) and eventual thickness data can be reached only by parameter fitting. Just adding a new “data flow” to the program was necessary.
To prepare simulated data, select the required elements and set up a structured model as described in the previous chapter. Invoke the *Intensity Simulation* window by the **Tools / Simulation…** command. If the intensity data set is not completely empty (i.e., all zero), a message warns the user that further actions may destroy the previously entered (either experimental or simulated) intensity data.
Select an experiment to store simulated intensity. New experiments can be added only to the end of the data set but any previously calculated experiment can be recalculated later. Enter the thickness of the layers (and optionally the coverage for the island-type models) and press the *Calculate* button. The inverse of the corrections selected in the *Parameters* window (cross section, IMFP, transmission, angle) are applied. Surface contamination can be implemented by defining a carbonaceous top layer.
You can assign a name, which is stored as the *Name* label of the selected experiment. If it were empty, the word “Simulated” is inserted. These automatically entered labels can be changed later in the *Intensity* window. Other labels, like *Time*, *Tilt*, etc., can also be added.
To calculate angle dependent experiments, enter the tilt angle values for each experiment as *Tilt* labels in the *Intensity* window before the simulation; and enter any number as intensity at least into each experiment, unless the automatic counting will delete it. If you want to create an angle dependent set, do not select the *Angle dependent experiment set* checkbox in the *Model* tab of the *Parameters* window during the simulation.
For the first time, it seems that the simulation can be used only for layered structures. However, intensity data of a homogeneous sample can be calculated as well. Define the required composition as the bulk of the model; define one, any kind of layer and set its thickness to zero. Again, surface contamination can be realized by a carbonaceous layer.
The simulated intensity values can also be perturbed by noise, within a given relative level.

Inelastic Mean Free Path

The inelastic mean free path values are one of the most important parameters of the quantitative XPS calculations, thus they should be selected very carefully. The recommended sources of IMFP data are (in this hierarchy):

- measured values from the reliable literature and databases
- experimentally based calculated values from the literature and databases
- values calculated by predictive formulae [9]
- values calculated by predictive formulae within XPS MultiQuant

The application of the IMFP values is slightly different for the homogeneous and the structured model calculations. For the homogeneous model, when the relative composition of the sample is calculated, instead of the absolute IMFP values, numbers proportional to the IMFP values can be used. Consequently, several straightforward methods are available, like the simple exponential approach or Jablonski's [7] method. Obviously, the actual IMFP values can also be used (*Explicit* method). XPS MultiQuant applies the selected method 'on the fly' for the calculations.
Conversely, for the structured models, when the thickness of the overlayers is calculated, knowledge of the actual IMFP values is essential. For these types of calculations, always the 'explicit' values are used. All other selectable methods [8-11] are applied to compute the IMFP values *prior* the layer thickness calculation.
Although there is only one location to set the IMFP correction method (i.e., the *IMFP* tab of the *Parameters* window), two different method names, one for the homogeneous and one for the structured models, are maintained. Only the methods associated with the model can be selected. The following table enumerates the selectable methods for each model type and also shows the source (the names of the windows in the program) of the IMFP data or the parameters to calculate them.

Models and methods	**Location of IMFP data**	**Location of parameters to calculate IMFP**
Homogeneous model		
None	–	–
Explicit	IMFP & Contamination	–
Exponential	–	Parameters
Jablonski	–	IMFP & Contamination *
Seah-Dench	–	IMFP & Contamination *
Gries	–	IMFP & Contamination *
Structured models		
Explicit	Model	–
Seah-Dench	Model	IMFP & Contamination
Tanuma-Powell-Penn	Model	IMFP & Contamination
Gries	Model	IMFP & Contamination
Cumpson-Seah *(AL)*	Model	Model

* When the same parameters are used for all experiments, values can be set in *IMFP* tab of *Parameters* window as well.

Carbonaceous Contamination

Presence of carbonaceous contaminant is typical on the surface of materials handled or stored in ordinary ambient. The effect of this layer on the composition of the otherwise homogeneous samples can be taken into account during the calculation. See the scientific background of the various methods in chapter “Contamination Correction”.

In most of the cases the bulk of the sample does not contain any carbon thus C concentration should be omitted from the 100 % sum of the percentage type composition results. Accordingly, when the selected correction method is *Evans*, *Mohai* or *Explicit*, C is omitted automatically. Although you can switch it back (by double clicking the symbol C), these composition values usually make no sense (even though it gives some estimate on the level of carbon contamination).

Correction methods can also be applied for carbon containing materials when the signal from the constituent carbon (e.g., carbonate or carbide types) can be separated by decomposition from the hydrocarbon type contamination (use different *State* settings). These correction methods cannot be applied to samples containing hydrocarbon type constituents, like most polymers. When the intensity of the adventitious carbon of an experiment is zero, no contamination correction is applied for that experiment.

As a generally applicable default contamination correction, method of Mohai [15] is suggested. It can be applied from clean to highly contaminated samples (up to approximately 6 nm hydrocarbon layer). See the changes of the atomic ratio of the otherwise stoichiometric samples in the following table.

Sample	**Correction**	**c factor**	**Na**	**Cl**
NaCl	None	0.0	1.00	0.96
clean	Evans	14.3	1.00	0.98
	Mohai	0.0	1.00	0.96
NaCl	None	0.0	1.00	0.90
highly	Evans	14.3	1.00	0.92
contaminated	Mohai	64.6	1.00	1.01
Sample	**Correction**	**c factor**	**Si**	**O**
SiO_2	None	0.0	1.00	2.01
slightly	Evans	14.3	1.00	2.25
contaminated	Mohai	4.3	1.00	2.08
SiO_2	None	0.0	1.00	1.31
highly	Evans	14.3	1.00	1.46
contaminated	Mohai	50.6	1.00	1.94

Such simple correction cannot be used for the structured models. Instead, you can explicitly define a hydrocarbon type contaminant layer on the top of the sample. Application of a layer with CH_2 composition, density of 0.8 g/cm^3 and *Polymer* material class is usually suitable. You can use ≈ 7.5 eV bandgap energy for the *Tanuma-Powell-Penn* IMFP calculations.

Miscellaneous Remarks

Mixing of Methods and Data

Every term of the sensitivity factors can be controlled independently; however, the user is responsible for the reliability of mixing the different methods and data. It is important to consider whether a sensitivity factor or your input data already contain correction for a phenomenon; do not apply any correction twice. Switch off all unnecessary features, e.g., if your instrument has 'magic angle' arrangement (54.73° excitation-analyser angle, where the term $^3/_2\, cos^2\varphi - ^1/_2$ is zero), do not apply angular correction.

Cross Section Correction

Evans' original cross section data [3] are measured with 90° excitation-analyser angle and this factor was not separated from the cross section values. Before angular correction, data are converted to the 4π sr solid angle but only when the *Data set* item in the *Cross section* tab of the *Parameter* window is set to *Evans*.

Wagner's sensitivity factors for the secondary lines are multiplied by 0.9 for Mg Kα and by 1.1 for Al Kα excitation, as suggested in [1], when the above item is set to *Wagner*. Thus, this item controls not only the library search but the correction of library data as well. If you use manually entered sensitivity factors, make sure to set this item to *None*.

Raw Composition

Determination of some terms of the sensitivity factors to calculate the chemical composition by the *Homogeneous* model requires the chemical composition itself. These are:

- Angular and elastic scattering correction by the *Reilman-Ebel* method,
- IMFP by the *Seah-Dench* method with the *Calculate mean atomic weight* option,
- IMFP by the *Gries* method,
- Contamination correction by the *Mohai* method.

The preliminary "raw composition" is calculated by simplified way, as listed in the last column of the next table. Then the composition calculated by the selected methods, with parameters based on the raw composition.

Correction	Selected method	"Raw" method
Angular	*None*	*None*
	Reilman *Reilman-Ebel*	*Reilman*
IMFP	*None*	*None*
	Exponential	*Exponential*
	Explicit *Jablonski* *Seah-Dench* *Gries*	*Jablonski*
Contamination	any	*None*
Multiline approach	any	*Average*

IMFP for Homogeneous Model

For the homogeneous model, instead of the *absolute* IMFP values, only their *ratios* are relevant. When the IMFP values are calculated by predictive formulae, like formula of Seah and Dench [8] or Gries [11], even at altering the parameters (mean atomic weight, density) in a wide range, the *ratio* of the different IMFP values remain almost unchanged and accordingly no differences can be observed in the composition results.

Thus for homogeneous model calculations precise knowledge of these parameters are not essential. However, for the *structured models*, knowledge of the actual IMFP values is *fundamental*.

Angle of Emission

If you perform a series of angle dependent ('tilt') experiments [3], where the angle of emission (take-off angle, the angle between the sample surface normal and the analyser axis) is other than zero (i.e., not perpendicular), select the *Tilt* label set and enter the angle values there. In the case of the *Homogeneous* model, it can be applied only as X-axis set. (However, if your data are depending on the tilt angle, it clearly proves that the sample is *not* homogeneous.) When one of the planar type structured models is applied, the angle values are taken into account in the equations (marked by θ) shown in chapter "Applied Methods". In case of curved surfaces, only the perpendicular view is permitted thus the angle values are not used. When you select the *Angle dependent experiment set* check box in the *Model* tab of the *Parameters* window, all of the experiments recorded at various angles are linked and the calculation of the layer thickness performed together.

Automatic and Manual Fitting of Layer Thickness

When you perform *Autofit* during layer thickness calculation, you may encounter that the Q_{sum} value becomes larger than previously reached manually. This can be caused by several factors and does not mean that the fit become worse.

- The *Autofit* procedure is more complex, not simply the least squares are minimised.
- The actual numeric value of Q_{sum} is depending on selection of the basis element. It is not necessarily the same at the manual and the automatic calculation.
- At manual calculation, Q_{sum} contains the contribution of all elements, including the omitted ones. During automatic calculation, omitted elements are neglected.

The fitting procedure 'knows' the mathematics only (i.e., not restricted by any physical consideration); results should be always revised by the experienced surface analyst.

Calculation of Coverage

Be careful when the coverage is calculated automatically in case of 'island' type models. Small changes in coverage may cause significant changes in the calculated intensity. The fitting procedure may be frequently trapped in 'local' minima. Always try to continue the calculation (click *Autofit* again) until there is no change in the results. Repeat the calculation with different starting values.

Always check whether a layer is really discontinuous. When the number of independent parameters is increased by the coverage, the numeric value of the fit may seem to be better but it does not necessary mean that it really is.

[3] It is also called 'angle resolved' XPS (ARXPS) but it is better to reserve this name for those experiments where the angle between the analyser and the excitation source is varied.

Density of Layers

A layer, deposited or developed on the surface of a substrate (e.g., a native oxide layer grown on a metal surface), may be far less dense than its bulk density. Using the latter value may decrease the calculated layer thickness significantly, as compared to the thickness measured by scanning probe microscopy or by optical methods.

Using of Undo Commands

The undo commands, as in other programs, are used to restore the accidentally changed data. There are two undo subsystems in XPS MultiQuant: one for cell and one for row editing. Cell editing commands, including **Cut Cells**, **Paste Cells** and DELETE key, have several levels of undo. The row editing commands, **Insert Row** and **Delete Rows,** have only one level. The table editing commands, **Paste Table** and **Clear Table**, use both subsystems at the same time thus they also have one level.

Due to the complex data structure of XPS MultiQuant, using of the undo commands is limited occasionally (e.g., when an element deleted, all corresponding intensity data will also be deleted). If the number of elements or experiments is changed or rearranged since the editing step to be undone, the program warns the user because the restored data may be placed into wrong locations (depending on the relative position of the items).

The best practice is to perform the necessary undo as soon as possible after the unwanted action (especially for the row and table editing) and avoid mixing of undoing the row and cell editing commands.

Step by Step

This chapter gives quick 'how to' instructions for some common tasks of XPS MultiQuant. Consult the chapter "Using of the Program" for hints and the chapter "Applied Methods" for the theoretical background. The *Data wizard* (activated by the **Tools / Data wizard** command) may also give short step-by-step instructions online.

Setting and Saving Default Parameters

1. On the **View** menu, click **Parameters**.
2. Click the **Cross Section** tab. Select the preferred cross section or sensitivity factor set. Set **Splitting** and **Scaling** to *None*.
3. Click the **IMFP** tab. Select the preferred inelastic mean free path correction method and fill the required (not greyed) parameters (for common use *Exponential* method with an exponent between 0.5 and 0.7 is suggested).
4. Click the **Angular** tab. Select the angular correction method (*Reilman*) if necessary. Enter the angle between the electron analyser and the X-ray source of the spectrometer.
5. Click the **Transmission** tab. Select the transmission type of the spectrometer and enter the necessary data.
6. Click the **Contamination** tab. Select the preferred contamination correction method (for common use *Mohai* is suggested).
7. Click the **Model** tab. Select the applied model (for common use *Homogeneous* is suggested). Set **Multiline approach** to *None*.
8. Click the **Labels** tab. Select the labels routinely used (e.g., *Name* or *Time*); select also the measure units.
9. Click the **General** tab. Select the routinely applied X-ray excitation source. If *Other* is selected, enter also the source energy. Select the **Enable library lookup** check box.
10. Click the **OK** button.
11. On the **File** menu, click **Save Defaults**.

Notes

- When the program is started at the first time, none of these parameters is set, i.e., numeric values are zeros and methods are *None*, etc.
- The default parameters are applied when a new calculation is started. Any of these parameters can be changed later at any stage of the calculation.

Setting up Simple Quantification

1. On the **File** menu, click **New**.
2. In the **Elements** window type the chemical symbols and line notations (into separate columns) of the elements involved in quantification (e.g., C 1s, O 1s, Cu 2p, etc.).
3. On the **Tools** menu, click **Library Lookup**.
4. On the **View** menu, click **Intensity**. Enter the integrated intensity (peak area) data for each experiment. Type the experiment labels (name, etch time, etc.) as well.
5. On the **View** menu, click **Results**.
6. On the **View** menu, click **Parameters**. Click the **General** tab *or*
   double click the **Title** (leftmost) panel of the status bar.
   Enter a descriptive title for the calculation and click the **OK** button.
7. On the **File** menu, click **Save As…** Enter a filename for the calculation and click the **Save** button.

Setting up Multiline Calculation

1. Setup simple quantification as described previously. Enter more than one photoelectron lines, if available, for each element (or as many, as possible, e.g., S2s *and* S2p, Cu2p *and* Cu3p *and* Cu3s, etc.).
2. On the **View** menu, click **Parameters**. Click the **Model** tab and select the required **Multiline approach** method (*Average* for good quality data, *Ebel* when the weak lines are less reliable).

Notes

- If the element calculated by multiple lines is present in more than one chemical states, data must be provided for all lines and all states (e.g., S2s and S2p for both S^{2-} and S^{6+}, i.e., totally four lines for sulphur).

Presenting Results in Various Forms

1. On the **View** menu, click **Results**.
2. Select the required result type in the dropdown list of the **Composition** window.
3. To omit an element from the 100 % sum of the ‘percentage’ results, double click the chemical symbol *or* right click the chemical symbol and check **Omit**.
4. To select a basis element of the ‘ratio’ results, double click the chemical symbol.
5. Click the up and down arrows of the **Number** box to change the quantity of basis atoms (for ‘ratio’ results).
6. Select the **Merge chemical states** check box to sum the concentration of different chemical states of the same elements.

Presenting Results Graphically

1. On the **View** menu, click **Results**.
2. On the **View** menu, click **Chart**.
3. In the **Composition** window, double click the label column headers to set X-axis.
4. In the **Composition** window, double click the sequence number of any experiment (point) to omit it from the chart *or* right click the sequence number and unselect **Visible**.
5. In the **Composition** window, right click any chemical symbol and unselect **Visible** to remove the element (series) from the chart.

Printing Reports

1. On the **File** menu, click **Print…**
2. Select the required data items to be printed.
3. Click the **OK** button.
4. If required, select other result type. On the **File** menu, click **Print Current**.
5. Double click the **Pending Page** icon on the status bar *or* on the **File** menu click **Print…** and click the **Eject Page** button.

Notes

- Selection of items to be printed can be saved by the **Save Defaults** command.
- For the first occasion click the **Option…** button, set the preferred print options (printer, page orientation, font) and save them by the **Save Defaults** command.

Editing Elements and Experiments

1. On the **View** menu, click **Elements**.
2. Click the sequence number of the element to highlight a row.
3. On the **Edit** menu, click **Delete Rows** to remove the selected element from the calculation.
4. On the **Edit** menu, click **Insert Row** to add a new empty element line above the selected row. Fill the line immediately.
5. On the **View** menu, click **Intensity**.
6. Click the sequence number of the experiment to highlight a row.
7. On the **Edit** menu, click **Delete Rows** to remove the selected experiment from the calculation.
8. On the **Edit** menu, click **Insert Row** to add a new empty experiment line above the selected row. Fill the line immediately.

Notes

- More than one elements or experiments can be highlighted in order to delete them simultaneously.
- To add a new element or experiment to the end of the calculation set, just fill the last empty line in the **Elements** or **Intensity** window.
- The **Delete Rows** can be revoked by an immediate **Undo Delete Rows** command.

Editing Content of Cells

1. Double click the cell to be edited.
2. Edit the cell. Use the arrow keys or the mouse to move the text cursor.
3. Click any other cell in the same window to leave cell edit mode.

Notes

- Cell editing is available in the **Elements**, **Intensity**, **IMFP & Contamination** and **Model** windows.
- Cell editing can be revoked by the **Undo** command.

Rearranging Elements and Experiments

1. On the **View** menu, click **Elements**.
2. Right click the sequence number of the element to be moved and drag the cursor to the sequence number of the destination position and release mouse button.
3. On the **View** menu, click **Intensity**.
4. Right click the sequence number of the experiment to be moved and drag the cursor to the sequence number of the destination position and release mouse button.

Notes

- During the drag and drop rearranging, the shape of the mouse cursor is changing, to indicate the operation in progress.

Setting up Structured Model

1. On the **View** menu, click **Parameters**.
2. Click the **General** tab. Select the **Measurement unit** as preferred.
3. Click the **Model** tab. Select the required model (other than *Homogeneous*). Set the **Sphere or Cylinder radius** to 0, set the **Multilayers** to 1. Click the **OK** button.
4. On the **View** menu, click **Model**.
5. Enter a descriptive name for each layer (**Layer 1** is the topmost one) and the bulk.
6. Enter the density (g/cm^3) for each layer and the bulk.

7. Specify the composition of the layers: enter the number of atoms for each element representing the atomic ratio (like the stoichiometric coefficients) for each layer, including hydrogen atoms, starting from the "**0 No. H**" row. Values can be integers or real numbers.
8. On the **Tools** menu click **Model** / **Calculate Molecular Weight**.
9. On the **Tools** menu click **Model** / **Mark Unused IMFPs**.
10. Enter IMFP values for each layer and the bulk for the kinetic energy of the lines of the elements, starting from the "**1 IMFP**" row. Fill all unmarked cells.
11. On the **Tools** menu click **Model** / **Test Model**. Correct the listed errors, if any.

Notes

- When the *Layers-on-Nanotube* model is used, both the **Sphere or cylinder radius** and the **Tube inner radius** must be entered.
- The geometry correction factors of the *Layers-on-Polyhedron* model should also be defined, as described later.

Calculating IMFP for Structured Models

1. On the **View** menu, click **Parameters**.
2. Click the **IMFP** tab. Select the required **Method** (*Seah-Dench*, *Tanuma-Powell-Penn*, *Gries*, *Cumpson-Seah*). Click the **OK** button.
3. On the **View** menu, click **IMFP & Contamination**.
4. Double click the **Material class** row for each layer and the bulk until the proper class is displayed *or* enter the first letter of the class names (*e*, *i*, *p*).
5. Enter the **Bandgap energy** values for each layer and the bulk (for the *Tanuma-Powell-Penn* method only).
6. On the **Tools** menu click **Model** / **Calculate Valence Electrons** (for the *Tanuma-Powell-Penn* method only).
7. Click the **Model** window.
8. On the **Tools** menu click **Model** / **Calculate IMFPs**.

Notes

- The **Density** and **Molecular weight** rows are the same as in the **Model** window.

Calculating Layer Thickness

1. On the **View** menu, click **Results**.
2. On the **View** menu, click **Chart**.
3. In the **Layer Thickness** window, double click the number of experiment to be calculated.
4. In the **Layer Calculation** window, double click the element symbol selected as basis element (an element of the bulk is suggested).

5. Type the estimated thickness of the first layer and press ENTER. Repeat with the remaining layers and optionally the coverage. After the last ENTER, the calculated intensity values are displayed and compared to the measured ones.
6. Repeat point 5 until reasonable $\mathbf{Q_{sum}}$ is achieved. To reuse a previously typed thickness value, press ENTER.
7. Click the **Autofit** button.
8. Click the **OK** button.

Notes

- To neglect an element during the automatic calculation, double click the **Omit** column in the **Model** window (an **X** appears).
- To neglect a layer during the automatic calculation (i.e., to keep the manually entered value) double click the **Link to** row in the **Model** window until *Fixed* appears.

Defining Islands

1. On the **View** menu click **Parameters**
2. Click the **Model** tab. Select the **Islands** check box.
3. Select the **Fit coverage automatically** check box (if required).
4. Setup the model as described previously.
5. In the **Model** window, double click the **Type** row to mark layers as *Layer* or *Island*.

Notes

- To calculate the coverage automatically, one layer in the islands must have at least two independent elements.

Defining Repeated Layer Structures

1. On the **View** menu click **Parameters**
2. Click the **Model** tab. Select one of the required 'layer' model types.
3. Click **Multilayers** and select the required repetition number.
4. Click the **OK** button.
5. Setup the model as described previously. Define one unit of the repetitive structure.

Defining Layers with Equal Thickness

1. Setup the model as described previously.
2. Double click the **Link to** row in the **Model** window until the sequence number of the layer to be linked appears.

Defining Angle Dependent Experiment Set

1. On the **View** menu click **Parameters**
2. Click the **Model** tab. Select one of the required 'planar' model types.
3. Select the **Angle dependent experiment set** check box.
4. Click the **Labels** tab. Click **Tilt**. Select the required angle unit.
5. Click the **OK** button.
6. Setup the model as described previously.
7. Calculate layer thickness as described previously.

Notes

- The data file must contain one set of corresponding experiments only.
- When the *Angle dependent experiment set* is selected, the results are displayed only in the first row of the *Layer Thickness* window.

Defining Polyhedral Surface Geometry

1. On the **View** menu click **Parameters**
2. Click the **Model** tab. Select the *Layers-on-Polyhedron* model.
3. Click the **Edit** button. The **Polyhedron Editor** window appears.
4. Select the required angles of polyhedron facets by the slider and enter the projected area for each type (as percentage value).
5. Click the **OK** button.

Notes

- To check or set the 100 % sum of the area values, click the **Normalise** button.
- To remove previously entered data, click the **Clear** button.

Setting up Oxide-Layer Model

1. On the **View** menu, click **Parameters**. Click the **Model** tab. Select the *Oxide-Layer* model. Click the **OK** button.
2. In the **Elements** window, type the chemical symbol and line notation (e.g., Si 2p) of the main constituent element of the bulk and the layer.

3. Copy the element to the next row.
4. Type "*Me*" and "*Ox*" into the **State** column *or* double click the cells of the **State** column to denote the different chemical sates of the same element (metal and oxide, respectively).
5. Enter intensity data, as described previously.
6. Set up structured model, as described previously. Define one layer only.
7. On the **View** menu, click **Results**.

Notes

- Results are calculated and displayed automatically.

Setting up Intensity Simulation

1. Setup a structured model, as described previously.
2. On the **Tools** menu, click **Simulation**.
3. In the **Intensity Simulation** window, select the experiment number where results to be stored.
4. Enter the thickness of the layers and the coverage.
5. Click the **Calculate** button.
6. Repeat points 3 – 5 to calculate further experiments.
7. To study the composition results, calculated by the *Homogeneous* model, select the **Show homogeneous composition** check box.
8. Click the **OK** button to finish simulation.

Notes

- If the status of the selected experiment is not *Empty*, previously entered intensity data will be overwritten.

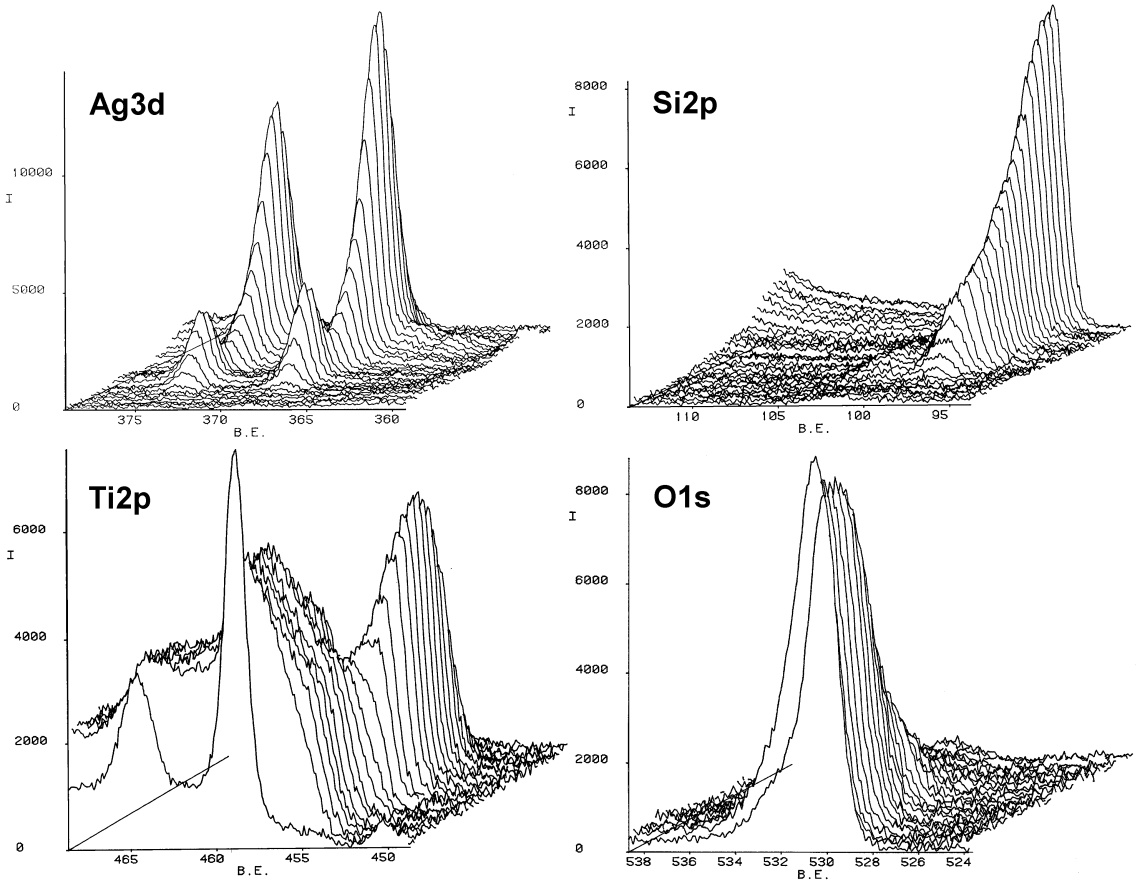
A photon checks into a hotel and the bellhop asks him if he has any luggage. The photon replies: "No, I'm traveling light".

Application Examples

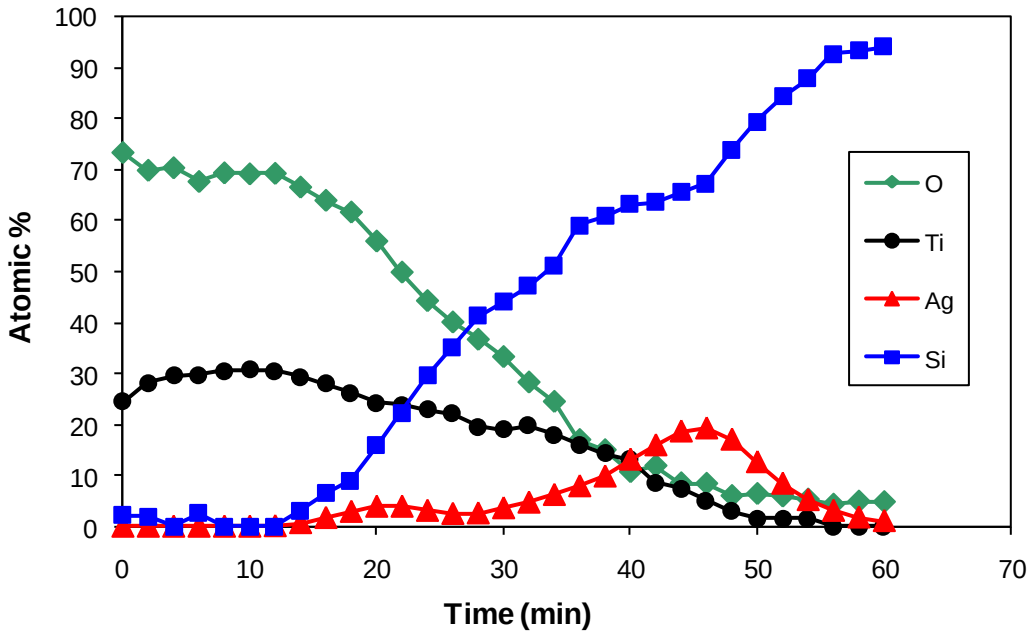
This chapter describes and gives hints on the sample XPS MultiQuant data files included in the distribution kit. These files are usually located in the \Program Files\XMQ\Samples folder. These examples illustrate the various features of the program. A brief description is also included into the *Notes* text of each file. Example files have some 'magic' when opened by the **Open Example…** command. The *Notes* window and other subwindows are activated automatically and the result format is set, as appropriate for the selected data.

Contact (Contact.mqd)

These XPS spectra were recorded on an electrical contact prepared on a silicon wafer from titanium and silver. The sample was heat treated causing diffusion of the components. The upper layers were oxidised and the top surface was contaminated by carbon. Ion etch series were performed by 2 keV Ar^+ ions in 2 min steps.



The ion etch depth profile reflects the changes seen on the previous figure. Beside the intensity (height) changes of the lines, consider alterations in FWHM as well; this explains the shallower concentration differences visible in the Ti profile. The reduction of the system can be seen from not only the chemical shift changes but the decreasing oxygen balance, as well.



This example illustrates of the simple handling and fast calculation of large data sets. Test the different results formats. When ratio types are used, be careful of the zero intensity data. The printed depth profile was prepared by Microsoft Excel as demonstrated by the ContactProfile.xls file.

NaCl – Simple Multiline (NaCl-multiline.mqd)

Spectra were measured on a freshly cleaved NaCl single crystal with low level of carbon and without oxygen impurities.
The concentration of sodium is calculated using either the 1s or 2s line; or both lines. In the latter case, the average of the raw results is calculated for all lines of matching elements and chemical states. The intensity and basic data are reliable for both sodium lines thus almost no difference can be observed when the multiline approach method is changed from *Average* to *Ebel*, as shown in the next table (atomic ratio).

	Na	**Cl**	**C**
Na1s only	0.95	1.00	0.04
Na2s only	1.00	1.00	0.04
Both (*Average*)	0.97	1.00	0.04
Both (*Ebel*)	0.97	1.00	0.04

Cu-Ag-Au Alloy – Weighted Multiline (CuAgAu.mqd)

A ternary Cu-Ag-Au alloy was prepared by grinding. XPS spectra were measured after 10 s Ar^+ ion sputtering, which removed majority of carbonaceous contamination. Intensity and all basic data, including cross sections, asymmetry parameters and transmission function, were obtained from the literature [6]. The measured Cu3p (MgK$\alpha_{1,2}$) line was superimposed with the Au4f (MgK$\alpha_{3,4}$) X-ray satellite; thus, the intensity of the Cu3p line was corrected by 10 % of the Au4f intensity ("Sat corr").
There are significant differences between the concentrations calculated with different lines (multiline approach method is set to *None*), thus application of weighted average (*Ebel*) is advisable.
The concentrations (mass %) calculated by the authors [6] and by XPS MultiQuant (satellite corrected), shown in the next table, are in good agreement.

	Cu	**Ag**	**Au**
Chemical analysis	40.0	50.0	10.0
No satellite correction	39.4	50.4	10.2
Satellite correction	39.2	50.6	10.2
XPS MultiQuant (*Ebel*)	40.7	49.5	9.8
XPS MultiQuant (*Average*)	37.6	51.4	10.9

NaCl – Scaling of Na1s Cross Section (NaCl-scaling.mqd)

Spectra were measured on a freshly cleaved NaCl single crystal. It was practically free from contamination with a low level of C and O impurities only.
This example illustrates of using of the *scaling* feature. The cross section data set of Evans does not contain data for the Na1s line. However, switching on *scaling*, rough results can be obtained. Compare the two scaling methods to the results calculated from the Na2s line.

Oxidised Si (Si-wafer.mqd)

Spectra were measured on a silicon wafer covered with a native oxide and a hydrocarbon contaminant layers.
The *Layers-on-Plane* model was applied to calculate the thickness of the layers. The composition of the layers was assumed to be SiO_2 and CH_x. For checking purposes, the layer thickness values were also calculated after the decomposition of the Si2p line into components representing the elemental and oxidised chemical states. Both calculations produced realistic and comparable results.

Calculation method	**d** $_{SiO_2}$ (nm)	**d** $_{CH_x}$ (nm)
from total intensity	1.39	2.27
from decomposed Si2p intensity	1.36	1.90

For details about how to perform of the calculations, see chapters "Application of Structured Models" and "Layer Calculation".

SiO_2 contamination (SiO2-contam.mqd)

XPS data were measured on a thermally oxidised Si wafer. The sample was totally oxidised and no elemental silicon could be detected. It was treated by low-pressure oxygen plasma to remove residual carbon and reach the stoichiometric Si:O = 1:2 ratio. After measuring the clean state of the sample, hydrocarbon contamination of increasing thickness was deposited by casting of polystyrene from benzene solution in subsequent steps. The compositions of the samples (atomic ratio) were calculated with different contamination correction methods.

Correction method	Sample treatment	Si	O	C	Difference from SiO_2
None	As is	1.00	1.76	0.43	-13.6 %
	O plasma	1.00	2.02	0.20	1.0 %
	Polymer 1	1.00	1.66	2.95	-20.5 %
	Polymer 2	1.00	1.49	3.81	-34.2 %
	Polymer 3	1.00	1.31	6.01	-52.7 %
Evans	As is	1.00	1.97	0.44	-1.5 %
	O plasma	1.00	2.26	0.21	11.5 %
	Polymer 1	1.00	1.85	3.07	-8.1 %
	Polymer 2	1.00	1.66	3.96	-20.5 %
	Polymer 3	1.00	1.46	6.25	-37.0 %
Mohai	As is	1.00	1.89	0.44	-5.8 %
	O plasma	1.00	2.08	0.20	3.8 %
	Polymer 1	1.00	2.18	3.24	8.3 %
	Polymer 2	1.00	2.04	4.26	2.0 %
	Polymer 3	1.00	1.91	6.85	-4.7 %

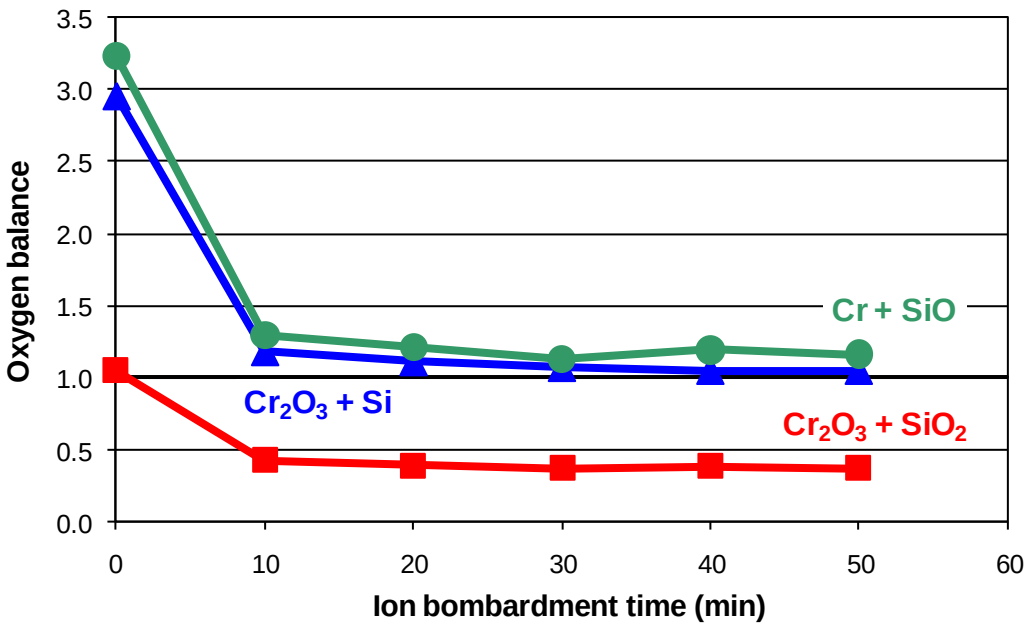
This example illustrates of application of the different contamination correction methods. Try to change methods in the *Contamination* tab in the *Parameters* window and compare the results.

Cr-O-Si Cermet Film (Cermet.mqd)

Cr-O-Si cermet films are widely applied in microelectronics devices. Such layers were prepared by RF-sputtering of a Cr:O:Si target with a nominal atomic ratio of 1:1:1 onto thermally oxidised silicon wafers.

XP spectra of the characteristic lines (Cr2p, Si2p, O1s, C1s) were recorded. Ion bombardments were performed by 2 keV Ar^+ ions. Composition, expressed in *Oxide molar ratio*, was calculated for assumed combinations: $\mathbf{Cr_2O_3+SiO_2}$, $\mathbf{Cr_2O_3+Si}$ and **Cr+SiO**. The *Oxygen balance* values of the different settings are depicted on the figure as a function of the bombardment time.

The chart revealed that the top surface is totally oxidised, i.e., $O_{obs}/O_{cal} \approx 1$ for the assumed $Cr_2O_3+SiO_2$ compounds. After 10 min bombardment, the top layer is removed and the former composition gives unrealistic oxygen deficiency. The new composition of the layer is close to either of the Cr_2O_3+Si or Cr+SiO (or also CrO+Si) supposed structures.



Further bombardment does not change the composition. Chemical shifts of the photoelectron lines will determine the correct chemical structure but this method can reduce the choice, discard unrealistic combinations and by this backs the peak decomposition procedure.
To calculate the *Oxygen balance* for the above assumed compositions (in three separate runs), set the *Valence* and *Oxygens* columns in the *Elements* window as follows:

	Cr ***Valence***	**Cr** ***Oxygens***	**Si** ***Valence***	**Si** ***Oxygens***
$Cr_2O_3 + SiO_2$	3	3	4	2
$Cr_2O_3 + Si$	3	3	0	0
Cr + SiO	0	0	2	1

Data of this sample are used to illustrate of pasting XPS MultiQuant data into Microsoft Word documents (see the CermetDocument.doc file).

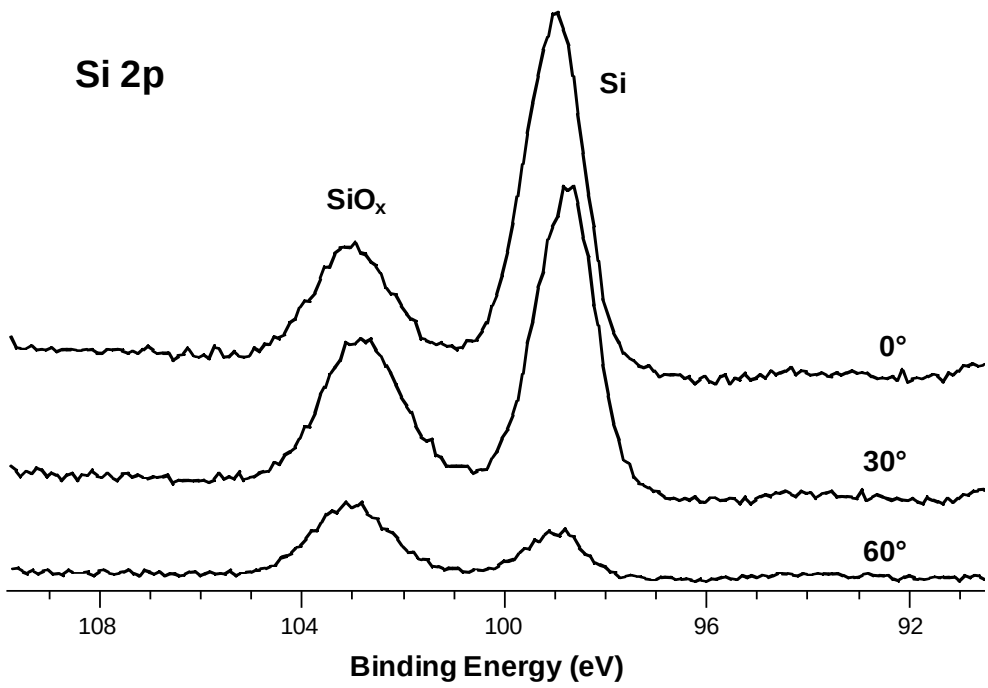
Al_2O_3 on Aluminium (Al-Layers.mqd, Al-Oxide.mqd)

XPS data recorded at 0 and 60 degrees take-off angles on rolled aluminium foil covered with oxide layer and carbonaceous contamination.
Thickness of the alumina layer was calculated both by the *Layer-on-Plane* model with various settings (with and without oxygen, as angle dependent set) and by the *Oxide-Layer* model.
To calculate the experiments together, select the *Angle dependent experiment set* check box in the *Model* tab of the *Parameters* window. To include and exclude oxygen, double click the "O" row of the *Omit* column in the *Model* window.
The results of the calculations are slightly different due to the oxygen surplus (OH groups) and the low intensity of metallic Al at 60° angle. The thickness values calculated by the *Oxide-Layer* model are the same as calculated by the *Layers-on-Plane* model without using of the oxygen.

	Tilt angle	d $_{CH_x}$ (Å)	d $_{Al_2O_3}$ (Å)
Layers-on-Plane	0°	14.29	67.01
(with oxygen)	60°	14.21	57.54
	ARXPS	14.27	67.02
Layers-on-Plane	0°	17.53	61.95
(without oxygen)	60	15.63	55.83
	ARXPS	16.41	63.26
Oxide-Layer	0°	–	61.95
	60°	–	55.83

Angle Dependent Set on Silicon Single Crystal (Si-ARXPS.mqd)

XPS data were recorded at various take-off angles (0°, 30°, 60°) on a silicon wafer covered with a native oxide and a hydrocarbon contaminant layers. The Si2p lines were decomposed to SiO_x and Si components.



Thicknesses of the oxide and contaminant layers were calculated by the *Layers-on-Plane* model with the *Angle dependent experiment set* feature.
The surface of the sample showed oxygen surplus, thus the composition of the oxide layer was selected as $SiO_2 \cdot SiO(OH)_2$. Applying of SiO_2 layer composition gives practically the same results but the differences between the measured and calculated oxygen intensity values are larger.
When *Angle dependent experiment set* is selected, all experiments calculated together and the results are displayed only in the first row of the *Layer Thickness* window.

Si_3N_4 Powder (SiN-powder.mqd)

XPS data were recorded on silicon nitride powder samples prepared by various manufacturers. These powders consisted of nearly spherical particles. The structure of the particles was assumed as follows: a core of Si_3N_4 is surrounded by a SiO_2 layer and a carbonaceous (CH_x) contaminant layer. Application of the *Layers-on-Sphere* model gives realistic results, while the *Layers-on-Plane* model overestimates the thickness of the layers providing higher, usually improbable values.

Sample	Spherical model		Planar model	
	d $_{CH_x}$ (Å)	**d** $_{SiO_2}$ (Å)	**d** $_{CH_x}$ (Å)	**d** $_{SiO_2}$ (Å)
A	10.83	1.84	16.92	2.36
B	3.95	16.51	6.73	23.50
C	4.82	8.39	8.06	12.12
D	5.06	1.56	8.46	2.27
E	7.32	19.16	11.88	26.14
F	6.89	3.75	11.23	5.28
G	12.74	2.51	19.59	3.19

Some hints to perform these calculations: First switch to *Homogeneous* model to estimate quantity of the different components. Higher oxygen content means higher SiO_2 layer thickness, etc. Then switch back to the *Layers-on-Sphere* model; estimate the layer thickness and step by step refine the fitting, minimising the Q_{sum} value.

Simulation of Angle Dependent Set (SiO2-simulation.mqd)

The assumed sample is a silicon wafer covered by silicon dioxide and carbonaceous contamination layers, measured at various tilt angles. The example file is ready for the angle dependent intensity simulation.
Angle values are already entered into the *Tilt* label set in the *Intensity* window before the calculation. The intensity of oxygen (or any other element) is set to 1 (or any other number larger than zero) to prevent deleting of empty (all zero) experiments by the automatic counting. During the simulation, do not select the *Angle dependent experiment set* checkbox in the *Model* tab of the *Parameters* window.
Invoke the *Intensity Simulation* window and enter identical set of thickness values for each experiment. (Keep in mind that these are corresponding experiments on the same sample.) When the calculations are ready, the *Angle dependent experiment set* checkbox can be selected to calculate the layer thickness based on all experiments.

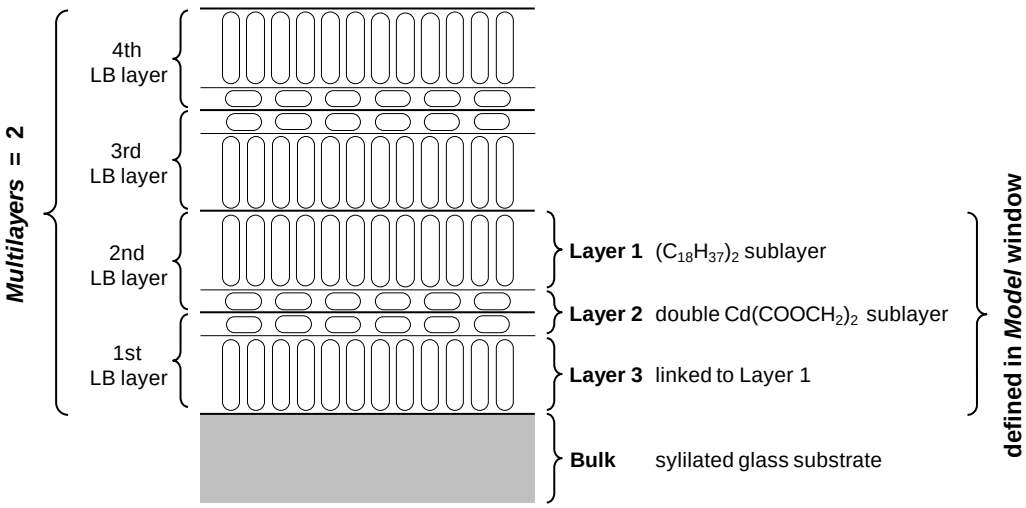
Surface Modified Carbon Nanotube (C-nanotube.mqd)

Commercial, thin multi-wall carbon nanotubes, with 9.5 nm external and 7 nm internal diameters were treated in low pressure RF plasma in N_2 flow. Negative DC bias of 50 V was applied through the sample holder.
The upper layers of the tube wall were converted into N-containing layer thus the *Modified tube layer* variant of the *Layers-on-Nanotube* model was applied to calculate the layer thickness.

The composition of the formed CN_x layer was selected as C_3N_2, based on measurements on similarly treated, freshly cleaved highly oriented pyrolitic graphite sample. The penetration depth of the N^+ ions with 25 eV energy in carbon was calculated by the SRIM 2006 program. The calculated depth (sum of the projected ion range & straggle) is 0.6 nm, which is very close to the layer thickness calculated from the intensity data of the XPS measurement (0.66 nm), confirming by this the validity of the calculation.

Langmuir-Blodgett film (LB-film.mqd)

Cadmium arachidate, $Cd(C_{19}H_{39}COO)_2$, Langmuir-Blodgett (LB) film with four monomolecular layers were deposited on trimethyl-silylated glass substrates [4].
The *Layers-on-Plane* model was applied with the following arrangement: the Cd-arachidate monolayer was considered as two sublayers due to the dissimilar nature of the two parts of the molecule. The physical constants (molecular mass, density, IMFP) of the octadecane ($C_{18}H_{38}$) and the cadmium acetate ($Cd(COOCH_3)_2$) were used for the hydrocarbon chain and the hydrophilic part of the molecule, respectively. In the program a double arachidate layer was implemented by three sublayers, as shown in the figure; and two of these structures were applied for the calculation of the 4L samples, setting the *Multilayers* attribute to 2.



Although the calculated monolayer thickness (26.7 Å) is less than the proper value (28 Å) reported in the literature [5], it can be explained by the tilted position of the molecules [4].

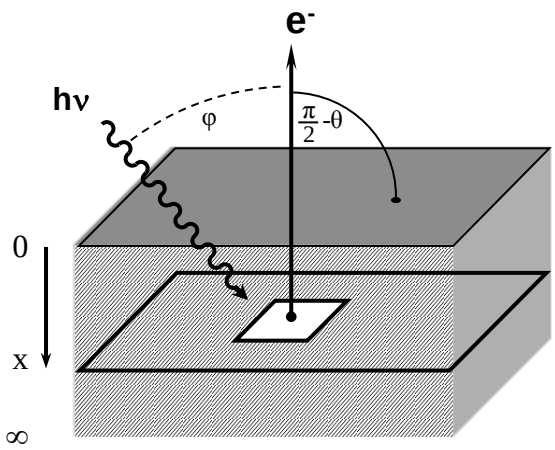
[4] M. Mohai, É. Kiss, A. Tóth, J. Szalma, I. Bertóti: *Preparation and Characterisation of Langmuir-Blodgett Type Arachidate Films*, Surf. Interface Anal. 34 (2002) 772.

[5] M. Sastry, P. Ganguly, S. Badrinarayanan, A. B. Mandale, S. R. Sainkar, D. V. Paranjape, K. R. Patil, S. K. Chaudhary: *Attenuation length measurements in lead arachidate Langmuir Blodgett films*, J. Appl. Phys. 70 (1991) 7073.

Applied Methods

This chapter summarises all calculation methods and formulae built into the XPS MultiQuant. All of the methods are described in details in the referred papers.

Homogeneous Model



The intensity of the photoelectron line excited from the infinitesimal thin layer of an infinitely thick sample is described by Equation (1):

$$dI = \Phi\sigma N k \exp\left(-x/\lambda\cos\theta\right)dx \qquad (1)$$

where I is the intensity, Φ is the X-ray flux, σ is the photoionisation cross section, N is the number of atoms per unit area, k is an instrument factor, λ is the inelastic mean free path (IMFP), θ is the angle between the exiting electrons and the surface normal and x is the distance perpendicularly below the sample surface [1, 2]. Integrating the above by x from 0 to infinity, the total intensity can be determined:

$$I^{\infty} = \Phi\sigma N k \lambda\cos\theta \qquad (2)$$

If the sample is covered with an overlayer of d thickness, e.g., surface contamination; Equation (1) must be integrated from 0 to d and from d to infinity to get the intensity from the surface layer (3) and the bulk (4):

$$I^{s} = \Phi\sigma N k \lambda \cos\theta \left[1 - \exp\left(-d/\lambda\cos\theta\right)\right] \qquad (3)$$

$$I^{b} = \Phi\sigma N k \lambda\cos\theta \exp\left(-d/\lambda\cos\theta\right) \qquad (4)$$

In the practice, instead of absolute intensity, intensity ratios are used thus the constant, i.e., energy independent parts of the equations ($\Phi k cos\theta$) can be neglected. The measured intensity should also be corrected by the transmission function of the analyser (and also detector sensitivity), by the cross section (which accounts for electrons exited into every directions, i.e., 4π sr solid angle) and for the angle of detection. Thus, the relative concentration of atom *i* in an infinitely thick homogeneous sample covered by surface contamination can be calculated from the total intensity by the following equations:

$$N_i = \frac{I_i}{F_i} \tag{5}$$

$$F_i = \sigma_i \cdot L(\varphi, \beta_i) \cdot \lambda_i \cdot T_i \cdot exp(-c_i/\lambda_i) \tag{6}$$

where I_i is the measured integral intensity of element *i* and F_i is the sensitivity factor which consist of the following terms: σ_i is the relative photoionisation cross section (function of photoelectron transition), $L(\varphi,\beta_i)$ is the angular correction factor (function of the asymmetry parameter, β and the direction of observation, φ), λ_i is the IMFP (function of the matter and kinetic energy), T_i the transmission correction (function of the kinetic energy) and *c* is the correction for surface contamination (proportional to the layer thickness).
Each term of the sensitivity factors can be controlled independently. When *None* is selected in the program for any of the above terms, the corresponding value is set to 1.

Cross Sections

Experimental cross section data of Evans [3] were measured with 90° excitation-analyser angle. To correct it to the 4π sr solid angle the Equation (7) is applied, which is derived from Equation (11) for 90° angle.

$$\sigma = \sigma_E \frac{1}{(1+\beta/4)} \tag{7}$$

where σ is the total relative photoionisation cross-section, σ_E is Evans' cross-section and β is the asymmetry parameter.
Wagner's sensitivity factors for the secondary lines are multiplied by 0.9 for Mg Kα and by 1.1 for Al Kα excitation [1]. The primary lines are the strongest ones while secondary lines are the 2s, 3p, 4p, 4d (except from Dy to Lu) and 5d lines.
When the experimental cross section or sensitivity factors are used, some data may be missing from the data set. In these cases, for rough approximation, *splitting* and *scaling* of experimental data are implemented in the program.
Cross section of the doublet lines of the experimental data can be split to its components, e.g., 3d to $3d_{3/2}$ and $3d_{5/2}$, using the corresponding theoretical ratio (Equation 8) or by the nominal ratio values (1:2 for *p* lines, 2:3 for *d* lines, etc.).

$$\sigma_i^{ex} = \sigma_{sum}^{ex} \frac{\sigma_i^{th}}{\sigma_1^{th} + \sigma_2^{th}} \tag{8}$$

where σ_i^{ex} is the (split) experimental cross section of either doublet component, σ_i^{th} is the theoretical cross section of the same doublet component and σ_{sum}^{ex} the experimental cross section of the doublet line.

When the data for a required line is not included in the experimental data set, the user may try to scale the available theoretical data to the applied set. This can be done by the ratio of the closest line (Equation 9) or by an average factor (Equation 10).

$$\sigma_i^{ex} = \sigma_i^{th} \frac{\sigma_j^{ex}}{\sigma_j^{th}} \tag{9}$$

$$\sigma_i^{ex} = \sigma_i^{th} \frac{1}{j} \sum_j \frac{\sigma_j^{ex}}{\sigma_j^{th}} \tag{10}$$

Although splitting usually provides reliable data, scaling is considered as a rough estimation only. Use scaled data only when there is no other possibility and restrict use for minor components. The 'closest' line can be as far as 1000 eV from the 'basis' line, so try both scaling methods and choose the more probable one.

Angular Correction

This correction is calculated by the method of Reilman et al. [4] using Equation (11):

$$L = \frac{1}{4\pi}\left[1 - \frac{\beta}{2}\left(\frac{3}{2}cos^2\varphi - \frac{1}{2}\right)\right] \tag{11}$$

where β is the asymmetry parameter and φ is the angle between the excitation source and the analyser entrance slit.

Correction for Elastic Scattering

This correction is calculated by the method of Ebel et al. [5, 6] using Equation (12):

$$\beta^* = \beta \cdot 1.0205 \cdot exp(-0.0093356 \cdot A) \tag{12}$$

where β^* is the effective asymmetry parameter and A is the atomic weight for elements or the effective atomic weight for compounds:

$$A_{eff} = \frac{1}{100} \sum_j x_j A_j \tag{13}$$

x_j is the atomic percent of element j. First x_j is calculated without correction. The effect of this factor is usually about a few percent or less.

Inelastic Mean Free Path (IMFP)

Beside the known and explicitly given inelastic mean free path values of the material examined, the IMFP can also be calculated by several methods.
The program expresses the calculated inelastic mean free path in Å or nm unit, as selected by the user (except the first two methods, where a proportional number is estimated instead of the proper IMFP value).

Exponential

A simple exponential function can be used, which is proportional to IMFP.

$$\lambda \propto E^{a} \tag{14}$$

where E is the kinetic energy (eV). The exponent a, being usually between 0.5 and 0.9, can be freely selected by the user.

Jablonski

Jablonski [7] also uses exponential approximation with pre-set exponents for three material classes, enumerated in the next table.

Material class	Exponent
Element	0.7283
Inorganic compound	0.7234
Polymer	0.7665

Seah-Dench

Seah and Dench [8] also calculate the IMFP for the three above classes using Equations (15)-(17) for elements, inorganic materials and polymers, respectively.

$$\lambda = \frac{538}{E^2} + 0.41 \cdot (aE)^{1/2} \qquad \text{[monolayers]} \tag{15}$$

$$\lambda = \frac{2170}{E^2} + 0.72 \cdot (aE)^{1/2} \qquad \text{[monolayers]} \tag{16}$$

$$\lambda = \frac{49}{E^2} + 0.11 \cdot E^{1/2} \qquad [\text{mg}\cdot\text{m}^{-2}] \tag{17}$$

where E is the kinetic energy (eV) and a is the average monolayer thickness in nm calculated by Equation (18).

$$a = \sqrt[3]{\frac{M}{\rho \cdot 602}} \tag{18}$$

where M is the mean molecular weight and ρ is the density in $g\cdot cm^{-3}$ unit. The numerical factor is derived from Avogadro's constant.

Gries

Gries [9, 11] developed the following G-1 Equations (19)-(21) for the prediction of the IMFP:

$$\lambda = 10\, k_1 \left(V_a / Z^*\right) E / \left(\log E - k_2\right) \tag{19}$$

where V_a is the atomic volume ($cm^3\cdot mol^{-1}$), Z^* is a parameter found empirically equal to $Z^{1/2}$, Z is the atomic number, k_1 and k_2 are parameters. The terms V_a and Z^* are generalised to apply for compounds, $A_pB_q\ldots C_r$:

$$Z^* = \left(pZ_A^{1/2} + qZ_B^{1/2} + \ldots + rZ_C^{1/2}\right) / (p + q + \ldots + r) \quad (20)$$

$$V_a = (pM_A + qM_B + \ldots + rM_C) / \rho(p + q + \ldots + r) \quad (21)$$

where *p*, *q*, … *r* are the stoichiometric coefficients of elements *A*, *B*, … *C*, respectively, *M* is the atomic weight, *ρ* is the density (g·cm^{-3}). The values of the *k* parameters for the different material classes are listed in the next table.

Material class		k_1	k_2
Elements	3d (Ti-Cu)	0.0020	1.30
	4d (Zr-Ag)	0.0019	1.35
	5d (Hf-Au)	0.0019	1.45
	other (also Y)	0.0014	1.10
Inorganic compounds		0.0019	1.30
Organic compounds		0.0018	1.00

For the *Seah-Dench* and *Gries* methods, if a material is actually an element, IMFP is always calculated with parameters of the *Element* class, despite of the selected one. While the material, selected to be as *Element*, is being in fact a compound (i.e., contains more than one element), parameters of the *Inorganic* class is applied. The significance of the calculations, according to the real and the selected material classes are summarised in the next table.

Selection of *Material class*	**Calculated IMFP when the material is**		
	Element	**Inorganic**	**Polymer**
Element	OK	acceptable	erroneous
Inorganic	acceptable	OK	erroneous
Polymer	acceptable	erroneous	OK

Tanuma-Powell-Penn

Tanuma, Powell and Penn [9, 10] proposed the following equations for calculating the IMFP as a function of electron kinetic energy and various material parameters. Equations (22)-(28) are collectively known as TPP-2M formula.

$$\lambda = \frac{E}{E_p^2\left[\beta\, ln(\gamma E) - (C/E) + (D/E^2)\right]} \quad (22)$$

where *E* is the kinetic energy (eV), E_p is the free-electron plasmon energy (eV) and

$$\beta = -0.10 + 0.944 / \left(E_p^2 + E_g^2\right)^{1/2} + 0.069\rho^{0.1} \quad (23)$$

$$\gamma = 0.191\rho^{-0.50} \quad (24)$$

$$C = 1.97 - 0.91U \quad (25)$$

$$D = 53.4 - 20.8U \quad (26)$$

$$U = N_v \rho / M = E_p^2 / 829.4 \tag{27}$$

$$E_p = 28.8 \left(N_v \rho / M\right)^{1/2} \tag{28}$$

where ρ is the density (g·cm^{-3}), N_v is the number of the valence electrons per atom or molecule, M is the molecular weight, E_g is the bandgap energy (eV).
For assessing of the uncertainties of the IMFP values calculated by the two latter methods, see literature [9] and the references therein.

Cumpson-Seah

Cumpson and Seah [12] developed the CS2 semi-empirical Equation (29) to calculate attenuation length in any solid over the energy range 100–2000 eV. These equations take account of the correct low-energy elastic scattering behaviour of large Z elements.

$$\lambda_{AL} = 0.316\, a^{3/2} \left(\frac{E}{Z^{0.45} \left[ln\left(E/27\right) + 3 \right]} + 4 \right) \tag{29}$$

where a is the lattice parameter (or monolayer thickness), calculated by Equation (18), E is the kinetic energy, Z is the average atomic number.

Transmission Function

In the first approximation, the analyser transmission (T) is proportional to a function of the kinetic energy. This function is usually exponential.

$$T \propto E^a \tag{30}$$

where a can be selected by the user or is pre-set for some frequent cases.
More precise approximation of the analyser transmission function can be applied by exponential, polynomial or rational [13] functions or the combinations of the above [14], optionally with different coefficient sets for different kinetic energy ranges. In the latter cases, transmission is calculated by Equations (31) – (34).

$$T \propto a_0 + a_1 E^{a_2} \tag{31}$$

$$T \propto a_0 + a_1 E + a_2 E^2 + \ldots + a_n E^n \tag{32}$$

$$T \propto \left(a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4\right) / \left(1 + b_1\varepsilon + b_2\varepsilon^2 + b_3\varepsilon^3 + b_4\varepsilon^4\right) \tag{33}$$

$$T \propto a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4 + b_1 E^{b_2} \tag{34}$$

For the last two equations ε is calculated by:

$$\varepsilon = (E - 1000)/1000 \tag{35}$$

The coefficients of the equations with the corresponding limits of energy ranges are stored in separate files. See chapter “Structure of the Transmission Files” in “Program References”.

When the transmission function is not available analytically, it can be provided in tabular form as well. The actual transmission factors are calculated by linear interpolation.
There is no separate term in the program to describe the detector sensitivity as the function of the kinetic energy. If this factor cannot be neglected (e.g., in the case of fixed retarding ratio analyser mode), it should be incorporated into the transmission function.

Contamination Correction

The surface contamination of the samples, which usually consists of carbonaceous material, can be taken into account by various methods. Evans [3] uses the

$$exp\left(-c/E^{0.5}\right) \tag{36}$$

factor with a constant c = 14.3 value. It can be applied for most of the cases when the sample is stored in ambient and a 'saturated' level of contamination is developed.
For clean, practically carbon free, e.g., freshly cleaved or ion etched samples, or on the contrary, for strongly contaminated ones this factor does not provide proper correction. In these cases method of Mohai [15] can be applied where c is a function of the normalised carbon concentration:

$$c = a \cdot [C_{at\%}] + b \tag{37}$$

Factors are calculated in two-step iteration. First $[C_{at\%}]$ is calculated with $c = 0$; next $[C_{at\%}]$ values are used to calculate c factors by Equation (37). This method is applicable up to ≈ 5 nm thickness of the contaminant layer.
To avoid the numerical misfit of the factors due to the various IMFP calculation methods, providing either the absolute or a proportional value, in the contamination correction term of Equation (6) instead of the applied IMFP, a value relative to the carbon is used (38).

$$F_i = \ \ldots \ \cdot exp\left(-c_i/\left(\lambda_i/\lambda_C\right)\right) \tag{38}$$

where λ_C is the inelastic mean free path of the C1s photoelectron line in the sample.
The user can also set the correction factors manually, i.e., enter values proportional to the thickness of the contaminant layer for each experiment.

Multiline Approach

The influences of statistical and systematic errors of XPS quantification can be reduced by introducing as many photoelectron lines as possible for each element and calculating the average of the results evaluated separately.
It can be done by simple averaging the unnormalised results for all lines of each element, as shown by Equation (39).

$$N_i = \frac{1}{k}\sum_k N_i^k \tag{39}$$

where N_i is the average unnormalised concentration of element i, N_i^k is the unnormalised concentration of element i calculated from line k.
When applying the method of Ebel et al. [6], data points are weighted by the square root of the intensity, representing the strong signals by heavier weight as compared to weak ones. To

find the optimal unnormalised concentration, the weighted error quantity, shown by Equation (40), is minimised for each element.

$$min \sum_{k} \left[\left(ln\left(\frac{I_i^k}{F_i^k} \right) - ln N_i \right) \sqrt{I_i^k} \right]^2 \tag{40}$$

where I is the measured integral intensity, F is the sensitivity factor, N is the unnormalised concentration. The i index stands for the elements and the k for the lines of that particular element.

Averaging can be ignored, even with multiple lines, by selecting the *Main* method: composition is calculated using only the main (most intensive) lines of the elements. The presence of elements with multiple lines and the selected *Multiline approach* method must be corresponding, as shown in the next table.

***Multiline approach* method**	**Elements with multiple lines**	
	Not present	**One or more present**
None	Normal calculation	Percentage results are meaningless, although the discrepancies among lines due to intensity uncertainties can be revealed.
Average, Ebel	No error, the calculated composition is accurate.	Average composition is calculated, as selected.
Main	No error, the calculated composition is accurate.	Composition is calculated using the most intensive lines only.

Normalisation of the Composition Results

The applied quantification gives relative concentrations thus the results should be normalised. The results can be displayed in various forms as required by the further applications. The meanings of R variables in the following equations are the same (i.e., normalised concentration), although their numeric values are different.

Atomic %

$$R_i = \frac{N_i}{\sum_j N_j} \cdot 100 \tag{41}$$

where N_i is the relative concentration of element i (from Equation 5) and R_i is the normalised relative concentration. The j index is varied from 1 to the number of elements.

Atomic Ratio

$$R_i = \frac{N_i}{N_b} \cdot n_b \tag{42}$$

where N_b is the relative concentration and n_b is the number of atoms of the selected ‘basis’ element. This mode supplies the coefficients of the stoichiometric formula.

Oxide Molar %

$$R_i = \frac{N_i \cdot o_i}{\sum_j N_j \cdot o_j} \cdot 100 \tag{43}$$

where o_i is the number of atoms i in one mol of oxide.

Oxide Molar Ratio

$$R_i = \frac{N_i \cdot o_i}{N_b \cdot o_j} \cdot n_b \tag{44}$$

Mass %

$$R_i = \frac{N_i \cdot w_i}{\sum_j N_j \cdot w_j} \cdot 100 \tag{45}$$

where w_i is the atomic weight of element i.

Mass Ratio

$$R_i = \frac{N_i \cdot w_i}{N_b \cdot w_j} \cdot n_b \tag{46}$$

Oxide Mass %

$$R_i = \frac{N_i \cdot o_i \cdot w_i}{\sum_j N_j \cdot o_j \cdot w_j} \cdot 100 \tag{47}$$

Oxide Mass Ratio

$$R_i = \frac{N_i \cdot o_i \cdot w_i}{N_b \cdot o_j \cdot w_j} \cdot n_b \tag{48}$$

When one of the ‘percentage’ forms is selected, any element can be omitted from the 100 % sum, and the remaining elements are re-normalised to 100 %. Any element can be selected as basis for the ‘ratio’ type results.

Oxygen Balance

When one of the ‘oxide’ normalisation is selected, the *oxygen balance* is also displayed, which is the ratio of the measured and calculated (required by the elements at the given stoichiometry and oxidation states) oxygen concentration. If the *oxygen balance* is less than 1, the surface is deficient in oxygen; if it is greater than 1, there is oxygen surplus.

Models for Structured Surfaces

When the surface of the sample is covered by one or more thin overlayers (the whole structure should be thinner than the information depth of the XPS measurement) and the compositions of these layers are known, the thickness of the layers can be estimated from the photoelectron intensity. The program solves the inverse task: the relative intensity values are calculated from the layer thickness.
The measured intensity data are corrected for cross section, angular distribution and analyser transmission using Equation (5) with the following sensitivity factor:

$$F_i = \sigma_i \cdot L(\varphi, \beta_i) \cdot T_i \tag{49}$$

The number of atoms per unit volume (N_i) is calculated by the following formula:

$$N_i = n_i \frac{\rho}{M} \tag{50}$$

where n_i is the stoichiometric coefficient of atom i, M is the molecular weight and ρ is the density in g·cm^{-3}.
Molecular weight and density values should be supplied for each layer, also stoichiometric coefficients and explicit IMFP values for each layer and element (i.e., kinetic energy). Contamination correction can be implemented by defining an explicit contaminant layer.
1 to 5 layers and the bulk can be defined in the program but for materials with repeated structure, the defined layer system can be multiplied also by a factor from 1 to 5.
The calculated intensity ratios can be fitted to the experimental ones either manually, by interactive iterations; or automatically by, least square fitting procedure. To help finding the best fit of the intensity, the difference (*Diff %*) between the calculated (I_{calc}) and measured (I_{obs}) intensity and the sum of the squares of the differences (Q_{sum}) are also calculated:

$$\text{Diff}\,\% = \frac{I_{calc} - I_{obs}}{I_{obs}} \cdot 100 \tag{51}$$

$$Q_{sum} = \sum_i |I_{calc} - I_{obs}|^2 \tag{52}$$

where the i index stands for the elements. *Diff%* is displayed only when smaller than ±100 %. Graphic tools are also available (see chapter “Model” in “Program References”).
The actual number of the applied equations calculating intensity depends on the number and distribution of the elements in the layers. For a definite system, where the number of independent equations is equal or greater than the number of variables, at least one independent element per layer is necessary ($n+1$ elements for n layers and bulk). For *Island* type models one more elements is necessary in one of the islands to calculate coverage. Intensity data of elements being present in more than one layers are summed unless its spectra can be decomposed into different chemical states (use the *State* column settings in the *Elements* window). Sometimes the system cannot be well defined, e.g., single element islands on a single element substrate. In these cases, consider applications of different calculation methods, like Tougaard’s QUASES program, or record spectra at more than one take-off angles.

The *Autofit* procedure minimizes the sum of the squares of m non-linear functions (number of layers) in n variables (number of elements, $m \leq n$) by a modification of the Levenberg-Marquardt algorithm [16]. The Jacobian matrix is calculated by a forward-difference approximation. The procedure is called repeatedly with decreasing tolerance limits until the best fit is achieved. Unless the model system is converging very slowly, this method supplies the optimal fit in one step.

If the convergence is slow, *Autofit* may stop due to reaching the allowed maximum number of iterations without obtaining a solution to the accuracy specified. Try to invoke *Autofit* some more times. The slow convergence may indicate that the model does not describe properly the examined system.

When the *Modified tube layer* variant of the *Layers-on-Nanotube* model is used, the above iterations are nested into an external cycle, which iterates the wall thickness of nanotube. As this model can be applied only for one layer, the convergence is usually not slower than in simple cases.

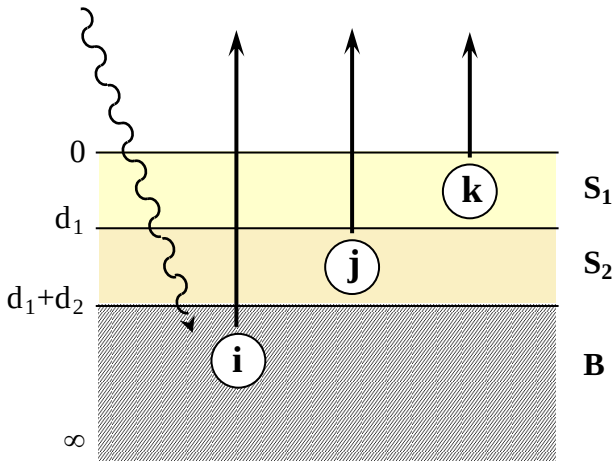
There are some other characteristics to assist defining more complex models. If there is some 'a priori' knowledge on the relation of the various layers, thickness of the different layers may be declared to be equal or can be kept constant. Elements or layers can be excluded from the automatic fit calculation, if necessary.

When a set of layers is repeated in sequence on the sample, it is enough to define one repeating unit and to set the number of the repetitions. E.g., two layers are defined in the *Model* window and the *Multilayers* attribute is set to 3 in the *Model* tab of the *Parameters* window, then a six-layer system is calculated, as illustrated in the next figure.

Defined Calculated

The fitting routine is not restricted by the physical meaning of the parameters. When any of the results seems to be unrealistic (e.g., a negative or too large layer thickness) a warning message is displayed.

Layers-on-Plane Model



The photoelectron intensity emitted from a flat, infinitely thick sample covered with overlayers of d_1, d_2 … thickness can be calculated by equations similar to (1)-(4).
For example, intensity of elements *i*, *j* and *k* from a flat bulk sample (*B*) covered by two overlayers (S_1 and S_2) are expressed by:

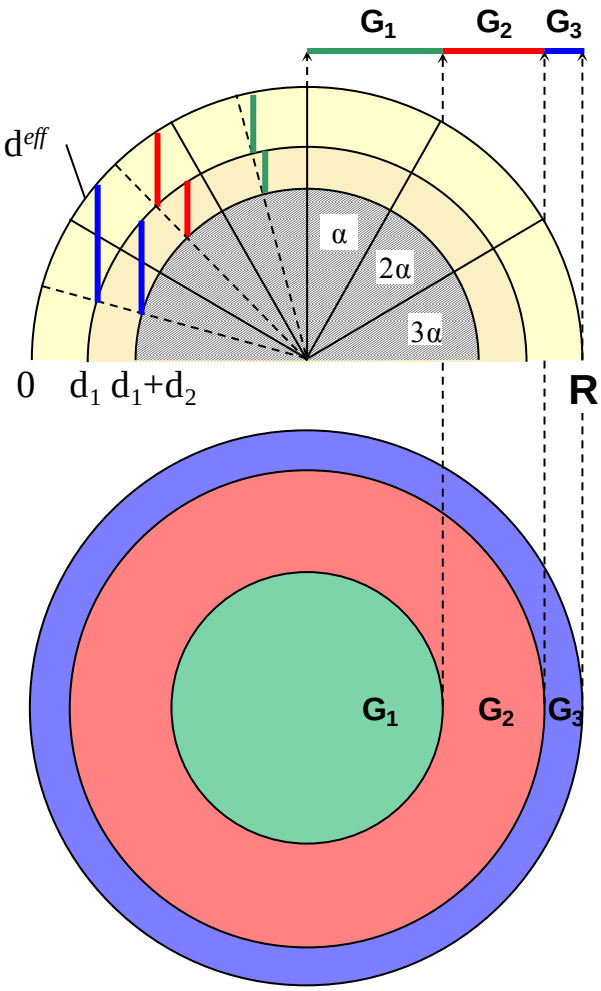
$$I_k^{S_1} = \int_0^{d_1} N_k \, exp\left(-x/\lambda_k^{S_1} cos\theta\right) dx = \\ = N_k \lambda_k^{S_1} cos\theta \left[1 - exp\left(-d_1/\lambda_k^{S_1} cos\theta\right)\right] \tag{53}$$

$$I_j^{S_2} = \int_{d_1}^{d_1+d_2} N_j \, exp\left(-x/\lambda_j^{S_2} cos\theta\right) dx = \\ = N_j \lambda_j^{S_2} cos\theta \, exp\left(-d_1/\lambda_j^{S_1} cos\theta\right)\left[1 - exp\left(-d_2/\lambda_j^{S_2} cos\theta\right)\right] \tag{54}$$

$$I_i^{B} = \int_{d_1+d_2}^{\infty} N_i \, exp\left(-x/\lambda_i^{B} cos\theta\right) dx = \\ = N_i \lambda_i^{B} cos\theta \, exp\left(-d_2/\lambda_i^{S_2} cos\theta\right) exp\left(-d_1/\lambda_i^{S_1} cos\theta\right) \tag{55}$$

where $\lambda_i^{S_1}$ means the inelastic mean free path of the electron emitted from element *i* in the matrix S_1, etc. Other symbols are defined at Equations (1)-(4).

Layers-on-Sphere Model



The calculation of photoelectron intensity excited from a spherical surface covered by overlayers is similar to the calculation of flat samples. However, the effective thickness of the layers (the virtual thickness seen from the direction of electron analyser) is varying from point to point along the sphere. Thus the intensity, originating from the various zones of the sample, should be weighted by a geometry correction factor, taking into account the projected areas corresponding to different thickness.

The integral describing the intensity of emission from a hemisphere cannot be solved analytically therefore the latter is divided into 9 segments of 10° [17, 18]. Every segment is represented its middle angle (5°, 15°, 25°, etc.). If the radius of the sphere is large enough (R > 1000 d), it can be neglected from the Equation (56) describing the effective d^{eff}.

$$d_i^{eff} = \frac{d_i}{\cos\alpha} \qquad (56)$$

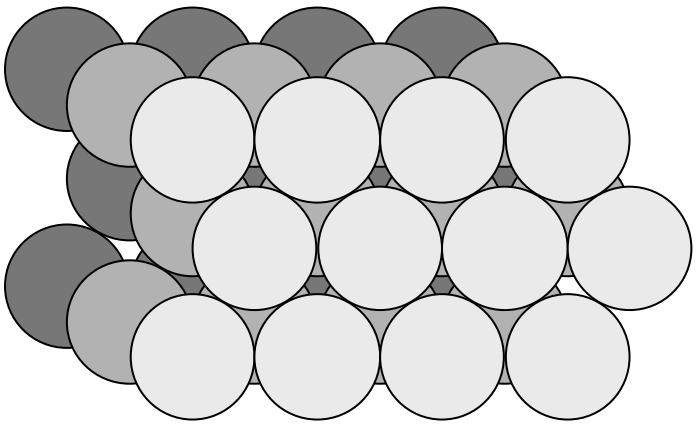
If the radius of the sphere is smaller (but still R >> 3λ), it must be supplied by the user and d^{eff} is calculated by Equation (57).

$$d_i^{eff} = \sqrt{cos^2\alpha\left(R - \sum_{j=1}^{i} d_j\right)^2 - d_i(d_i - 2R)} - cos\,\alpha\left(R - \sum_{j=1}^{i} d_j\right) \qquad (57)$$

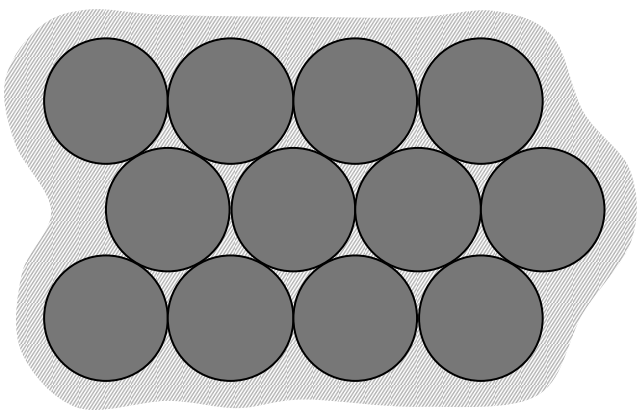
where R is the total radius (bulk plus layers) and the term $R\text{-}\Sigma d_j$ stands for the radius of the core under the current layer. If the radius is even smaller, i.e., $R \approx 3\lambda$, this model cannot be applied because there is no 'bulk-like' material.

After intensity values being calculated for every segment, they are weighted by the corresponding geometry correction factors (G_1, G_2, etc.; see the previous figure) describing the projected area of the spherical zones.

The flattened surface of powder samples is similar to the closest packed plane of the hexagonal lattice. The specific feature of this section is that some parts of the second and third rows of spheres below the top one are also visible partially, as illustrated in the following figure. The geometry correction factors (G_i) also include these contributions.

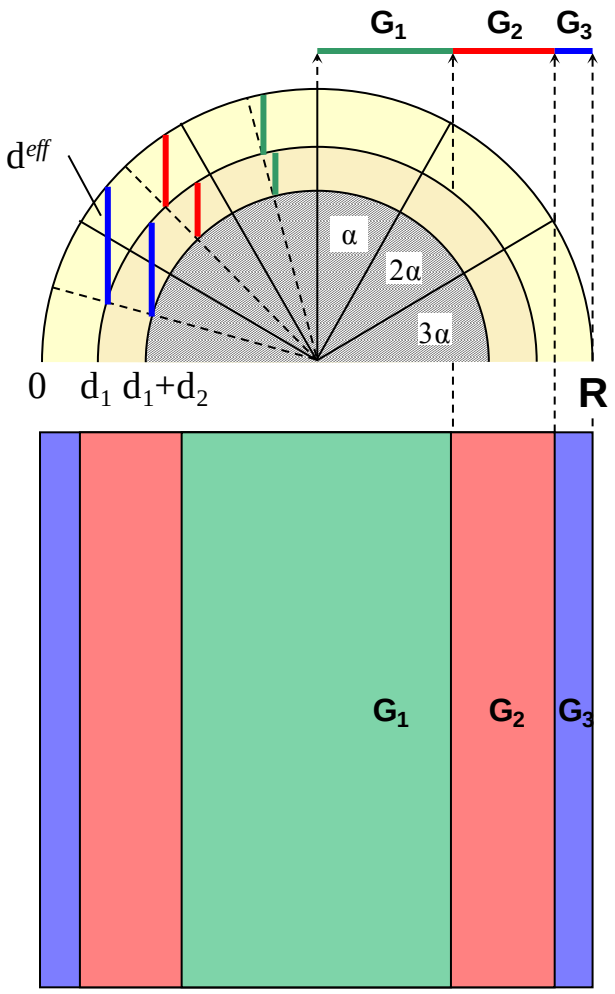


If the sample consists of relatively large spheres (e.g., small balls) arranged in one row, the latter correction can be turned off. In this case, the material of the sample holder is visible among the spheres, thus it should not contain any element of the sample, including the possible contaminations (carbon, oxygen, etc.). Using a piece of gold foil is usually advisable.

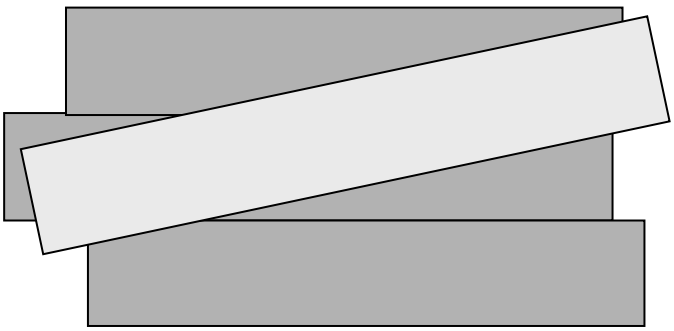


When this model is applied, the angle of emission (take-off angle) cannot be varied, i.e., the sample must be observed from the direction of the surface normal (θ is zero and $cos\theta = 1$).

Layers-on-Cylinder Model

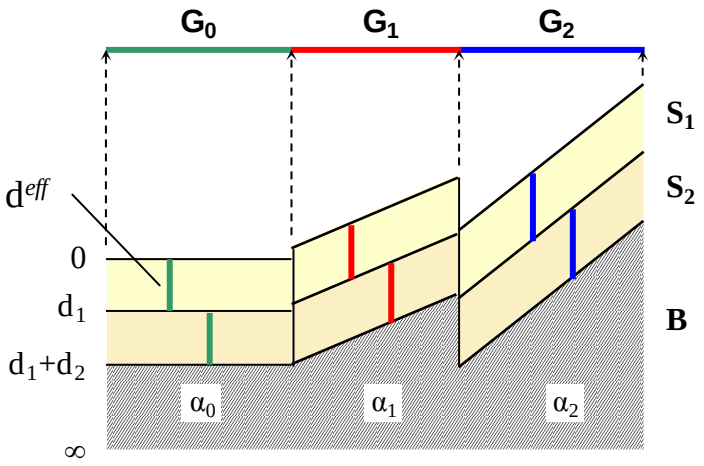


The description of photoelectron intensity from a cylindrical surface covered by overlayers is similar to the spherical ones [18]. In this case, the shapes of the projected surfaces are rectangles instead of annuli for spheres (see the figure above) and in closely packed arrangement the lower rows are not visible partially; even in the case of crossing cylinders.



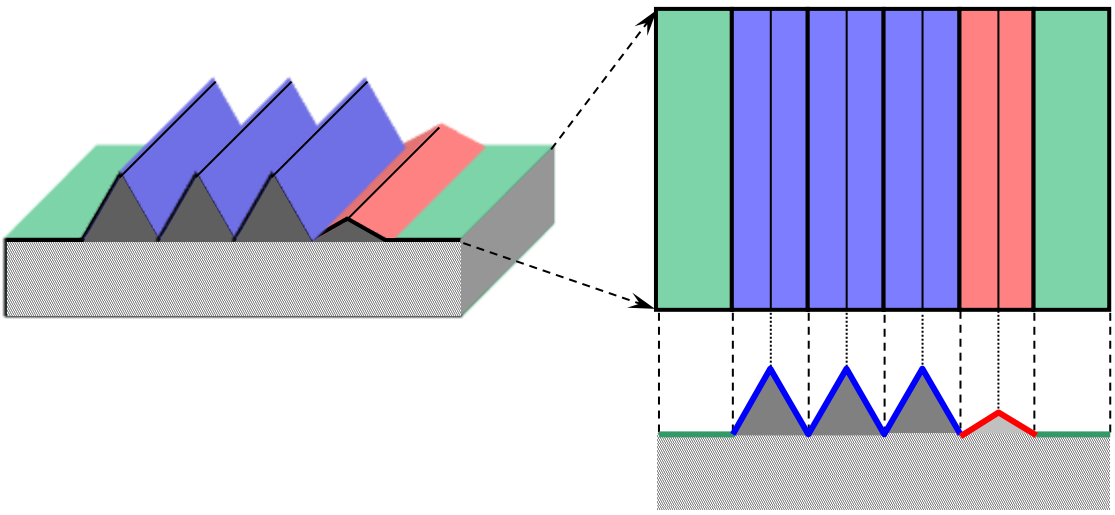
Thus, the way of the calculation for spheres and cylinders, performed by the program, are similar but the values of the geometry correction factors are different. This kind of sample must also be observed from the direction of the surface normal.

Layers-on-Polyhedron Model

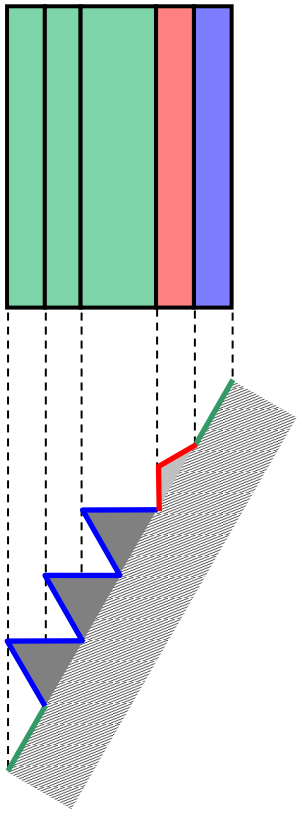


Rough surfaces with macroscopic or microscopic structures can usually be modelled by small planar units at different angles, i.e., facets of one or several types of polyhedra. The *Layers-on-Polyhedron* model [19] allows defining various surface geometry. From the point of view of quantification, only the relative sizes of the projected areas and the tilt angles of the different facets (measured from the base plane normal) are relevant. (The projection plane is the virtual base plane of the sample supporting the polyhedra.

The calculation of photoelectron intensity values excited from a polyhedral surface covered by overlayers is similar to the calculation of other structured models but while in case of spherical and cylindrical models the geometry correction factors are predefined, here the factors should be defined by the user. The effective thickness of the layers is varying from facet to facet positioned at different angles. Thus the intensity data, originating from the various facets of the sample, are weighted by a geometry correction factor, accounting for the projected areas. Similarly to the other structured models, the size of the surface features must be greater than thickness of the layers.



The surface should be inspected by naked eye or by microscope and the tilt angles of the facets together with their corresponding relative area should be measured (e.g., by optical methods, goniometer or image analysis, etc.) or estimated.
The above example shows a grooved surface with roof-shaped features. The projected areas could be derived from the top view while the tilt angles from the side view. The relative projected area data to be included into the model are shown in the next table.

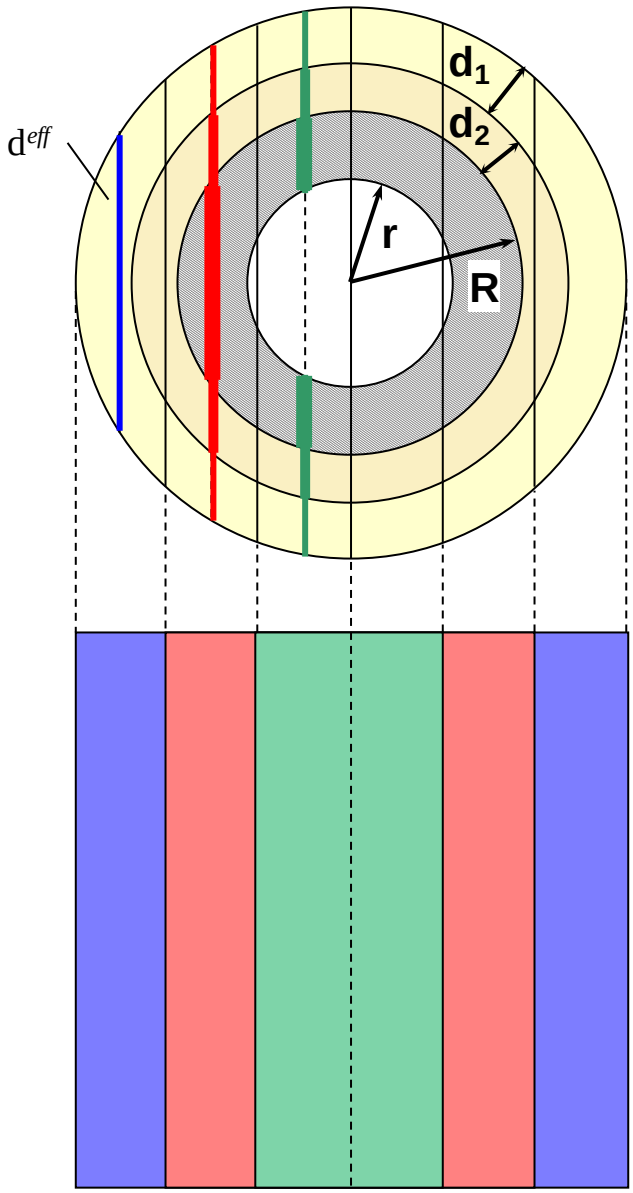


When angle dependent experiments are performed, the model geometry must be redefined, as the effect of tilt on the different features are unpredictable, in general. It is strongly depending on relation of tilt direction with the position of facets, on the self-shading effects of the features, etc.

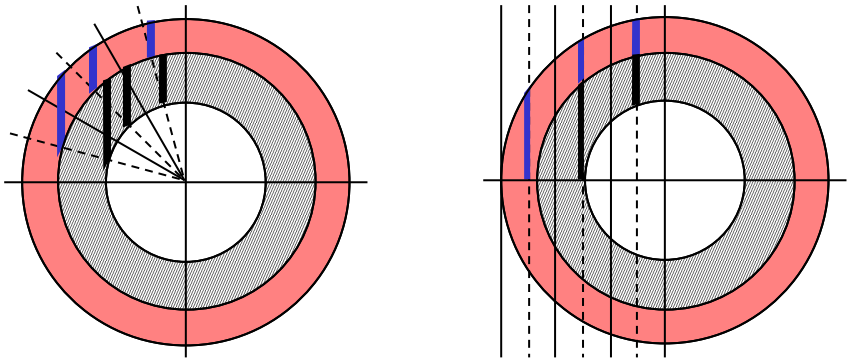
Facet tilt angle	**Projected area at sample tilt**	
	0°	**60°**
0°	33.3 %	66.6 %
30°	16.7 %	16.7 %
60°	50.0 %	16.7 %

As shown in the above table, the relationship between the projected areas and the original surface is quite different at various sample tilt angles.

Layers-on-Nanotube Model



The description of intensity of photoelectrons emitted from cylindrical surfaces covered by overlayers, despite the simplicity of the shape, cannot be applied directly for nanotubes [20]. In this latter case, the diameter of the nanotubes and the thickness of the tube wall are commensurable with the thickness of the layers. This means that there is no “bulk like”, i.e., infinitely thick, material, the electrons are emitted from the bottom part of the nanotubes, and they can be emerged from several rows of tubes and passing through the top one. The algorithm of the calculation, used for the cylindrical model, cannot be applied either. In that case, the cross section of the tube is divided into segments of equal angles. When this division is applied to nanotubes, the matching effective thickness values, originated from the layers and the tube wall (read at the middle angle of segments), are misaligned, as shown in the next figure, and would give erroneous results. Thus, tubes must be divided into segments of equal width instead of equal angle.



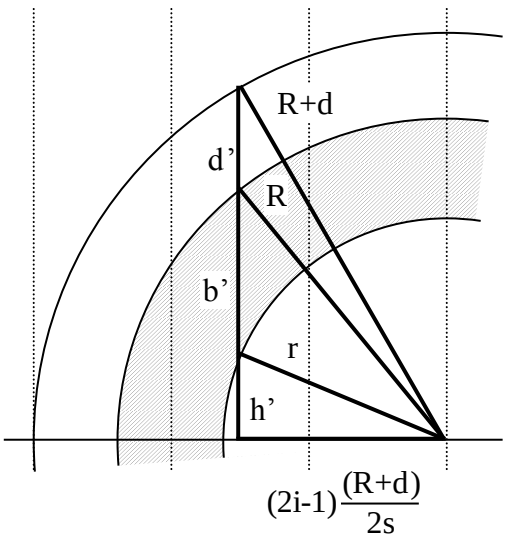
The size of the tube cannot be neglected, as well. Both the outer (*R*) and inner (*r*) radii must be known. They are usually determined by transmission electron microscopy. For nanofibres, the inner radius may be set to zero. In case of carbon nanotubes, their given absolute outer radius [21] and wall thickness [22] are also tested.
The effective thickness values of the layers and the wall for each segment are calculated by Pythagorean Equations (58)-(60):

$$d'+b'+h' = \sqrt{(R+d)^2 - \left((2i-1)\frac{(R+d)}{2s}\right)^2} \tag{58}$$

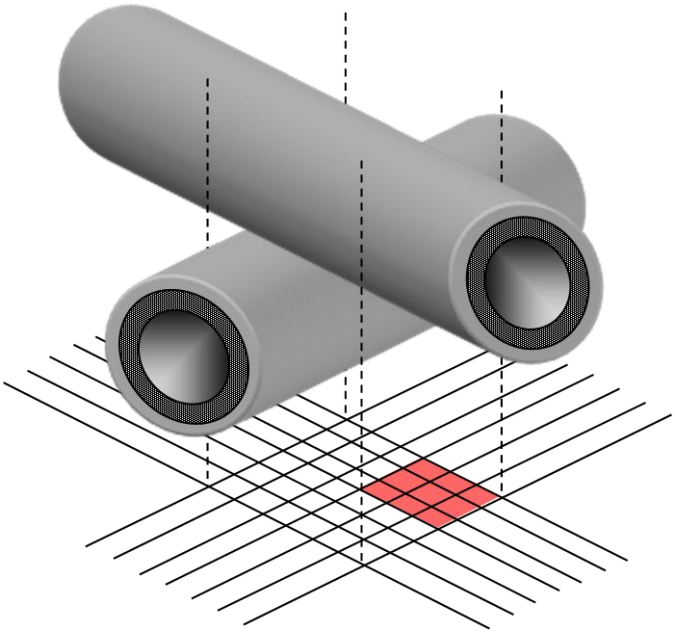
$$b'+h' = \sqrt{R^2 - \left((2i-1)\frac{(R+d)}{2s}\right)^2} \tag{59}$$

$$h' = \sqrt{r^2 - \left((2i-1)\frac{(R+d)}{2s}\right)^2} \tag{60}$$

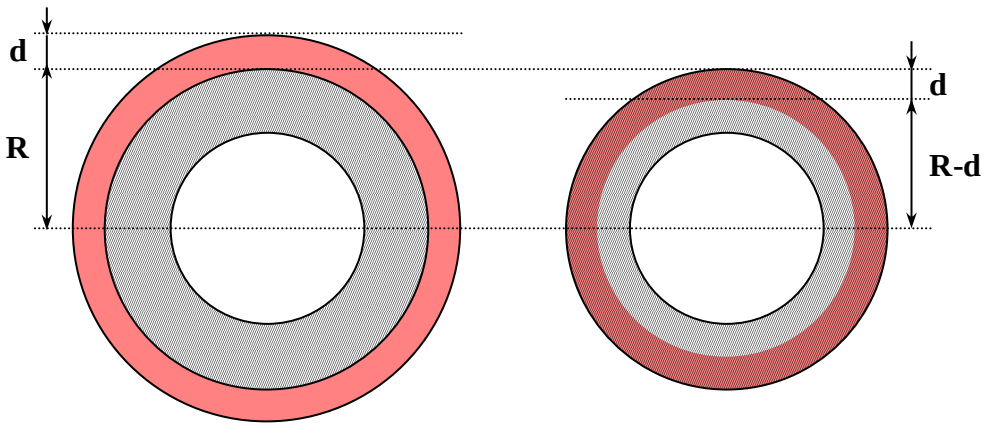
where *R* is the outer and *r* is the inner radius of the nanotube, *d* is the layer thickness, *d'*, *b'* and *h'* are the effective thickness values of the layer, wall and the hole of the tube, respectively. *s* is the number of segments (9) and *i* is the index of the actual segment (varying from 1 to *s*). The triangles used for these calculations are illustrated in the next figure.



The most characteristic arrangement of the randomly piled nanotubes is not the parallel but the crossing position at various angles. When two tubes are in such position, all segments of the two tubes are overlapping with each other. The projected areas of the overlapped segments are equivalent and their ratio is invariant to the crossing angle of the tubes, as illustrated in the next figure. The further underlying tube rows are supposed to be parallel with the corresponding upper rows (1st with 3rd, 2nd with 4th, etc.). The latter assumption does not really affect the accuracy of the calculations because the contribution of the lower rows is usually less than one percent.



The segments are situated symetrically on both sides of the tubes, thus only one quadrant of the crossing tubes (9×9 segments; only 3×3 shown) needs to be calculated.
When the layer on the nanotubes is prepared by modification of the tube material (e.g., by plasma or chemical treatment), the overall original diameter of the tube is unchanged but the thickness of the undisturbed tube wall is decreasing with the increasing thickness of the modified part; their sum is equal with the original thickness of the tube wall.

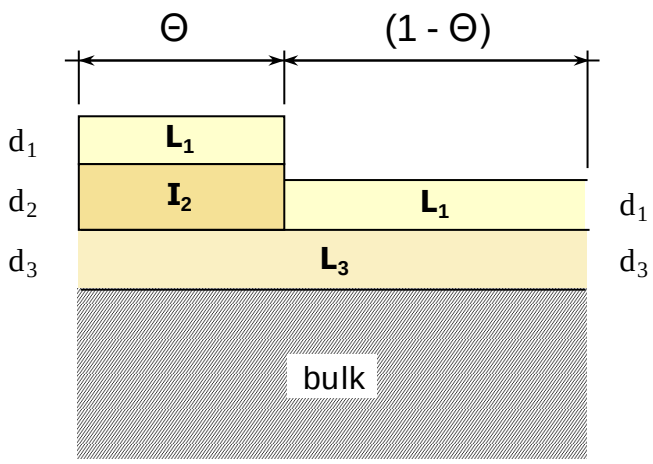


During this type of calculations, the total thickness is kept constant and the actual wall thickness is also iterated. This latter variant of the model can be applied for one layer only.
The number of rows of nanotubes to be involved in the calculation (n_{row}) is determined by the following empirical Equation (61).

$$n_{row} = \left\lfloor 3.4 \cdot \left(d_w / \lambda_w^{max} \right)^{-0.4} + 0.75 \right\rfloor \qquad (61)$$

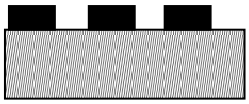
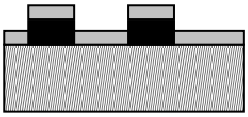
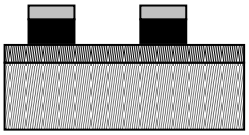
where d_w is the thickness of the nanotube wall and λ_w^{max} is the largest IMFP in the material of the wall. The formula (intentionally) overestimates the number of necessary rows, n_{row}, which falls between 1 and 6.

Island Type Models

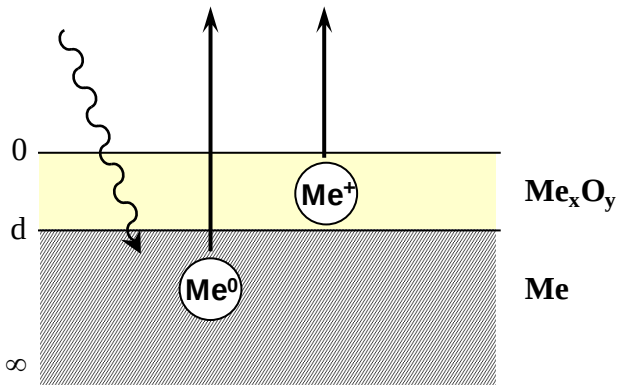


Frequently, one or more of the surface layers covering the surface are not continuous, forms 'islands' on the bulk material. An additional parameter, the coverage (Θ), varying from 0 to 1, describes the relative area of the islands. Any of the overlayers can be present as island (marked by $\mathbf{I}_i$ in the figure) but the coverage must be the same for all of them. In addition to the islands, continuous layers may also be present ($\mathbf{L}_i$). The intensity calculations, using the same equations as those applied for the *Layers* type models, are performed in two steps. The 'island' and 'non-island' parts are computed separately then weighted by Θ and (1-Θ), respectively. The corresponding intensity values of the two calculations are summed.
The same method is used for the curved surfaces (*Islands-on-Sphere, Islands-on-Cylinder, Islands-on-Polyhedron*) thus the following restrictions are assumed: the islands are relatively thin and small comparing to the radius of the surface and uniformly distributed on the spheres or cylinders, i.e., the same amount of 'island' and 'non-island' areas are present on any part of the surface. The sidewalls of the islands, getting visible on the high-angle segments of the curved surfaces (or at tilting of the planar samples), are left out of consideration. When the islands are thin enough, as compared to their area, this effect is usually negligible. In case of the *Islands-on-Plane* model, the angle of emission (*Tilt*) is applied.

Since a new independent variable is introduced to the calculations, the system may be ill-defined (the number of independent equations is less than the number of variables, e.g., both the island and the substrate contain single element only). In this case, either the island thickness or the coverage should be supplied from other measurements.
A few examples for some of the possible arrangements are given in the following table.

Type of the overlayers		
1: Island	1: Layer 2: Island	1: Island 2: Island 3: Layer
		
Islands on a substrate.	Islands on a substrate, covered by a contaminant layer.	Substrate is covered by a continuous layer and two-layer islands.

Oxide-Layer Model



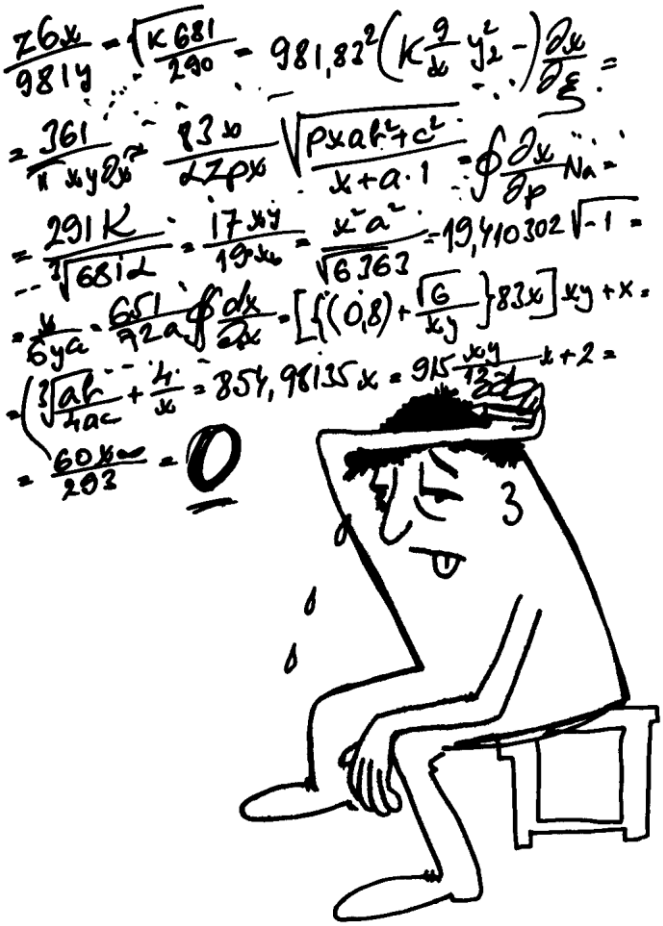
In the simplest cases, when the layer and the bulk contain the same element in different chemical states, the layer thickness (*d*) can be expressed analytically [23, 24]. A typical example is a metal surface covered with a single and uniform layer of its (native) oxide; and the intensity of the photoelectron peaks of the metallic (I_{me}) and oxidic (I_{ox}) chemical states of the same metal (element) can be resolved, the intensity ratio can be written as:

$$\frac{I_{me}}{I_{ox}} = \frac{N_{me}\,\lambda_{me}}{N_{ox}\,\lambda_{ox}} \cdot \frac{exp\left(-d/\lambda_{ox}\,cos\,\theta\right)}{1-exp\left(-d/\lambda_{ox}\,cos\,\theta\right)} \qquad (62)$$

where N is the number of atoms per unit volume, λ is the inelastic mean free path, d is the layer thickness, and θ is the tilt angle (from the surface normal). Indexes *me* and *ox* refer to the bulk (metal) and layer (oxide), respectively.
Solving Equation (62) for the layer thickness, it can be calculated directly:

$$d = \lambda_{ox} \cos\theta \, ln\left(\frac{N_{me}\,\lambda_{me}}{N_{ox}\,\lambda_{ox}} \cdot \frac{I_{ox}}{I_{me}} + 1\right) \tag{63}$$

Parameters of the model should be defined similarly to the other structured models but here only one layer is permitted. As the involved intensity originated from the same element, practically at same binding energy, no corrections are required for cross section, transmission or contamination. The number of atoms per unit volume (N_{me} and N_{ox}) is calculated by Equation (50) as in the case of other structured models.
Unlike the other models, no parameter fitting is required, thus results are calculated and displayed immediately.



Library Data

The library of XPS MultiQuant includes all necessary basic data for the calculations (data for elements, photoelectron lines, angular correction, etc.). Any data extracted from the library can be overwritten manually.

Chemical Elements

The atomic number, element symbol, name, atomic weight (1981 Table of Standard Atomic Weights), density and valence data of the elements were extracted from the literature [25]. The valence and number of oxygen atoms refer to the most common, usually the most stable, oxide.

Photoelectron Lines

The kinetic energy of the photoelectron lines were taken from Reference [26] and converted to binding energy. Some data were taken from Reference [27].
The energy of the doublet lines is the mean of the two components, weighted by their nominal intensity ratio (1:2, 2:3 and 3:4 for the *p*, *d* and *f* lines, respectively), as shown by Equation (64).

$$E_{mean} = \frac{E_a - E_b}{I_a + I_b} \cdot I_a + E_b \qquad (64)$$

where *E* is the binding energy, *I* is the nominal intensity, indexes *a* and *b* refer to the higher ($p_{1/2}$, $d_{3/2}$, $f_{5/2}$) and lower ($p_{3/2}$, $d_{5/2}$, $f_{7/2}$) binding energy components, respectively. This approach provides proper base for the IMFP and transmission corrections.
The values, although usually refers to elemental states, are precise enough only for transmission and IMFP approximation. Never use them for chemical state determination.

Cross Sections and Sensitivity Factors

Five different theoretical and experimental data sets are available in the library for most of the elements and photoelectron lines. Any other cross section or sensitivity factor values can be entered manually. All data are based on peak areas and not peak heights.

Scofield

The data of *Scofield* [28] are theoretically calculated cross sections (using relativistic single-potential Hartree-Slater atomic model). Separate sets are available for Mg Kα and Al Kα

excitation sources. Data are relative to C1s = 1 (22200 barn and 13600 barn, respectively). XPS MultiQuant chooses the data set according to the selected excitation source. When the source energy is specified by the user, the Al Kα set is selected.
Lines from 1s to 4f (when applicable) are included in the library. If experimental data are available (from Hg to U), the 5d lines are also included.

Evans

The data of *Evans et al*. [3] are experimentally based relative differential cross sections relative to F1s = 1. Data were measured with Mg Kα radiation, fixed retard ratio (FRR, CRR) analyser mode and at 90° analyser-excitation angle. The angular dependency of data was not eliminated (see Equation 7). Cross sections were calculated using $\propto E^{1/2}$ IMFP and $\propto E$ transmission dependency.

Wagner

The data of *Wagner et al.* [1, 29] are experimentally based relative sensitivity factors. Measurements were performed with Mg Kα and Al Kα radiation, fixed analyser transmission mode (FAT, CAE), at 84° analyser-excitation angle (and also with CMA analyser). Values are average for Mg and Al radiation; the strongest lines are insensitive to the excitation while secondary lines should be corrected by factors of 0.9 and 1.1 for Mg Kα and Al Kα, respectively. The secondary lines include the 2s, 3p, 4p, 4d (except from dysprosium to lutetium) and 5d lines.

Nefedov

The data of *Nefedov et al*. [30, 31] are experimentally based relative sensitivity factors relative to Na1s = 1. Data were recorded with Al Kα radiation, fixed analyser transmission mode (FAT, CAE).

Average Scale Factors

The three average scale factors (*Evans/Scofield*, *Wagner/Scofield* and *Nefedov/Scofield*), for scaling the cross sections or sensitivity factors, are calculated as the average of the ratio of *all* available corresponding photoelectron line pairs (158, 200 and 57 items, respectively; see Equation 10).

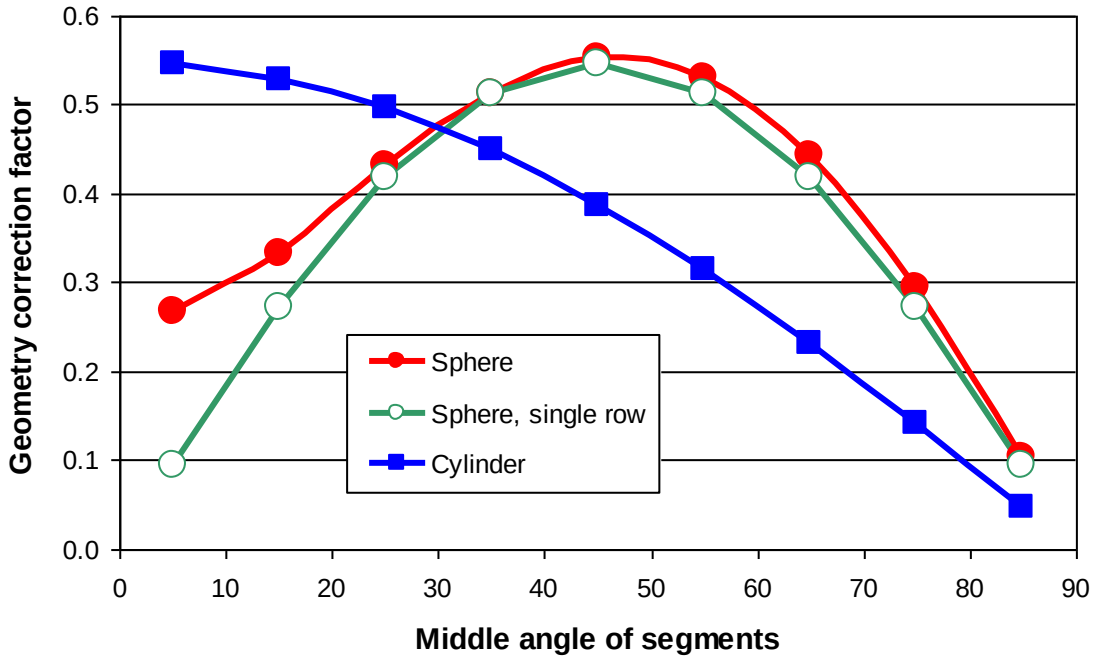
Asymmetry Parameters

The theoretically calculated asymmetry parameters of *Reilman et al*. are given in reference [4] in tabulated form for the different transitions in five atomic number steps. Polynomials with order of 6 were fitted to every asymmetry parameter set and the coefficients together with the transition names and the ranges of validity (atomic numbers) are stored in the library. Separate data set are available for Mg Kα and Al Kα excitation sources.

Number of Valence Electrons

The numbers of valence electrons of the elements recommended by *Powell et al.* for the TPP-2 formula are extracted from the literature [9, 25]. The contributions of the 4f electrons of the rare earth elements are excluded, as suggested [9].

Geometry Correction Factors



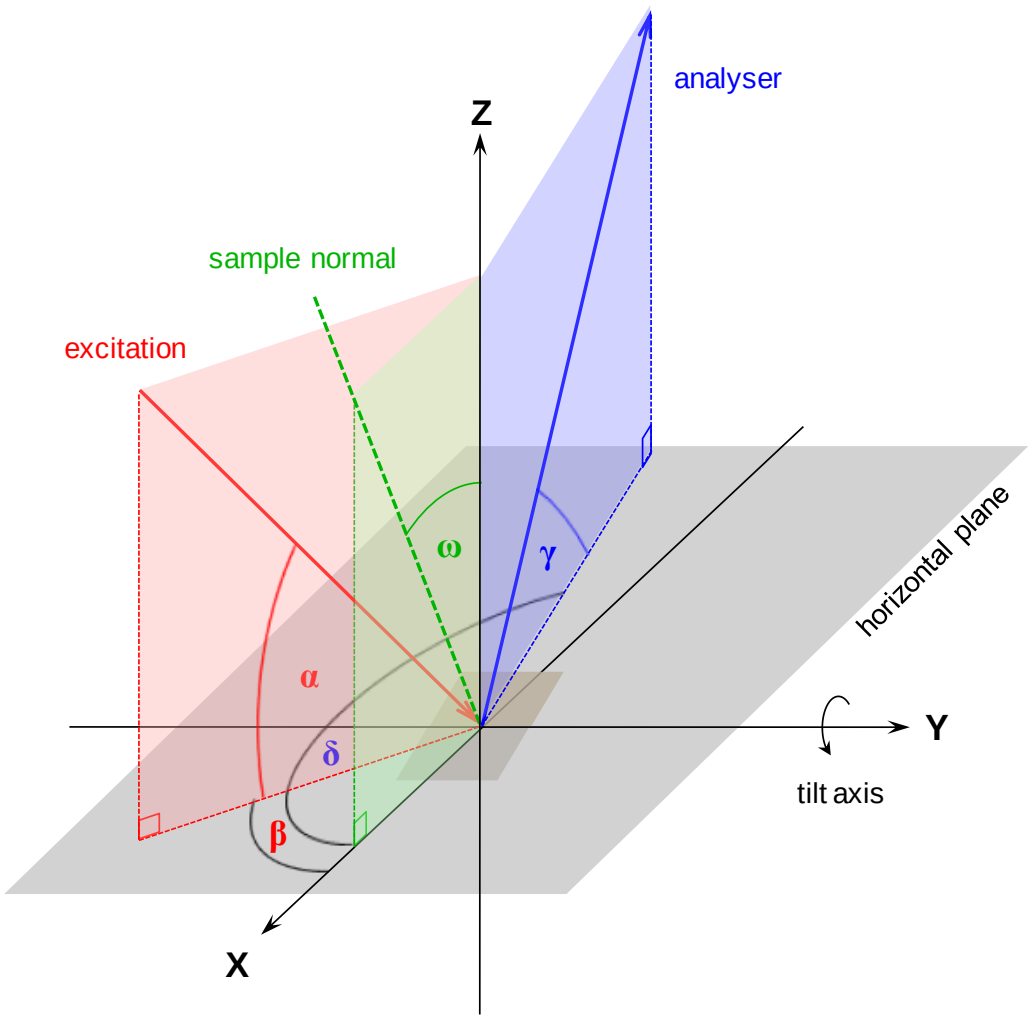
The geometry correction factors, for calculating photoelectron intensity values from layer thickness on curved surfaces, were calculated by *Varsányi et al.* [17, 18] for sphere and by *Mohai* for cylinder [18]. These factors are based on pure geometry considerations.

An atom says to his friend,
"Man, I think I've lost an electron."
The friend says "Are you sure?"
He answers: I'm positive!

Tips and Tricks

Transforming Angles

Commercial photoelectron spectrometers are manufactured with various geometry. For the quantitative evaluation of the spectra, the angles between the axis of the excitation source and the axis of the analyser (φ) must be known. The emission angle (θ), i.e., the angle between the sample surface normal and the analyser is also very important, especially for ordinary samples possessing in-depth inhomogeneities near to the surface.
Sometimes these angles can hardly be recognised unless the axis of the excitation and the analyser and the sample normal are in one plane. If this is not the case, these angles can be derived, however, from other angles measured (or specified by the manufacturer) on the instrument.



In the figure, the sample surface is in the X-Y plane of the coordinate system, which is horizontal; the Y axis is the tilt axis of the sample (being perpendicular to the sample normal). The direction of the excitation source is defined by its elevation (α) and azimuthal (β) angles, while the direction of the analyser also by its elevation (γ) and azimuthal (δ) angles. Measuring these angles, the excitation − analyser angle (φ) can be calculated by Equation (65).

$$\varphi = arccos\frac{A^2 + B^2 - E^2}{2AB} \tag{65}$$

where

$$A = 1/sin\,\alpha \tag{66}$$

$$B = 1/sin\,\gamma \tag{67}$$

$$C = 1/tan\,\alpha \tag{68}$$

$$D = 1/tan\,\gamma \tag{69}$$

$$E^2 = C^2 + D^2 - 2CD\,cos(\delta - \beta) \tag{70}$$

The emission angle (θ) can also be calculated from the above data and the sample tilt angle (ω, measured on axis Y) by Equation (71).

$$\theta = arccos\frac{A^2 + B^2 - E^2}{2AB} \tag{71}$$

where

$$A = 1/sin\,\gamma \tag{72}$$

$$B = 1/cos\,\omega \tag{73}$$

$$C = 1/tan\,\gamma \tag{74}$$

$$D = 1/tan\,\omega \tag{75}$$

$$E^2 = C^2 + D^2 - 2CD\,cos\,\delta \tag{76}$$

The equations are similar; differences are due to the different definitions of angles (elevation angles are measured from the horizontal plane, azimuthal angles from axis X, tilt angle from axis Z).

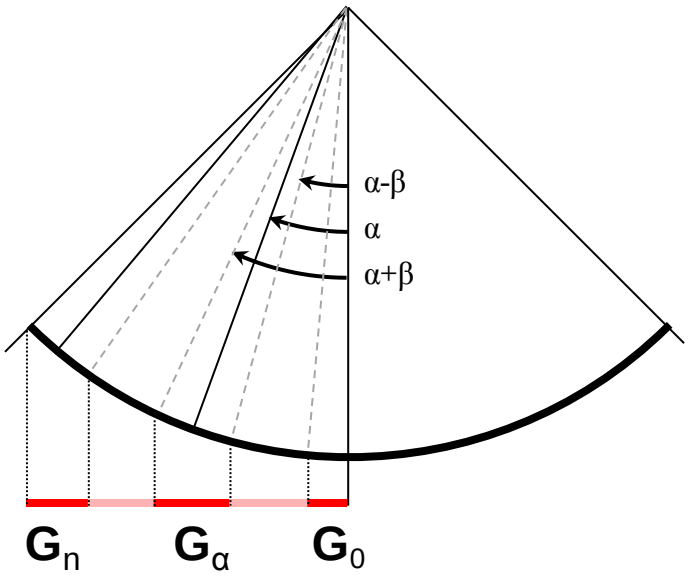
Layers Inside a Tube

Sometimes layers on (or in) a tubular sample have to be measured, e.g., on an inside-coated tube, on a fluorescent lamp or on an inside-coated medicinal ampoule. Although the sample is cylindrical, the *Layers-on-Cylinder* model cannot be applied because it takes into account whole cylinders, while in a practical case of bulky samples only a part of a cylinder (usually a

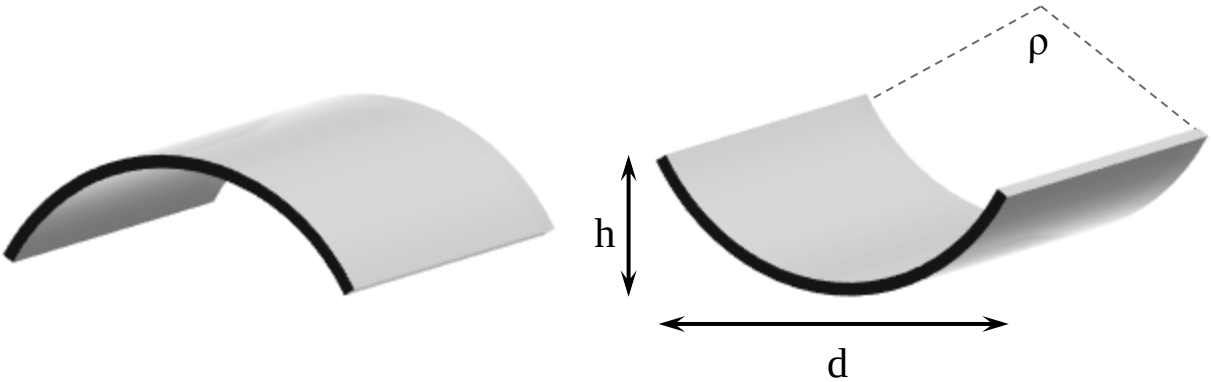
third or a quarter) is cut out for measurement. Fortunately, application of the *Layers-on-Polyhedron* model may help. The geometry correction factors (the relative sizes of the projected areas of the facets at different angles) in the *Layers-on-Polyhedron* model, set by the user, can be applied to describe any kind of non-planar surface (see chapter "Layers-on-Polyhedron Model" for details).
The geometry correction factors of the tube segment can be calculated by Equation (77),

$$G_{\alpha}^{tube} = sin(\alpha+\beta) - sin(\alpha-\beta) \qquad (77)$$

where G_α is the geometry correction factors for facet at angle α, while β is the half of the angle increment between facets (β is 5° in XPS MultiQuant), as illustrated in the next figure.

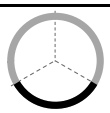
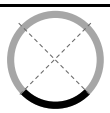
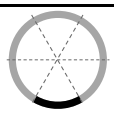


Due to the symmetry of the tube section, only half of it should be taken into account. For the same reason, the first factor (G_0) is calculated from 0 to β, while the last one (G_n) from α-β to α+β or from α-β to α, depending on how the angle increment (2β) can be fit into the central angle (ρ) of the segment.
The central angle (ρ) of the tube section can be easily calculated from its width (d) and height (h) by Equation (78), as illustrated in the next figure. The width (d) of the segment is delimited either by the sample size itself when spot size of the instrument is larger than the size of the sample or by the field of view of the spectrometer (for small spot size instruments).



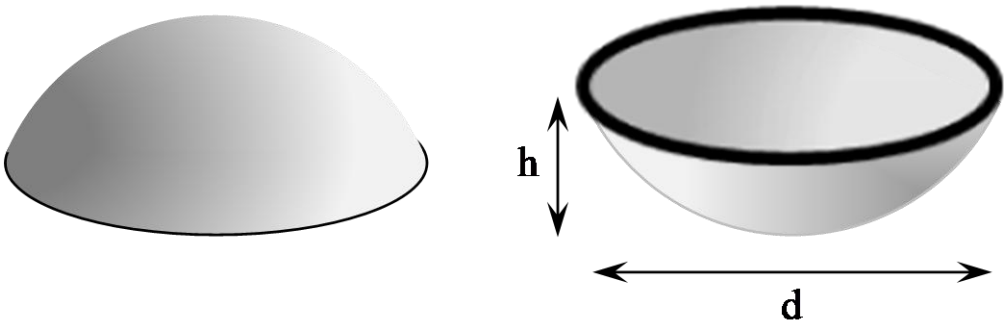
$$\rho = 2\,arcsin\frac{dh}{(d/2)^2 + h^2} \tag{78}$$

The required geometry correction factors for the most common cases, when the tube is cut into three, four or six parts are enumerated in the next table (normalised to 100 %). These numbers can be simply entered into the *Polyhedron Editor* window.

Facet tilt angle	 **120°**	 **90°**	 **60°**
0°	10.1 %	12.3 %	17.4 %
10°	19.8 %	24.3 %	34.3 %
20°	18.9 %	23.2 %	32.8 %
30°	17.4 %	21.3 %	15.5 %
40°	15.4 %	18.9 %	
50°	12.9 %		
60°	5.4 %		

Layers on Domes

Similar evaluation can be performed when the inside or outside of a part of spherical samples (domes) are measured, like coated optical lenses, small light bulbs, round bottom of ampoules, etc. The way of calculation is the same; the values of the geometry correction factors are, however, different. The central angle (ρ) of the dome can also be calculated from its width (d) and height (h) by Equation (78), as illustrated in the next figure.

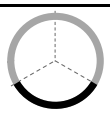
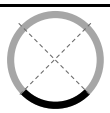
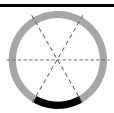


The geometry correction factors of the spherical segment can be calculated by Equation (79),

$$G_{\alpha}^{dome} = sin^2(\alpha + \beta) - sin^2(\alpha - \beta) \tag{79}$$

where G_α is the geometry correction factors for facet at angle α and β is the half of the angle increment between facets (5°), as defined in case of tubes. Here the user should apply all symmetry considerations listed in case of tube sections.

The geometry correction factors for the most common cases, when the central angle of the sphere section is 120, 90 or 60° are enumerated in the next table (normalised to 100 %).

Facet tilt angle	 **120°**	 **90°**	 **60°**
0°	1.0 %	1.5 %	3.0 %
10°	7.9 %	11.9 %	23.8 %
20°	14.9 %	22.3 %	44.6 %
30°	20.1 %	30.1 %	28.6 %
40°	22.8 %	34.2 %	
50°	22.8 %		
60°	10.5 %		

Testing Layers

Evaluating measured intensities for a sample allegedly having one or more overlayers, while composition and even sequence of those are not exactly known, the user can easily test several potential layers and compositions.

To simplify and speed up the trials, a number of test layers with their estimated composition and sequence can be defined at the same time. To neglect unnecessary ones, declare it *Fixed* (in the *Link to* row of the *Model* window) and set its thickness to zero (in the *Layer Calculation* window). This layer will be “invisible” for the calculations.

In the next figure, example is shown of calculating A-B then B-A layer sequences.

		Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Bulk	Omit
	Name	A	B	A			C	
	Link to			Fixed				
	Mol. weight	10.00	40.00	10.00				
	Density	1.000	2.000	1.000				

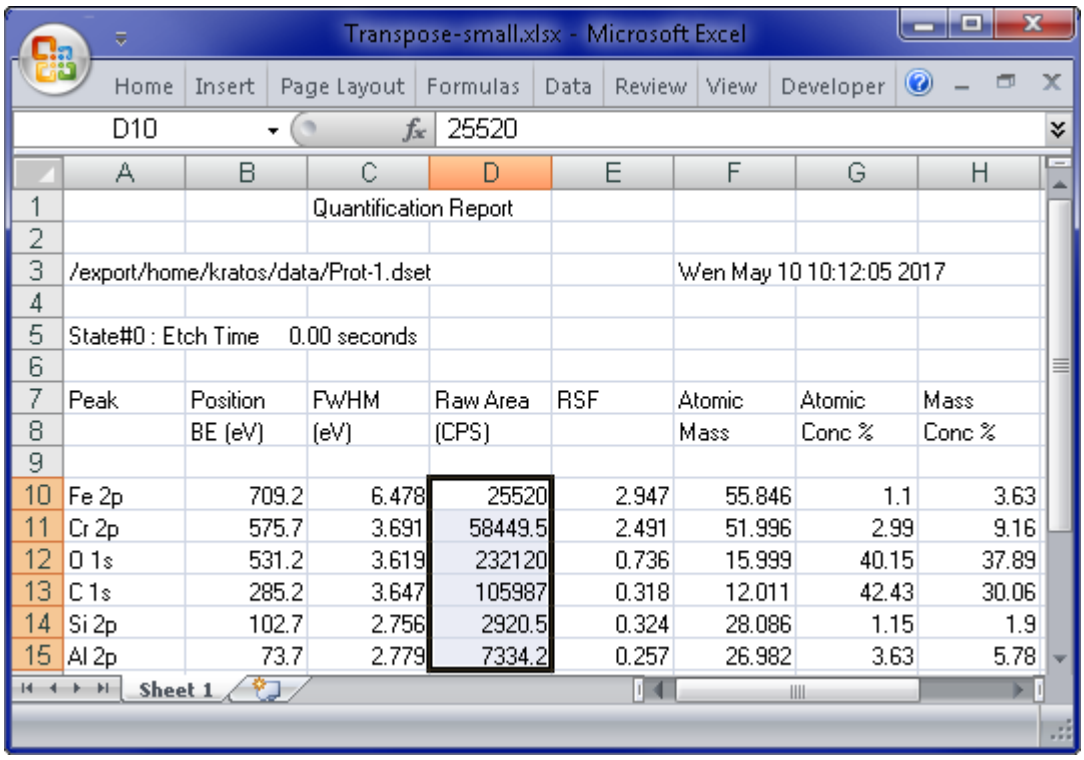
	Layers	[nm]
1	A	1
2	B	1
F	A	0

		Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Bulk	Omit
	Name	A	B	A			C	
	Link to	Fixed						
	Mol. weight	10.00	40.00	10.00				
	Density	1.000	2.000	1.000				

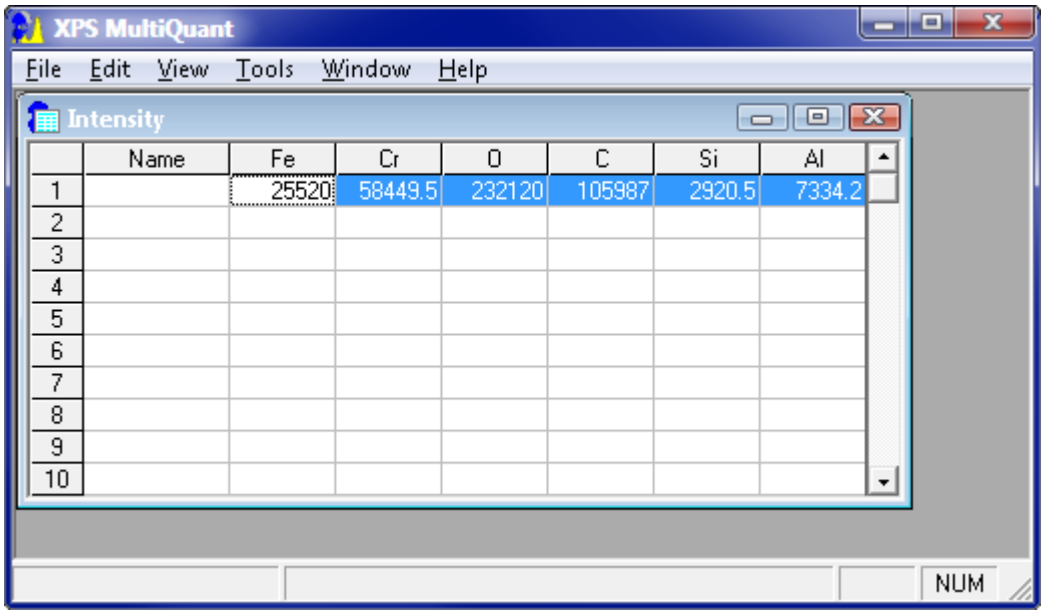
	Layers	[nm]
F	A	0
2	B	1
3	A	1

Transposing Cells

If input data of the quantification, e.g., peak area values, are available as structured text, like an Excel or Origin file, a table in Word document or comma delimited file, arrangement of items can be transposed thus a row can be pasted as a column, or a column as a row. Table of data (matrix) cannot be transposed by this way.

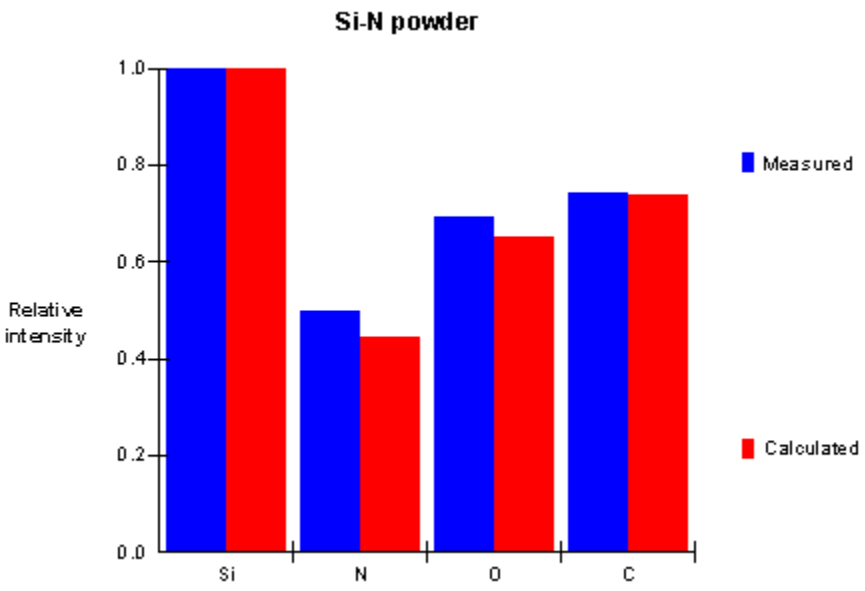


Copy the group of cells in the source program, then select a range in the wanted direction in any input window of XPS MultiQuant and perform the **Paste** command.



Exporting Comparison Chart

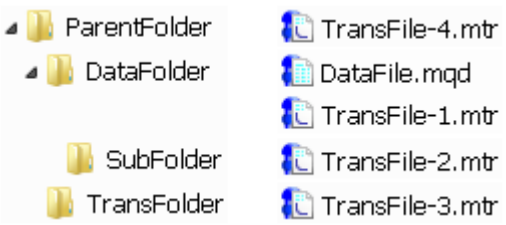
During layer thickness calculation the *Chart* window displays a bar graph, comparing the measured and calculated relative intensity values of the elements. When the *Chart* window is clicked after the calculation, the content is switching back to the regular chart. However, if you want to save the bar graph, e.g., to illustrate the quality of the fit, it can be done by the following way: after closing the *Layer Calculation* window, immediately right click the *Chart* window and select the **Copy Chart** command.



The bar graph is copied to the clipboard as Windows Metafile and can be pasted into documents, as illustrated above. Do not left click or do not try to move or resize the *Chart* window.

Relative Path for Transmission Files

Although XPS MultiQuant stores the full (absolute) path of the transmission files in the data files, user can remove or edit the path in *Transmission* tab of the *Parameters* window. Using a relative path may be useful if the data file is moved together with the transmission file. Some examples of denoting the relative path of the different transmission files for the *DataFile.mqd* are illustrated in the next figure.



..\TransFile-4.mtr

TransFile-1.mtr

.\SubFolder\TransFile-2.mtr

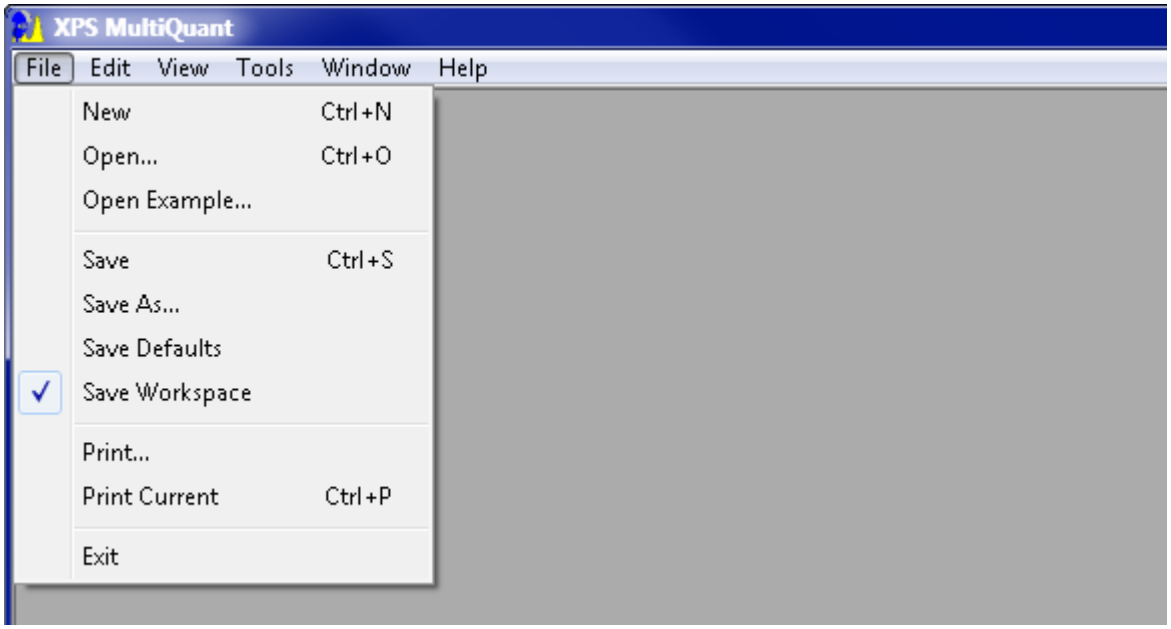
..\TransFolder\TransFile-3.mtr

Program References

Menu Commands

Use menu commands to control XPS MultiQuant. Click the menus or press ALT and type the access key (underlined) or press the shortcut key to perform some commands directly.

File Menu



New

Deletes all previously entered data from all windows and displays the *Elements* window. Prints any pending page. Settings of the parameters are unchanged, except *Title*.

Open…

Invokes the *Open Data* dialog box for selecting previously saved XPS MultiQuant data files, XPS MultiQuant template files or XPS Reduced Data Exchange files.

Open Example…

Invokes the *Open Example Data* dialog box for selecting example XPS MultiQuant data files, XPS MultiQuant template files or XPS Reduced Data Exchange files. The *Notes* window and other subwindows are opened automatically and the result format is set, as appropriate for the selected file.

Save

Saves data in the current XPS MultiQuant data file (shown in the status bar). If data are not yet saved, the *Save Data As* dialog box will be invoked.

Save As…

Invokes the *Save Data As* dialog box for entering name for a new XPS MultiQuant data file or XPS MultiQuant template file. When an example file is saved, it loses its 'magic' and acts as an ordinary data file.

Save Defaults

Saves the initial settings of the *Parameters* (except *Title*), *Print* and *Print Options* windows in the registry.

Save Workspace

When selected, the name of the current data file, the position, size and other attributes of all open windows are saved on exit. Next, when the program started without command line (filename) parameter, the file is loaded and the layout of all windows are restored.

Print…

Invokes the *Print* window for selecting items to be printed, forcing printing of the pending page and setting printing options. If no printer is installed to the computer when the program is started, this item is not available.

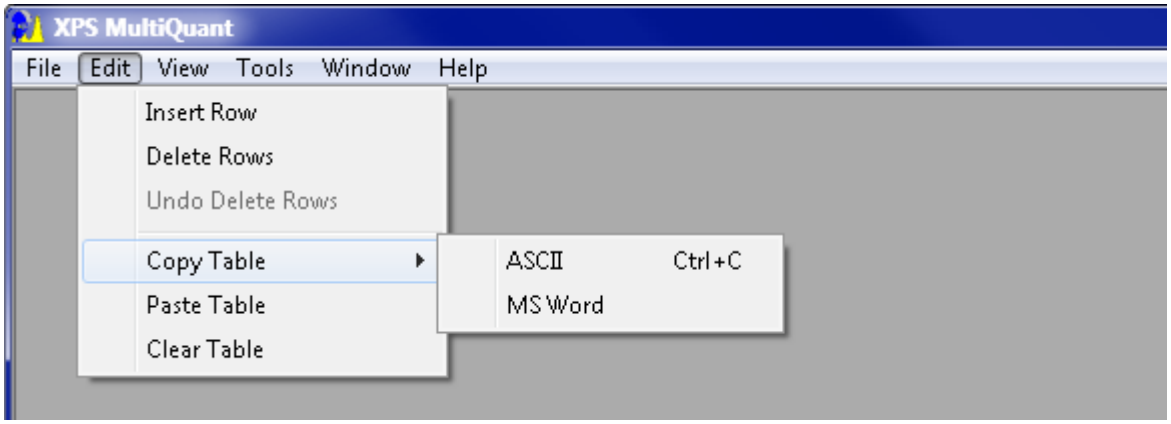
Print Current

Prints the active window to the printer. If no printer is installed to the computer, this item is not available (including shortcut). The content of the *Chart* or *Model Layout* windows is printed immediately (not spooled) on a separate page; the previously printed pending page is printed before the figure.

Exit

Quits XPS MultiQuant. Pending page is printed. The current size and position of the main window is saved in the registry.

Edit Menu



Insert Row

Inserts one empty row into the active input windows (*Elements* or *Intensity*) before the selected (coloured) line. To select a row click the sequence number of elements or experiments. The blank row should be filled immediately.

Delete Rows

Deletes one or more selected rows from the active input windows (*Elements* or *Intensity*). Remainder lines are closed up. To select rows click the sequence number of the first row then drag or SHIFT+click the last one.

Undo Delete Rows

Revokes the last **Delete Row** command. There is only one level of undo either for elements or for experiments. When the number of elements or experiments was changed since the last delete, a warning message is displayed, because undo may corrupt the last entered data.

Copy Table ▸

Copies the content of the active window to the clipboard, including row and column headers. If the SHIFT key is pressed, tables are copied without heading.

ASCII

To paste data into an ASCII file (e.g., Notepad) or Excel worksheet, select the **ASCII** subcommand. Data items are separated by tabulator (TAB) characters, lines are terminated by carriage return – line feed (CRLF) characters.

MS Word

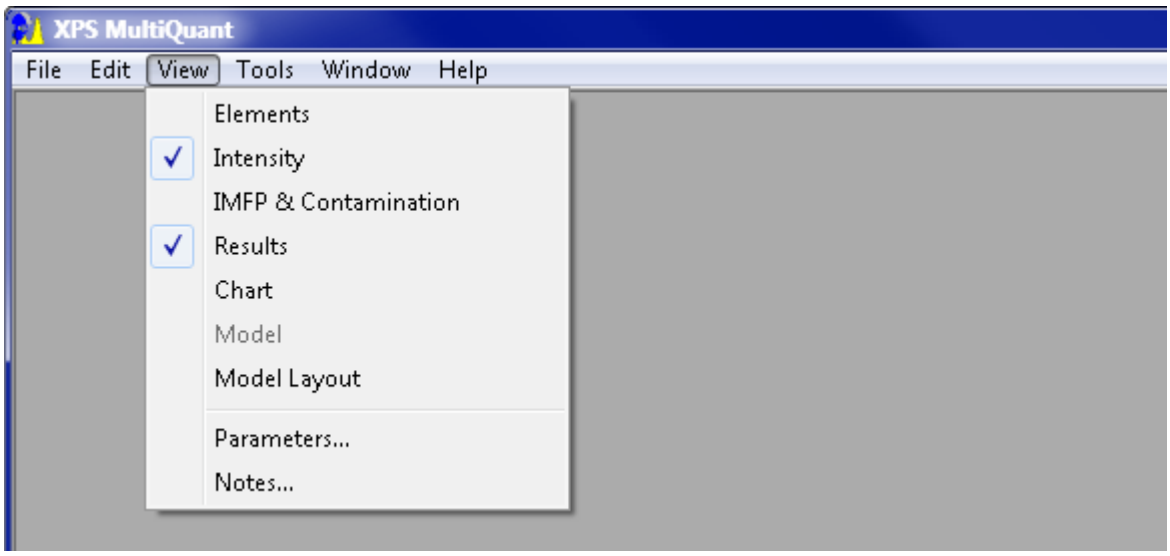
To paste data into a Microsoft Word document, converting it to a table, select the **MS Word** subcommand. Data items are separated by TAB characters, lines are terminated by vertical tabulator (VT) characters (manual line break) and table is terminated by CRLF characters.

Paste Table
Pastes the content of the clipboard to the active input window (*Elements*, *Intensity*, *IMFP & Contamination* or *Model*). The original content of the table can be recovered by an immediate **Undo** command of the pop-up menu.

Paste Table
Pastes the content of the clipboard to the active input window (*Elements*, *Intensity*, *IMFP & Contamination* or *Model*). The original content of the table can be recovered by an immediate **Undo** command of the pop-up menu.

Clear Table
Clears the whole content of the active input window (*Elements*, *Intensity*, *IMFP & Contamination* or *Model*) or the results of the structured model calculations. Cleared windows can be recovered by an immediate **Undo** command of the pop-up menu.

View Menu



Elements
Displays or hides the *Elements* window.

Intensity
Displays or hides the *Intensity* window. Available only if elements are already entered into the *Elements* window.

IMFP & Contamination
Displays or hides the *IMFP & Contamination* window. Available only if elements are already entered into the *Elements* window.

Results
Displays or hides the *Composition* or *Layer Thickness* windows. Available only if elements and intensity data are already entered.

Chart
Displays or hides the *Chart* window. Available only if the *Composition* or the *Layer Thickness* window is displayed.

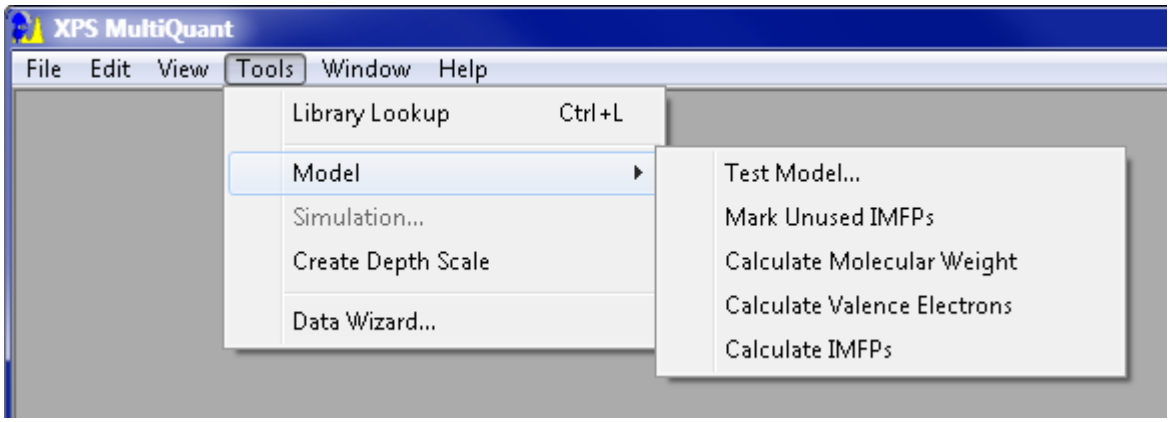
Model
Displays or hides the *Model* window. Available only if the selected model type is one of the structured ones (the *Model* textbox in the *General* tab of the *Parameters* window).

Model Layout
Displays or hides the *Model Layout* window.

Parameters…
Displays the *Parameters* window.

Notes…
Displays the *Notes* window.

Tools Menu



Library Lookup
Searches XPS MultiQuant's library for element and photoelectron line data for the elements given in the *Elements* window according to the settings in the *Parameters* window. Library must be enabled. Search can be performed either for the whole content of the window or for selected elements only. To select elements, click the line number of the first line then drag or SHIFT+click the last one. This command works only when invoked from the *Elements* window.

Model ▸

This menu contains tools, which help and automate filling of the structured model data. These commands usually work only when invoked from the *Model* window.

Test Model

Performs the model data consistency tests and displays the results and possible error messages in the *Model Summary* window. These tests are normally performed only at closing of the *Model* window.

Mark Unused IMFPs

Marks the positions in the IMFP matrix of the *Model* window, which are unnecessary for calculating of the specified layer structure.

Calculate Molecular Weight

Calculates and fills the molecular weight values of the layers according to atomic weights given in the *Element* window and stoichiometric coefficients given in the atom location matrix of the *Model* window. This command can be invoked either from the *Model* or from the *IMFP & Contamination* window.

Calculate Valence Electrons

Calculates the number of the valence electrons for the TPP-2M formula according to the composition given in the *Model* window. This command must be invoked from the *IMFP & Contamination* window.

Calculate IMFPs

Calculates the IMFP values using the method selected in the *Parameters* window. Results are put into the IMFP matrix of the *Model* window. Parameters of the calculation are taken from the *IMFP & Contamination* window. Calculation can be performed for all layers and the bulk or only for a selected single layer. To select a layer, click its column header.

Simulation…

Displays the *Intensity Simulation* window.

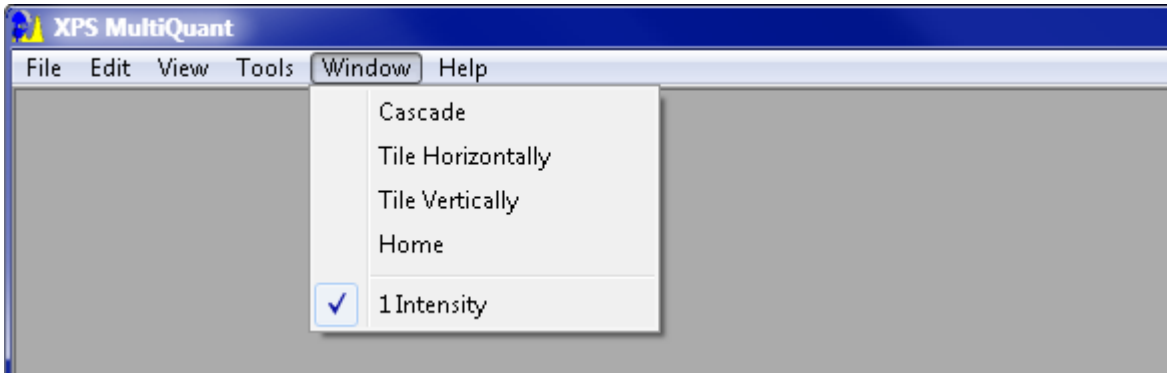
Create Depth Scale

Calculates a depth scale from the *Time* labels and the *Sputter rate* value from the *Labels* tab of the *Parameters* window. Depth values are permanently stored in the *Other Numeric* label set. Warning message is displayed when the *Other Numeric* labels are not empty or the sputter rate and time data are not entered. It works only when performed from the *Composition* window.

Data Wizard…

Invokes the *Data Wizard* window. The Data Wizard helps to enter data for a simple XPS MultiQuant calculation by giving step-by-step instructions. To leave the wizard perform this command again or press the close button.

Windows Menu



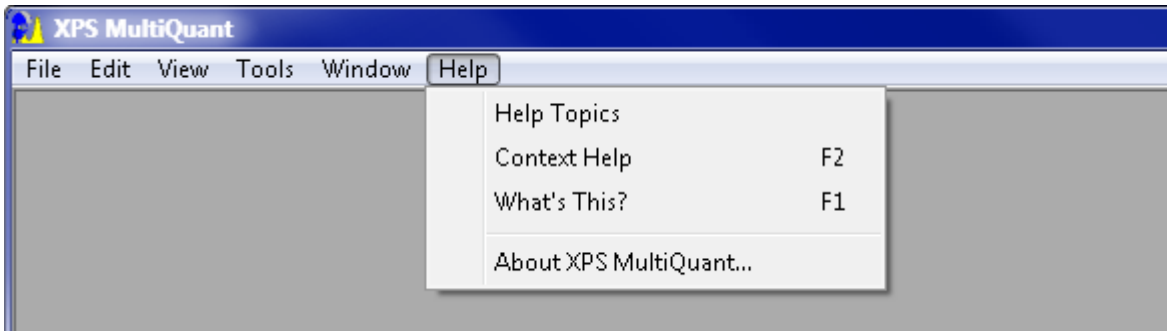
Cascade
Arranges the open windows in cascade form.

Tile Horizontally
Arranges the open windows horizontally tiled.

Tile Vertically
Arranges the open windows vertically tiled.

Home
Moves the active window to the home position (upper left corner of the main window).

Help Menu



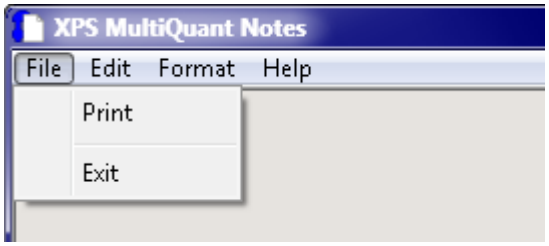
Help Topics
Displays the table of content of XPS MultiQuant Help.

Context Help
Displays context sensitive help.

What's This?
Changes the mouse pointer to "What's This" pointer (question mark). Click an item to display its context sensitive help in a pop-up window.

About XPS MultiQuant…
Displays the program's *About* box. It shows the version numbers of the program, library and data files.

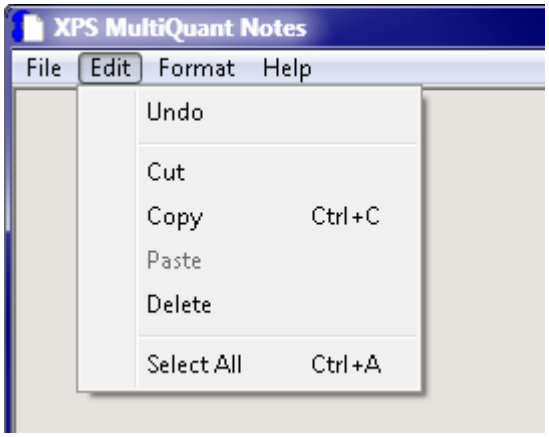
File Menu (Notes window)



Print
Prints the notes text and saves the last editing.

Exit
Closes the *Notes* window after prompting to save any unsaved editing. To permanently save notes, use the **File / Save** command to save the current XPS MultiQuant data file.

Edit Menu (Notes window)



Undo
Revokes the last editing action. There is only one level of undo.

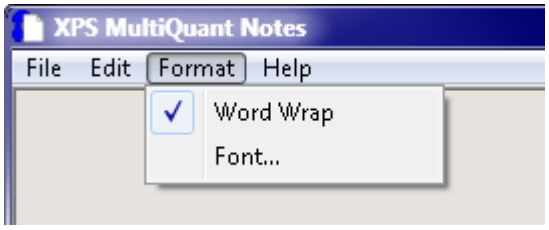
Cut, Copy, Paste, Delete

These commands provide standard editing functions to cut, copy, paste, or delete text. They can also be accessed via pop-up menu (right click).

Select All

Highlights the entire *Notes* text.

Format Menu (Notes window)



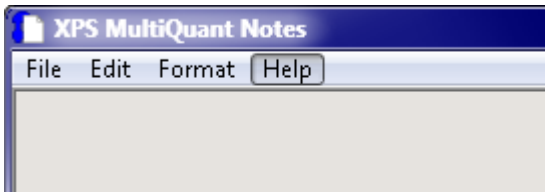
Word Wrap

Wraps text to the width of the *Notes* window. It does not affect the way text appears when it is printed. A check mark appears when word wrap is turned on.

Font…

Changes the font style and size of the *Notes* window. An example of how the selected font will look appears in *Sample*. The selected font and its size are stored with the default parameters while other elements (style, colour, etc.) are not retained.

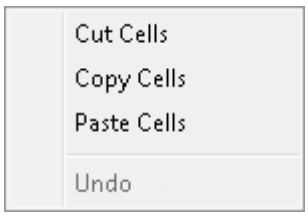
Help Menu (Notes window)



Help

Invokes the help topic of the *Notes* window.

Pop-up Menu (input windows)



A pop-up menu, activated by a right mouse click, is available in the input windows (*Elements*, *Intensity*, *IMFP & Contamination*, *Model*) to cut, copy and paste the content of the active cell or range of cells to or from the clipboard. Data can be exchanged within XPS MultiQuant or between other Windows applications.
When the pop-up menu commands are invoked in one of the mentioned windows, only the selected cells are affected. Multiple rows and columns can be selected by clicking one of the corners and dragging to the opposite corner or by pressing the SHIFT + ARROW keys.
If there are more cells in the selected range than are in the clipboard, the remaining cells are cleared. If there are more cells in the clipboard than in the selected range, the unused portion of the clipboard is ignored.
The structure of the clipboard text is described at the **Copy Table** command.

Cut Cells

The content of the active cell or the selected range is copied to the clipboard then the selected region is cleared. When the entire content of two (or more) lines of the *Elements* or *Intensity* windows are cleared by the **Cut Cells** command, the content of the underlying lines may be lost because of the automatic counting of elements and experiments.

Copy Cells

The content of the active cell or the selected range is copied to the clipboard. The selected region remains unchanged. This command is also available in the *Composition* and *Layer Thickness* windows.

Paste Cells

The content of the clipboard is pasted to the active cell or to the selected range. The selected range is overwritten. Available only when the clipboard contains text data. Alphabetic text pasted into the numeric cells is treated as zero. Direction of cells can be transposed thus a row can be pasted as a column, or a column as a row. If the cells to be pasted contain space characters (i.e., spaces are not item separators), press the SHIFT key during pasting.

Undo

Revokes the last cell- or table-editing command (DELETE, **Cut Cells**, **Paste Cells**, **Paste Table** and **Clear Table**). When the number of elements or experiments changed since the last editing command, a warning message is displayed, because undo may corrupt the recently entered data. If the destination cell of the undo command is non-existing due to removed elements, another warning message is displayed and the command cannot be performed. There are ample levels of undo.

Pop-up Menu (result windows)

This pop-up menu, activated by a right mouse click in the column header (element symbols) or in the row header (experiment sequence numbers), is available in the *Composition* and *Layer Thickness* windows.

Omit

When selected, the element is omitted from the 100 % sum of the percentage composition, while the remaining elements are re-normalised. **Omit** is enabled only for 'percentage' results. The effect of the command is the same, as double clicking the element symbol.

Visible

Controls the visibility of elements or experiments in the *Chart* window. If unselected, the element (series) or experiment (points) disappears from the composition chart. When this menu is activated on the element symbols, it affects the elements; when activated on the sequence numbers of experiments, the experiments. (Invisible elements, unlike in case of the **Omit** command, are still included in the 100 % sum.)

Reset All

When the menu is activated on the element symbols, it resets the *Omit* and *Visible* items of all elements to default (*Omit* off, *Visible* on). When activated on the sequence numbers of experiments, it resets the all the data points (experiments) omitted from composition chart.

Pop-up Menu (Chart window)

This pop-up menu, activated by a right mouse click, is available in the *Chart* window.

Copy Chart

Copies the content of the *Chart* window to the clipboard in Windows Metafile (WMF) format.

Colours

Switches on or off the colours of the chart.

Pop-up Menu (Model Layout window)

This pop-up menu, activated by a right mouse click, is available in the *Model Layout* window.

Copy Figure

Copies the content of the *Model Layout* window to the clipboard in device independent bitmap (DIB) format. To obtain the best quality (higher resolution) picture, adjust the size of the *Model Layout* window before copying.

Colours

Switches on or off the colours of the model layout figure.

Legend

Switches on or off the legend text (layer names) of the model layout figure.

Windows

Users enter input data and also get results in different windows. Windows can be invoked by the **View** menu command. Data can be entered into the textboxes, alternatives can be selected from the drop down lists and can be set by check boxes or option buttons. When large amount of data is necessary for the calculation, enter them into the tables. User can navigate in the tables by the arrow keys or mouse clicks. The BACKSPACE key deletes the last character in a cell while the DELETE key deletes the whole content of a cell. To edit flexibly the content of a cell in a table, double click it. In this mode the arrow keys moves the text cursor within the cell. To leave the edit mode, click any other cell in the same window.
In numeric cells, either point or comma typed, always the current decimal mark is entered, as set in Windows. Where a number is expected in a table, two numbers, connected with an arithmetic operator, can also be used. The numbers may have sign, decimal separator and exponent with optional sign.
Windows can be repositioned and resized within the main window. XPS MultiQuant adjusts the optimal size of each window when they are opened and resize them when it is necessary (e.g., when elements are inserted or deleted, *Oxygen Balance* column is displayed, etc.). However, when the user resizes any window manually, it will keep its new size and will not be resized automatically until it is closed and reopened again.

Elements

Elements

	Symbol	Line	State	B. E.	Cross s.	Asymm.	Atomic w.	Valence	Oxygens
1	O	1s		531.0	0.624	2.000	16.00	2	0
2	Cr	2p		574.0	2.340	1.459	52.00	3	3
3	C	1s		285.0	0.225	2.000	12.01	4	0
4	Si	2p		99.0	0.230	1.106	28.09	4	2
5									
6									
7									
8									
9									
10									

Enter element symbols and photoelectron line assignations of the elements required for the calculations. Use the 2p, 3d, 4f, etc. notation for the doublet lines and the 2p3, 3d5, 4f7, etc. for the $2p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$ components, respectively. Capitalisation errors of the element symbols are corrected automatically. Use the *State* column to distinguish the different chemical states of the same element. Data can be extracted from the library by the **Tools / Library Lookup** command or can be entered manually. Data taken from the library can also be overwritten. The *Valence* column is the valence of the element at the given chemical state and the *Oxygens* column is the number of oxygen atoms in a mol of such oxide. When the window is left or closed, the data in the table are checked and a message may be displayed about possible errors. The number of elements is determined automatically thus empty lines are not allowed in the table.

Special cases of the *State* entries:

- The C1s line of carbon contamination must be left ***empty*** when the automatic contamination correction (*Mohai*) is selected.
- The two chemical states of the main constituent element must be ***Ox*** (oxide, oxidic, oxidised, oxidized) and ***Me*** (met, metal, metallic) when the *Oxide-Layer* model is used. (Only the first two characters are significant.)

Clicking some cells in the *Element* window assists in entering data conveniently. Double clicking a cell of the *Line* column inserts the notation of the lines actually available in the selected cross section data set, rotating transitions in increasing binding energy order. By double clicking the cells of the *State* column, one can enter the standard chemical state types for the *Oxide-Layer* model (Me, Ox, *empty*).
Double clicking the *B. E.* column header, the energy scale will be temporarily switched to kinetic energy. The K.E. values cannot be edited. The values are changing back automatically to binding energy when any mouse or keyboard action is taken.

	Symbol	Line	State	K. E.	Cross s.	Asymm.
1	O	1s		722.6	0.624	2.000
2	Cr	2p		679.6	2.340	1.459
3	C	1s		968.6	0.225	2.000
4	Si	2p		1154.6	0.230	1.106
5						

The order of the elements can be rearranged by right clicking the sequence number of the element to be moved, then dragging the cursor to the required new position (sequence number). During the drag and drop the cursor is changed, as illustrated in the next figure (e.g., moving Si to position 1), and the number of source element is marked by a dotted frame.

	Symbol	Line	State	B. E.	Cross s.	Asymm.	
1	O	1s		531.0	0.624	2.000	— Destination
2	Cr	2p		574.0	2.340	1.459	
3	C	1s		285.0	0.225	2.000	
4	Si	2p		99.0	0.230	1.106	— Source
5							

Elements cannot be moved to empty positions and empty lines cannot be inserted this way.

Intensity

Intensity

	Time (min)	O	Cr	C	Si
1	0	837624	669910	41853	213533
2	10	467572	936964	20378	296118
3	20	436508	936100	21494	293938
4	30	422376	938868	15150	302254
5	40	424544	955776	16565	290347
6	50	417772	942724	13359	292522
7					
8					
9					
10					

Enter the integral photoelectron line intensity data into this table, as supplied by the spectrum processing software. XPS MultiQuant distinguishes the empty and zero cells so zero value can be used to emphasise the lack of an element. Data of several experiments can be entered and calculated simultaneously. The 'experiment' may be an item in a series, e.g., ion bombardment, heat treatment, time dependence or simply a different (but usually similar) sample. The number of the experiments is determined automatically thus empty lines are not allowed in the table.

Labels for the experiments can also be entered into this table. Labels are used either to identify experiments or to supply additional information, e.g., the treatment time or tilt angle, etc. They also act as a source of X-axis values for charts. Select or define the required type of labels in the *Labels* tab of the *Parameters* window.

The content of the header row (chemical symbol, line assignation and chemical state) may vary, according to the actual elements and lines.

The order of the experiments can be rearranged by right clicking the sequence number of the experiment to be moved, then dragging the cursor to the required new position (sequence number). During the drag and drop the cursor is changed, as illustrated in the next figure, and the source experiment is marked by a dotted frame.

	Time (min)	O	Cr	C	Si
1	0	837624	669910	41853	213533
2	10	467572	936964	20378	296118
3	20	436508	936100	21494	293938
4	30	422376	938868	15150	302254
5	40	424544	955776	16565	290347
6	50	417772	942724	13359	292522
7					

— Destination

— Source

Experiments cannot be moved to empty positions and empty lines cannot be inserted this way.

IMFP & Contamination

IMFP & Contamination

	Time (min)	O	Cr	C	Si	Contam.
1	0	30	26	34	37	
2	10	27	26	31	34	
3	20	27	26	31	34	
4	30	27	26	31	34	
5	40	27	26	31	34	
6	50	27	26	31	34	
7						
8						
9						
10						

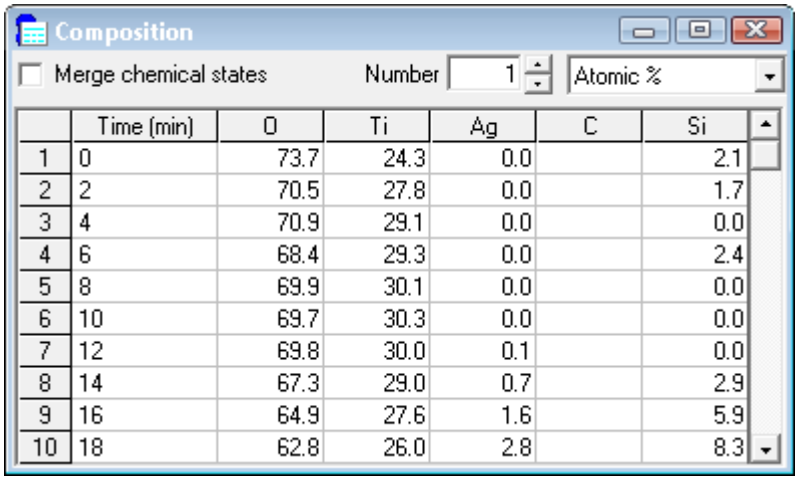
Data from the *IMFP & Contamination* window are applied when separate values are used for each experiment to calculate the IMFP. The layout of the window is depending on the selected calculation method.
Enter the inelastic mean free path data into the columns marked by element symbols for *Explicit* values into the above table. Parameters for the *Jablonski*, *Seah-Dench* or *Gries* methods (material class, density (g/cm^3) and mean atomic weight) can be entered into the next style table.

IMFP & Contamination

	Time (min)	Class	At. weight	Density	Contam.
1	0	Polymer		1	
2	10	Inorganic		2.5	
3	20	Inorganic		2.5	
4	30	Inorganic		2.5	
5	40	Inorganic		4.2	
6	50	Inorganic		4.2	
7					
8					
9					
10					

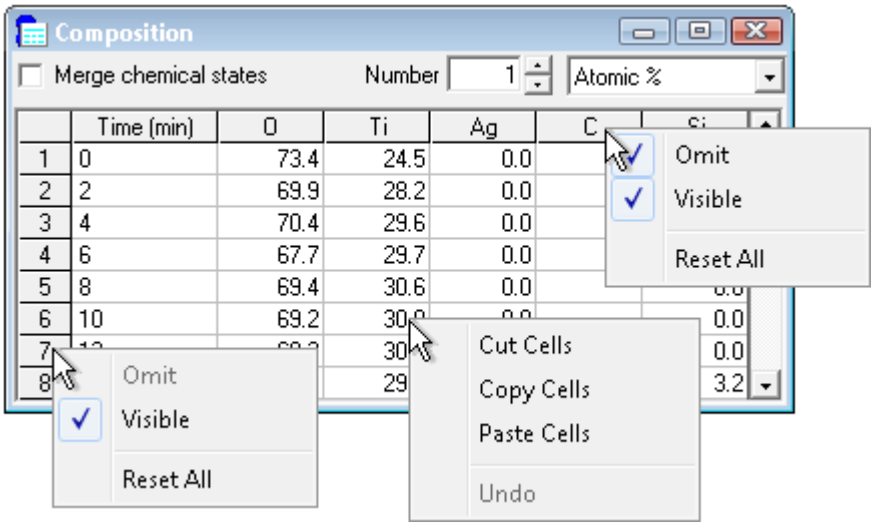
Also, enter contamination correction factors for *Explicit* type correction. Data from this table are used only when the corresponding calculation methods are selected in the *Parameters* window. Although these data are not always used, all data are always preserved and stored in data files. Labels cannot be edited in this window.
The content of the header row (chemical symbol, line assignation and chemical state) may vary, according to the actual elements and lines. If the header seems to be improper, double click the table.

Composition

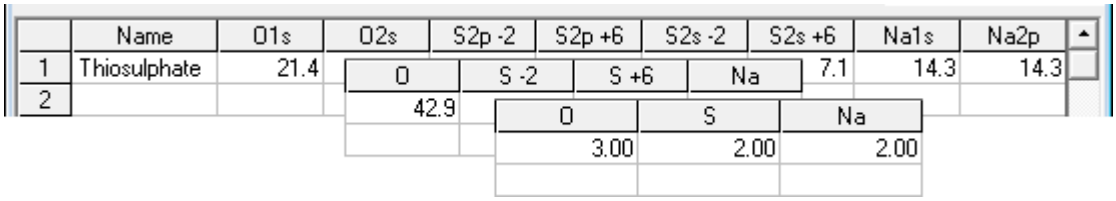


	Time (min)	O	Ti	Ag	C	Si
1	0	73.7	24.3	0.0		2.1
2	2	70.5	27.8	0.0		1.7
3	4	70.9	29.1	0.0		0.0
4	6	68.4	29.3	0.0		2.4
5	8	69.9	30.1	0.0		0.0
6	10	69.7	30.3	0.0		0.0
7	12	69.8	30.0	0.1		0.0
8	14	67.3	29.0	0.7		2.9
9	16	64.9	27.6	1.6		5.9
10	18	62.8	26.0	2.8		8.3

When all necessary input data are entered, invoke the *Composition* window by the **View / Results** command to see the harvest of the quantitative calculations. Results can be displayed in various forms. From the dropdown list *Atomic %*, *Atomic ratio*, *Oxide molar %*, *Oxide molar ratio*, *Mass %*, *Mass ratio*, *Oxide mass %* or *Oxide mass ratio* can be selected as adequate for the application of data.
For the percentage type results, any element can be omitted from or introduced to the 100 % by double clicking the element symbol while for the ratio type of data the basis element can be selected also by double clicking the element symbol. The number of basis atoms can be set in the *Number* textbox by clicking the arrow buttons or typing the number. See chapter "Normalisation of the Composition Results" for details.
If elements are present in more than one chemical state, the different states of the same elements can be added by selecting the *Merge chemical states* check box. This option is not available when any of the oxide result types is selected but in these cases the *Oxygen balance* is calculated and displayed in the last column of the window. The *Oxygen balance* is the ratio of the measured and calculated (required by the other elements at a given oxidation state and chemical formula) oxygen concentrations.

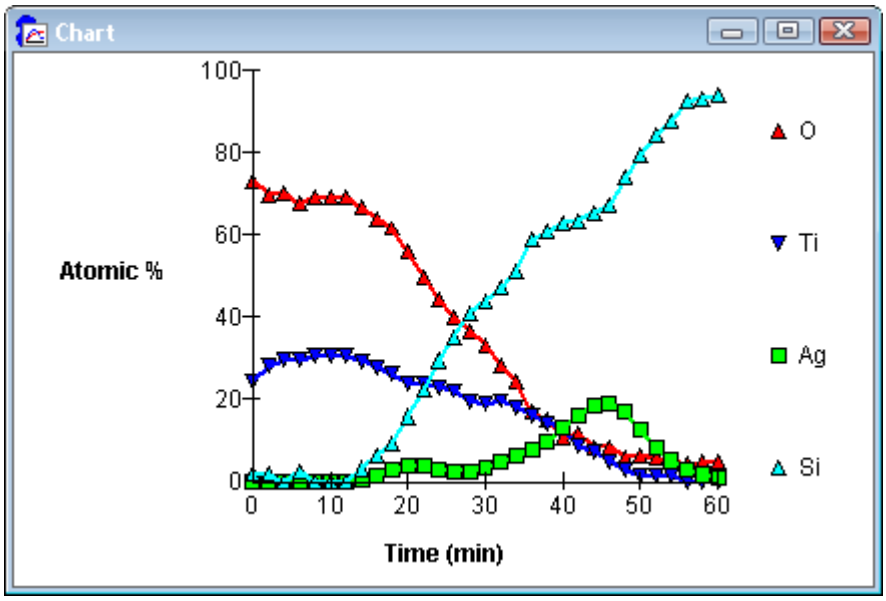


Various popup menus can be activated at different locations of the *Composition* window, as illustrated above. The menus are applied for copying cells, for controlling omission of elements from the percentage results and for controlling visibility of elements and experiments in the *Chart* window. See details in chapter “Menu Commands”.



The content of the header row (chemical symbol, line assignment, chemical state, oxide formula) may vary, as shown above, according to the type of calculation (multiline, merged, oxide, etc.).

Chart



The results of the quantification can be displayed in graphical forms as well. This window interacts with the *Composition* or the *Layer Thickness* windows.
X-axis is set as initially selected in the *Labels* tab of the *Parameters* window and Y-axis as the result type selected in the *Composition* or the *Layer Thickness* windows. When settings are changed in the latter windows, it will be reflected in the *Chart* window immediately or when clicking it. Data of the X-axis can be changed easily by double clicking the label column header (except the *Sequence number*; it can be preselected only in the *Labels* tab).
Experiments, i.e., data points, can be omitted from the chart by double clicking the sequence number of the experiment or by the **Visible** popup menu command, activated on the sequence number of the experiment. The number changes to **X**. Elements, i.e., data series, can also be omitted by the **Visible** popup menu command, activated on the chemical symbol. Elements omitted from percentage calculation are also omitted from the chart even if the result type is

set to ratio. If only one experiment is entered instead of the line chart, a pie chart is displayed. No chart is shown when only one element is specified.
A pop-up menu, activated by a right mouse click, is available to copy the content of the window to the clipboard in Windows Metafile format. The chart can be printed by the **File / Print Current** menu command. The chart is not spooled; it is printed immediately on a separate page. The pending page is printed before the chart.
The *Chart* window is also applied to compare the measured and calculated relative intensity values at the layer thickness calculations (see chapter "Layer Calculation").

Model

Model

		Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Bulk	Omit
	Name	CH-1	Pb-Ac	CH-2			SiO2	
	Type	Layer	Island	Layer				
	Link to			Layer 1				
	Mol. weight	432.36	319.24	432.36			60.09	
	Density	0.780	3.250	0.780			2.200	
0	No. H	72.00	4.00	72.00				
1	O		4.00				2.00	X
2	Pb		1.00					
3	C	36.00	4.00	36.00				
4	Si						1.00	
1	IMFP O	25.17	18.75	25.17			21.08	
2	Pb	35.56	26.12					
3	C	31.73	23.40	31.73				
4	Si	36.53	26.81	36.53			30.18	

Atom location matrix

IMFP matrix

When one of the structured model types is selected in the *Model* tab of the *Parameters* window, the composition and other parameters of the layers must be described in the *Model* window. Assign name to the layers and the bulk in the *Name* row. Although the name stands for administrative purposes, it indicates the presence of the layer for the program. Fill the molecular weight and density rows. The *Type* row is displayed only in case of *Island* type models. Enter I or L or double click to choose the *Island* or *Layer* type.
The next section is the atom location matrix: it shows the stoichiometry of the layers, i.e., the number of different atoms in a molecular unit. The 0th element is the hydrogen, which is, obviously, not part of the quantification but can be included for the molecular weight and IMFP calculations. The last section is the IMFP matrix; it shows the inelastic mean free path values for each layer and for each kinetic energy represented by the selected lines of the elements. Use the measure unit selected in the *Measurement unit* box of the *General* tab of the *Parameters* window. The molecular weight and calculated IMFP data can be obtained automatically by the **Tools / Model** commands.
When the automatic least square parameter fitting (*Autofit*) is used, layer thickness values can be *fixed* (kept constant during the fitting procedure) or can be *linked* (declared to be equal with another, neither fixed nor linked layer). To change the linking of the layers, double click the cells of the *Link to* row until the required notice is visible. Elements can also be omitted from the automatic calculation. To omit an element, double click the *Omit* row in the atom location matrix (an **X** appears).

Both the link and omit condition can be removed by the DELETE key as well.
The following figures show some examples of application of linking and fixing of layer thickness during automatic parameter fitting. Some erroneous combinations are also illustrated.

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to			

✓ No link is defined.
Each layer thickness is calculated independently.

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to		Layer 1	

✓ Layer 2 is linked to Layer 1.
The thickness of the layer B is kept equal to A during calculation.

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to	Layer 2	Layer 1	

✗ Layers 1 and 2 are linked to each other. *Cross link* is not allowed.

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to		Layer 1	Layer 1

✓ Layers 2 and 3 are linked to Layer 1. The thickness of both the B and C layers are equal to A

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to		Layer 1	Layer 2

✗ Layer 3 is linked to Layer 2, which is linked to Layer 1. *Chain* is not allowed.

Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to		Fixed	

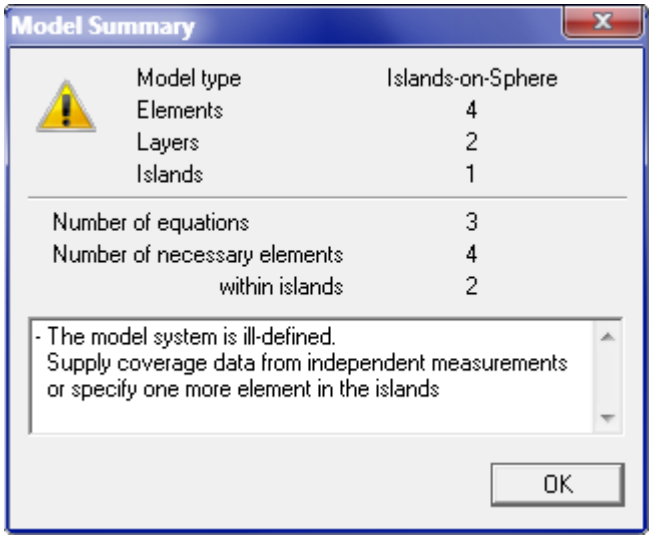
✓ Layer 2 is fixed. The thickness of B will not be changed during calculation.

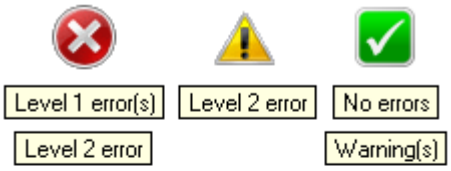
Model

		Layer 1	Layer 2	Layer 3
	Name	A	B	C
	Link to	Layer 2	Fixed	

✗ Layer 1 is linked to Layer 2, which is fixed. Target of a link cannot be a fixed layer.

Model Summary





The *Model Summary* window, invoked by the **Tools / Model / Test Model…** command, shows a brief summary and the results of the consistency tests of the data describing the current model. The icon is varying, according to the severity of the error. Pointing to it, the level of error is displayed in a tooltip box, as shown in the right hand side of the figure. Level 1 errors include wrong numeric range of data, correspondence of composition and IMFP values, validity of links, etc.; while level 2 errors indicate the insufficient number of equations, omitted elements, etc. The tests for level 2 errors are executed only when no errors in level 1 are present. These tests are normally performed only at closing the *Model* window thus by the above command the model can be checked as necessary without closing and re-opening the window.

IMFP & Contamination of Structured Models

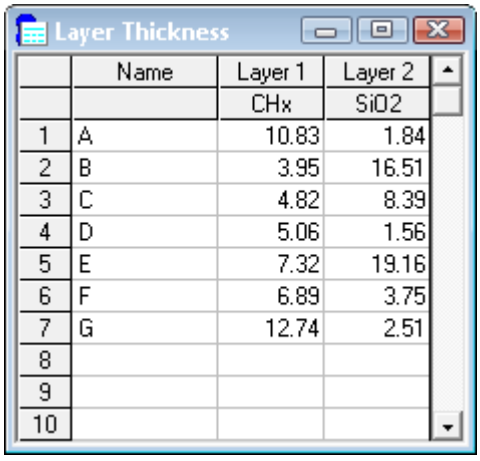
IMFP & Contamination

	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Bulk
Name	CH-1	Pb-Ac	CH-2			SiO2
Material class	Polymer	Inorganic	Polymer			Inorganic
Molecular weight	432.36	319.24	432.36			60.09
Density	0.780	3.250	0.780			2.200
Bandgap energy	6.000	6.000	6.000			6.000
Valence electrons	144	44	144			16

The parameters of the IMFP calculations for the structured models are taken from the *IMFP & Contamination* window. The molecular weight and density data are the same as in the *Model* window and can be change in either of them. If *Element* is selected as material class for a layer when its density row is empty, the value is automatically extracted from the library. To change the material class of the layers, double click the appropriate row or enter

the initial letter (e, i, p). Providing of the bandgap energy and the number of the valence electrons are required by the *Tanuma-Powell-Penn* method only.
The number of the valence electrons can be calculated automatically by the **Tools / Model / Calculate Valence Electrons** command.

Layer Thickness

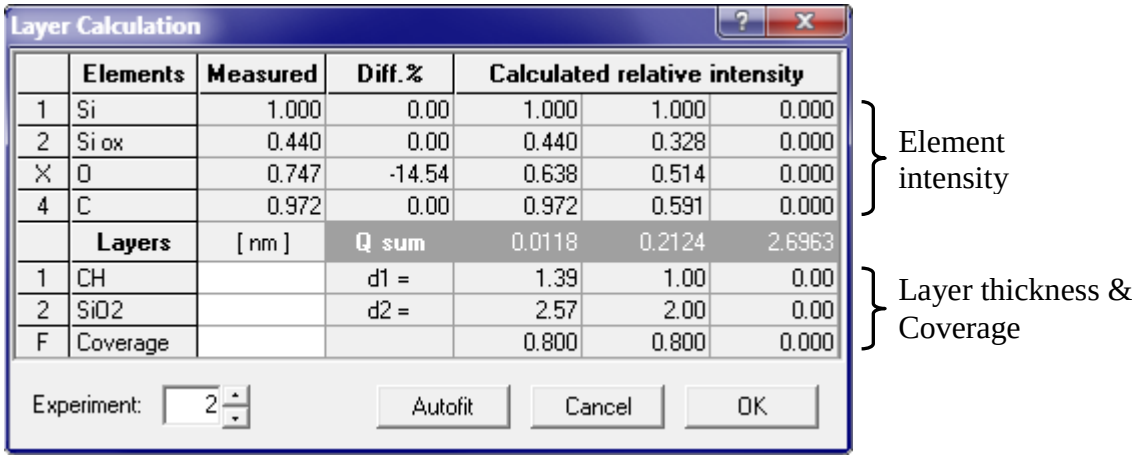


Layer Thickness

	Name	Layer 1	Layer 2
		CHx	SiO2
1	A	10.83	1.84
2	B	3.95	16.51
3	C	4.82	8.39
4	D	5.06	1.56
5	E	7.32	19.16
6	F	6.89	3.75
7	G	12.74	2.51
8			
9			
10			

The results of the layer structure calculations are summarised in the *Layer Thickness* window, invoked by the **View / Results** command. Layer thickness is shown in the same unit as selected in the *Model* window. The columns have double header lines showing both the type and number and also name of the layers. The *Coverage* column is displayed only when one of the *Island* type model is selected.
Since layer thickness values are not calculated automatically the table is empty when first displayed. The calculated layer thickness values, unlike other results, are stored in the XPS MultiQuant data files.
To invoke the layer calculation, double click the sequence number of the required experiment. To select an experiment for displaying in the *Model Layout* window, click the sequence number.
When an angle dependent experiment set is calculated, results will be appear only in the first row; indicating that all of the experiments are handled together. Calculation can be initiated by double clicking any experiment of the set but the intensity results, calculated for the whole set, is compared to the selected experiment only.
Popup menus, like in the *Composition* window, can be activated at different locations of the *Layer Thickness* window to copy cells and controlling visibility of elements and experiments in the *Chart* window. See details in chapter “Menu Commands”.

Layer Calculation



	Elements	Measured	Diff.%	Calculated relative intensity		
1	Si	1.000	0.00	1.000	1.000	0.000
2	Si ox	0.440	0.00	0.440	0.328	0.000
X	O	0.747	-14.54	0.638	0.514	0.000
4	C	0.972	0.00	0.972	0.591	0.000
	Layers	[nm]	Q sum	0.0118	0.2124	2.6963
1	CH		d1 =	1.39	1.00	0.00
2	SiO2		d2 =	2.57	2.00	0.00
F	Coverage			0.800	0.800	0.000

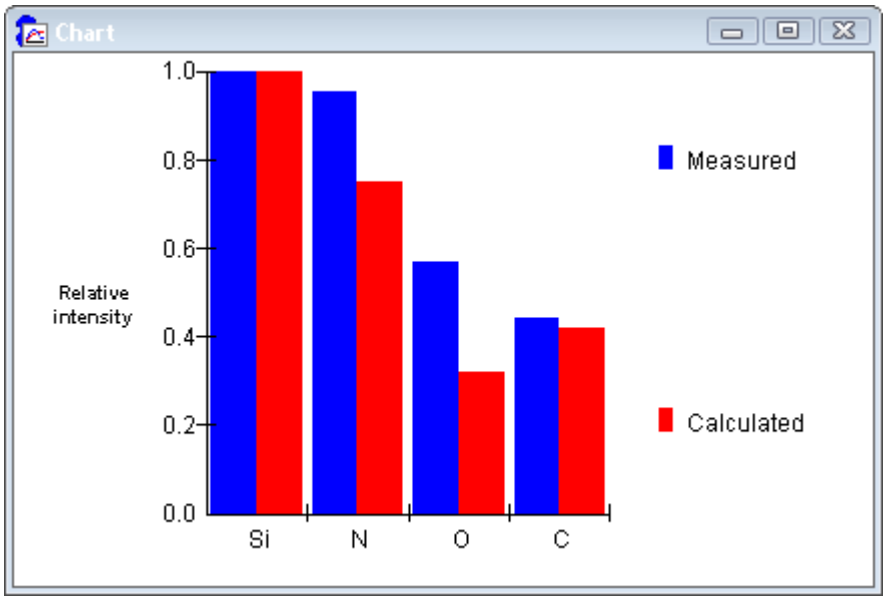
The upper part of the table shows the results of the intensity calculations. The *Measured* column shows the measured intensity ratio as described in chapter "Models for Structured Surfaces". The basis element can be changed by double clicking the element symbol. When an element is omitted from the automatic calculation, instead its sequence number an **X** is shown in the first column. The omit sate can also be changed in the *Layer Calculation* window by double clicking the sequence number of the element.
The lower part of the table shows the actual and previously entered layer thickness and coverage values. When two layers are linked, they indicated by the same layer number. Values for the linked layers entered automatically. When a layer is fixed or the coverage not fitted automatically, a letter **F** is displayed instead of the layer number.
After typing the layer thickness values into the entry cells of the table (press ENTER after each number), the results of the calculation are displayed in the first column of *Calculated relative intensity* columns. The *Diff%* column shows the percentage difference between the calculated and measured intensity. Negative *Diff%* value means that the calculated intensity is lower than the measured. *Diff%* is displayed only when smaller than ±100 %. The Q_{sum} row shows the sum of the squares of the differences, indicating the precision of the fit.
When all of the new layer thickness values are entered, the previously calculated intensity values are shifted to right, preserving the two previous sets for comparison. To minimise the difference between the measured and calculated intensity, the user can vary the layer thickness manually or can use the automatic least square fitting feature. The *Coverage* row is displayed only in case of *Island* type models.

Experiment
Selects the next or previous experiment for calculation without leaving the *Layer Calculations* window. The result of the current experiment is stored in the *Layer Thickness* window. This item is not available in case of angle dependent experiment set.

Autofit
Starts the automatic least square fitting procedure of model parameters.

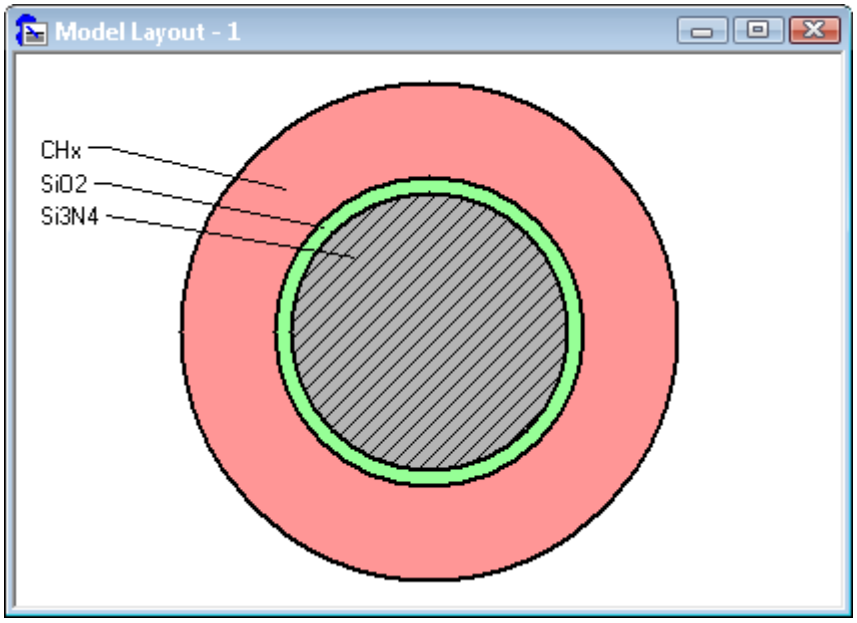
Cancel
Closes the *Layer Calculations* window without saving last results.

OK
Closes the *Layer Calculations* window and stores the last results into the *Layer Thickness* window.

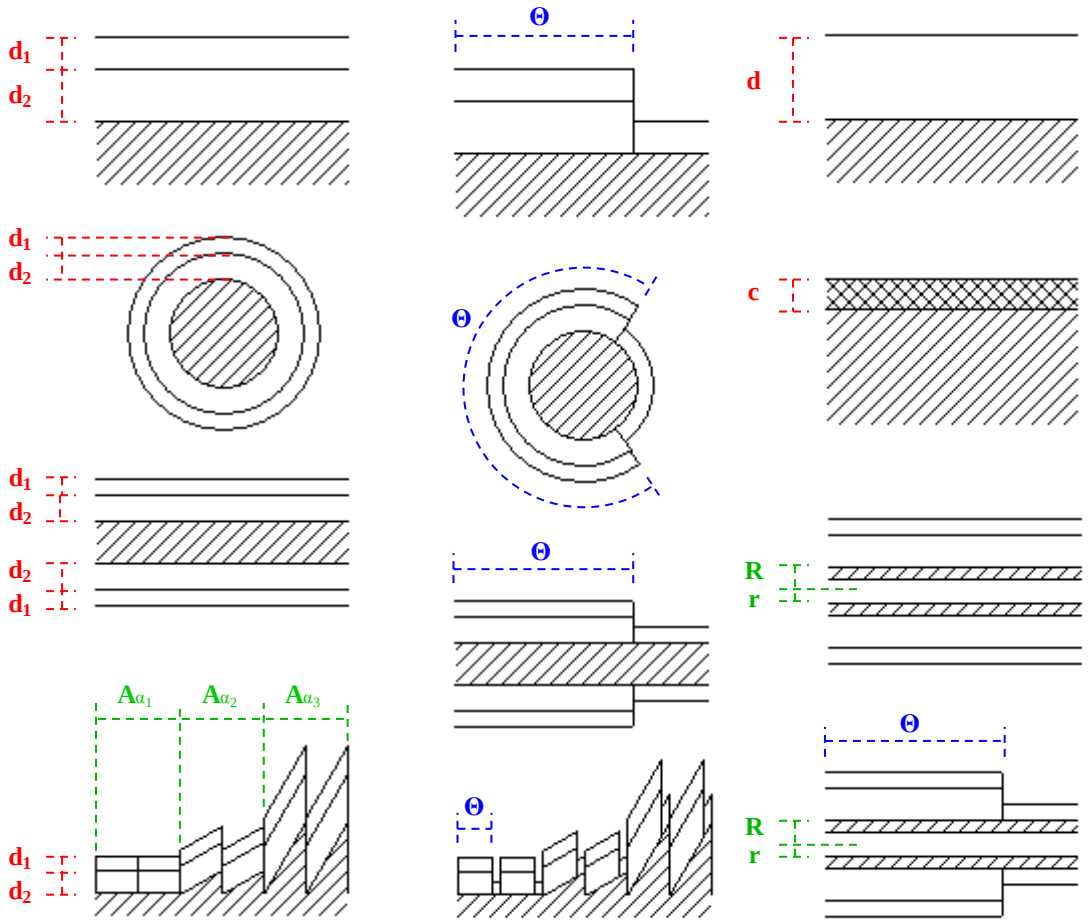


If the *Chart* window is displayed when the *Layer Calculation* window is invoked, the content of the *Chart* window is changed to a bar graph, as shown above. The graph compares the measured and calculated relative intensity values of the elements. This feature helps to find the optimum of the layer thickness and coverage values. Adjust the size and position of the *Chart* window as convenient before the *Layer Calculation* window is invoked.

Model Layout



The *Model Layout* window displays the geometric scheme of the applied quantification model. Keep in mind that it gives a graphical representation of the results of the structured model calculations only and not a realistic picture of the examined sample.
The various information represented graphically in the *Model Layout* window are summarised in the next figure.

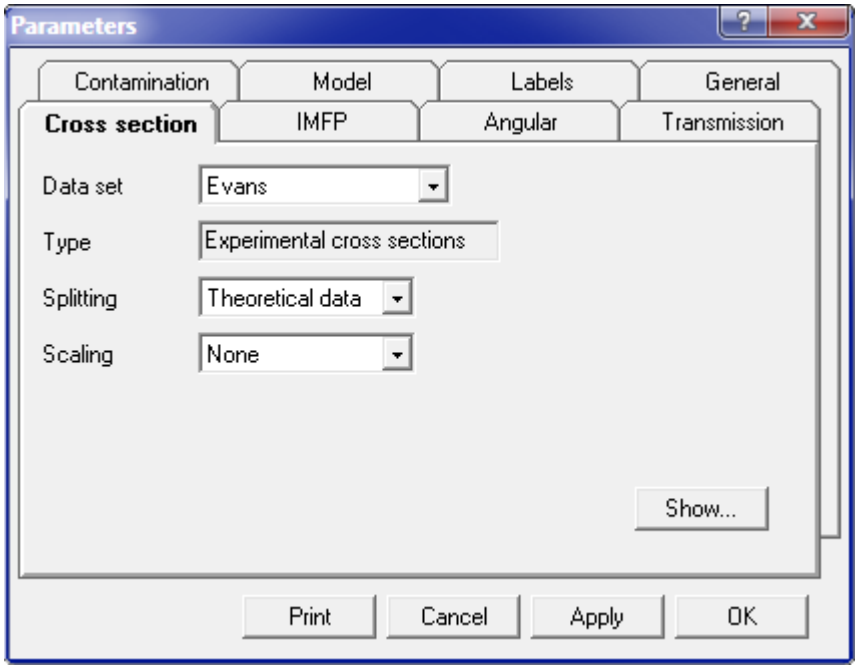


The thickness of the drawn layers *(d_1, d_2)* are proportional to each other but, in case of the spherical or cylindrical models, the layers are oversized relative to the bulk. For the *Homogeneous* model, the thickness of the contaminant *(c)* is proportional to the contamination correction factor. In case of the *Island* type models, the widths of the island and non-island parts are proportional to the coverage *(Θ)*. In case of the *Layers-on-Nanotube* model, the inner and outer radii of the tube *(r, R)* are proportional to each other (but not to the layer thickness). When the *Layers-on-Polyhedron* model is used, the total width of similar segments *(A_{α_1}, A_{α_2}, A_{α_3})* is approximately proportional to the geometry correction factors. Minor facets (with small projected area) may not be displayed in the figure.
The window displays the recently calculated experiment. To show other experiments, click the sequence number of the required experiment in the *Layer Thickness* window. The number of the selected experiment is displayed in the title bar.
A pop-up menu, activated by a right mouse click, is available to copy the content of the window to the clipboard as device independent bitmap and to switch on or off the colours and the legends of the figure. The content of the window can be printed by the **File / Print Current** menu command; it is printed immediately on a separate page. The pending page is printed before the figure.

Parameters

Most of the parameters of the calculations are set in this window (consult chapters "Setting Parameters" and "Setting and Saving Default Parameters"). The whole set of *Parameters* (except *Title*) can be stored in the registry as default by using the **File / Save Defaults** command. Items not applicable in the current parameter set are dimmed; however, their values are saved. After entering or selecting data in every necessary tab, press the *OK* button to accept the actual values or the *Cancel* button to reject the changes. By pressing the *Apply* button, changes of parameter can be accepted without closing the window. Press the *Print* button to print the current parameter set. After printing, parameter changes cannot be rejected, even by pressing the *Cancel* button.
The *Show…* buttons found on some tabs show the actual values of quantification parameters. Recent changes are appearing in the tables only after pressing *Apply*.

Cross Section Tab



Data set
Select the cross section or sensitivity factor set.

None	none of the library sets are looked up and no correction is applied
Scofield	theoretical relative differential cross sections, separate sets for Mg Kα and Al Kα excitations
Evans	experimentally based relative differential cross sections for Mg Kα excitation (correction applied)
Wagner	experimentally based relative sensitivity factors for Mg Kα and Al Kα excitation (correction applied)
Nefedov	experimentally based relative sensitivity factors for Al Kα excitation

Type
Displays the type of the above data set (*theoretical* or *experimental cross section*, *experimental sensitivity factor*, *user defined*).

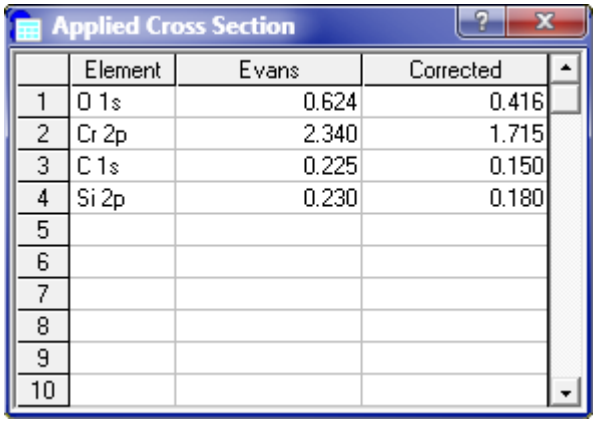
Splitting
Select the method of splitting of experimental cross sections of doublet lines into components.

None	no splitting is applied
Theoretical data	doublets are split by the ratio of the corresponding theoretical cross section data
Nominal values	doublets are split by the the nominal ratio values (1:2, 2:3 and 3:4 for *p*, *d* and *f* lines, respectively)

Scaling
Select the method of scaling of the theoretical cross sections into the experimental data sets in case of missing experimental values.

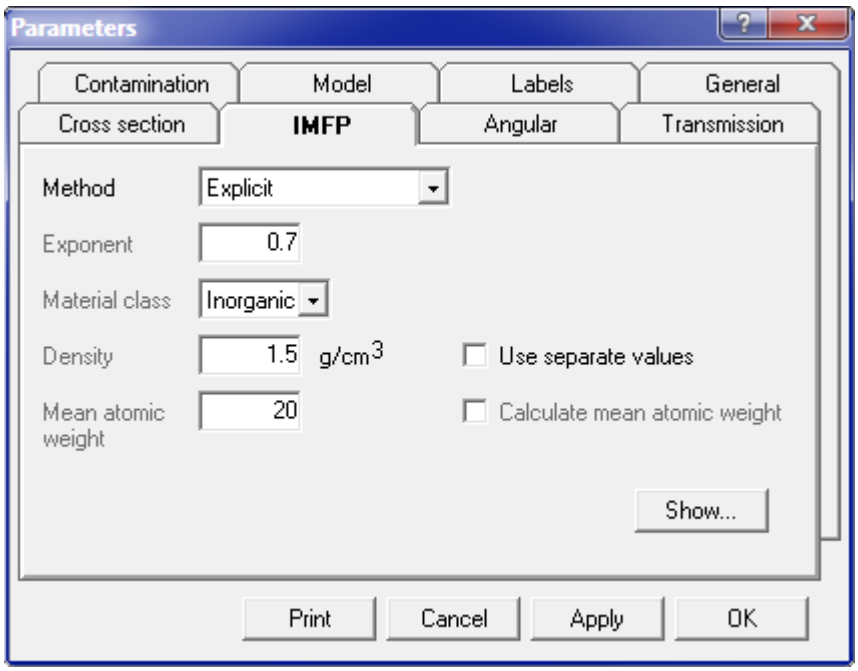
None	no scaling is applied
Closest line	scaled by the ratio of the closest line
Average factor	scaled by the average of the ratio of all available line pairs

Show…
Displays the table of the original (entered) and actually applied (corrected) cross section values, according to Equation (7), as illustrated in the next figure. Corrections are made for *Evans* and *Wagner* data sets only.


Applied Cross Section

	Element	Evans	Corrected
1	O 1s	0.624	0.416
2	Cr 2p	2.340	1.715
3	C 1s	0.225	0.150
4	Si 2p	0.230	0.180
5			
6			
7			
8			
9			
10			

IMFP Tab



Method
Select the applied inelastic mean free path correction method.

None	no IMFP correction
Explicit	exact IMFP values, given by the user, are used
Exponential	exponential approach
Jablonski	Jablonski's exponential approach with pre-set exponents
Seah-Dench	formula of Seah and Dench
Tanuma-Powell-Penn	TPP-2M formula of Tanuma, Powell and Penn
Gries	G-1 formula of Gries
Cumpson-Seah	CS2 formula of Cumpson and Seah (*attenuation length*)

Exponent
Enter the exponent of the *Exponential* approach.

Material
Select the material class for the *Jablonski*, *Seah-Dench* and *Gries* methods when the same values are used for all experiments. It can be *Element*, *Inorganic* or *Polymer*.

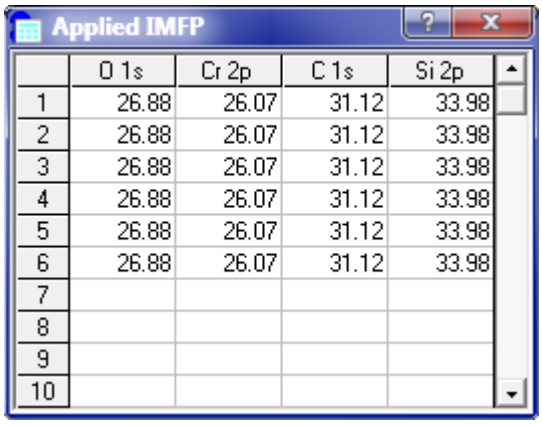
Density
Set the density of the material in g/cm^3 for the *Seah-Dench* and *Gries* methods when the same values are used for all experiments.

Mean atomic weight
Set the mean atomic weight of the material for the *Seah-Dench* method when the same values are used for all experiments.

Use separate values
Select this check box if separate material class, density and mean atomic weight values are specified for each experiment in the *IMFP & Contamination* window for the *Explicit*, *Jablonski*, *Seah-Dench* or *Gries* methods. Apply this feature when the experiments were performed on different materials or the samples were changed during measurements or treatments.

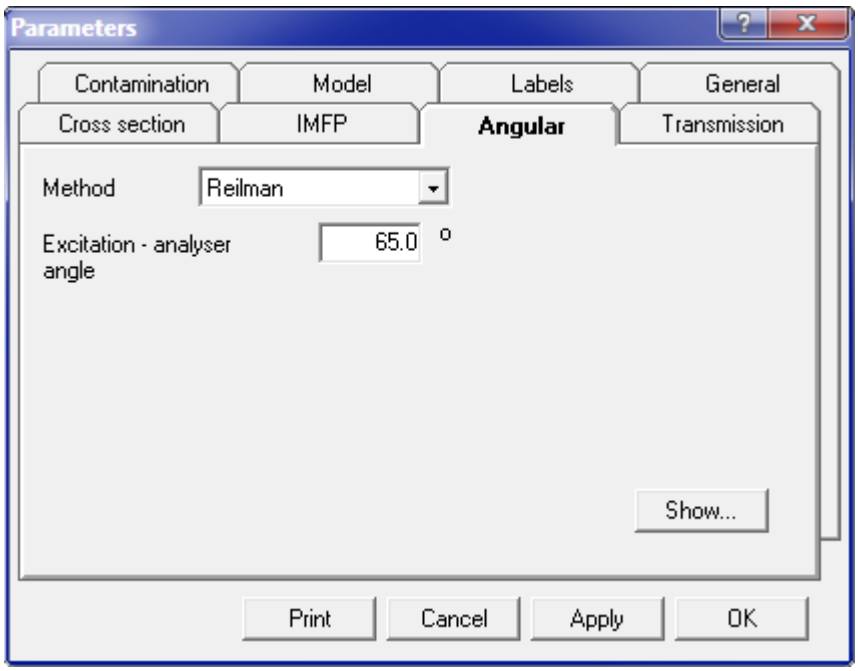
Calculate mean atomic weight
Select this check box to calculate the mean atomic weight values automatically in a two-step iteration for the *Seah-Dench* method.

Show…
Displays the table of the actually applied IMFP values (or numbers proportional to IMFP), as illustrated in the next figure.


Applied IMFP

	O 1s	Cr 2p	C 1s	Si 2p
1	26.88	26.07	31.12	33.98
2	26.88	26.07	31.12	33.98
3	26.88	26.07	31.12	33.98
4	26.88	26.07	31.12	33.98
5	26.88	26.07	31.12	33.98
6	26.88	26.07	31.12	33.98
7				
8				
9				
10				

Angular Tab

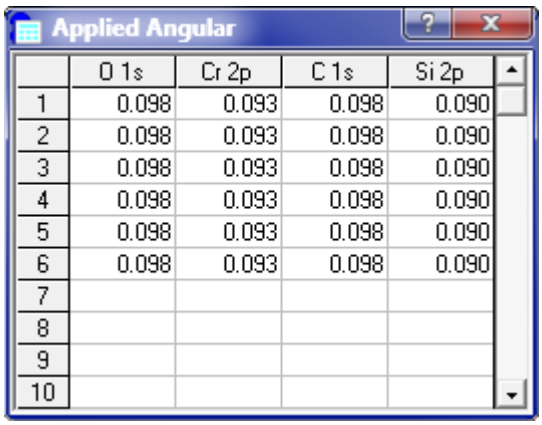


Method
Select the applied angular correction method.

None	no angular correction
Reilman	method of Reilman
Reilman-Ebel	method of Reilman with correction for elastic scattering

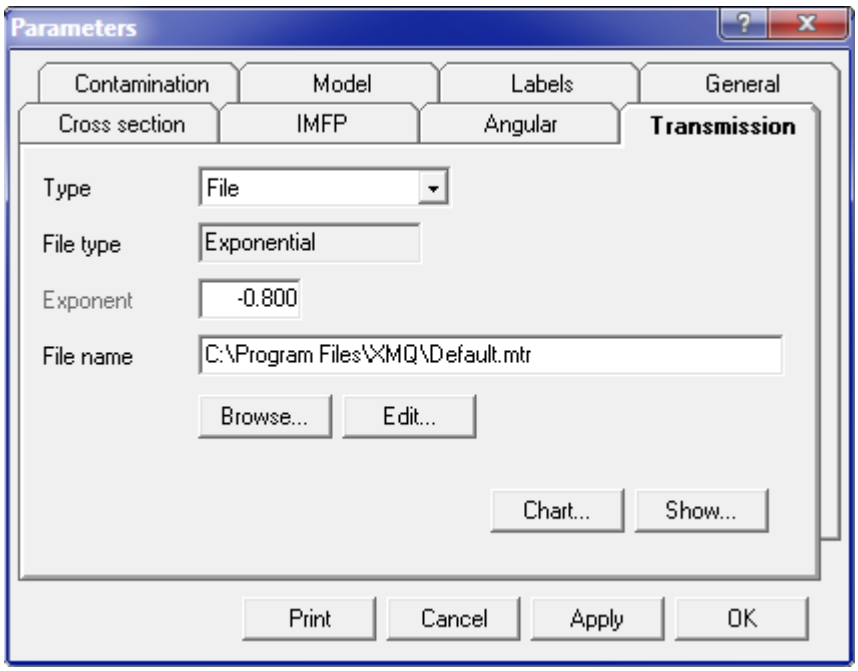
Excitation-analyser angle
Set the angle between the excitation source and the axis of the analyser in degrees.

Show…
Displays the table of the actually applied angular correction values, according to Equation (11), as illustrated in the next figure.



	O 1s	Cr 2p	C 1s	Si 2p
1	0.098	0.093	0.098	0.090
2	0.098	0.093	0.098	0.090
3	0.098	0.093	0.098	0.090
4	0.098	0.093	0.098	0.090
5	0.098	0.093	0.098	0.090
6	0.098	0.093	0.098	0.090
7				
8				
9				
10				

Transmission Tab



Type
Select the type of the transmission function.

None	no transmission correction
FAT, CAE	fixed analyser transmission or constant analyser energy mode (E^{-1})
FRR, CRR	fixed retarding ratio or constant retarding ratio mode (E^{1})
Exponential	exponential function is applied with the selected exponent (E^{a})
File	various types of functions can be applied, which are described in separate file

File type
Displays the type of the transmission function defined in the current transmission file *(Exponential, Polynomial, Rational, Combined* or *Tabulated).*

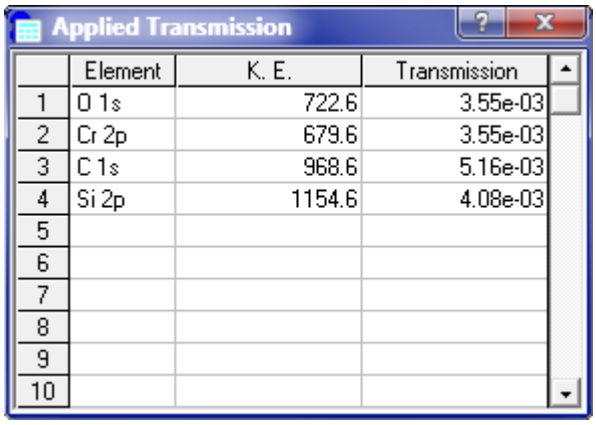
Exponent
Set the exponent for the exponential type transmission function.

Filename
Set the name of the transmission function file.

Browse…
Invokes the *Open* dialog box to browse and select transmission function file.

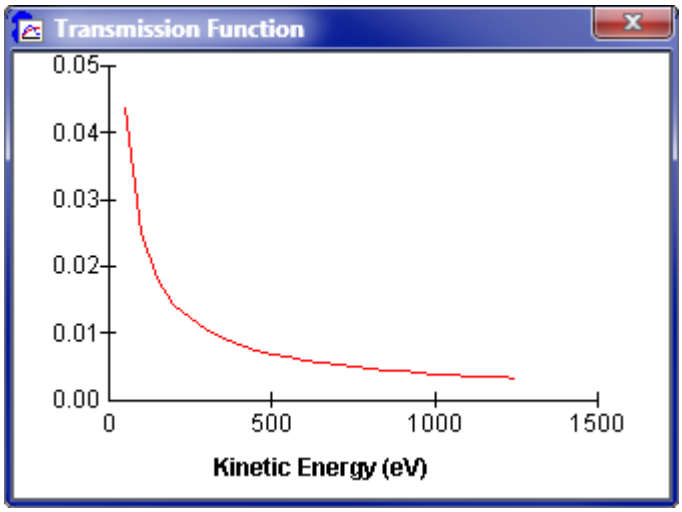
Edit…
Opens the current transmission function file in the internal editor (similar to *Notes* window). To create a new transmission file or save the file with different name, use Notepad or other simple text editor program.

Show…
Displays the table of the kinetic energy and the actually applied transmission correction values, according to Equations (30)-(34), as illustrated in the next figure.



	Element	K. E.	Transmission
1	O 1s	722.6	3.55e-03
2	Cr 2p	679.6	3.55e-03
3	C 1s	968.6	5.16e-03
4	Si 2p	1154.6	4.08e-03
5			
6			
7			
8			
9			
10			

Chart…
Displays the transmission function, as illustrated in the next figure.



Structure of the Transmission Files

The analyser transmission files of XPS MultiQuant are simple ASCII files with *.mtr* extensions. They can be created and edited with Notepad or other simple text editor programs. Existing files can be modified with the internal editor of XPS MultiQuant.
The first, header line of the file must be "XPS MultiQuant Transmission". Comment lines, starting with number sign (#), can be inserted after the header. The first line after the comments defines the type of the applied function, which can be EXP, POLY, TAB, NPL or UNI. The first three types allow defining separate coefficient sets for different energy ranges. The number of coefficient sets must be between 1 and 40. A single set of coefficients is valid for the whole range for the last two types of functions. In the subsequent lines of the file, give the coefficients of the applied function, separated with commas or semicolons and optionally spaces. The decimal separator must be point; digit grouping is not allowed.
Transmission files must be carefully checked for typing errors. Although the files are thoroughly tested by the program, some kinds of errors cannot be detected, leading to unexpected results; e.g., numbers are truncated at the accidentally entered non-numeric characters.
The numbers in the following example transmission files are illustrations only.

Exponential Function

```
XPS MultiQuant Transmission
#
EXP
100,   1.0, 20, -0.60
800,   1.0, 10, -0.50
1500,  1.0,  7, -0.45
```

The exponential transmission function is marked by **EXP** in the file. Subsequent lines of the file contain the kinetic energy and the list of coefficients (here 1 and 3 items). Coefficient sets are applied in the kinetic energy range from the given starting energy (inclusive) and extending up to the starting energy of the next range.

Polynomial Function

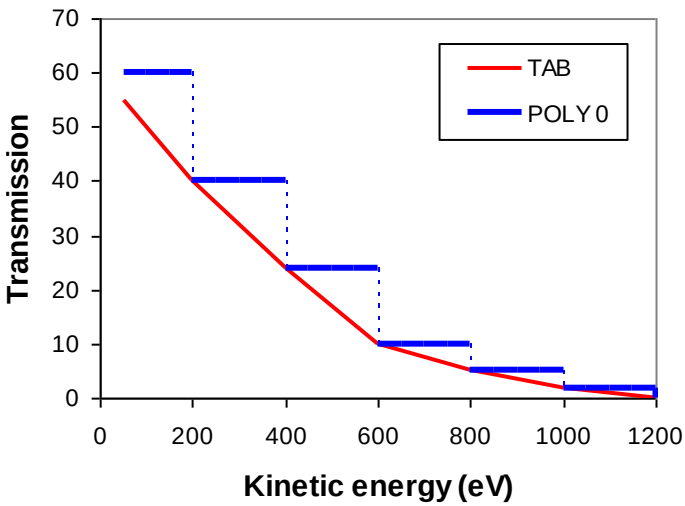
```
XPS MultiQuant Transmission
#
POLY 3
100,  2.0, -0.001, 8.5e-04, 5.0e-07
800,  2.0, -0.001, 8.5e-04, 5.0e-07
1500, 5.0, -0.003, 9.5e-04, 4.0e-07
```

The polynomial transmission function is marked by **POLY n,** where **n** is the order of the polynomial, which may vary between 0 and 6. Subsequent lines of the file contain the kinetic energy and the list of coefficients (1 and n+1 items). Coefficient sets are applied in the kinetic energy range from the given starting energy (inclusive) up to the starting energy of the next range.

Tabulated function

```
XPS MultiQuant Transmission
#
TAB
300,  35
600,  12
900,   5
1200,  4
```

The tabulated transmission function is marked by **TAB**. This function is simple enumeration of the transmission values for the different kinetic energy values (1 and 1 items). Between the given energy values, transmission is calculated by linear interpolation.
At first glance, the zero order polynomial and the tabulated functions, having the same coefficients, seem to be identical.




```
XPS MultiQuant
#
# Polynomial
#
POLY 0
0,    60
200,  40
400,  24
600,  10
800,   5
1000,  2
1200,  0.1
```

```
XPS MultiQuant
#
# Tabulated
#
TAB
0,    60
200,  40
400,  24
600,  10
800,   5
1000,  2
1200,  0.1
```

However, in the first case, a constant transmission is used in each energy range ("step-like" function), while in the second case, transmission is calculated by linear interpolation within the ranges. The differences are illustrated in the figure above.

Combined (UNIFIT) Function

```
XPS MultiQuant Transmission
#
UNI
0, -1.0, 1.0, 1.0, 0.1, 1.0, 0.1
```

The combined polynomial-exponential type transmission function, introduced at the University of Leipzig [14], is marked by **UNI** in the file. The coefficients of this type of function ($a_0 - a_4$, b_1, b_2) of Equation (34) must be entered in one line (7 items). Parameters of this kind of function can be calculated from recorded spectra by the *Unifit for Windows* [14] program. This function is valid for the whole energy scale thus no energy ranges are presented in the file.

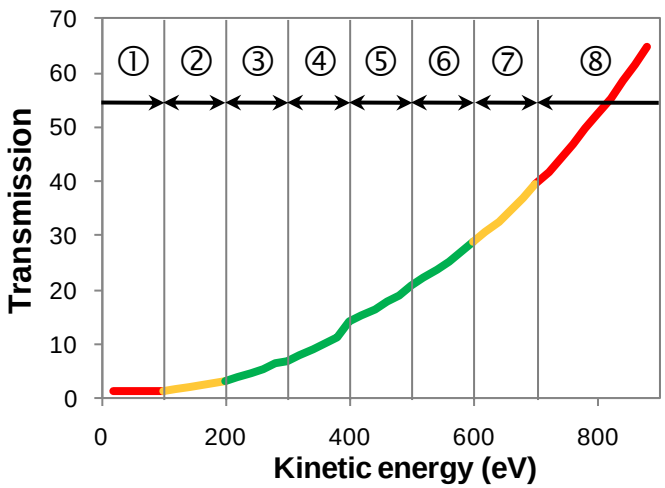
Rational (NPL) Function

```
XPS MultiQuant Transmission
#
NPL
1.4, -23, 40, 50,  60
1,   -15, 19, 18, -21
```

The fourth order rational transmission function, developed at National Physical Laboratory, UK [13], is marked by **NPL** in the file. For this function, the two sets of coefficients for the numerator ($a_0 – a_4$) and denominator (1, $b_1 – b_4$) of Equation (33) must be entered in two lines (5 items in each). The b_0 coefficient, which is always one, must also be enumerated. Coefficients of this type of function can be determined from experimental data by the *NPL XPS Intensity Calibration System* [13] software. This function is valid for the whole energy scale thus no energy ranges are presented in the file.

Extrapolation

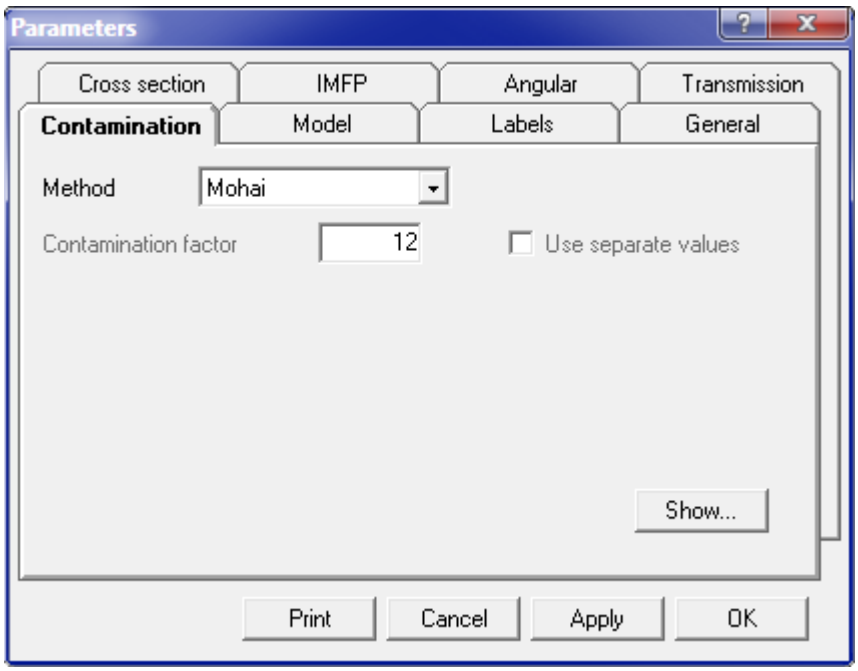
The applicability of the transmission functions, where energy ranges are given (*Exponential*, *Polynomial*, *Tabulated*), is extended by extrapolation. In this case the coefficients of the previous or next energy range are used. The range of the valid extrapolation is the same as the next or previous energy range in the transmission file.




```
XPS MultiQuant Transmission
POLY 3
200,  1.5, -0.01, 8.5e-5, 5.0e-8   ③
300,  3.7, -0.02, 9.0e-5, 4.0e-8   ④
400, 13.0, -0.04, 1.0e-4, 2.0e-8   ⑤
500, 17.0, -0.05, 1.1e-4, 1.0e-8   ⑥
600
```

In the example above, energy ranges 3-6 are specified in the transmission file. In range 2, coefficients of range 3 are used. The width of range 2 is equal with range 3. The same is suitable for ranges 7 and 6. In ranges 1 and 8 transmission calculation are not allowed, because the energy distance is too large for the reliable extrapolation.

Contamination Tab



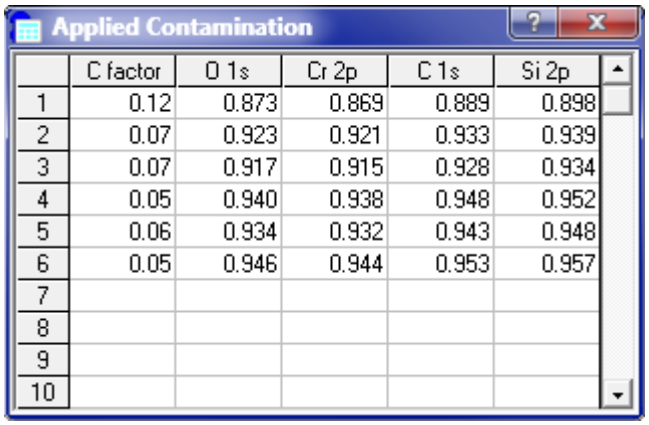
Method
Select the applied contamination correction method.

None	no contamination correction
Evans	static method of Evans
Mohai	dynamic method of Mohai. Intensity data for C1s line must be present.
Explicit	factors for contamination correction are entered into the *IMFP & Contamination* window

Contamination factor
Set the contamination factor for the *Explicit* method when the same values are used for all experiments.

Use separate values
Select this check box if separate contamination factor values are specified for each experiment in the *IMFP & Contamination* window for the *Explicit* method.

Show…
Displays the table of the actually applied contamination factors and correction values, according to Equations (36)-(38), as illustrated in the next figure.

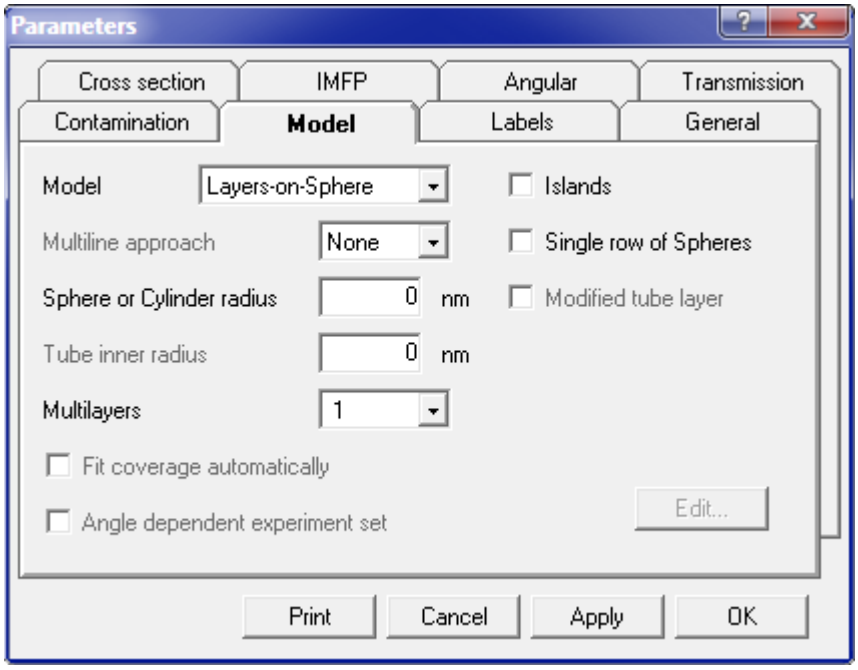


Applied Contamination

	C factor	O 1s	Cr 2p	C 1s	Si 2p
1	0.12	0.873	0.869	0.889	0.898
2	0.07	0.923	0.921	0.933	0.939
3	0.07	0.917	0.915	0.928	0.934
4	0.05	0.940	0.938	0.948	0.952
5	0.06	0.934	0.932	0.943	0.948
6	0.05	0.946	0.944	0.953	0.957
7					
8					
9					
10					

If the automatic contamination correction method (*Mohai*) is selected, a C1s line with empty *State* column (i.e., the contaminant) must be present in the *Element* window.
When the intensity values of the adventitious carbon of some experiments are zero, no contamination correction is applied for those experiments. If application of the correction is even necessary (e.g., for test purposes), enter a negligible carbon intensity.

Model Tab



Model
Select the required model for the sample.

Homogeneous	infinitely thick homogeneous sample, optionally with surface contamination
Oxide-Layer	planar samples with one overlayer, containing different chemical states of the same element
Layers-on-Plane	planar sample with known composition covered by 1 to 5 overlayers
Layers-on-Sphere	spheres in closest packed or single row arrangement with known composition (e.g., coated powder pellets) covered by 1 to 5 overlayers
Layers-on-Cylinder	cylinders with known composition (e.g., coated fibres) covered by 1 to 5 overlayers
Layers-on-Polyhedron	rough surface modelled as planar facets of polyhedrons covered by 1 to 5 overlayers
Layers-on-Nanotube	randomly piled nanotubes covered by 1 to 5 overlayers

Islands
Select this check box if non-continuous overlayers (islands) are present on the sample.

Single row of Spheres
Select this check box if the relatively large spheres of the sample are laid in one row.

Modified tube layer
Select this check box if the layer on the nanotube was prepared by modification of the tube material (i.e., the *Sphere or cylinder radius* is the sum of the layer thickness and the unchanged radius of the tube).

Multiline approach
Select the applied multiline calculation method for the *Homogeneous* model.

None	no multiline calculation
Average	simple average of raw data for all lines of each element and chemical state
Ebel	weighted average of raw data for all lines of each element and chemical state
Main	composition calculated using only the most intensive line of each element and chemical state

Sphere or cylinder radius
When the radius of the sphere or cylinder is set to zero, it means that the radius of the curved surfaces is much larger (1000 times or more) than the layer thickness. In this case, the simplified formula, Equation (56), is used for calculations. In other cases, enter the actual radius in the same unit used for the layer thickness and IMFP. The outer radius of the nanotubes must always be specified.

Tube inner radius
Enter the inner radius of the nanotubes. In case of nanofibres or nanowires (where is no hole), enter zero.

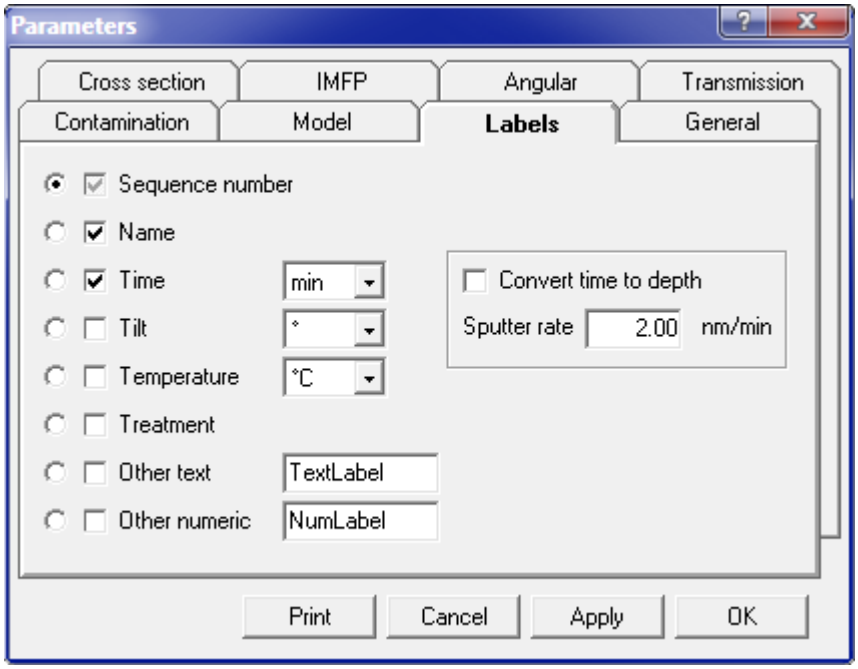
Multilayers
Set the number of repetition of the layer structures defined in the *Model* window.

Fit coverage automatically
When this check box is selected, the coverage of the *Island* type models is refined during the autofit procedure.

Angle dependent experiment set
When this check box is selected, all experiments, recorded at various take-off angles, are linked and the thickness of the layers calculated together. This feature is available for the *Layers-on-Plain* and *Islands-on-Plain* models.

Edit…
Invokes the *Polyhedron Editor* window. Available only when the *Layers-on-Polyhedron* model is selected.

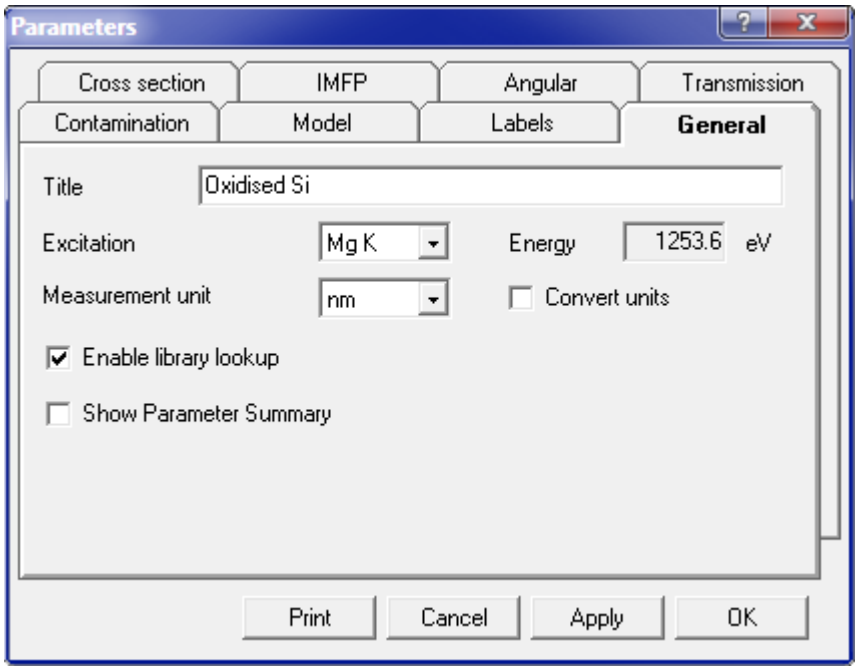
Labels Tab



Select the check boxes of labels to be displayed. Select the measure from the dropdown lists for the numeric type labels. Enter the name of the user definable label sets into the textboxes. Preselect one of the labels as X-axis value of the charts (sequence number can be selected by this way only). Unselected label sets cannot be chosen as X-axis. All label values entered in the *Intensity* window are stored even after deselected in this tab.
When the *Layers-on-Plane* or *Islands-on-Plane* model is applied, tilt angle (θ) values are taken from the *Tilt* label set.

If both the *Time* and *Convert time to depth* check boxes are selected, time data will be multiplied by the *Sputter rate* value and, instead of time, depth is displayed temporarily in the *Composition* and *Chart* windows. Numeric data are not converted automatically when a measure is changed.

General Tab



Title
Identify the whole calculation set. If it is not entered here, it is asked before the data file is saved. Title can also be edited by double clicking the status bar.

Excitation
Select the excitation source (energy). It can be *Mg Kα*, *Al Kα* or *Other*. When the latter is selected user must specify the source energy.

Energy
Set the energy of the excitation source when the *Excitation* is set to *Other*

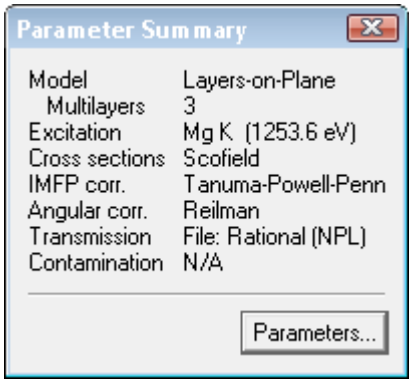
Measurement unit
Select the measurement unit of the inelastic mean free path, thickness values and sphere, cylinder or nanotube radius (Ångström or nanometer).

Convert units
Select this check box to convert the previously entered IMFP and thickness values when changing the measure unit (Å to nm or nm to Å). The converted items are: IMFP data of the *Homogeneous* model, IMFP matrix of the structured models, results of the structured model calculations, radius of the sphere, cylinder or nanotube, sputter rate, temporary depth scale. The permanent depth scale, stored in the *Other numeric* label set, however, is not converted automatically. To convert it, repeat the **Tools / Create Depth Scale** command.

Enable library lookup
Unselect this check box to prevent the quantification data set from overwriting by an accidental library lookup. If lookup is not enabled, a warning message is displayed when the **Tools / Library Lookup** command issued.

Show Parameter Summary
Select this check box to show the *Parameter Summary* window.

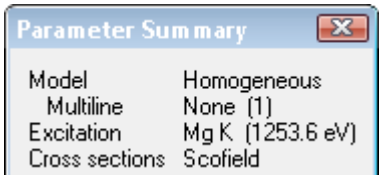
Parameter Summary



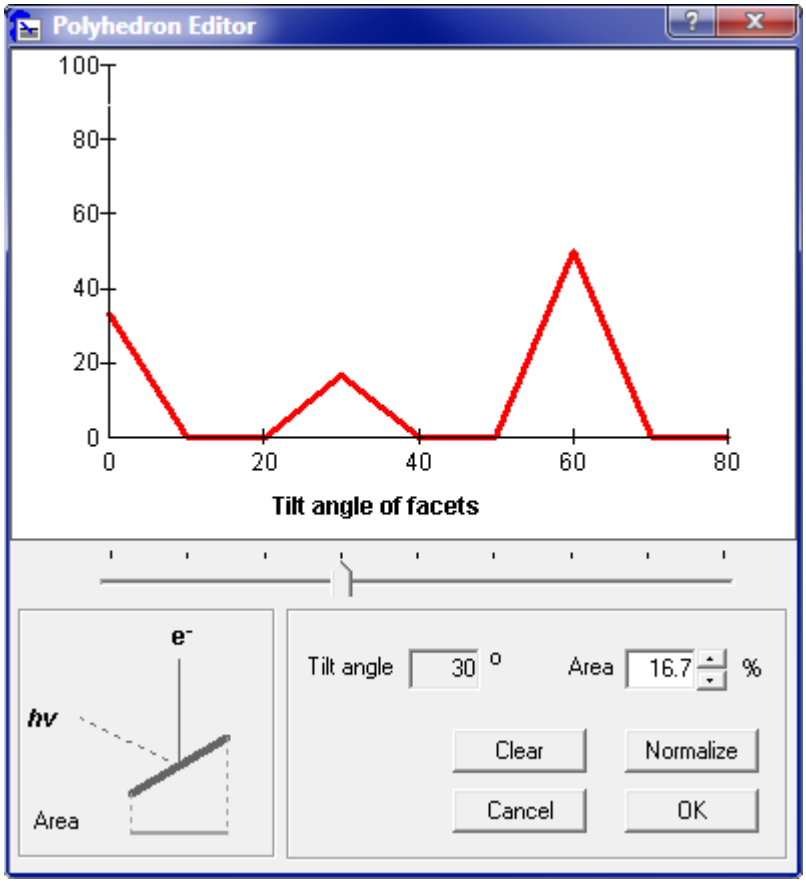
The *Parameter Summary* window summarizes the selected values of the most important parameters. It is useful when calculation of various experiments require different parameter settings. Displaying of the *Parameter Summary* window can be preselected by the *Show Parameter Summary* checkbox in the *General* tab of the *Parameters* window. Although the window can be discarded by its close button, it reappears when a data file is loaded or the **File / New** command is performed. The window is not shown when the *Data Wizard* is active or an example file is loaded.
Double click anywhere in the *Parameter Summary* window to locate it to the upper right corner of the main window.

Parameters…
Invokes the *Parameters* window.

The additional information on the model (*Multilayers*, *Multiline*, *Variant*) is displayed only if it is applicable. However, to emphasize the wrong combination of parameters, when the *Multiline approach* is off but element(s) are present with multiple lines, still the *None* setting is shown with the number of elements involved (in parenthesis).



Polyhedron Editor



The parameters of the sample geometry model, describing the surface by small facets at different angles, can be created or modified in the *Polyhedron Editor* window.
User can select each tilt angle (in steps of 10°) by moving the slider and enter the corresponding percentage ratio of its area, projected to the base plane of the sample supporting the polyhedra (i.e., the geometry correction factors).
The chart shows all the geometry correction factors as the function of tilt angles. The figure on the left illustrates the direction of the incoming X-ray and the ejected electron beams and also the angular position of the surface facets at the selected tilt angle. The *Area* line represents the projected area of the current facet.

Tilt angle
Shows the tilt angle selected by the slider.

Area
Enter the percentage of the projected area corresponding to the surface elements with the selected tilt angle. Numbers can be set in the textbox by clicking the arrow buttons or typing.

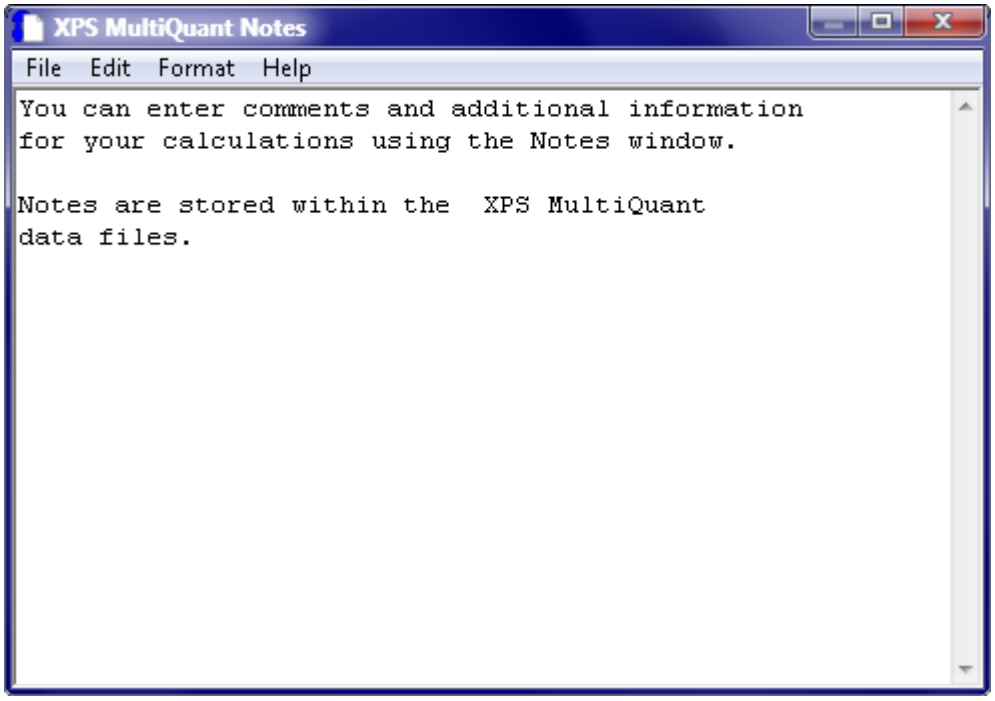
Clear
Deletes all data of the polyhedron. To recover accidentally deleted data, click the *Cancel* button immediately.

Normalize
Normalize the entered area data to 100 % sum.

Cancel
Discards the last changes, including clearing, and closes *Polyhedron Editor* window.

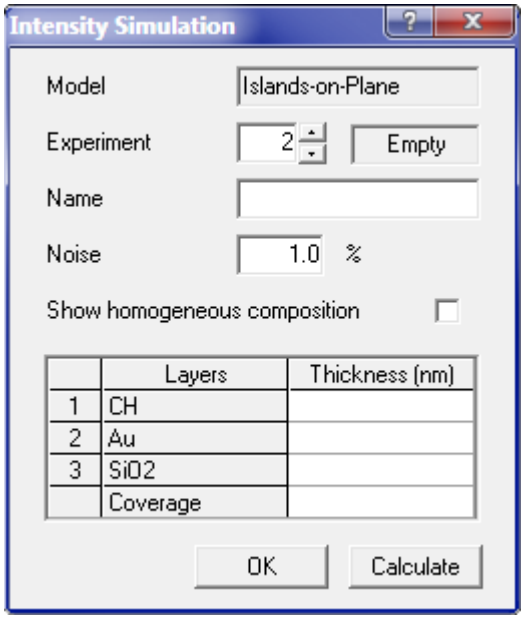
OK
Keeps the last changes, normalizes data and closes *Polyhedron Editor* window.

Notes



Enter comments and additional information connecting to the calculations to store together with the XPS MultiQuant data. This window is not restricted to the main window; it can be kept open and remarks can be written continuously during analysis of data. Editing functions are available via standard or pop-up menus (see chapter “File Menu (Notes window)”). A similar window is applied for editing the current transmission file.

Intensity Simulation



The input data (layer thickness and coverage) of the intensity simulation calculations can be entered into the small table of the *Intensity Simulation* window. If the intensity data set is not empty (i.e., all zero), a warning message is shown before displaying the window.

Model
Displays the name of the current quantification model.

Experiment
Select the sequence number of experiment where the results of the simulation (intensity values) are stored. The status of the current experiment can be *Filled* if at least one intensity value of the current experiment is not zero (either manually entered experimental or simulated); can be *Empty*, if all values are zero; or temporarily *Calculated*, to indicate that calculation with the current data just has been done.

Name
Enter the name of the simulated experiment to store in the *Name* label set. If it were left blank, the word "Simulated" is inserted. The automatic labels can be edited and other labels can be added later in the *Intensity* window.

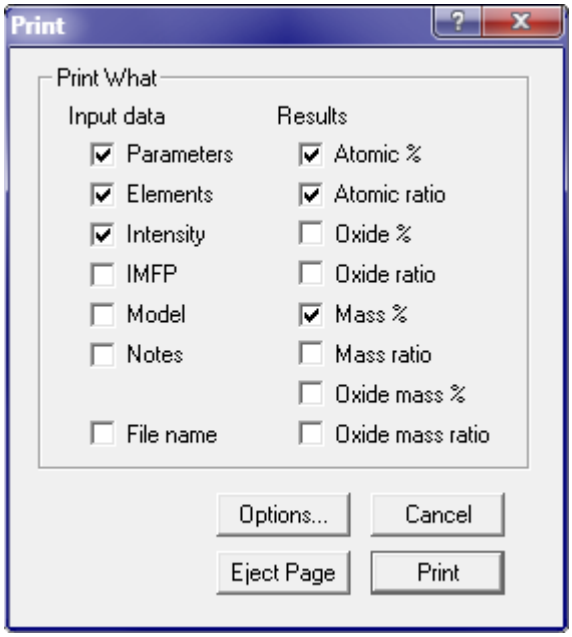
Noise
Set the level of relative noise of the simulated intensity data. A random number, within the interval of $\pm\, Noise / 100 \cdot Intensity$, is added to each calculated intensity. The value of *Noise* is not saved between sessions.

Show homogeneous composition
Temporarily shows the composition results calculated by the *Homogeneous* model for the currently simulated data. When the composition is being displayed, neither the simulation can be continued nor the *Intensity Simulation* widow can be closed.

OK
Closes the *Intensity Simulation* window.

Calculate
Calculates intensity values with the current thickness and coverage data and stores them in the selected experiment.

Print



Print What
Select the items to be printed. When *File name* is selected, the name of the current data file is printed after the header. These settings are stored in the registry when the **File / Save Defaults** command performed.

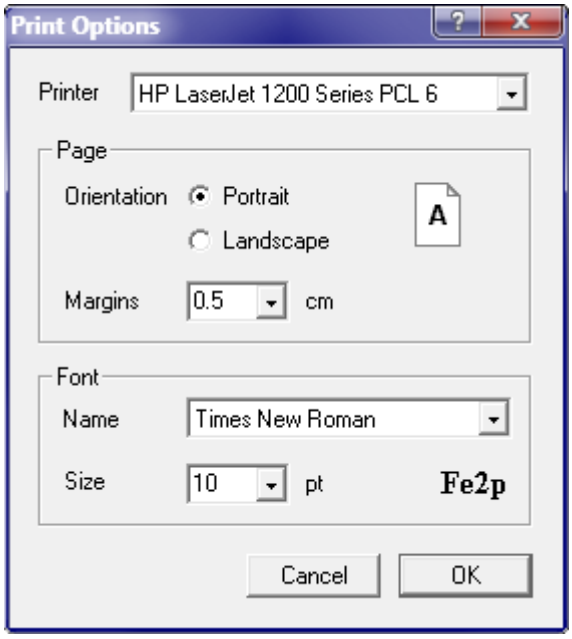
Options…
Invokes the *Print Options* window.

Cancel
Closes the window without printing.

Eject Page
Prints of the pending (the last unfinished) page.

Print
Prints the select the items. Only full pages are printed using the spooling feature of the operating system. Unfinished pages are printed only when the *Eject Page* button is pressed, the *Pending page* icon is double clicked in the status bar or the **File / New** or **File / Exit** command is issued.

Print Options



Printer
Select one of the installed local or network printers. Default is the Windows' default printer.

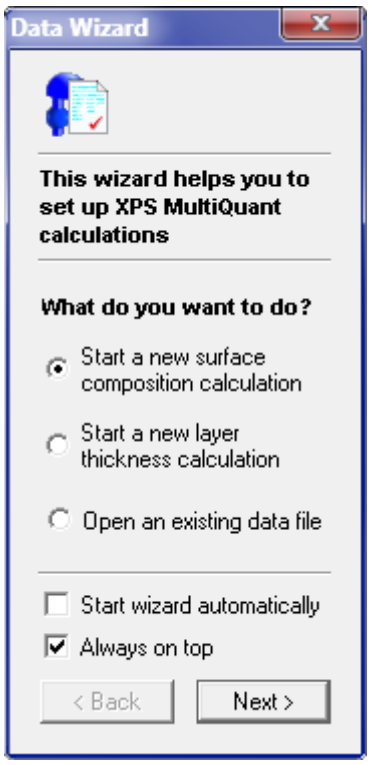
Page
Set the orientation and margins of the page. The size of the paper can be set in the Control Panel of the Windows operating system. Margins can be varied from 0.5 to 5 cm.

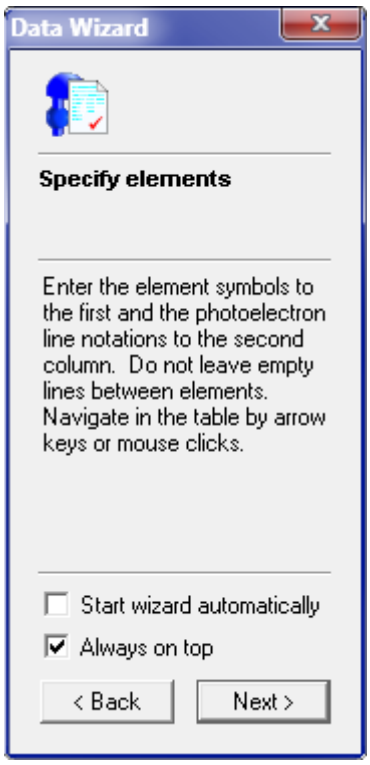
Font
Select or set the name and size of the font for printing. In the *Name* list, all fonts of the selected printer are shown. The font size can be selected between 4 and 36 points. An example of how the font will look also appears (it may be improper when no matching screen font is installed).

Cancel
Closes the window without changing options.

OK
Closes the window and accepts new options.

Data Wizard



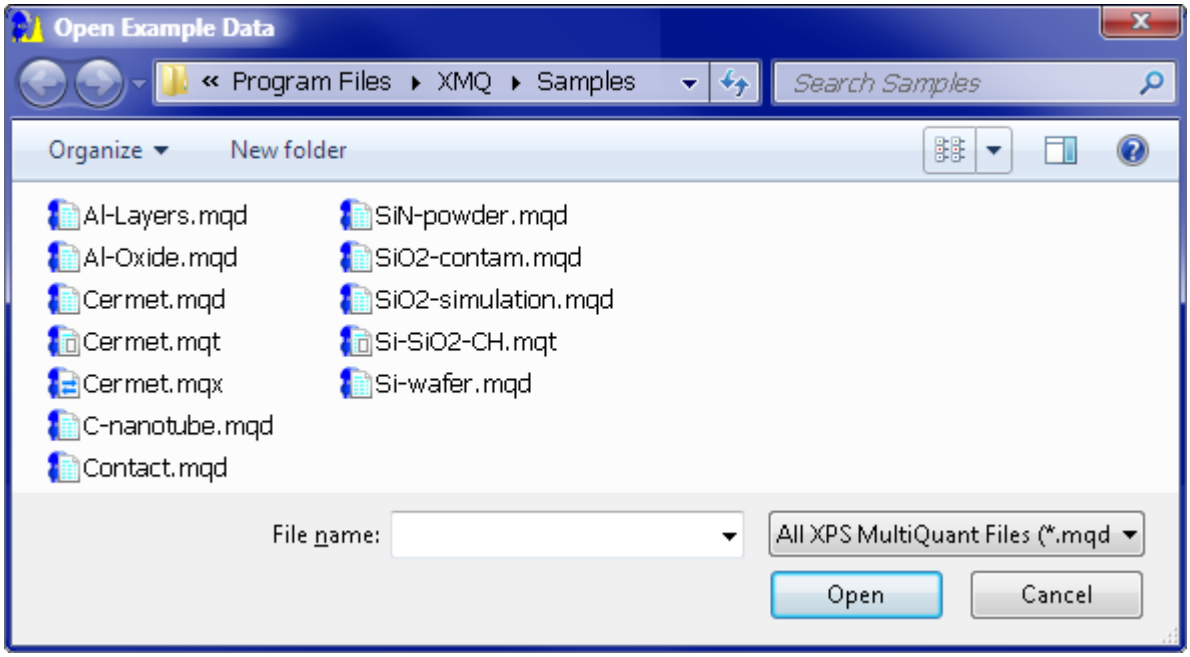


The *Data Wizard* window helps the unfamiliar users walking through the different phases of setting up an XPS MultiQuant calculation by giving step-by-step instructions.
Starting the wizard, user should select the type of calculation. To recall this very first step again, restart the wizard after a **File / New** command.
The upper panel shows the title of the current step, while the lower panel provides a brief description of the action and also an error message, if necessary.
Follow the instructions of the wizard, enter the required data then press the *Next* button. When an error is occurred, a warning signal is displayed and, beside the standard messages of the program, the wizard gives the short explanation of the problem. Press the *Back* button and revise the entered data. Consult the online help or the User's Manual for further clues. The *Back* and *Next* buttons are enabled only when the previous step was completed successfully (however, the wizard cannot prevent from all potential errors).
When the *Always on top* check box is selected, the wizard's window is kept on the top of all other windows, including other applications. This window is not restricted to the main window of the program; it can be positioned anywhere on the screen. Double click anywhere in the *Data Wizard* window to locate it to the upper right corner of the main window.
The wizard can be switched off at any time by the **Tools / Data Wizard** command or by its close button.

Start wizard automatically
Select this check box to start *Data Wizard* automatically when XPS MultiQuant is started.

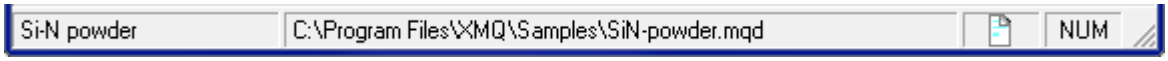
Always on top
Select this check box to keep the wizard's window on the top of all other windows.

Open – Save As



This is a standard Windows dialog box for opening and saving XPS MultiQuant data files, template files, transmission files or XPS Reduced Data Exchange files. The default file extension is *.mqd*, *.mqt*, *.mtr* and *.mqx* for the data, template, transmission and exchange files, respectively. Select or type the proper file name or navigate in the folders as usual in Windows. The common Windows pop-up menu (right click) is also available for file deleting, renaming, etc. Files on mapped network drives can be opened only with writing permission. This window may look different in the various versions of the operating system.

Status Bar



The status bar, located at the bottom of the main window, shows some important information of the program. It is divided into four panels. The panels show:

- The title of the calculation. To change or edit the title, double click the panel or use the *General* tab of the *Parameters* window.
- The name and the path of the current data file. If the path is long and the filename cannot be read, double click to alter the alignment of the text.
- The presence of a pending (unfinished) page or a pending error condition. To print the pending page, double click the icon or press the *Eject Page* button in the *Print* window. To show the category of the error, point to the icon. The cell edit mode is also indicated.
- The status of the NUMLOCK key. Double clicking this panel, the tooltip displays the decimal symbol and list separator set in the operating system.

Keyboard Commands

Shortcut Keys

CTRL + N	Reset XPS MultiQuant and start new calculation
CTRL + O	Open an XPS MultiQuant data file
CTRL + S	Save current calculation
CTRL + P	Print the content of the active window
CTRL + C	Copy the content of the active window to the clipboard in ASCII form
CTRL + L	Search the library for element and line data
ALT + F4	Exit program
F1	Invoke *What's This* Help
F2	Display context sensitive help

Editing Keys

DELETE	Delete the content of the current cell in a table
BACKSPACE	Delete the last character of the current cell or a textbox
ARROW keys	Move the current cell in a table or the text cursor in a textbox
ENTER	Move the current cell right or to the beginning of the next row in a table
TAB	Move the current cell right or to the beginning of the next row in a table
PAGE UP	Move the current cell up by one window
PAGE DOWN	Move the current cell down by one window
HOME	Move the current cell to the beginning of the row
END	Move the current cell to the end of the row

Menu Access Keys

Access keys allow the user to open a menu by pressing the ALT key and then type the underlined letter. Once the menu is open, the user can choose a control by pressing the letter (the access key) assigned to it. Underlines are visible only when the menu is opened by the ALT key.

Messages

Bad file name.
The specified filename is invalid.

Change or edit title.
Change or edit the title text. Title can also be edited on the *General* tab of the *Parameters* window.

Clear all data from [*title*] window. Are you sure?
Confirm deleting the whole content of an input table. Deleted data cannot be recovered.

Coverage must be between 0 and 1.
The entered coverage value is less than zero or larger than one. Enter the correct value.

Data file error(s): - Erroneous block header found. Data may be corrupted.
The length of the data block, specified in the block header, is not matching that of expected by the data type and indexes. Check all data and enter missing items.

Data file error(s): - File shorter than expected. Data may be corrupted.
The end of the data file reached before all data blocks, expected by the program, is read or the end mark of the file is not found. Some data items may be missing. Check all data and enter missing items.

Data file error(s): - Number of parameters fewer than expected.
The number of parameter items in the data file is fewer than the program expects. Check parameters and enter missing items.

Data file error(s): - Number of parameters larger than expected.
The number of parameter items in the data file is larger than those the program expects. Excess parameters will be ignored. The file might be correct, although it can be invalid as well. Inspect all parameters.

Data file error(s): - Unidentified data block found.
A syntactically valid data block with unknown identifier was found in the file. The block will be ignored. All other data items are presumably correct.

Data file error(s): - Unrecognized data found. Data may be corrupted.
Unrecognizable, damaged block structure or excess data items were found in the data file. The invalid data is skipped, reading is continued from the next valid block. Some data items are almost certainly missing. Examine data for missing items.

Data file not found.
The specified data file cannot be found in the current folder. Use the browsing feature of the *Open* dialog box to locate the file.

Division by zero occurred at fitting of parameters (*N*). Check model and refine initial data.
An attempt was made to divide a number by zero during the least square fitting of model parameters. It may be caused by wrong initial data or that the model is not properly describe the measured data.

Division by zero occurred at model calculation (*N*).
An attempt was made to divide a number by zero during calculation of intensity of structured models.

Do you want to open existing workspace?
The *Save Workspace* menu command is selected while the program detected a previously saved workspace. Select *Yes* to load the data file and to restore the layout of windows; or *No* to discard it. In the latter case, the workspace file will be overwritten at exit. Obviously, the data file, registered in the workspace, will not be disturbed.

Do you want to save changed Notes text?
The text in the Notes window has been changed. Select *Yes* to save changes, *No* to discard changes or *Cancel* to continue editing. To save notes permanently, save the current XPS MultiQuant data file.

Do you want to save changed Transmission file?
The text in the transmission file editor window has been changed. Select *Yes* to save changes, *No* to discard changes or *Cancel* to continue editing.

Do you want to save your changes?
The content of the calculation has been changed since the last save. Select *Yes* to save changes, *No* to discard changes or *Cancel* to continue work.

Element error(s): - Invalid line notation at element [*symbol*].
The line notation at the indicated element is either non-existing (e.g., 3z) or the shell, subshell and doublet items are not matching (e.g., 3f, 2p5).

Element error(s): - *N* element parameter(s) out of the expected range.
Some of the element data is out of the expected range, e.g., density is greater than 22.5 or atomic mass is less than 1, etc. Despite the warning calculation is continued.

Element error(s): - Photoelectron lines - chemical states mismatch at element [*symbol*].
When more than one photoelectron lines are used to calculate the concentration of the same element (*Multiline approach*) and the chemical states are also distinguished, each state must be present for each line. E.g., the S2p(6+), S2p(2-), S2s(6+), S2s(2-) set is valid, while the S2p(6+), S2p(2-), S2s(total) set is deficient.

Element error(s): - Photoelectron line [*symbol line*] duplicated with identical chemical state at line *N*.
The same element with the same photoelectron line can be present only in different chemical states. Delete one of the lines in the *Element* window or change one of the states.

Element [*symbol*] not found.
The specified element cannot be found in the library. Check the element symbol for typing errors.

Elements or experiments have been rearranged since the last Delete Rows command. Do you want undo anyway?
The elements or experiments have been rearranged since the last *Delete Rows* command. Execution of the undo command can be forced but data may be inserted into wrong positions because the order of rows or cells is changed. Press *Yes* to force the undo command, *No* to discard the undo data of this editing step or *Cancel* to cancel undo but keep the data.

Enter composition before calculating IMFP.
The *Tools / Model / Calculate IMFPs* command was selected before entering the composition data into the atom location matrix.

Error *N* [*error description*]
An unexpected fatal program error occurred. The program stops. Report the error number, the location (window), the command used and other circumstances to the author.

Error in XPS Reduced Data Exchange file: [*filename*]. Loaded data may be incorrect.
There are one or more errors in the loaded *XPS Reduced Data Exchange file*. Several other error messages may follow this message. Consult the manufacturer of the source application, which generated the file. Information and software tools to analyse the invalid file are available at the homepage of XPS MultiQuant.

[*Error description*] occurred at fitting of parameters (*N*). Check model and refine initial data.
Unexpected program error occurred during the least square fitting at step *N*. Fitting is abandoned.

[*Error description*] occurred at model calculation (*N*).
Unexpected program error occurred during the calculation of model intensity.

Estimate initial layer thickness values before Autofit.
Guess and enter initial values for layer thickness and coverage before invoking the Autofit procedure. The Q_{sum} of the initial data should be 50 or less.

File not found.
The specified file cannot be found in the current folder.

"Gries" is applied as default IMFP calculation method. Default setting(s) can be altered in the Parameters window.
When user selects the *Start a new layer thickness calculation* item in the first step of the wizard and no suitable inelastic mean free path calculation method is preselected, the program uses the *Gries* method as default. This can be changed in the *IMFP* tab of the *Parameters* window at any time.

Illegal exchange file header.
The header of the specified exchange file is not valid. The file should be damaged or the file is not an XPS Reduced Data Exchange file even the extension is .mqx.

Illegal or damaged library file header.
The header of the library is not valid. The file should be damaged or the file is not the valid XPS MultiQuant library file.

Improper IMFP method selected.
The current IMFP correction method cannot be applied for the selected quantification model.

Incompatible data file version.
This version of data or template file is not supported.

Incompatible library. Library version should be *N*.
The version of the library is too old. Libraries of the different versions are not compatible. Use the library supplied with the program.

Incorrect dataset. Intensity always 0.
No valid experimental intensity data was found at the layer thickness calculation. Check or enter the content of the *Intensity* window.

Intensity data set is not empty. Do you want to overwrite?
The *Intensity Simulation* window was invoked but some intensity data are larger than zero (either measured or simulated). Simulation may overwrite the selected experiment without further warnings.

Invalid procedure call (e.g., square root of negative number) occurred at fitting of parameters (*N*). Check model and refine initial data.
The argument of the function was out of the expected range (e.g., square root of a negative number). It may happen when the radius of the spheres or cylinders, given in the *Model* tab of the *Parameters* window, are not zero (i.e., structures are relatively small) and during the iterations of the least square fitting one of the layer thickness values became negative. This error may also indicate that the model does not describe properly the measured data. To solve the problem, set the radius to zero; try to fit parameters; reset the radius to its correct value and fit parameters again.

Invalid procedure call (e.g., square root of negative number) occurred at model calculation (*N*).
The argument of the function was out of the expected range (e.g., square root of a negative number).

"Layers-on-Plane" is applied as default model.
Default setting(s) can be altered in the Parameters window.
When user selects the *Start a new layer thickness calculation* item in the first step of the wizard and no suitable model type is preselected, the program uses the *Layers-on-Plane* model as default. This can be changed in the *Model* tab of the *Parameters* window at any time.

Layer thickness must be non-negative.
Negative numbers cannot be entered as layer thickness values.

Library access error.
Fatal software or hardware error occurred during library lookup.

Library disabled.
Library lookup is not allowed. Enable searching of the library in the *General* tab of the *Parameters* window.

Library not found. File XMQ.LIB must be in the application's folder.
The library file cannot be found in the application's folder. Move the library to the correct location or reinstall it from the distribution media.

Line [*symbol*] not found.
The selected photoelectron line of the specified element is not included in the selected cross section data set. Select other line from the list of the available lines, select other cross section set or try the *splitting* and *scaling* features.

Maximum number of iterations reached.
The allowable number of iterations has been met without obtaining a solution to the accuracy specified in the program. Very slow convergence may be indicated. Try to invoke *Autofit* again.

Model error(s): - Angle values must be unique for angle dependent experiments.
At calculating angle dependent experiment set, each experiment must be recorded at different angle; the difference must be at least 1°. Check *Tilt* labels for repeated angle values.

Model error(s): - Bulk or layer element not marked.
When the *Oxide-Layer* model is used, the chemical states of the main constituent element must be denoted by "*Me*" for the bulk and by "*Ox*" for the layer.

Model error(s): - Geometry correction factors of the Layers-on-Polyhedron model not specified.
The *Layers-on-Polyhedron* model is selected but the geometry correction factors are not specified. Invoke the *Polyhedron Editor* window from the *Model* tab of the *Parameters* window and edit geometry data.

Model error(s): - Inner radius of the nanotube is too large.
The inner radius of the nanotube is equal or greater than the outer radius.

Model error(s): - Invalid angle values in the angle dependent experiment set.
At calculating angle dependent experiment set, the angle values must be specified and should be between 0° and 90°. Check *Tilt* labels for missing or mistyped numbers.

Model error(s): - Layer *N* not defined.
Definition (name) of the Nth internal layer is missing. There is an empty column between the defined layers.

Model error(s): - Link error at Layer *N*: chains or cross-links.
The target of a link cannot be a linked or fixed layer, neither directly nor indirectly. Chains (e.g., Layer 1→Layer 2→Layer 3) or cross links (e.g., Layer 1↔Layer 2) are not allowed. Inspect the *Link to* row in the *Model* window.

Model error(s): - Missing IMFP data.
One or more IMFP data is missing from the Model window. Apply the *Tools / Model / Mark Unused IMFPs* command and fill all unmarked cells.

Model error(s): - Model structure not defined.
One of the structured model types is selected but no layer structure is defined in the *Model* window. Select the *Homogeneous* model or define the layer structure. This message can also be displayed alone.

Model error(s): - No bulk defined.
When structured models are used at least one layer and the bulk must be specified. The *Name* field must be filled in the *Model* window.

Model error(s): - No independent parameter.
All layer thickness and coverage parameters are fixed or linked. Check the *Link to* line in the *Model* window and the *Model* tab in the *Parameters* window.

Model error(s): - Only one layer allowed for the Oxide-Layer model.
When the simple *Oxide-Layer* model is used, only one overlayer on the bulk can be defined. If more layers are necessary, use the *Layers-on-Plane* model.

Model error(s): - Radius of the nanotube must be specified.
The external radius of the nanotubes cannot be omitted as in case of spheres or cylinders.

Model error(s): - Some parameters out of the expected range.
Some of the layer data is out of the expected range, e.g., molecular weight is less than 1 or density is greater than 22.5, etc.

Model error(s): - The composition of bulk not specified.
The stoichiometric coefficients of the bulk material in the atom location matrix of the *Model* window are not set or all are zero. Enter the missing values.

Model error(s): - The composition of layer [*name*] not specified.
The stoichiometric coefficients of the indicated layer in the atom location matrix of the *Model* window are not set or all are zero. Enter the missing values.

Model error(s): - The same element and line must be selected in two different chemical states.
When the *Oxide-Layer* model is used, the selected main constituent element and its photoelectron line must be the same for both the bulk and the layer.

Model error(s): - The model system is defined but too many or necessary elements omitted.
The described model is defined but neglecting the elements marked as ‘Omit’ in the *Model* window, it became ill-defined. Remove the omit marks until the system becomes defined again.

Model error(s): - The model system is ill-defined. Specify at least *N* independent elements.
The described model is ill-defined. The equation system cannot be solved. Each layer and the bulk must have at least one independent element. For automatic fitting of the coverage, one of the islands must have two independent elements.

Model error(s): - The model system is ill-defined. Supply coverage data from independent measurements or specify one more element in the islands.
None of the islands has at least two independent elements. Automatic fitting of the coverage is not possible unless one more element is specified in one of the islands.

Model error(s): - Tilt label set must be selected for angle dependent experiments.
At calculating angle dependent experiment set, angle values are taken from the *Tilt* label set which must be selected in this case.

Nanotube warning(s): - Radius of the carbon nanotube seems to be too small.
The absolute radius of the carbon nanotube is smaller than the minimal value specified in the literature. This message can also be listed in *Model error(s)*.

Nanotube warning(s): - Thickness of the carbon nanotube wall seems to be too small.
The absolute wall thickness of the carbon nanotube is smaller than the minimal value specified in the literature. This message can also be listed in *Model error(s)*.

No element specified.
Some features of the program cannot be accessed before the elements are specified. Enter all elements first.

No independent parameter to fit.
All layer thickness and coverage parameters are fixed or linked. Check the *Link to* line in the *Model* window and the *Model* tab in the *Parameters* window.

No transmission file specified.
The transmission type was set to *File* in the *Transmission* tab of the *Parameters* window but no file name was given in the *Filename* box.

Number of elements or experiments has been changed. Do you want undo anyway?
The number of elements or experiments has been changed since the last cell or table editing command. The undo action may not be properly performed. Execution of the undo command can be forced but data may be inserted into wrong cells. Press *Yes* to force the undo command, *No* to discard the undo data of this editing step or *Cancel* to cancel undo but keep the data.

Number of elements or experiments has been changed since the last Delete Rows command. Do you want undo anyway?
The number of elements or experiments has been changed since the last *Delete Rows* command. Execution of the undo command can be forced but data may be inserted into wrong positions because the order of rows or cells is changed. Press *Yes* to force the undo command, *No* to discard the undo data of this editing step or *Cancel* to cancel undo but keep the data.

Numeric label set is not empty. Do you want to overwrite?
The *Tools / Create Depth Scale* command was selected but the target label set stores previously entered data. Press *OK* to overwrite.

Overflow during calculating intensity ratio. Layer *N* seems to be too thick.
There is enormous difference between the intensity values of one of the calculated and the basic elements. It is usually caused by a large layer thickness or an extreme measured intensity value (possibly miswritten). The second sentence is displayed only when the thickness of the concerned layer is at least 25 times larger than the largest IMFP value.

Overflow during calculation. Check input data.
Overflow was occurred during calculations. One of the input data is larger than can be stored in the variables of the program (larger than $3.4 \cdot 10^{38}$). Check the contents of the input windows.

Overflow. Too large number in transmission file.
One of the coefficients of the transmission function is larger than can be stored in the corresponding variable. Edit the transmission file.

Overflow occurred at fitting of parameters (*N*). Check model and refine initial data.
Overflow was occurred during least square fitting of the model parameters. It may be caused by wrong initial data or that the model is not properly describe the measured data.

Overflow occurred at model calculation (*N*).
Overflow was occurred during calculation of intensity of structured models.

Parameter error(s): - Invalid transmission exponent.
The exponent of the *Exponential* transmission correction method is too large. Calculating the transmission function with this value would cause overflow.

Parameter error(s): - No transmission file specified.
The transmission type was set to *File* in the *Transmission* tab of the *Parameters* window but no file name was given in the *Filename* box. Type the filename or use the *Browse* button.

Parameter error(s): - The excitation - analyser angle is invalid.
The *Reilman* type angular correction was selected but the analyser-excitation angle is not set, smaller than 0° or larger than 360°. Enter the proper angle value of the applied spectrometer and save it as default.

Parameter error(s): - The excitation energy is invalid.
The *Other* excitation source was selected but the excitation energy is not set, zero or negative. Set the proper energy of the applied source.

Parameter error(s): - The IMFP exponent must be between 0 and 2 .
The *Exponential* type IMFP correction method was selected but the value of the exponent is unrealistic. Set other value (usually between 0.5 and 0.9) or select another method.

Path not found or incorrect.
The path specified is either not existing or containing errors. This error may also occur when an existing read-only file is attempted to overwrite.

Printer error.
The printer is not ready, out of paper or an error is occurred during printing or spooling.

Refine layer thickness values until Q sum is less than 50.
The *Autofit* button is pressed but the Q_{sum} value of the current parameters is greater than 50. Try to select other basis element. Vary the layer thickness and coverage data until Q_{sum} is less than 50 then invoke *Autofit* again.

Results error(s): - Adventitious carbon not found. No contamination correction.
Mohai's contamination correction method is selected but no C1s line with empty *State* field was found. Select different method, add C1s line or clear the *State* field of the adventitious carbon.

Results error(s): - Invalid transmission data. No transmission used.
Some of the coefficients in the transmission file are too large to calculate the transmission function or some of the calculated factors are negative or zero. Edit the transmission file to fix the error.

Results error(s): - Oxygen not found in experiment *N*.
One of the oxide normalisation types is selected but oxygen was not found in the Nth experiment (the oxygen intensity is zero or empty; there is no oxygen among the elements).

Some of the results are out of the expected range. Refine initial data or modify the model.
Although the fittings of the parameters was successful mathematically, some of them has no physical meaning; e.g., negative layer thickness, layer thickness greater than five times of the largest IMFP value, coverage less than zero or greater than one.

Some parameters of the IMFP calculation are missing or invalid.
Some parameters of the inelastic mean free path calculations are out of the expected range, e.g., the material class or is not set or the density is zero or greater than 22.5, etc. The error is reported only if the parameter is necessary for the selected method (e.g., bandgap energy is required only for the *Tanuma-Powell-Penn* method).

Sputter rate not set.
The *Tools / Create Depth Scale* command was selected but the sputter rate on the *Label*s tab of the *Parameters* window is not set or zero. Enter sputter rate first.

Subscript out of range occurred at fitting of parameters (*N*). Check model and refine initial data.
A reference was made to a non-existing array element during the least square fitting of model parameters. Check model definition in the *Model* window and the *Model* tab of the *Parameters* window.

Subscript out of range occurred at model calculation (*N*).
A reference was made to a non-existing array element during calculation of intensity of structured models.

The [*symbol*] line cannot be excited by the selected source. Line energy changed to give positive kinetic energy.
The binding energy of the selected line is higher than the energy of the excitation source. The specified energy of the line was changed to excitation energy minus one to give positive kinetic energy value. This line cannot be present in the spectra thus delete it in the *Elements* window.

The cosine of the angle between the function values and the columns of the Jacobian matrix is at tolerance.
The cosine of the angle between the solution vector and any column of the Jacobian matrix is at the tolerance specified in the program in absolute value. It means possible numerical convergence but the precision of calculation is limited or the convergence is very slow.

The data file is set to read-only.
Read-only files cannot be overwritten. Save the file with different name or remove the read-only attribute and repeat the *Save* command.

The excitation energy (*N* eV) is not plausible. Do you want to keep this value?
Although the value of the excitation energy is not restricted, the current value is lower (Y Mζ, 132.3 eV) or higher (Cr Kα, 5417.0 eV) than the energy of the regular sources applied in XPS. Press *Yes* if the energy is correct; or *No* to alter it. Once approved, this warning will not be displayed again, unless the excitation energy is changed.

The thickness of the modified layer is higher than the thickness of the nanotube wall.
The *Modified tube layer* feature was selected, where the thickness of the modified layer cannot be larger than the original wall thickness (i.e., the wall is transformed to layer). Enter smaller value or unselect this feature.

The solution is orthogonal to the columns of the Jacobian matrix to machine precision.
The solution vector is orthogonal to the columns of the Jacobian matrix to machine precision. The task cannot be solved with the present initial data.

The tolerance limit is reached. No further improvement in the approximate solution is possible.
The relative error between two consecutive iterates is at the tolerance limit specified in the program, i.e., there are no further changes in the approximate solution.

The tolerance limit is reached. No further reduction in the sum of squares is possible.
Both the actual and predicted relative reductions in the sum of squares reached the tolerance limit specified in the program.

The transmission file is not found in its specified location ([*path*]) but found in the [*data file / application*] folder. Do you want to keep the original invalid path?
XPS MultiQuant stores the full path of the transmission file in the data files. If the transmission file is not found at the given location (e.g., it was moved or the path was renamed), the program attempts to find a file with similar name first in the folder of the current data file, next in the folder of the application (usually *\Program Files\XMQ*). Select *Yes* to keep the original improper path, stored in the data file, or *No* to store the new path. When the transmission file is found in either of the default locations, always verify whether its content appropriate for the present calculations.

The window cannot be closed while "Show homogeneous composition" is selected.
Unselect the *Show homogeneous composition* checkbox before closing the *Intensity Simulation* window.

Time data not set.
The *Tools / Create Depth Scale* command was selected but the *Time* labels are empty. Select *Time* labels and enter data in the *Intensity* window.

Title must be entered.
No title entered in the *General* tab of the *Parameters* window. Enter the title now.

Too many elements omitted.
The described model is defined but with the elements marked as 'Omit' in the *Model* window, it became ill-defined. Remove the omit marks until the system becomes defined again.

Transmission file not found.
The specified transmission file cannot be found. Use the *Browse* button to locate the file manually.

Transmission function error(s): - Excess lines found in the transmission file.
After reading the maximum number of transmission coefficient sets, extra lines are detected in the transmission file. Although excess lines are ignored, check the validity of the file. E.g., in case of tabulated transmission function, if the energy step size is too small, the number of data points can easily go above the allowed maximum.

Transmission function error(s): - Invalid transmission data for line [ ].
The calculated transmission factor of the line is negative or zero. Test and edit the transmission file to correct the error.

Transmission function error(s): - Invalid type of transmission function.
Non-existing type of function is specified in the transmission file. Edit the transmission file to correct the error. Valid types are *EXP*, *POLY n*, *NPL*, *UNI* and *TAB*.

Transmission function error(s): - No valid transmission coefficients for line [ ].
The kinetic energy of the line is out of the energy ranges specified in the transmission file. The energy distance is too large for extrapolation. Extend the energy ranges in the transmission file.

Transmission function error(s): - The exponent of transmission function is too large.
The exponent of the *Exponential* or *Combined (Unifit)* type transmission function is too large to calculate the transmission factors. The maximum value of the exponent is 12.

Transmission function error(s): - The order of polynomial of transmission function is invalid.
The order of the polynomial for the *Polynomial* type transmission function is too large to calculate the transmission factors. The maximum order is 6.

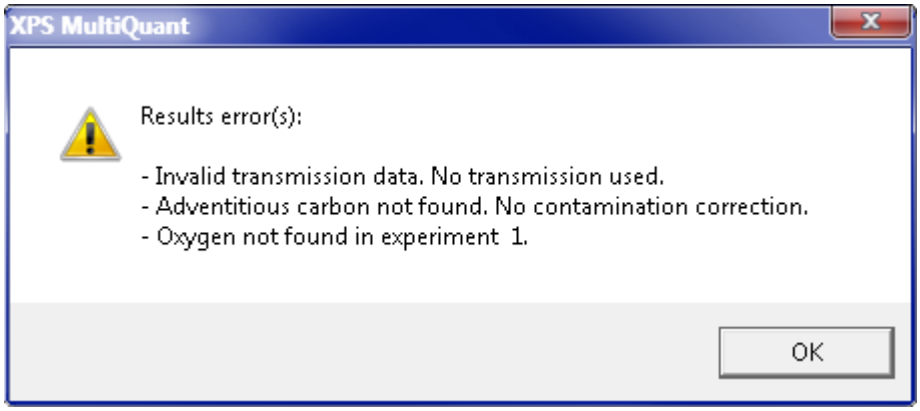
Transmission function error(s): - Wrong number of coefficients of transmission function.
The number of coefficients of transmission function is smaller or larger than required by the type of function. Edit the transmission file to correct the error.

Transmission function warnings(s): - Transmission data extrapolated for line [ ].
The kinetic energy of the line is out of the energy range specified in the transmission file but close enough for the reliable extrapolation. Although it is a warning message only, it is advisable extend the transmission function to the required energy.

Undo cannot be performed because destination cells are removed from the table.
The destination cells of the undo command are no more existing in the *Intensity* window, due to removed elements. The undo command cannot be performed and the undo data of this editing step are lost.

Error collections

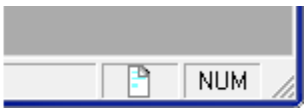
Some of the error and warning messages are organised into "error collections". If two or more errors of the same collection occur, messages are displayed together, as illustrated in the next figure.



The following collections are defined:

- Data file errors
- Element errors
- Model errors
- Nanotube warnings
- Parameter errors
- Results errors
- Transmission function errors
- Transmission function warnings

Pending Errors



If parameters of the elements or of the IMFP and transmission calculations are missing or invalid, an error message is shown and the erroneous data are replaced by default values. In this situation the calculated results are usually incorrect, therefore indicated by a small red page icon on the status bar (left hand side figure above). When a pending page (right hand side) is also waiting for printing, the icon represents both conditions (middle). Pointing to the icon, the tooltip shows the category of the error.

Release Notes

7.80 Improved data import facility: miscellaneous delimited texts can be pasted without any previous modification. Testing of input data was enhanced: even less disturbing error messages. The program's workspace can be saved and restored. Checking of obligatory elements for island type models was corrected. New data file version (3.0) with new, robust structure and new file error messages. Transmission files are identified by header line. The cell edit mode is indicated in the status bar. Several minor bugs were corrected.

7.70 The *Data Wizard* was enhanced; parameters of the IMFP calculations are requested, if necessary. The pending error condition is displayed in the status bar. Selection of parameters of the *Seah-Dench* IMFP calculation method is modified (similar to *Gries* one). In numeric cells, either dot or comma typed, always the current decimal separator is entered. Double clicking the *State* column in the *Element* window changes the standard chemical states only for the *Oxide-Layer* model. Direction of cells can be transposed during pasting. Code was reorganised to prevent redundant error messages. Minor bugs were corrected.

7.60 The *Islands-on-Nanotube* model variant was added. The *Show homogeneous composition* feature was added to *Intensity Simulation*. Icons were redesigned. Double clicking the *Line* cells in the *Elements* window, only items of the actually available transitions are rotated, instead of the most frequently used ones. Testing of *Angle dependent experiment set* was improved. New messages. Minor bugs were corrected.

7.51 Minor errors of the wizard and the nanotube simulation were corrected. None of them disturbed the calculated results.

7.50 The following error was corrected: at extrapolating the tabulated transmission function, calculated values were invalid. New transmission error messages were added. The actual values of the terms of the sensitivity factors can be displayed. The energy scale the *Elements* window can be temporarily switched to kinetic energy. Selection of parameters of the *Gries* IMFP calculation method is modified. Cells in the input windows can be edited. Several minor bugs were corrected.

7.41 The following error was corrected: when the number of (Elements × Experiments) exceeds the maximum number of elements at calculating *Angle dependent experiment set*, the "Subscript out of range" error occurred. Several minor bugs were corrected.

7.40 The undo features for the cell, row and table editing commands were enhanced. The levels of undo were increased. The order of elements or experiments can be

rearranged by drag and drop in the *Elements* and *Intensity* windows. Elements can be removed from chart. All omit and visible states can be reset to default. All data file versions supported again.

7.30 The *Data Wizard* was enhanced, a new starting window was added. Noise can be added to the simulated intensity values. Positioning of the *Data Wizard* window was corrected. Selection error of the initial folder of the *Open...* command was corrected.

7.22 The thickness of a linked layer is entered automatically in the *Layer Calculation* window. A very infrequent window refresh error, causing program crash, was corrected. New chapter *(Tips and Tricks)* in the User's Manual.

7.21 The following errors were corrected: for elemental materials the IMFP calculations by the *Gries* method may have provided erroneous values due to wrong parameter selection. When clicking the folder icon in the address line of the *Open* dialog box in Windows 7, the program crashed.

7.20 The *Parameter Summary* window was added. Older data files (versions 1.x) are no more supported. New data file version (2.31): the measurement unit is stored when the *Homogeneous* model selected. Minor bugs were corrected. New application example. New chapters *(Carbonaceous Contamination, Parameter Summary)* and figures in the User's Manual.

7.10 New feature: when the intensity of the adventitious carbon of an experiment is zero, no contamination correction is applied. The following error was corrected: in spite of changing the IMFP method of the *Homogeneous* model, values may be calculated with the originally selected one. Minor bugs of the *Model Layout* window were corrected. An erroneous library item was corrected.

7.00 The *Layers-on-Nanotube* model was added, including the *Modified tube layer* variant. The single row variant of the *Layers-on-Sphere* model was implemented. Intensity simulation was implemented. The *Model Layout* window was enhanced; drawing errors were corrected. Reorganised *Parameters* window. Results windows were renamed. New data file version (2.3). Several new messages. Minor bugs were corrected. New chapters in the User's Manual *(Intensity Simulation, Layers-on-Nanotube Model).*

6.13 The following, rare errors were corrected: when an *XPS Reduced Data Exchange* file is opened and the default model type is not *Homogeneous*, an error occurred. When a modified example file is saved, always the *Save As…* command invoked.

6.12 When the *Composition* (former *Results*) window is minimized and a new line is inserted into the *Elements* or *Intensity* window, the program crashed. Sizing errors of *Chart* and *Transmission* windows were corrected.

6.11 The following, very infrequent error was corrected: when an *XPS Reduced Data Exchange* file contains unidentifiable element entries, the sum of the percentage composition may exceed the 100 %.

6.10 The *Open Example…* command was added. The 'magic' of example files was implemented. The omit state of elements can be changed in the *Layer Calculation* window. When a line cannot be found in the library, available lines are listed in the error message window. Redesigned *Model Summary* window. The *Save As…* command offers the user's document folder.

6.00 New transmission file types were implemented *(NPL, Unifit, Table, Poly 0)*. Improved IMFP calculation for the *Homogeneous* model (*Gries* method, extended *Separate* options). Displaying the calculated IMFP values of the *Homogeneous* model. Redesigned *Layer Calculation* window. New items in *Parameters* window. New data file version (2.2). The *Data Wizard* can be started automatically. Minor bugs were corrected.

5.04 An error of loading results of structured models (may cause crash) is corrected.

5.03 The annoying error of the *Paste Table* command (inserting non-printable characters into cells) was corrected. The SHIFT + *Copy Table* command was implemented.

5.02 A window sizing error (causing crash) was corrected.

5.01 The improper handling of file extensions of *Template* files and the error in *Model Layout* window when the polyhedral model is not defined, were corrected. Enhanced checking of equations at island type models using *Angle dependent experiments*.

5.00 The *Layers-on-Polyhedron* model type was added. The *Multiline approach* for the homogeneous model was added. Reorganised *Parameters* and *Notes* windows. Internal editing of transmission files. The *Template* file type was introduced. Improved error checking of element data. Data entry accelerator in *Element* window. Rewritten, enhanced window handling and auto/manual resizing. Enhanced HTML-based help system. Cell copy from *Composition* (former *Results*) window. New data file version (2.1). Several new messages. New application examples. Minor bugs were corrected. New chapters in the User's Manual (*Template Files, Multiline Approach, Layers-on-Polyhedron Model, Polyhedron Editor Window*).

4.10 Reading of *XPS Reduced Data Exchange File* version 1.1 was implemented.

4.00 The *Oxide-Layer* model type was added. New AL calculation method was added (*Cumpson-Seah*) for the structured models. The input window calculator was added. IMFP and thickness measure conversion was added. Enhanced selection of Autofit initial parameters (fewer overflow error). Reading of *XPS Reduced Data Exchange File* (version 1.0) was implemented. Extended library (version 4.0) with more line entries; erroneous library items were corrected. New data file version (1.43). Minor bugs were corrected. New application examples. New chapters in the User's Manual (*Calculator in the Input Windows, Oxide-Layer Model, Contact*).

3.00 Experiments recorded at various angles of emission can be calculated together (*Angle dependent experiments set*, 'ARXPS'). New IMFP calculation methods were added (*Tanuma-Powell-Penn, Gries*) for the structured models. New data file version (1.42). New library version (3.0). Minor bugs were corrected. New chapters in the User's Manual (*Inelastic Mean Free Path, Step by Step*).

2.10 The *Model Layout* window was added. The content of the *Chart* window can be copied and printed directly. New normalisation types (*Oxide mass %, Oxide mass ratio*). Minor bugs were corrected.

2.01 Parameters error caused by data files prior to version 1.20 was corrected. Layer forward link data handling bug was corrected.

2.00 The least squares fitting of the model parameters (*Autofit*) feature was added. New model types (*Islands-on-Sphere*, *Islands-on-Cylinder*). Multilayer (repeated layer structures) feature. Enhanced data and model checking. Several new messages. New data file version (1.30). Reorganised *Parameters* window. Colours of the program components are controlled by the system colours set in the Control Panel of the operating system.

1.20 The *Data Wizard* was added to help filling the tables. Drag and drop file open. The start bitmap and data file icons were merged into the application file.

1.12 The development was migrated to Visual Basic 6.0. Minor printing and window handling errors were corrected. The items of the atom location matrix in the *Model* window can be real numbers instead of integers. New data file version (1.20). Title editing feature and new messages were added.

1.11 Pop-up menu for editing cells in input windows was added. Few minor bugs were corrected (found by the author's four-year-old son).

1.10 The *Islands-on-Plane* model was added. The intensity comparison graph was introduced to help layer thickness calculations. User selectable source energy. Improved help file and manual. New data file version (1.12). Several minor bugs were corrected.

1.00 This was the first release of XPS MultiQuant. It was developed using Microsoft Visual Basic Version 4.0 Professional Edition.

Predecessors

MultiQuant for DOS A quantification program written for DOS. It could calculate 33 experiments with 15 elements; the results could be displayed as *atomic %, atomic ratio, oxide ratio* or *mass %*. Two label sets (*Name* and *Time*) could be assigned to the experiments. Library with three cross section sets (*Evans* and *Scofield Mg Kα* and *Al Kα*) was also included. The program could apply a few structured models (*Layers-on-Plane* and *Layers-on-Sphere*) with maximum three layers as well but only with interactive (manual) parameter fitting. It had no graphic capabilities and help system was not available.

LAYERS A DOS program to calculate the intensity and intensity ratio of electrons excited from planar or spherical samples covered with overlayers. Maximum three layers with 6 elements could be calculated.

QUANT-140 This quantification program could handle a simplified homogeneous model. It was an overlay program system, consisting of five programs *(QUANT-140, WEIGHT-140, EDIT-140, FACTOR-140, ENERGY-140)*, written for a Texas Instruments TI-59 pocket calculator with magnetic card reader and printer. One experiment with 14 elements could be calculated; results could be expressed as atomic % or atomic ratio. A real gem!

Specifications

Library Specifications

Number of element entries	103
Number of photoelectron line entries	1,068
Number of cross section and sensitivity factor sets	5
Number of cross section and sensitivity factor data items	2,475
Number of asymmetry coefficient parameter sets	2
Number of geometry correction factor sets	3

Program Limitations

Number of quantification models	14
Number of concentration result types	8
Maximum number of elements	20
Maximum number of experiments	40
Maximum number of layers	5
Maximum of multilayer factor	5
Maximum number of transmission file items	40
Maximum order of transmission polynomial	6
Maximum length of label text (characters)	15
Maximum length of notes text (characters)	32,766
Largest integer number allowed	32,767
Largest real number allowed	$3.4 \cdot 10^{38}$

Basic Parameter Ranges

Asymmetry parameter	-1	–	2
Atomic weight	1	–	260
Bandgap energy (eV)	> 0	–	10
Cross section	> 0	–	100
Density ($g \cdot cm^{-3}$)	> 0	–	22.59
Inelastic mean free path (nm or Å)	> 0	–	
Molecular weight	1	–	
Oxygen atoms	0	–	8
Valence electrons	1	–	
Valence	0	–	8

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Contact

The author would be indebted if you send him comments and suggestions on further development of the program. Reports on errors of library data (possibly with the suggested new value) and program bugs are also accepted. Reprints of papers (electronic or printed) referring to XPS MultiQuant are highly appreciated.

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If you find the program useful, please refer to the following works of the author (or to other ones, if applicable) in your papers:

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Index

A

Adventitious carbon 6, 26, 115, 136, 142
Analyser-excitation angle 13, 27, 47, 70, 135
Angle dependent experiment set 9, 23, 24, 28, 42, 43, 44, 62, 100, 101, 132, 134, 143
Angle of emission 14, 24, 28, 44, 59, 61, 62, 66, 68, 73, 75, 76, 93, 117, 120
ARXPS 9, 23, 24, 28, 42, 43, 44, 62, 100, 101, 132, 134, 143
ASCII 20, 81, 111, 127
Asymmetry parameter 6, 40, 47, 48, 70
Atom location matrix 84, 97, 130, 133, 144
Atomic % 19, 53, 95
Atomic ratio 19, 95
Attenuation length 25, 51, 106, 143
Autofit 23, 28, 35, 55, 56, 97, 101, 129, 130, 131, 132, 135, 136, 143, 144

B

BACKSPACE key 91, 127
Bandgap energy 26, 51, 100, 136
Bar graph 78, 102
Basis element 19, 20, 23, 28, 31, 34, 95, 101, 136
Binding Energy 13, 14, 68, 69, 92, 137
Bulk material 22, 24, 26, 29, 33, 34, 36, 46, 55, 57, 59, 63, 66, 67, 68, 84, 97, 103, 132, 133, 134

C

CAE 70, 109
Calculator 15, 143
Cell editing 33
Chart window 19, 23, 78, 83, 89, 96, 97, 100, 102, 118, 144
Chemical states 14, 19, 24, 31, 39, 40, 55, 67, 69, 91, 92, 93, 94, 95, 96, 116, 129, 132, 133, 141
CH_x contamination 40, 44
Clipboard 20, 78, 81, 82, 88, 89, 90, 97, 103, 127
Combined (UNIFIT) function 9, 17, 109, 112, 138, 143, 148
Command 13, 14, 15, 16, 18, 19, 20, 22, 24, 30, 32, 33, 38, 77, 78, 80, 81, 82, 83, 84, 86, 88, 89, 91, 95, 96, 97, 99, 100, 103, 104, 118, 119, 123, 125, 129, 130, 133, 134, 135, 136, 137, 138, 139, 142, 143
Composition window 19, 31, 32, 84, 95, 96, 100
Concentration 14, 19, 26, 31, 39, 47, 52, 53, 54, 129, 146
Constant Analyser Energy 70, 109
Constant Retarding Ratio 70, 109
Contamination 6, 13, 14, 15, 24, 25, 26, 27, 30, 33, 34, 38, 40, 41, 42, 43, 44, 46, 47, 52, 55, 67, 68, 82, 88, 92, 94, 99, 103, 114, 115, 116, 136, 142
Converter programs 16
Copying 14, 16, 17, 20, 78, 81, 88, 144
Correction
  Angular 27, 30, 47, 55, 69, 70, 108, 120, 135
  Contamination 6, 13, 14, 24, 26, 30, 40, 41, 42, 44, 46, 47, 52, 68, 92, 94, 103, 114, 115, 116, 136, 142
  Elastic scattering 48, 147, 148
  IMFP 6, 13, 14, 15, 16, 24, 25, 26, 27, 28, 30, 33, 34, 45, 46, 47, 48, 49, 50, 51, 52, 55, 57, 66, 68, 69, 70, 82, 84, 88, 94, 97, 99, 106, 107, 114, 116,

118, 130, 131, 133, 135, 136, 140, 141, 142, 143
Transmission function 6, 10, 11, 14, 24, 30, 40, 47, 51, 52, 55, 64, 68, 69, 70, 78, 109, 110, 111, 112, 113, 121, 126, 129, 134, 135, 136, 137, 138, 139, 140, 141, 143, 146
Cross section 6, 13, 24, 27, 30, 40, 46, 47, 55, 63, 68, 69, 70, 92, 104, 105, 132, 144, 146
CRR 70, 109
CS2 formula 51, 106
Cumpson, P. J. 25, 34, 51, 106, 143, 148
Cylindrical surface 22, 60, 61, 63, 73, 103

D

Data file 9, 12, 13, 15, 16, 20, 24, 36, 78, 80, 86, 94, 118, 119, 123, 126, 127, 128, 129, 131, 137, 141, 142, 143, 144
Data Import 16
Data Wizard 13, 30, 84, 119, 125, 130, 131, 141, 142, 143, 144
Delete
Element 14, 29, 32, 33, 81, 130, 134
Experiment 14, 29, 32, 33, 81, 130, 134
DELETE key 14, 29, 32, 33, 81, 87, 88, 91, 98, 127, 129, 130, 134
Dench, W. A. 25, 27, 28, 34, 49, 50, 94, 106, 107, 141, 147
Density 24, 26, 28, 29, 33, 45, 49, 50, 51, 55, 69, 94, 97, 99, 106, 107, 129, 133, 136
Depth scale 84, 118
Detector sensitivity 47, 52
Diff % 23, 55
Doublet 13, 15, 47, 69, 91, 105, 129

E

Ebel, H. 14, 27, 31, 39, 40, 48, 52, 53, 108, 116, 147
Edit menu 14, 81, 86
Edit Menu (Notes window) 86
Editing keys 127
Effective asymmetry parameter 48
Eject Page command 20, 32, 123, 126
Elastic scattering 48, 147, 148
Elements 6, 14, 49, 50, 69, 84, 92, 99, 106, 115, 129, 130, 139, 141, 143
Elements window 13, 14, 24, 31, 36, 42, 55, 79, 82, 83, 137, 141
Empty and zero cells 14, 93
Empty row 81
ENTER key 23, 35, 101, 127
Evans, S. 26, 27, 40, 41, 47, 52, 70, 104, 105, 114, 144, 147
Example files 44, 80, 119, 142, 143
Excel 2, 9, 16, 20, 39, 77, 81
Excitation energy 30, 70, 118, 144
Excitation source 13, 27, 28, 30, 47, 48, 70, 72, 73, 104, 108, 118, 135, 137
Excitation-analyser angle 13, 27, 47, 70, 135
Experiments 11, 13, 14, 16, 19, 23, 24, 25, 26, 28, 29, 31, 32, 33, 34, 36, 37, 42, 43, 44, 52, 62, 81, 88, 89, 93, 94, 96, 100, 101, 103, 106, 107, 114, 115, 117, 119, 122, 123, 130, 131, 132, 134, 136, 141, 142, 143, 144, 145, 146
Explicit 25, 26, 27, 55, 94, 106, 107, 114
Exponential 9, 13, 25, 27, 30, 49, 51, 106, 109, 111, 112, 113, 135, 138
Extracting data 16

F

FAT 70, 109
File menu 79, 86, 121
File Menu (Notes window) 86, 121
Fixed Analyser Transmission 70, 109
Fixed Retarding Ratio 52, 70, 109
Flat surface 6, 16, 22, 57, 58
Font 20, 32, 87, 124
Format Menu (Notes window) 87
FRR 52, 70, 109

G

G-1 formula 49, 106
Geometry correction factors 34, 59, 60, 61, 71, 74, 75, 76, 103, 120, 132
Graphical intensity comparison 23, 78, 97, 102
Gries, W. H. 25, 27, 28, 34, 49, 50, 94, 106, 107, 130, 141, 142, 143, 148

H

Hardware requirements 19
Help menu 85, 87
Help Menu (Notes window) 87
Hesse, R. 148
Hexagonal lattice 59
Homogeneous model 13, 22, 23, 25, 27, 28, 30, 33, 37, 44, 46, 103, 116, 118, 122, 133, 142, 143
Hydrocarbon contamination 14, 26, 40, 41, 43, 45

I

IMFP 6, 13, 14, 15, 16, 24, 25, 26, 27, 28, 30, 33, 34, 45, 46, 47, 48, 49, 50, 51, 52, 55, 57, 66, 68, 69, 70, 82, 84, 88, 94, 97, 99, 106, 107, 114, 116, 118, 130, 131, 133, 135, 136, 140, 141, 142, 143
IMFP & Contamination window 14, 82, 84, 94, 99, 107, 114
IMFP matrix 84, 97, 118
Importing data 16
Inelastic Mean Free Path 6, 13, 14, 15, 16, 24, 25, 26, 27, 28, 30, 33, 34, 45, 46, 47, 48, 49, 50, 51, 52, 55, 57, 66, 68, 69, 70, 82, 84, 88, 94, 97, 99, 106, 107, 114, 116, 118, 130, 131, 133, 135, 136, 140, 141, 142, 143
Infinitely thick homogeneous sample 6, 47, 116
Inorganic materials 49, 50, 106
Insert
  Element 14, 29, 32, 81
  Experiment 14, 29, 32, 81
Installed files 8
Installing 7, 8, 11
Instrument factor 46
Intensity 6, 14, 15, 16, 22, 23, 24, 26, 28, 29, 31, 32, 33, 35, 37, 39, 40, 42, 43, 44, 45, 46, 47, 52, 53, 55, 57, 58, 59, 61, 63, 66, 67, 68, 69, 78, 81, 82, 83, 84, 88, 93, 97, 100, 101, 102, 113, 114, 115, 117, 122, 123, 129, 130, 131, 135, 136, 138, 139, 141, 142, 144, 145, 149, 150
Intensity comparison 23, 78, 97, 102
Intensity Simulation 24, 37, 44, 84, 122, 131, 141, 142
Intensity Simulation window 24, 37, 44, 84, 122, 123, 131, 138
Intensity window 14, 15, 24, 33, 44, 82, 88, 117, 122, 131, 138, 139, 142
Island type models 55, 97, 101, 103, 117
Islands-on-Cylinder model 66, 144
Islands-on-Nanotube model 141
Islands-on-Plane model 66, 117, 144
Islands-on-Polyhedron model 66
Islands-on-Sphere model 66, 144

J

Jablonski, A. 25, 27, 49, 94, 106, 107, 147

K

Keyboard commands 13, 127
Kinetic Energy 34, 47, 49, 50, 51, 52, 55, 69, 97, 110, 111, 112, 137, 138, 139
Kinetic energy scale 92, 141

L

Labels 11, 13, 14, 15, 17, 19, 24, 28, 30, 31, 32, 36, 44, 84, 93, 94, 96, 117, 118, 122, 132, 134, 135, 136, 138, 144, 146
Langmuir-Blodgett films 23, 45
Layer thickness calculation 23, 34, 40, 76, 78, 97, 101, 102, 142, 143
Layer Thickness window 23, 34, 36, 43, 83, 88, 89, 96, 100, 101, 102, 103
Layers 16, 22, 23, 24, 25, 26, 28, 29, 33, 34, 35, 36, 37, 40, 41, 42, 43, 44, 45, 46, 47, 52, 55, 56, 59, 64, 65, 66, 67, 68, 71, 76, 78, 84, 90, 97, 98, 99, 100, 101, 102, 103, 116, 117, 122, 130, 131, 132, 133, 134, 135, 136, 137, 142, 144
Layers-on-Cylinder model 60, 73, 116
Layers-on-Nanotube model 34, 44, 56, 63, 103, 116, 142
Layers-on-Plane model 40, 42, 43, 44, 45, 57, 116, 117, 131, 133, 144
Layers-on-Polyhedron model 34, 36, 61, 74, 103, 116, 117, 132, 143
Layers-on-Sphere model 44, 58, 116, 142, 144

Least square fitting 23, 28, 35, 55, 56, 97, 101, 129, 130, 131, 132, 135, 136, 143, 144
Library 6, 7, 9, 13, 14, 27, 30, 31, 69, 70, 83, 86, 91, 99, 104, 119, 127, 130, 131, 132, 142, 143, 144, 146, 150
Library Lookup 13, 30, 31, 83, 91, 119, 131
Limitations 146

M

Magic 27, 38, 80, 143
Magic angle 27
Margins 124
Mass % 19, 54, 95
Mass ratio 19, 95
Material class 26, 49, 50, 94, 99, 106, 107, 136
Me (metal) chemical state 8, 24, 37, 92, 132
Mean molecular weight 49
Menu access keys 127
Menus
  Edit menu 14, 81, 86
  Edit Menu (Notes window) 86
  File menu 79, 86, 121
  File Menu (Notes window) 86, 121
  Format Menu (Notes window) 87
  Help menu 85, 87
  Help Menu (Notes window) 87
  Pop-up Menu (result windows) 89
  Tools menu 83
  View menu 82
  Windows menu 85
Merge chemical states 19, 31, 95
Messages 128
Model Layout window 20, 23, 80, 83, 90, 100, 103, 142, 143, 144
Model Summary window 84, 99, 143
Model window 22, 23, 24, 33, 34, 35, 36, 42, 56, 76, 83, 84, 97, 99, 100, 117, 132, 133, 134, 136, 138, 144
Models 6, 22, 23, 24, 25, 28, 34, 40, 55, 56, 61, 66, 68, 99, 101, 103, 117, 141, 143, 146
  Homogeneous 13, 22, 23, 25, 27, 28, 30, 33, 37, 44, 46, 103, 116, 118, 122, 133, 142, 143
  Islands-on-Cylinder 66, 144
  Islands-on-Nanotube 141
  Islands-on-Plane 66, 117, 144
  Islands-on-Polyhedron 66
  Islands-on-Sphere 66, 144
  Layers-on-Cylinder 60, 73, 116
  Layers-on-Nanotube 34, 44, 56, 63, 103, 116, 142
  Layers-on-Plane 40, 42, 43, 44, 45, 57, 116, 117, 131, 133, 144
  Layers-on-Polyhedron 34, 36, 61, 74, 103, 116, 117, 132, 143
  Layers-on-Sphere 44, 58, 116, 142, 144
  Oxide-Layer 24, 36, 42, 43, 67, 92, 116, 132, 133, 141, 143
Modified tube layer 44, 56, 116, 137, 142
Mohai, M. 2, 7, 13, 14, 26, 27, 30, 41, 45, 52, 71, 92, 114, 115, 136, 148, 149, 150
mqd file extension 9, 10, 11, 12, 19, 38, 39, 40, 41, 42, 43, 44, 45, 78, 126
mqt file extension 9, 10, 15, 126
mqx file extension 9, 10, 126, 130
mtr file extension 9, 10, 111, 126
Multiline Approach 14, 27, 30, 31, 39, 40, 52, 53, 116, 119, 129, 143, 147

N

Native oxide 29, 40, 43
Nefedov, V. I. 70, 104, 149
NLP (rational) function 9, 51, 109, 111, 113, 138, 143
Noise 24, 122, 142
Normalisation 52, 53, 54, 75, 76, 89, 136, 144
  Atomic % 19, 53, 95
  Atomic ratio 19, 95
  Mass % 19, 54, 95
  Mass ratio 19, 95
  Oxide mass % 19, 95, 144
  Oxide mass ratio 19, 95, 144
  Oxide molar % 19, 95
  Oxide molar ratio 19, 41, 95
Notes window 19, 20, 38, 80, 83, 86, 87, 109, 129, 143

O

Omit element 19, 28, 99
Omit experiment 19, 96
Open data 15, 19, 20, 23, 80, 85, 121, 127, 129, 144
Origin 2, 16, 20, 77
Overlayers 22, 23, 24, 25, 46, 55, 57, 58, 60, 61, 63, 66, 67, 76, 116, 133, 145
Ox (oxide) chemical state 24, 37, 92, 132
Oxidation state 54, 95
Oxide mass % 19, 95, 144
Oxide mass ratio 19, 95, 144
Oxide molar % 19, 95
Oxide molar ratio 19, 41, 95
Oxide-Layer model 24, 36, 42, 43, 67, 92, 116, 132, 133, 141, 143
Oxygen balance 19, 39, 41, 42, 54, 95

P

Parameter Summary window 119, 142
Parameters
  Angular tab 108
  Contamination tab 114
  Cross Section tab 104
  General tab 118
  IMFP tab 106
  Labels tab 117
  Model tab 115
  Transmission tab 109
Parameters window 14, 15, 19, 22, 23, 24, 25, 28, 41, 42, 44, 56, 78, 83, 84, 93, 94, 96, 97, 119, 126, 128, 130, 131, 132, 133, 134, 135, 136, 138, 142, 143, 144
Pasting 14, 17, 18, 20, 77, 78, 88, 141
Pending error 126, 141
Pending page 13, 20, 79, 80, 97, 103, 126, 140
Penn, D. R. 25, 26, 34, 50, 100, 106, 136, 143, 148
Photoelectron intensity 22, 24, 55, 57, 58, 60, 61, 71
Photoelectron line transition 47
Photoelectron lines 31, 42, 46, 52, 69, 70, 83, 91, 93, 129, 132, 133, 146
Photoionisation cross section 6, 13, 24, 27, 30, 40, 46, 47, 55, 63, 68, 69, 70, 92, 104, 105, 132, 144, 146
Polyhedral surface 61, 143
Polyhedron Editor 36, 75, 117, 120, 121, 132, 143
Polymers 26, 41, 49, 50, 106
Polynomial 51, 109, 111, 112, 113, 138, 146
Pop-up Menu (result windows) 89
Pop-up menus 14, 20, 82, 87, 88, 89, 90, 97, 103, 121, 126
Powell, C. J. 25, 26, 34, 50, 71, 100, 106, 136, 143, 147, 148, 149
Print Current command 20, 32, 80, 97, 103
Print Options window 20, 80, 123
Print window 20, 80, 126
Printer 10, 124, 136

Q

Q_{sum} 23, 28, 35, 44, 55, 101, 130, 136

R

Radius 33, 34, 58, 59, 64, 66, 116, 117, 118, 131, 132, 133, 134
Rational (NPL) function 9, 51, 109, 111, 113, 138, 143
Raw composition 27
Rearranging
  elements 14, 33, 92, 141
  experiments 14, 33, 93, 141
Registry entries 8
Reilman, R. F. 27, 30, 48, 70, 108, 135, 147
Results type
  Atomic %, 19, 53, 95
  Atomic ratio 19, 95
  Mass % 19, 54, 95
  Mass ratio 19, 95
  Oxide mass % 19, 95, 144
  Oxide mass ratio 19, 95, 144
  Oxide molar % 19, 95
  Oxide molar ratio 19, 41, 95

S

Save Data As… 80
Scaling 9, 40, 47, 48, 70, 105, 132

Scofield, J. H. 69, 70, 104, 144, 149
Seah, M. P. 25, 27, 28, 34, 49, 50, 51, 94, 106, 107, 141, 143, 147, 148
Sensitivity factor 13, 27, 30, 47, 53, 55, 69, 70, 104, 105, 141, 146
Sequence number 14, 19, 23, 32, 33, 36, 81, 89, 92, 93, 96, 100, 101, 103, 117, 122
SHIF key 17, 20, 81, 83, 88
Shortcut 12, 19, 79, 80
Shortcut keys 127
Show 37, 104, 105, 107, 108, 110, 114, 119, 122, 138, 141
Show homogeneous composition 37, 122, 138, 141
Simulation 24, 37, 44, 84, 122, 131, 141, 142
Source energy 30, 70, 118, 144
Special State entries 92
Spherical surface 22, 44, 58, 59, 60, 61, 75, 103, 145
Splitting 47, 48, 105, 132
State column 14, 24, 37, 55, 91, 92, 115, 141
State entries, special 92
Status bar 13, 19, 20, 31, 32, 80, 118, 123, 126, 140, 141
Structured models 15, 25, 26, 28, 61, 68, 99, 118, 129, 133, 135, 136, 143, 144

T

Take-off angle 14, 24, 28, 44, 59, 61, 62, 66, 68, 73, 75, 76, 93, 117, 120
Tanuma, S. 25, 26, 34, 50, 100, 106, 136, 143, 148
Template files 9, 10, 15, 79, 80, 126, 131, 143
Tilt angle 14, 24, 28, 44, 59, 61, 62, 66, 68, 73, 75, 76, 93, 117, 120
Title 11, 13, 15, 31, 79, 80, 103, 104, 118, 125, 126, 128, 138, 144
Tools menu 83
Tougaard, S. 2, 55
TPP-2M formula 50, 71, 84, 106
Transmission function 6, 10, 11, 14, 24, 30, 40, 47, 51, 52, 55, 64, 68, 69, 70, 78, 109, 110, 111, 112, 113, 121, 126, 129, 134, 135, 136, 137, 138, 139, 140, 141, 143, 146
Transmission function files 10, 11, 78, 111, 126, 143
Transposing cells 77, 88, 141

U

Undo 14, 29, 33, 81, 82, 86, 88, 130, 134, 139, 141
UNIFIT (combined) function 9, 17, 109, 112, 138, 143, 148
Uninstalling 8

V

Valence 51, 69, 71, 84, 91, 100
Valence electrons 51, 71, 84, 100
Varsányi, G. 71, 148, 150
View menu 82
Visible element 96, 100

W

Wagner, C. D. 27, 47, 70, 104, 105, 149
Windows 15, 20, 25, 79, 80, 81, 82, 85, 88, 91, 96, 125, 129, 135, 141, 142, 144
  Chart 19, 23, 78, 83, 89, 96, 97, 100, 102, 118, 144
  Composition 19, 31, 32, 84, 95, 96, 100
  Elements 13, 14, 24, 31, 36, 42, 55, 79, 82, 83, 137, 141
  IMFP & Contamination 14, 82, 84, 94, 99, 107, 114
  Intensity 14, 15, 24, 33, 44, 82, 88, 117, 122, 131, 138, 139, 142
  Intensity Simulation 24, 37, 44, 84, 122, 123, 131, 138
  Layer Thickness 23, 34, 36, 43, 83, 88, 89, 96, 100, 101, 102, 103
  Model 22, 23, 24, 33, 34, 35, 36, 42, 56, 76, 83, 84, 97, 99, 100, 117, 132, 133, 134, 136, 138, 144
  Model Layout 20, 23, 80, 83, 90, 100, 103, 142, 143, 144
  Model Summary 84, 99, 143
  Notes 19, 20, 38, 80, 83, 86, 87, 109, 129, 143

Parameter Summary 119, 142
Parameters 14, 15, 19, 22, 23, 24, 25, 28, 41, 42, 44, 56, 78, 83, 84, 93, 94, 96, 97, 119, 126, 128, 130, 131, 132, 133, 134, 135, 136, 138, 142, 143, 144
Print 20, 80, 126
Print Options 20, 80, 123
Windows menu 85
Wizard 13, 30, 84, 119, 125, 130, 131, 141, 142, 143, 144
Word 9, 16, 20, 42, 77, 81, 87
Workspace 9, 11, 20, 80, 129, 141

X

X (category) axis 19, 28, 32, 93, 96, 117
XPS MultiQuant data files 9, 10, 11, 12, 19, 23, 38, 39, 40, 41, 42, 43, 44, 45, 78, 79, 80, 100, 126
XPS Reduced Data Exchange File 9, 10, 16, 79, 80, 126, 130, 142, 143
X-ray flux 46

Y

Y (value) axis 19, 96

Z

Zero and empty cells 14, 93

Herr Prof. Dr. Röntgen