030.0098.01.0

EasyCal

Eval2

Innovation with Integrity

Handheld XRF

Table of Contents

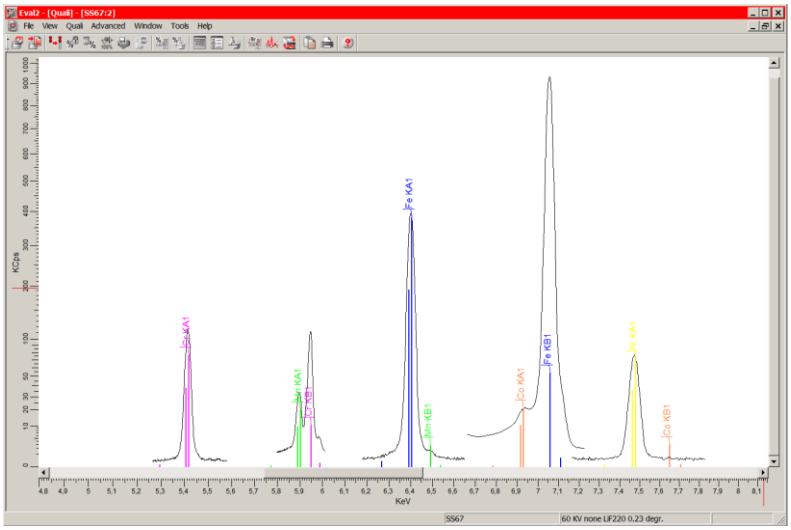
1. Getting Started

1.1. Aim of EVAL2

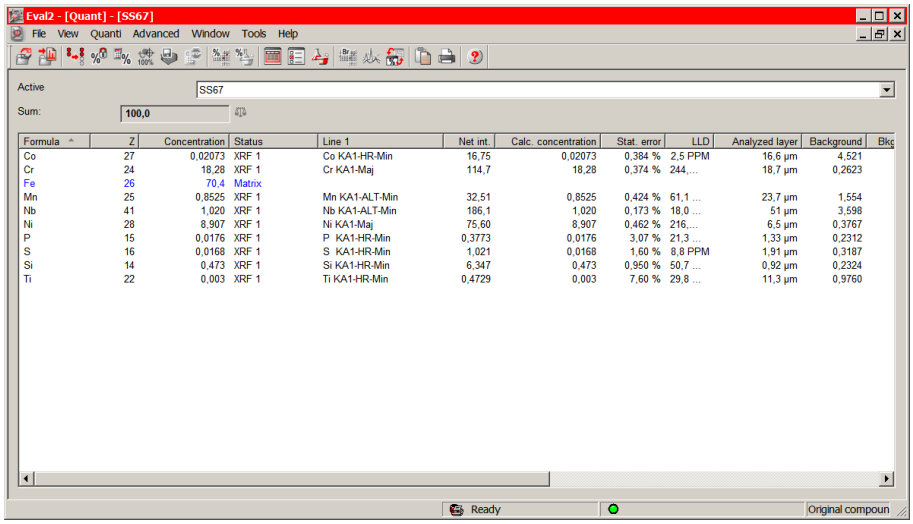
EVAL2 is a tool for analyzing measured files (extension ssd).

The program consists of two main parts, graphical evaluation and quantitative evaluation:

- If a sample is measured in scan mode the software offers options for graphical evaluation and interactive work. Elements are identified and labelled automatically. There will be produced a qualitative result.



- In the quantitative part of EVAL2 various functions and features to calculate results from the measured intensities are offered. Important parameters like sample preparation and calibration files can be checked and if necessary be modified.



At the completion of a measurement, the concentrations are automatically computed ; this is the Automatic Evaluation. In X-ray fluorescence, it is necessary to give a physical model of the sample in order to calculate these concentrations. Some hypotheses are mandatory (e.g. the sample must be homogeneous); some other can be adjusted:

- the preparation parameters;
- the concentration of the elements that are not measured, or that are also measured with another analysis method;
- the line used to evaluate the elements.

Some of the parameters can differ between the unknowns and the standard samples. In case of standardless measurements, the software cannot know some of these parameters. SPECTRA EDX therefore gives the possibility to modify these parameters and make a new evaluation — this is the Interactive Evaluation.

1.2. Interaction with the other SPECTRA EDX files

When a calibration is done, the calibration coefficients can be stored:

- in the line library (S*X*-LineLibrary.FLL), in case of the default calibration for the lines;
- in a calibration file (FCL file).

When performing an interactive evaluation, QUANTEVL2 retrieves the default parameters for the evaluation from the application (evaluation model, EVM file), the Results database (Measure.MDB) and the line library (S*X*-LineLibrary.FLL). The intensities that will be used for the evaluation are stored in a SSD file.

Once the evaluation performed, it can write the result in the Results database (Measure.MDB).

1.3. Starting EVAL2

You can start EVAL2 from:

Spectra Launcher icon

- The SPECTRA EDX Launcher:
  1. start the SPECTRA EDX Launcher;
  2. when no SPECTRA EDX session is running, a warning message appears; click **OK**, then in the SPECTRA EDX Login dialog box, type your **User name** and **Password** and click **OK**;

Evaluation button

  3. the SPECTRA EDX Launcher dialog box appears; click **Evaluation**;
  4. the Select Sample(s) for Evaluation dialog box appears (see section 3.1 "How to import a sample"); once the sample is selected, click **Interactive quant** or **Interactive quali**.

Fig. 1-3 SPECTRA EDX Launcher dialog box

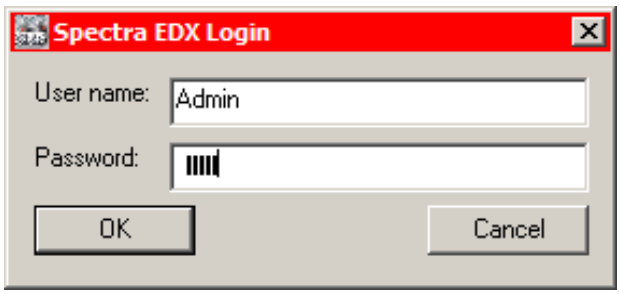


Fig. 1-4 SPECTRA EDX Login dialog box

Like for any other Windows®-based application:

EVAL2 icon

- EVAL2 can be launched from the Windows® Explorer or My Computer, by double-clicking the icon.
  EVAL2.EXE is in the drive and folder set during installation. If you used the default setup, it is in `C:\Program Files\SpectraEDX\`

2. EVAL2 windows and documents

2.1. Overview of the EVAL2 windows

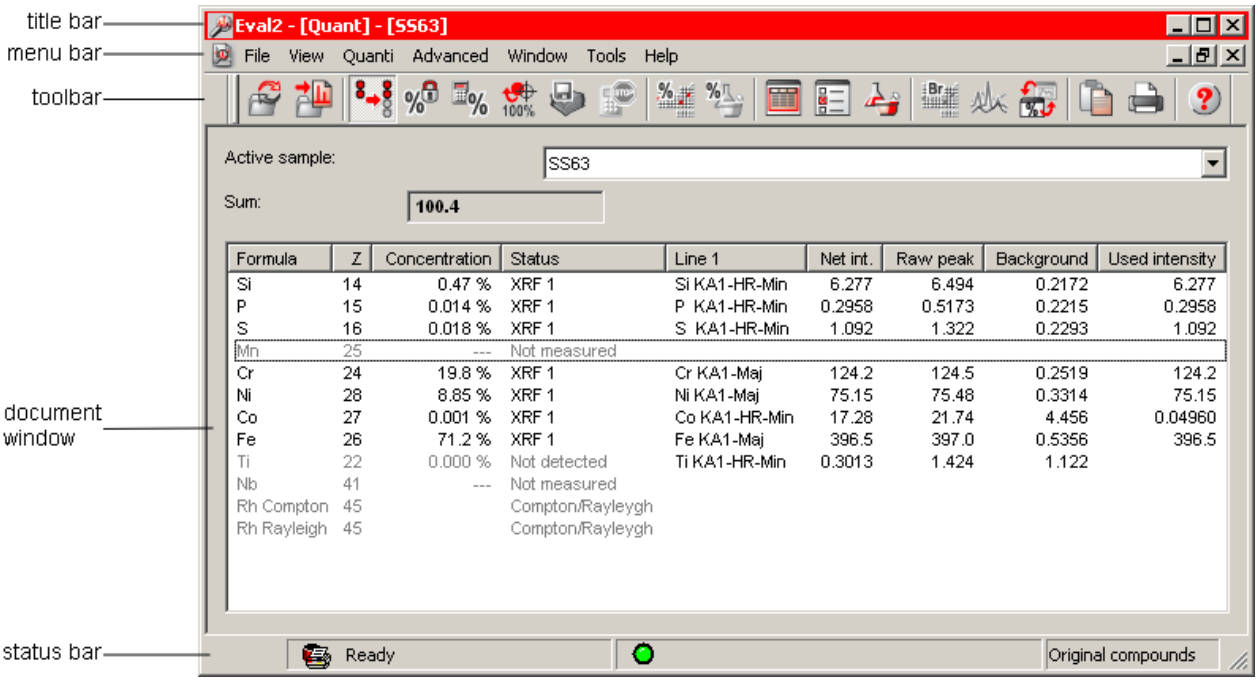


Fig. 2-1 EVAL2 window

The EVAL2 window consists in five parts:

- the Title bar, which contains the name of the selected Document window;
- the Menu bar, which contains all the commands;
- the Toolbar, with the shortcut buttons to the most important commands;
- a Document window, which can be a Quant window or a Quali window;
- the Status bar, which displays the calculation status.

Alternative mode window button

The **Alternative mode window** button allows switching between the various Quant and Quali windows of an EVAL2 document. The **CTRL+F6** and **CTRL+TAB** key combinations can also be used to switch from a window to the other, including between EVAL2 documents.

Restore button

The **Restore** button puts the Document windows (Quant and Quali windows) in the "cascade" display mode. It is then possible to click directly in the window of interest.

Maximize button

Click the **Maximize** button of any Document window to get back to the initial display mode.

To know more about	see
the Document windows	section 2.3

2.2. EVAL2 documents

Overview of the EVAL2 documents

An EVAL2 document is a composite document that can contain:

- raw measurement data (e.g. a copy of SSD files);

- evaluation data:
  - parameters for the quantitative evaluation and its result: the initial application (EVM file) and the adjusted parameters (fixed concentration, chemical bonds, matrix…), calculated concentrations;
  - parameters for the qualitative evaluation and its result: chemical filter, energy/wavelength range, found elements…
- graphical parameters: color of the spectra, zoom, labels…

In the EVAL2 window, the EVAL2 document is displayed as one or several Document windows. There are two types of Document windows: the Quant windows and the Quali windows. By default, an EVAL2 document is made of a single Quant window.

The EVAL2 documents are saved in files whose file name extension is .EVAL2

e.g. the `doc1` document is stored in the `doc1.EVAL2` file.

By default, the name of the document is the sample ID of the first imported sample (see section 3 "Importing a sample"); it can be changed when saving the document.

To know more about	See
The EVAL2 window	section 2.1
The Document windows (Quant and Quali windows)	section 2.3
How to save an EVAL2 document	section 2.2.2

Managing documents

The usual procedure is:

1. create a new EVAL2 document
   — or —
   open an existing document.
2. import one or more samples.
3. process the data (quantitative or qualitative evaluation).
4. print the result, save the result in the Results database and/or save the EVAL2 document.
5. close the EVAL2 document.

The present section is about creating, opening, saving and closing an EVAL2 document.

To know how to	See
Import a sample	section 3
Perform a quantitative evaluation	section 4
Perform a qualitative evaluation	section 5
Print the result and save it in the Results database	section 5.6

Creating a new document

An empty document is automatically created when EVAL2 is opened.

To create a new empty document:

- click the **New** command in the **File** menu
  — or —
  use the shortcut key combination **CTRL+N**

Opening an existing document

When an EVAL2 document was saved (see below), it is possible to retrieve it.

To open an existing EVAL2 file:

1. click the **Open** command in the **File** menu
   — or —
   use the shortcut key combination **CTRL+O**;
2. in the Open dialog box, browse to the directory where the file was saved;
3. select the EVAL2 file and click **Open**.

Saving a document

It is possible to save an EVAL2 document, e.g. when it is not possible to process the data in a continuous session, or to be able to reprint the spectra with the same layout.

To save a document with the current document name:

- click the **Save** command of the **File** menu
  — or —
  use the shortcut key combination **CTRL+S**;

To save a document with a different name:

1. click the **Save As** command of the **File** menu;
2. in the Save As dialog box, select the file path (directory) where the file will be saved;
3. in the **File name** text box, type in the name of the file; the .EVAL2 file name extension is automatically added;
4. click **Save**.

Closing a document

Several documents can be opened at the same time in EVAL2. However, to avoid errors (e.g. performing an operation on the wrong document), it is recommended to close a document before opening a creating another one.

To close a document:


Close button

- click the **Close** command of the **File** menu
  — or —
  close all the windows of the document with the **Close** button in the Menu bar when the windows are maximized, or in their Title bar when they are in cascade mode (see section 2.1 "Overview of the EVAL2 windows").

2.3. Document windows

A Quant window is a window used for the quantitative evaluation, i.e. the calculation of the concentrations from the measured spectrum and the Application.

A Quali window is a window used for the graphical display of the spectrum and the qualitative evaluation, i.e. the detection of the elements from the spectrum.

By default, an EVAL2 document is made of a Quant window.

Another Quant window can be added, e.g. to compare several quantitative evaluation. To do this:

- in the **Window** menu, choose **New Quant window**.

A Quali window can be added in one of the following ways


Alternative Mode Window button

- in the **Window** menu, choose **New Quali window**;
  — or —
  in a Quant window, click the **Alternative Mode Window** button.

The name of the window is written in the Title bar: the Title bar of the EVAL2 window when the document windows are maximized, or the Title bar of the document window when they are minimized or in adjustable size mode. The name of the window is:

`[Mode] - [Document name:n]`

where

- *Mode* is "Quant" or "Quali", depending of the type of window;
- *Document name* is the name of the EVAL2 document;
- *n* is the number of the window in the order of creation.

To switch between the different windows of a document:


Alternative Mode Window button

- use the **CTRL+F6** or **CTRL+TAB** key combination
  — or —
  click the **Alternative Mode Window** button.

To close a document window:


Close button

- click the **Close** button in the window Menu bar when the Document window is maximized, or of the Title bar of the Document window when it is in cascade display mode (see section 2.1 "Overview of the EVAL2 windows").

The Quant windows

The main part of a Quant window is the Concentration list, i.e. list of calculated concentrations with additional information.

Some buttons of the EVAL2 Toolbar are specific of the Quant windows and are disabled for other windows; these are shortcuts to the commands of the **Quanti** and **View** menus. Other commands are accessed with a right-click the items of the Concentration list (context-sensitive menu).

The color of a line changes with its status: the compound is in blue when it is a matrix, and in red when it is fixed to zero.

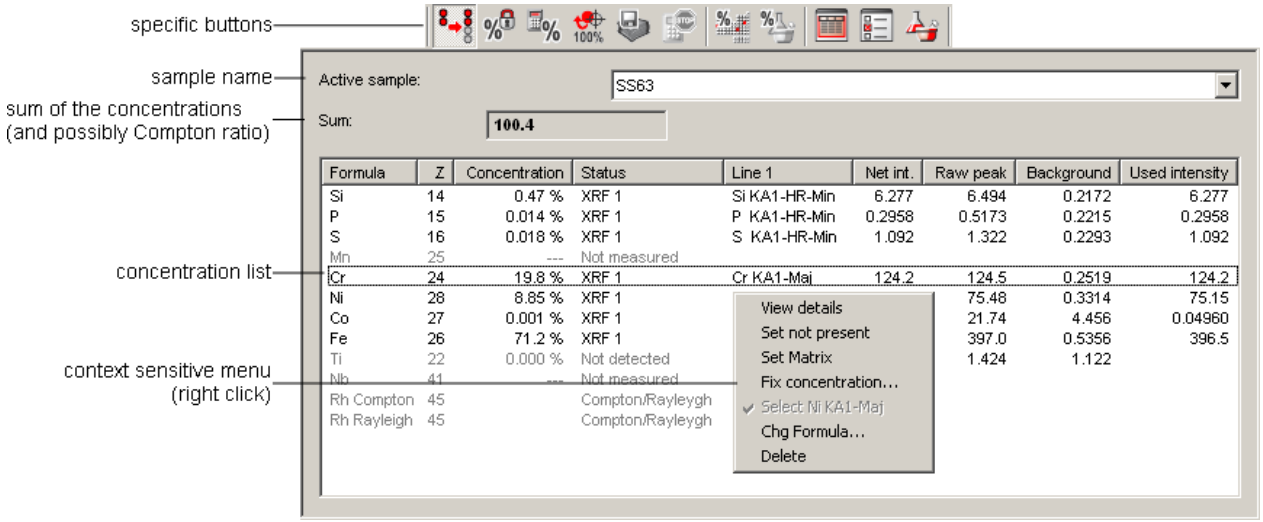


Fig. 2-2 Quant window

Columns of the Concentration list

Column name	Description
Formula	chemical formula of the compound
Z	atomic number of the key element of the compound
Concentration	concentration of the compound in the sample
Status	the way the compound is evaluated:
Line *n*	XRF line used for the evaluation
Net Int.	net intensity of the line *n*
Calc. concentration	concentration calculated with the line *n*
Stat. Error	statistical error on the intensity (fluctuation of the signal following the Poisson's law) converted into a concentration with the calibration coefficient and the matrix correction
LLD	lower limit of detection, determined from the background level (the smallest detectable peak must be above the fluctuations of the signal)
Analyzed layer	thickness of the sample that absorbs 90% of the intensity of the XRF line of interest

2.3.2 The Quali windows

The Quali window consists in a graphical window; it is possible to zoom in and out, to change the color of the objects…

Some buttons of the EVAL2 Toolbar are specific of the Quali windows and are disabled for other windows. Other commands are accessed with a right-click the graphical objects (spectrum, Element stick), on the background or on the axis.

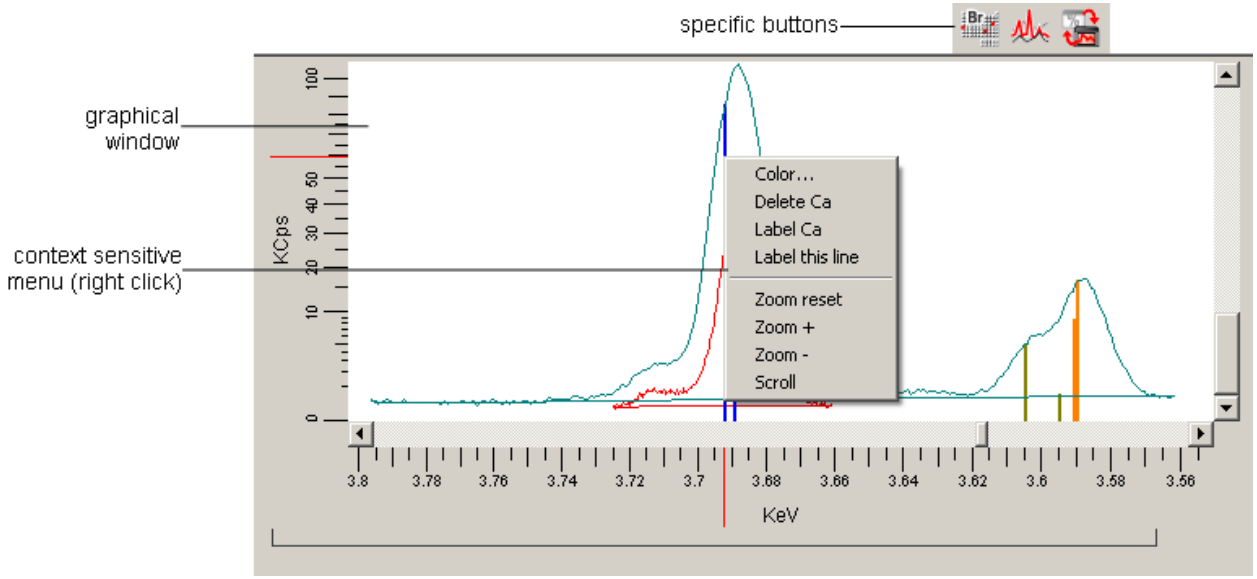


Fig. 2-3 Quali window

See also

- section 5.2: "Creation of a Quali window and import of a spectrum"

Organizing the windows

EVAL2 uses "floating" windows for the most useful dialog boxes, i.e.

- for a quantitative evaluation (with a Quant window): the Sample Properties and the Evaluation Methods dialog boxes;
- for a qualitative evaluation or the graphical display (with a Quali window): the XRF Lines dialog box.

It is possible to display and hide these windows at will, with the corresponding buttons or with the commands of the **View** menu. But it is also possible to keep them always onscreen, besides the main EVAL2 window; mind in this case that it is recommended to hide the windows of other programs, or the windows from the different programs may hide each others'. This all depends on your habits and on the size and resolution of your screen.

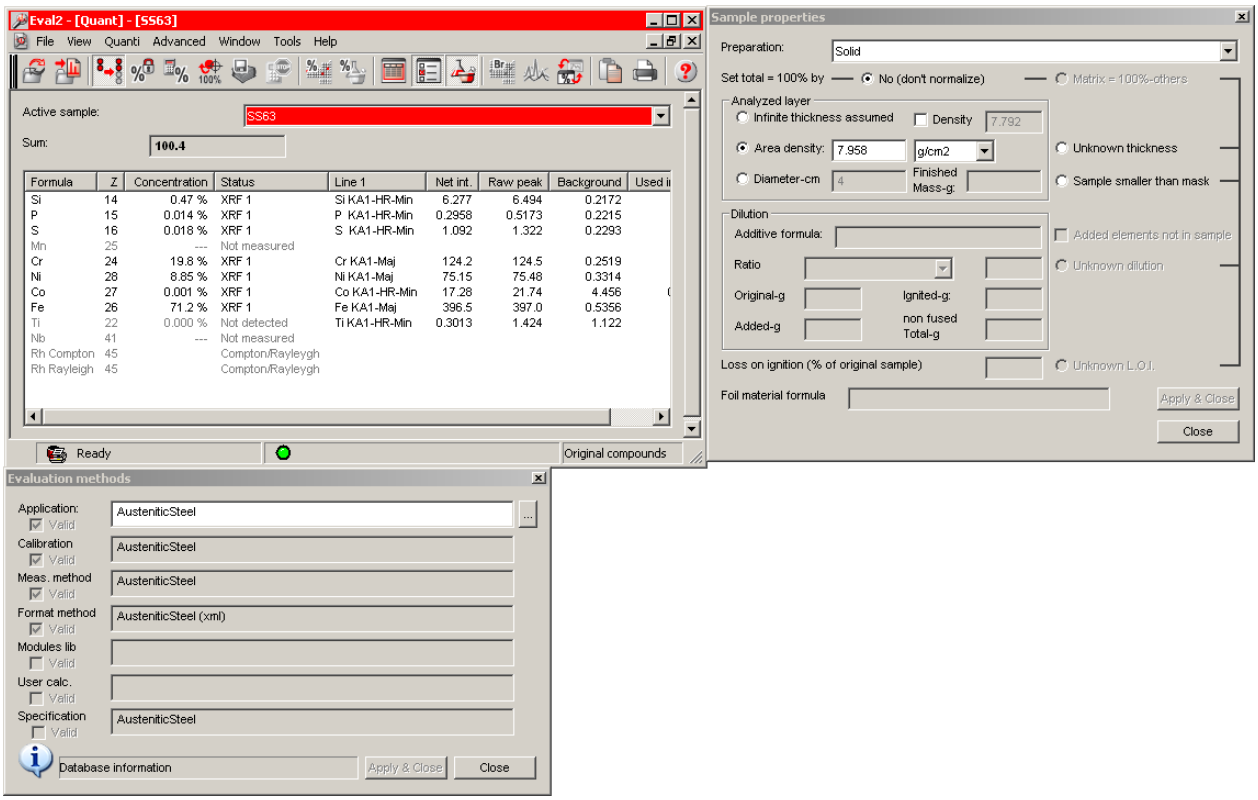


Fig. 2-4 Example of the organization of the screen with a Quant window and Sample Properties and Evaluation Methods floating windows

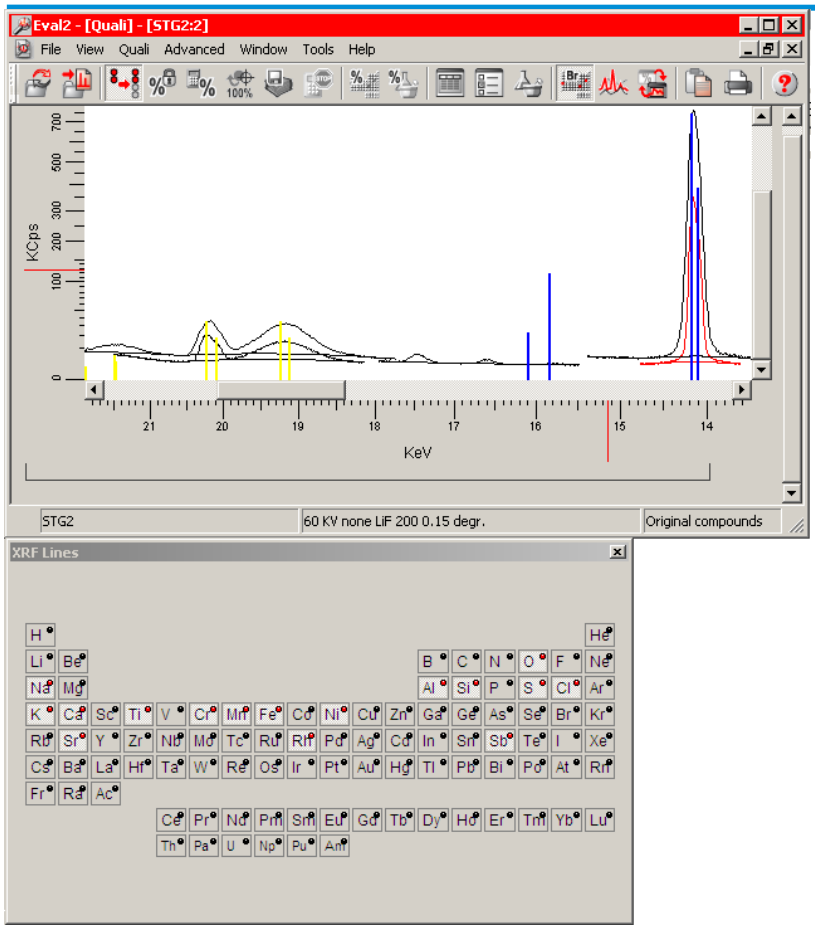


Fig. 2-5 Example of the organization of the screen with a Quali window and the XRF Lines floating window

3. Importing a sample

3.1. How to import a sample

The first operation to perform is to import a sample, i.e. the SSD file corresponding to the measurement. When EVAL2 is opened by the SPECTRA EDX LAUNCHER, it automatically displays the Select Sample(s) for Evaluation dialog box; otherwise:

Import raw data and **Next document** button

- click the **Import raw data** or **Next document** button
  — or —
  use the **Import raw data/Next document** option in the **File** menu.

There are two import buttons and two import options:

- **Import raw data**,  : this button permits to overlay the scans of different samples. It is useful for graphical work and overlay features;
- **Next document**,  : remove the former SSD file and replace it by the new one.

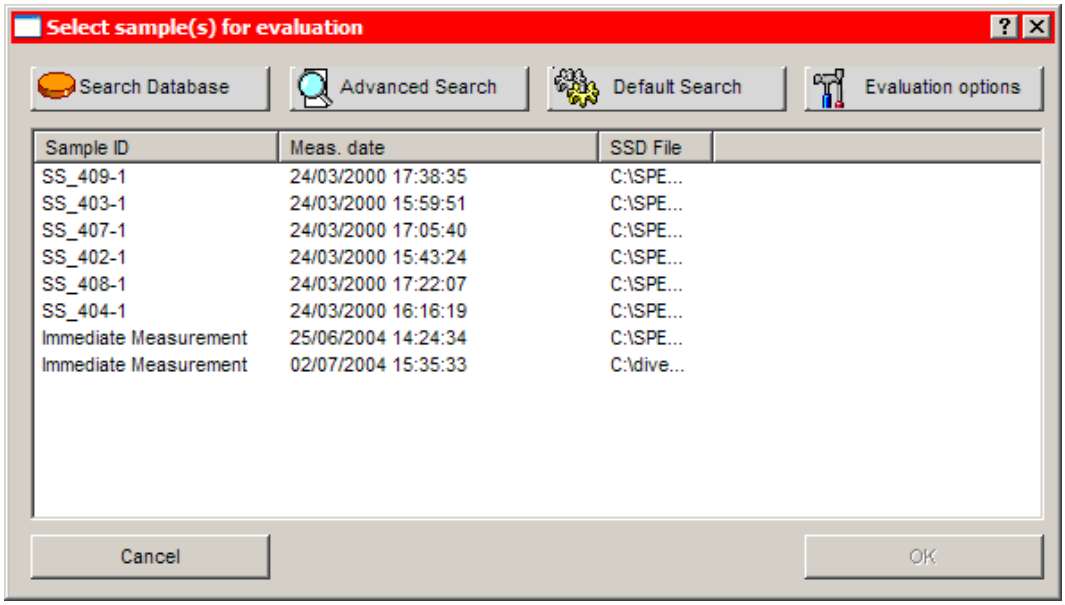


Fig. 3-1 Select Sample(s) for Evaluation dialog box

When the sample of interest is displayed in the list, click its line and then **OK**, or, if the evaluation was launched from the SPECTRA EDX Launcher, with the **Interactive quant** or the **Interactive quali** button.

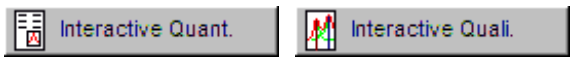


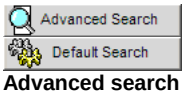
*Fig. 3-2 **Interactive quant** and **Interactive quali** buttons in the Select Sample(s) for Evaluation window, when EVAL2 is launched from the SPECTRA EDX Launcher*

If you want to modify first the evaluation parameters (change the calibration file, the preparation or fix a parameter), click the **Evaluation option** button.It is also recommended to click this button to check the evaluation parameters any time you evaluate a sample.

When it does not appear in the list, you can set different options to retrieve it: click **Advanced search**.

Display option

You can set which columns are displayed in the Sample list. For this:



Advanced search or **Default search** buttons

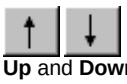
1. click **Advanced search** or **Default search**;
2. in the Advanced Search or the Default Search Option dialog box, click the **Sample list columns** button;
   this displays the Select Samples List Column dialog box; the names of the columns of the Samples list are listed in the right list, in the same order as the display; the parameters, that are available but not displayed, are in the left list;


Add button

3. to add a column to the display, click the name of the column in the left list and click the **Add** button;


Remove button

4. to remove a column to the display, click the name of the column in the right list and click the **Remove** button;


Up and **Down** buttons

5. to change the order of the column, click the name of the column of interest on the right list, and click the **Up** or **Down** button.
6. click **OK**.

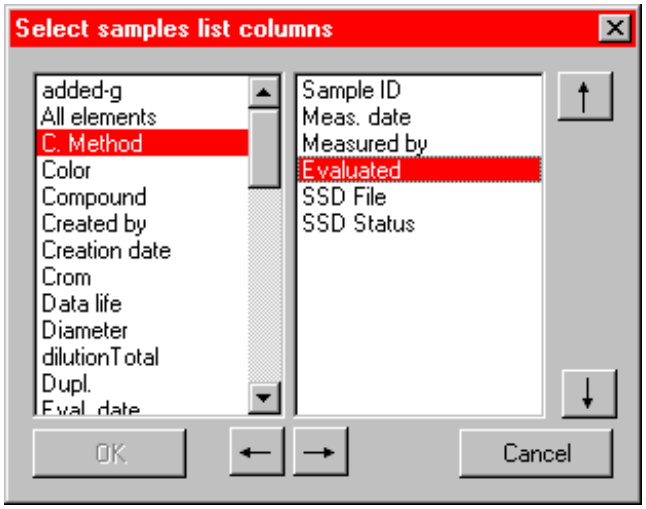
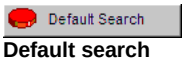


Fig. 3-3 Select Samples List Columns dialog box

Error at the import

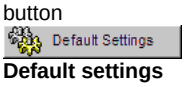
The SSD file is retrieved through it path and name in the Results database. If the SSD file was moved, deleted, or its name changed, a "SSD file not found" error message appears in the Status bar and most commands are disabled.

3.2. 3.2 Search options



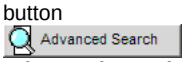
Default search button

When the **Default search** button is used, EVAL2 searches in the Results database for samples that match criteria. These criteria can be set with two dialog boxes:



Default settings button

- the Default Search Options dialog box: it is displayed when you click **Default settings**; the criteria are used by default for all queries;



Advanced search button

- the Advanced Search dialog box: it is displayed when you click the **Advanced search** button; this dialog box allows setting the search options for one single search only.

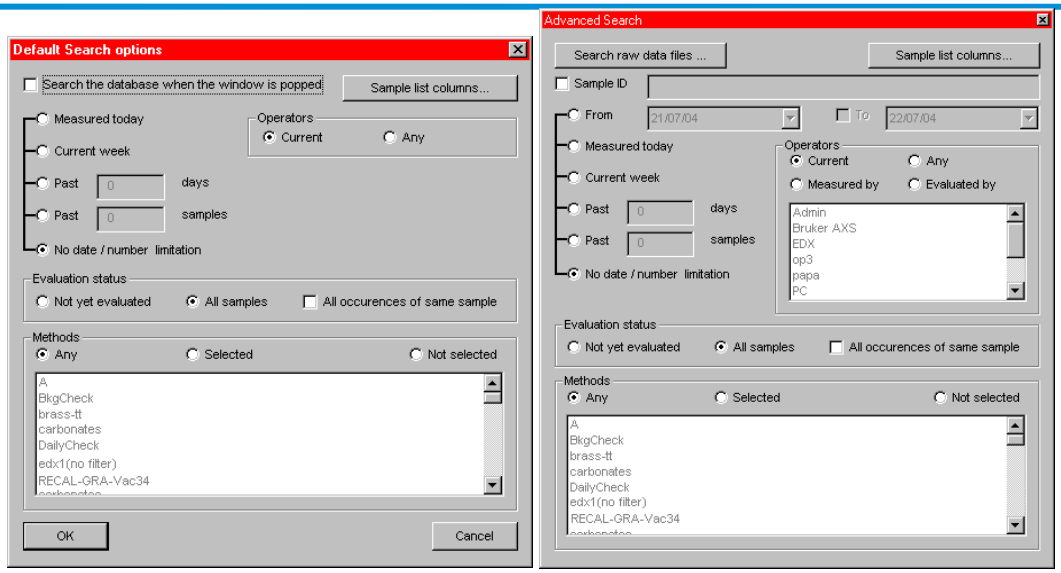
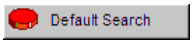


Fig. 3-4 Default Search Option and Advanced Search dialog boxes

To set the default search criteria

Default settings button

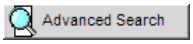
7. display the Select Sample(s) for Evaluation dialog box (see the section 3.1 "How to import a sample");
8. click the **Default settings** button; this displays the Default Search Options dialog box;
9. change the options;
10. click **OK**.



Default search button

These options will be used when clicking the **Default search** button.

To set specific search criteria for a single search



Advanced search button

11. display the Select Sample(s) for Evaluation dialog box (see section 3.1 "How to import a sample");
12. click the **Advanced search** button; this displays the Advanced Search dialog box;
13. change the options;
14. click **Apply and Close**.

Description of the search options

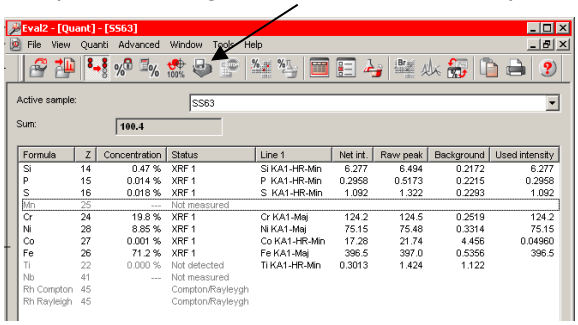
The following options are used to search in the Results database (Measure.MDB). The same options appear in the Default Search and in the Advanced Search Options dialog box.

A single sample can be displayed several times:

- if it was measured several times (with the same sample name);

Save results button

- if it was interactively evaluated; there is then one result for the automatic evaluation (at the completion of the measurement), and one for every interactive evaluation (when clicking the **Save results** button).

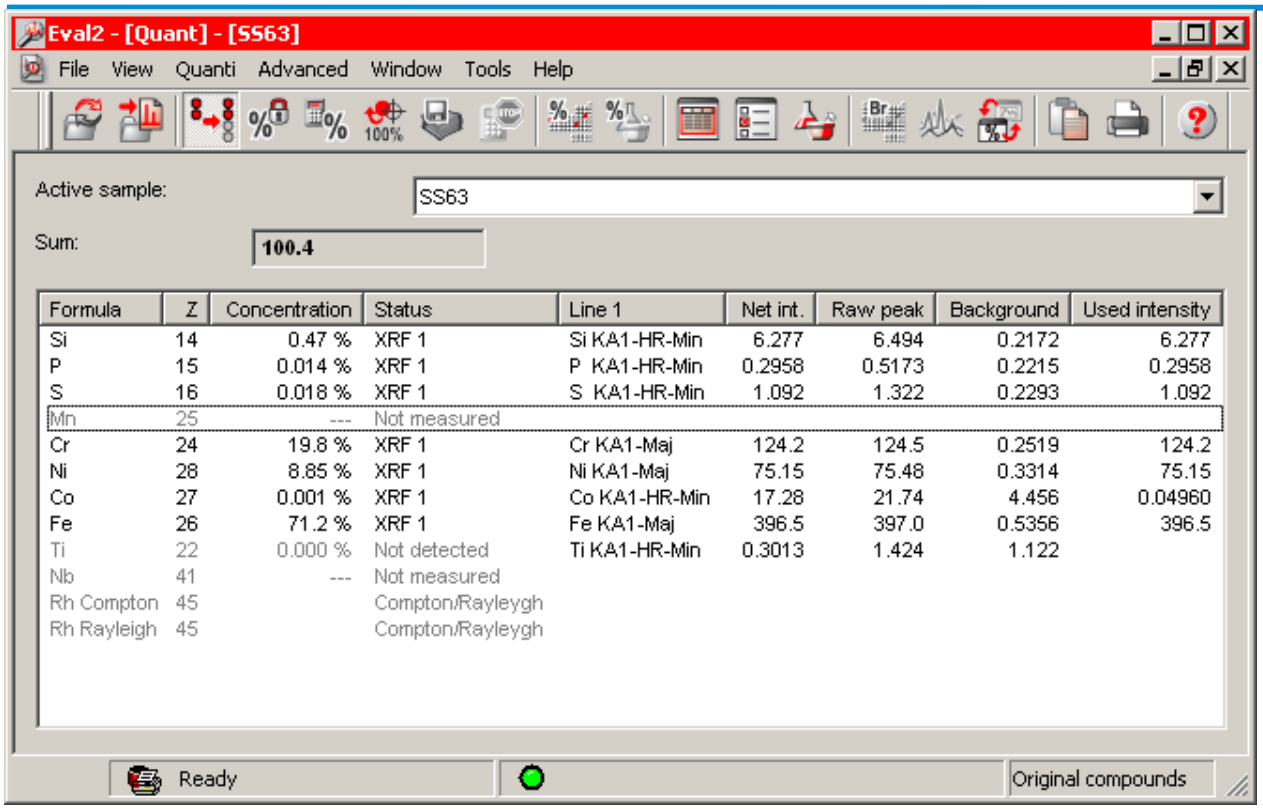


Option	Description
Date	sort the measurements by date; five options are available: • **Measured today**: only the samples measured the current day • **Current week**: only the samples measured the current week • **Past *x* days**: only the samples measured in the last *x* day • **Past *x* samples**: only the *x* last samples • **No date/number limitation**: the samples are not sorted by date
Operator	select only the samples measured or evaluated by a given operator (this is the login name of the SPECTRA EDX Login); there are four options: • **Current**: sample measured or evaluated by yourself • **Measured by**: in the list, choose the operator that was logged when the measurement was performed • **Evaluated by**: in the list, choose the operator that was logged when the interactive evaluation was performed • **Any**: the samples are not sorted by operator
Evaluation status	whether the sample was evaluated • **Not yet evaluated**: • **All samples**: • **All occurrences of the same sample**
Applications	name of the application (EVM file)

4. Quantitative evaluation

The aim of the quantitative evaluation is to compute the concentrations from the measured spectra, using a calibration (default calibration in case of a standardless method). In EVAL2, it is possible to adjust some parameters, i.e. to change interactively the application.

The quantitative evaluation is performed in a Quant window (see section 2.3.1).



Formula	Z	Concentration	Status	Line 1	Net int.	Raw peak	Background	Used intensity
Si	14	0.47 %	XRF 1	Si KA1-HR-Min	6.277	6.494	0.2172	6.277
P	15	0.014 %	XRF 1	P KA1-HR-Min	0.2958	0.5173	0.2215	0.2958
S	16	0.018 %	XRF 1	S KA1-HR-Min	1.092	1.322	0.2293	1.092
Mn	25	---	Not measured					
Cr	24	19.8 %	XRF 1	Cr KA1-Maj	124.2	124.5	0.2519	124.2
Ni	28	8.85 %	XRF 1	Ni KA1-Maj	75.15	75.48	0.3314	75.15
Co	27	0.001 %	XRF 1	Co KA1-HR-Min	17.28	21.74	4.456	0.04960
Fe	26	71.2 %	XRF 1	Fe KA1-Maj	396.5	397.0	0.5356	396.5
Ti	22	0.000 %	Not detected	Ti KA1-HR-Min	0.3013	1.424	1.122	
Nb	41	---	Not measured					
Rh Compton	45		Compton/Rayleygh					
Rh Rayleigh	45		Compton/Rayleygh					

Fig. 4-1 Quant window

4.1. Principles of the evaluation

This section gives an overview of the general principles of the evaluation, to show the integration of these concepts in EVAL2. Please refer to appropriate literature for details.

Concentrations, intensities and matrix effects (theoretical background)

When an atom is excited by an incident X-ray photon, its de-excitation emits an X-ray photon (or an Auger electron, especially for the light elements) with a specific energy; this emitted photon is called "fluorescent photon", and the energy is called the "specific line". The energy of the specific line only depends on the type of atom; each element can emit several lines. The rate of photon that is detected by the spectrometer depends on:

- the rate of incident photon that strike the atom,
  - reduced by the absorption by the sample (primary absorption);
  - enhanced by the lines emitted by the neighboring atoms (over-excitation or secondary fluorescence);
- the absorption by the sample of the emitted photons on their way out (secondary absorption.)

The intensity of a line thus depends not only on the concentration of the atoms that emit the line, but also on the concentration of other atoms (absorption and secondary fluorescence). These effects are called the "matrix effects".

This can be summed up by the Lachance-Traill formula (1966):

$$I_i = m_i \cdot c_i \times \left(1 + \sum_{j \neq i} \alpha_{ij} \cdot c_j\right)$$

in which

- i is the element of interest, c_i is its concentration and I_i is the measured intensity of the line of i used for the evaluation;
- m_i is the calibration coefficient for the considered line;
- the c_j are the concentrations of the other elements j;
- α_{ij} is an integral expression that depends on all the concentrations, and that represents the influence of j on the intensity measured for i; it is called "inter-element coefficient" or "matrix coefficient".

This formula is derived from the Sherman's equation (1955).

It is easy to compute the intensities knowing the concentrations, but the contrary requires

- either to consider that the alpha coefficients are fixed; this is the "Fixed Alphas" method;
- or to use an iterative calculation algorithm; this is the "Variable Alphas" method.

The Variable Alphas method computes the alpha coefficients from the concentrations (estimated by the previous iteration) and from the fundamental parameters (absorption coefficients, fluorescence yield…).

The basic equation to calculate the concentrations from the measured intensities is:

$$C_i = A0 + A1 \times I \times (1 + \sum_{i \neq j} \alpha_{ij} \times C_j)$$

in which

- C_i is the element concentration and I the measured intensity of the corresponding line;
- the C_j are the concentrations of the other elements j;
- $A0$ and $A1$ are the coefficients of the calibration regression line, respectively offset and slope. They are stored either in the Line library if a default calibration is used or in the calibration file if a specific calibration is used;
- α_{ij} are the interelement matrix coefficients. They can be calculated “theoretically” based on “fundamental” physical values like absorption coefficients and secondary fluorescence enhancement

This a simplified model of the physical reality.

The calculations are performed as follows:

- Step 1:

$$C = A0 + A1 \times I$$

- Step 2:

$$C_i = A0 + A1 \times I \times (1 + \sum_{i \neq j} \alpha_{ij} \times C_j)$$

And so on! The iteration cycles are performed as long as the compared iteration steps are below a given value.

Evaluation of the intensities

The spectrometer records a "number of counts" N versus 2θ, the position of the detector. This 2θ position can be converted in the wavelength λ of the radiation with the Bragg's law, and in the energy the photons E (the energy of the photons and the wavelength of the radiation are linked by the Planck's constant).

The number of counts is assumed to be proportional to the number of photons (linearity of the detector); the proportionality factor determines the sensitivity of the spectrometer for a given energy. The number of counts is divided by the measurement time t to give the count rate I, or intensity.

A spectral line is represented by a peak in the (2θ,I) diagram (spectrum). The intensity is normally the net height (i.e. gross peak height minus background height); in some cases, the gross height can be used.

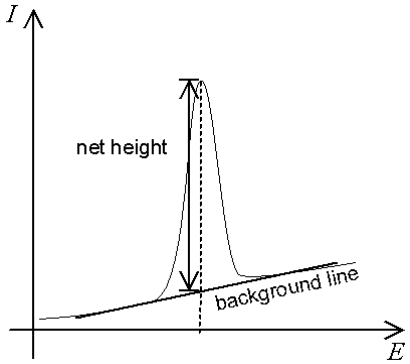


Fig. 4-2 Evaluation of the intensity by the net height

The peak and background can be determined in two ways:

- when the sample is measured in fixed position, one point gives the gross height, and one r several points give the background level;
- when the sample is measured in scan mode, a parabola is adjusted (fitting) to the peak to determine the gross height, and the background level is determined by a polynomial.

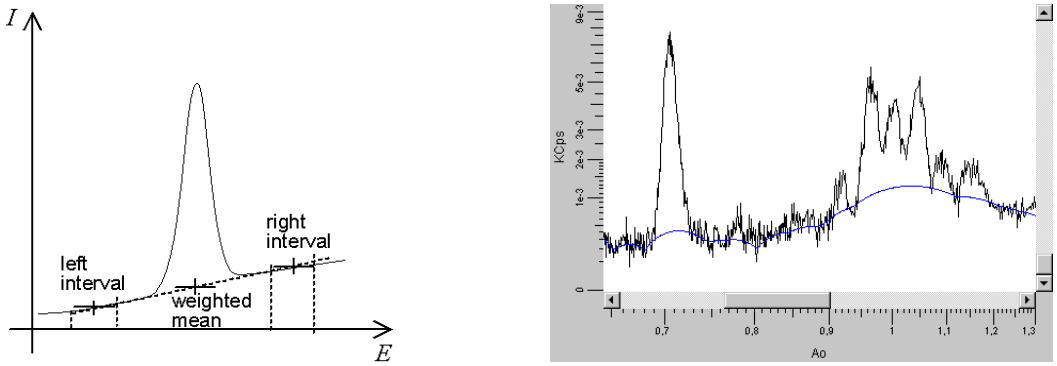


Fig. 4-3 Models for the determination of the background level: fixed position (left) and fitting of a polynomial (right)

The model that is used depends on the measurement method (MM file).

The application (EVM file)

Application icon

The application is a set of parameters used for the evaluation of unknown samples. It is stored in an EVM file, created by APPLICATION SETUP, usually at the **Evaluation model** step of APPLICATION WIZARD.

An application consists of:

- a "collection" of files:
  - in case of a user-made calibration: a calibration file (FCL file), created with APPLICATION WIZARD;
  - in case of a precalibrated method: a measurement method (MM file), created with S2 MEASMETHOD
  - a format method (WZM file), created with the Result Manager (QUERY RES), usually at the Results formatting step of APPLICATION WIZARD; this defines the way the results are displayed and printed;
  - possibly a module file (MLB file), i.e. calculations made from the concentrations, created with MODULES;
  - possibly a user batch (BAT file) or script (VBS, JS… file) for additional operation (e.g. writing the results in a user database); this batch or script is executed at the completion of an automatic evaluation (e.g. at the end of the measurement), or when saving the results in the Results database in EVAL2;
- a list of parameters:
  - the preparation: this defines the additive (e.g. flux, wax, solvent…) that modify the matrix effects and dilute the sample, the absorption by the polymer foil for liquid or powder samples, the loss on ignition (LOI) for fused samples, the sample thickness and density to take the analyzed thickness into account…
  - fixed concentrations;
  - matrix compound, i.e. compound evaluated by balance to 100% from the other compounds instead of an evaluation with its XRF lines;
  - calculation options: neglecting low intensity lines or low concentration compounds, optimizing a sample characteristic (sum of all concentrations equal to 100%) by adjusting a sample parameter (dilution, thickness, a given concentration);
  - iteration parameters: maximum number of iterations, variation of concentrations between two iterations below which the result is considered as stable…
  - specification: conditions on concentrations a sample should meet (out of range concentrations can be highlighted on the display or printout).

Preparation: foil, dilution and loss on ignition

The preparation is the procedure that transforms the raw material into a measurable sample. There are four types of preparation:

- solid (no preparation): the material is measured without any preparation;
- pressed pellets: the material is a powder that is mixed with a binder (e.g. wax, cellulose…) and that is pressed to form the measurable sample;

- liquid or powder: the material is a liquid or powder that is poured on a polymer film, or foil; if it is a liquid, it may be diluted;
- fused bead: the material is dissolved in a flux to form a homogeneous glass sample.

The preparation must be declared for five reasons:

1. when a compound is added, it does not belong to the original material, so it must be subtracted from the results, but it must be taken into account for the matrix effects;
2. the additive dilutes the original material, so the final result must be corrected to display the concentrations in the original material;
3. the foil absorbs the X-rays, so the intensities must be corrected before the calculation, it is therefore necessary to know the type of material of the foil (.e.g. polypropylene, Mylar, Prolene…), its density and its thickness;
4. when a sample is heated (fused bead), some material can be volatile or form a volatile oxide, this is the loss on ignition (LOI); the software corrects this effect and displays the concentrations in the original material (i.e. before fusion);
5. when the sample is thin compared to the analyzed thickness, the intensity changes with the thickness; this thickness effect must be taken into account.

When the raw material is mixed with an additive, the mass of raw material is **Original-g**, the mass of additive is **Added-g**, and the mass of the final sample is **Finished Mass-g**:

Original-g + Added-g = Finished Mass-g.

When the dilution is expressed by the ratio a of additive (i.e. Added-g/Original-g), then the concentration $C_{i\,orig}$ of the element i in the sample is linked with the concentration $C_{i\,prep}$ in the prepared sample by the formula:

$$C_{i\,orig} = (1+a)\cdot C_{i\,prep}$$

and

$$a = \frac{1}{\sum_i C_{i\,prep}} - 1$$

the program first computes the $C_{i\,prep}$ concentrations, then transforms them into the $C_{i\,orig}$ for the display.

When a sample is fused, there are two ways to compute the LOI:

- by measuring the mass lost during the calcination of the raw material; the mass of raw material is **Original-g**, the mass of calcinated raw material is **Ignited-g**, and the LOI is:
  LOI = 1 - Ignited-g/Original-g
- by comparing the mass of the sample before and after fusion; the mass before fusion is **Non-fused Total-g** (it is the sum of the raw material mass and of the flux mass), the mass of the measured sample is **Finished Mass-g**, and the LOI is
  LOI = 1 - (Finished Mass-g - Added-g)/Original-g

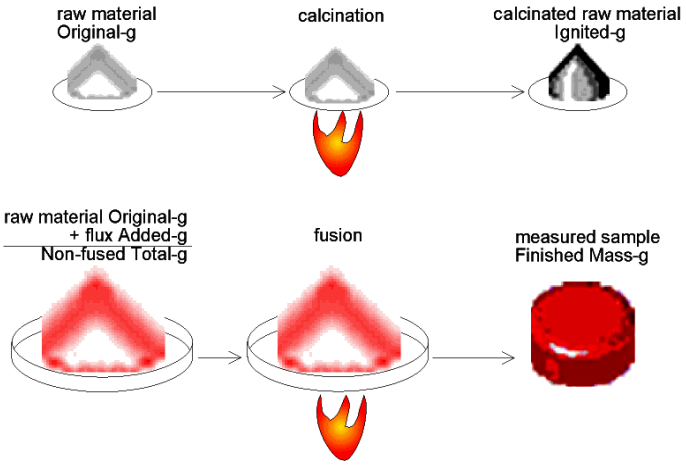


Fig. 4-4 Two ways of calculating the loss on ignition

When a_0 is the nominal ratio of additive (i.e. Added-g/Original-g), then the real ratio of additive a (Added-g/Ignited-g) is linked to the LOI by

$$a = a_0 /(1\text{-LOI})$$

By default, the concentrations displayed in the result are those in the original material, without any preparation (i.e. before addition, dilution, mixing or fusion). It is also possible to display the concentrations of the elements in the measured sample, these are the "prepared elements concentrations".

Optimization: adjusting the sample parameters

When samples parameters, such as the thickness, the sample diameter… are likely to vary, it is possible to let the calculation algorithm adjust them, provided the matrix correction is performed with the Variable Alphas method: these sample parameters are taken into account for the calculation of the concentrations. As the number of equations must always be equal or greater than the number of parameters, EVAL2 uses the fact that the sum of all concentrations must be equal to 100% . This adjustment is called "optimization".

4.2. Performing the first evaluation

Prerequisites

To perform an interactive quantitative evaluation, it is necessary to have an application (EVM file) adapted to the evaluation that will be performed, i.e. using the right method (peak/background or spectrum), see the APPLICATION SETUP manual for more details. The other parameters (such as the calibration, the preparation, the fixed concentrations…) can be changed interactively.

The first steps consist in:

- creating an EVAL2 new document or opening an existing EVAL2 document (see the section 2.2.2 "Managing documents");
- importing a measurement (see the section 3 "Importing a sample").

Choosing the initial application

Warning:	When clicking **Apply**, this changes the parameters in the Results database, i.e. the evaluation parameters that were chosen become the default evaluation parameters. If the sample was evaluated before, EVAL2 works on a copy of it so the original record of the database is not modified. If the sample has never been evaluated, EVAL2 modifies the original record. If you do not want to change the records of the database, see the section 4.3 "Adjusting the parameters".

The default application (EVM file) is the same one used for the original measurement (as defined in the LOADER). EVAL2 knows which application was used because the system stores this information in the Results database (Measure.MDB).

The application to be used can be changed at import of the sample in EVAL2:

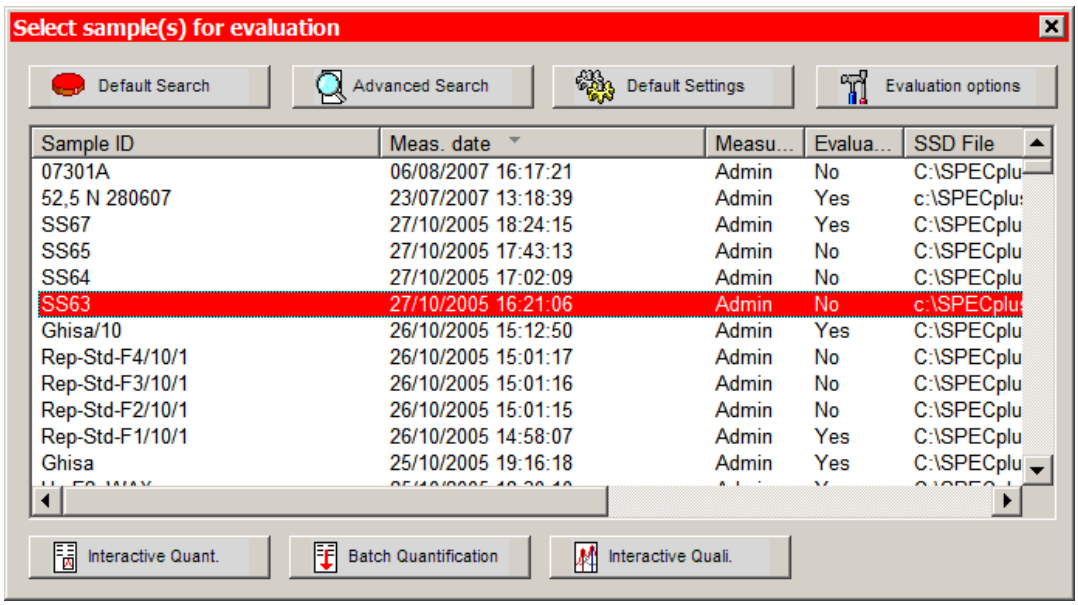
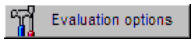


Fig. 4-5 Selection of the sample to be imported



Evaluation options button

1. In the Select Sample(s) for Evaluation dialog box, select the sample of interest;
2. Click the **Evaluation options** button;

3. In the Advanced evaluation Option dialog box that appears, check the **Force calibration** box;
4. Use the corresponding **Browse** button to retrieve the EVM file of interest;
5. Click **Apply**.

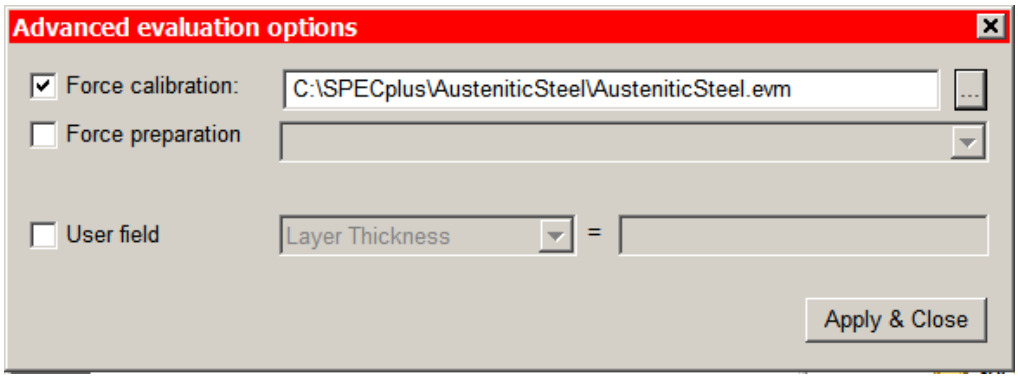


Fig. 4-6 Choosing another EVM file

It is also possible to simply change the evaluation parameters, without changing EVM file referenced in the Results database. It is possible to:

Browse button

- use different calibration than the one defined in the default application:
  1. check the **Force calibration** box;
  2. click the **Browse** button;
  3. in the **File of type** drop-down list, select **Calibration files** for a user-made calibration (FCL file) or **Measurement method files** (MM file) for a standardless evaluation;
  4. browse to the file of interest, then click **Open**;
- use a different preparation than the one defined in the default application:
  1. check the **Force preparation** box,
  2. select the new preparation in the drop-down list;
- use different sample specific parameters
  these parameters are defined by the user at the measurement; these adjustable parameters depend on the method and can be the sample size, the loss on ignition…
  1. check the **User field** box;
  2. select the parameter in the drop-down list;
  3. type the value in the text box.

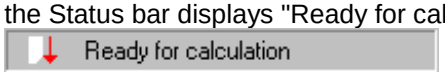
Launching the first evaluation

Once a sample is imported (see section 3 "Importing a sample") and the application is defined (see above), it is possible to start the evaluation.

The first calculation is made in two steps:

Initialize button

- initialize the calculation, with the **Initialize** command of the **Quanti** menu,
  — or —
  with the **Initialize** button;
  the Status bar displays "Ready for calculation";

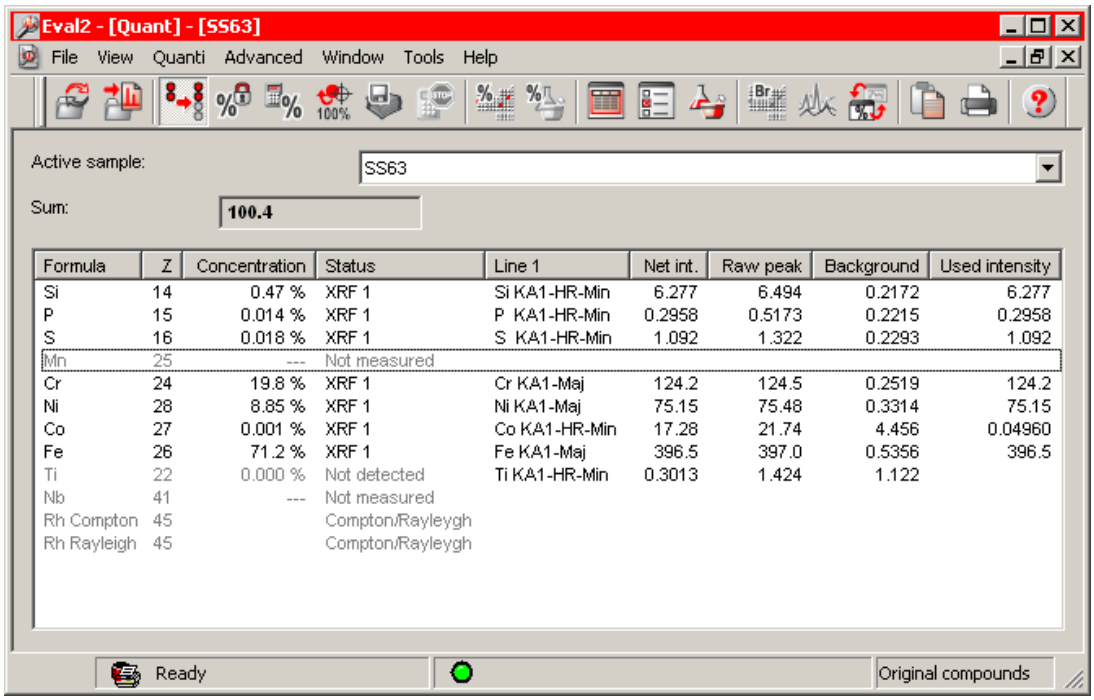


Compute concentrations button

- launch the calculation with the **Compute** command of the **Quanti** menu
  — or —
  click the **Compute concentrations** button;

Stop calculation button

- if you want to interrupt the calculation (when it lasts a long time), press the **Stop calculation** button. As the calculation is not completed, it will not be possible to print or save it.



The results are displayed in the Quant window (see section 2.3.1 "The Quant windows").

Fig. 4-7 Quant window with the results of the evaluation

Note:	The initialization and the first computation can be performed automatically at the import. For this: open the Quantitative Options dialog box (**Tools | Options**), and in the **Calculation** tab, check the two options.

4.3. Adjusting the parameters

Several parameters can be interactively set to adjust the evaluation.

How to change the application

Warning:	When the EVAL2 document is saved, the parameters are modified in the Results database, i.e. the evaluation parameters that were chosen become the default evaluation parameters. If the sample was evaluated before, EVAL2 works on a copy of it; the original record of the database is thus not modified. If the sample has never been evaluated, EVAL2 modifies the original record. Do not save the EVAL2 document if you do not want to modify the Results database.

To change an application:

Toggle method bar button

Browse button

Close button

1. when the Evaluation Methods dialog box is not on screen: choose the **Evaluation methods** command of the **View** menu
   — or —
   click the **Toggle method bar** button;
2. click the **Browse** button at the right of a file's text box to select a new file;
3. if you want to remove the Evaluation Methods dialog box from the display, click the **Close** button.

   — or —
   click again on the **Toggle method bar** button.

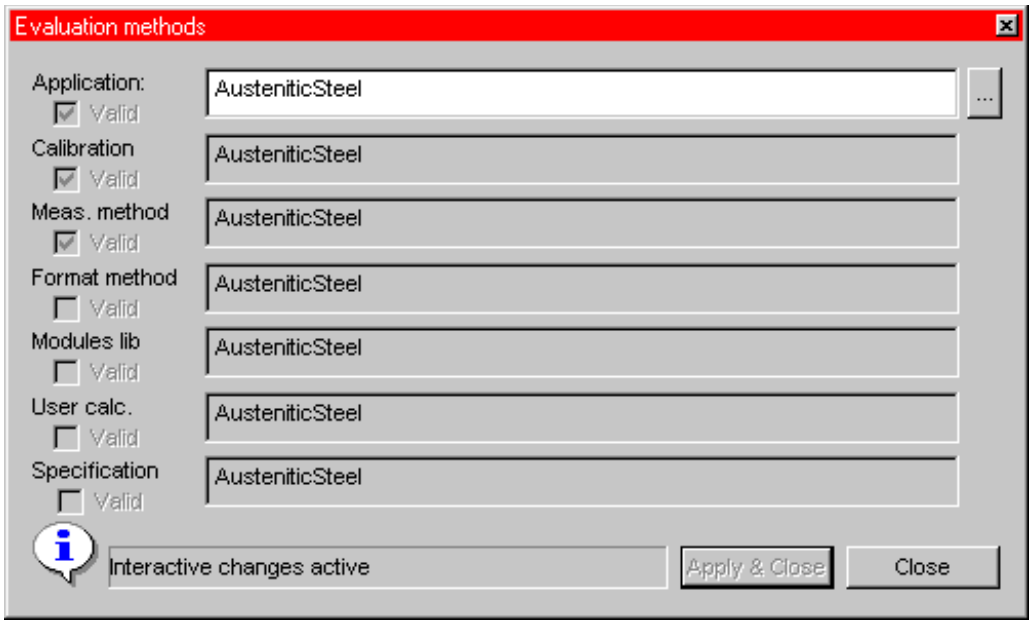


Fig. 4-8 The Evaluation Methods dialog box

How to change the sample properties

To display the Sample Properties dialog box:

Toggle sample properties button

- choose the **Sample properties** command in the **View** menu
  — or —
  click the **Toggle sample properties** button.

It is then possible to:

- change the preparation:
  select the new one in the **Preparation** drop-down list;
- change the parameters of the current preparation (for this evaluation only, this does not change the preparation in the Materials database):
  choose the options and edit the text boxes.

Parameter	Description and options
Analyzed layer	• Infinite thickness assumed: the sample thickness is greater then the analyzed thickness for every line; • Area density: the sample does not have an infinite thickness for every lines; the "thin sample" effect is determined with the area density, i.e. the mass of the sample divided by the analyzed area (in g/cm^2); • Diameter/Finished mass: the sample does not have an infinite thickness for every lines; the "thin sample" effect is determined with the diameter of the sample (in cm, assuming a cylinder) and its mass (in g).
Additive formula	chemical formula of the additive (see the section 4.1.3 Preparation: foil, dilution and loss on ignition). • **Added element not in sample**: when this box is checked, the elements contained in the additive are forced to 0
Ratio	dilution of the original material, expressed by the ratio between one of the following mass (see the section 4.1.3 Preparation: foil, dilution and loss on ignition): • **Additive**: mass of added material (Added-g); • **Original**: initial mass of sample, before preparation (Original-g); • **Total**: final mass of sample, i.e. Original + Additive (Finished Mass-g); Choose the ratio in the drop-down list and its value in the text box — or — type the initial mass of sample in the **Original-g** text box, ad the mass of additive in the **Added-g** text box.
Loss on ignition	for a Fused bead preparation only (see the section 4.1.3 Preparation: foil, dilution and loss on ignition): • **Ignited-g** is the mass of original sample, after calcination; • **Non-fused Total-g** is the mass of uncalcinated sample+flux before the fusion; • **Loss on ignition (% of original sample)** is the LOI

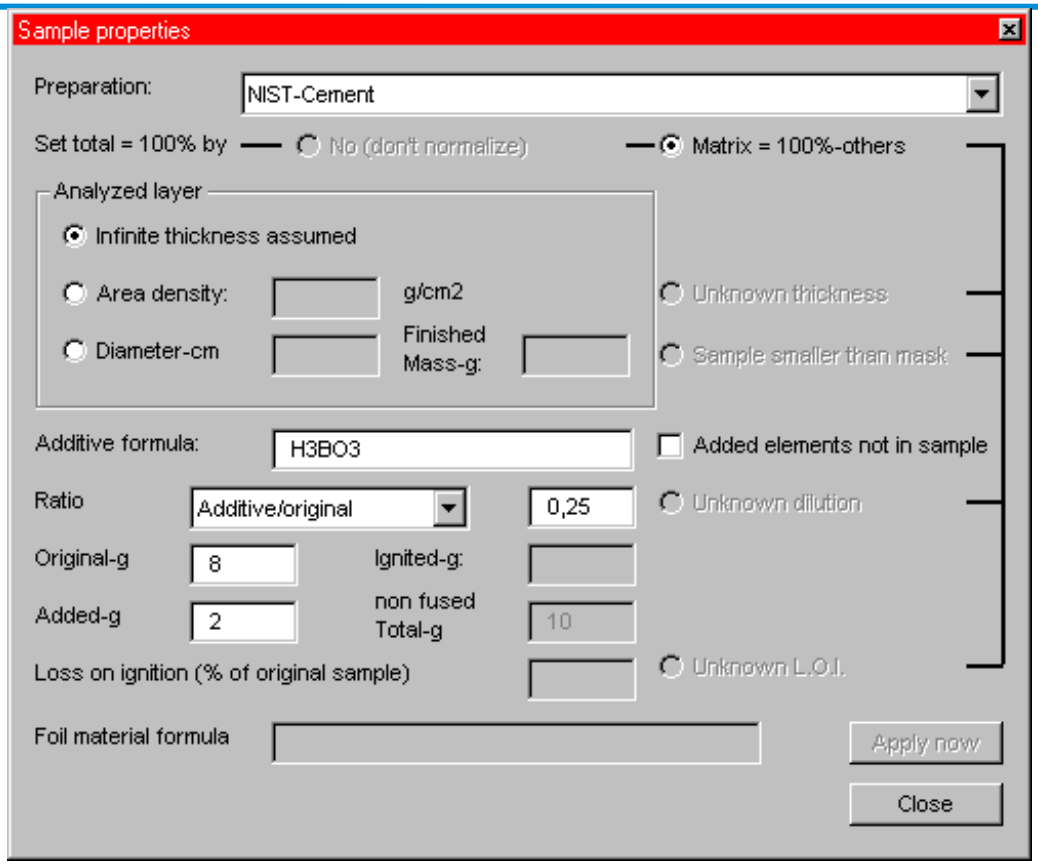


Fig. 4-9 Sample Properties dialog box: adjusting the sample parameters

4.3.3 How to change the optimizations (automatic adjustment of sample parameters)

The optimization options are in the Sample Properties box (see figure 4-9). To display this box:

Toggle sample properties button

- choose the **Sample properties** command in the **View** menu
  — or —
  click the **Toggle sample properties** button.

The available options depend on the application:

- when a matrix is defined (compound evaluated by balance to 100%), no other optimization is possible;
- the **Sample smaller than mask** option is not available for liquid samples;
- the **Unknown dilution** option is available only when an additive is defined;
- the **Unknown L.O.I.** option is only available for fused beads.

Option	Description
No (don't normalize)	no normalization is performed, the sum of all concentrations can be different from 100%
Matrix = 100%-others	one of the compounds is evaluated by balance to 100%
Unknown thickness	when the sum of all concentrations exceeds 100%, the thickness is decreased; it is increased when the sum is below 100%
Sample smaller than mask	when the sum of all concentrations is below 100%, all the intensities are multiplied by a common factor
Unknown dilution	the amount of additive is adjusted so the sum of all concentrations (in the original material) is equal to 100% (this modifies the matrix effects)
Unknown L.O.I.	the LOI, and thus the real dilution, is adjusted so the sum of all concentrations (in the original material) is equal to 100%

4.3.4 How to set a concentration

It is possible to set a specific value to a concentration (e.g. when it is known by another analysis, or set to 0 when it is absent), or to define a specific way of calculation (e.g. choice of a given line or calculation by balance to 100%).

This choice can be made by a right-click the line of the compound in the Quant window (context-sensitive menu).

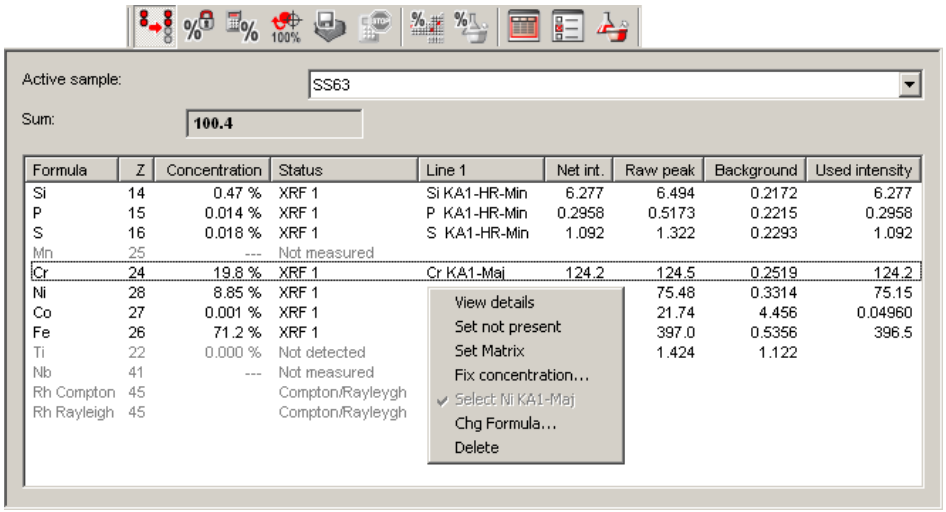


Fig. 4-10 Context-sensitive menu to set a concentration

Option	Description
Set not present	force the concentration to 0; it is displayed in red in the list
Set matrix	the compound is computed by balance to 100% from the sum of the other compounds; it is displayed in blue in the list
Fix concentration	the concentration is fixed to a value; it is displayed in red in the list
Select *line*	the concentration is evaluated using this line
Chg formula	change the chemical formula of the compound
Delete	removes the compound from the list; it does not appear even when the **Show all elements** option is selected

Adjustable display parameters

Choosing the columns of the Concentration table

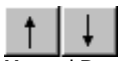
It is possible to define which data appear in the Concentration table. This does not influence the printout.

To change the columns:

Quant columns button

Add button

Remove button



Up and **Down** arrow buttons

- display the Select Quantitative Window Columns dialog box: select the **Quant columns** command in the **View** menu
  — or —
  click the **Quant columns** button;
- to add an element to the display: select this element in the left-side list, and then click the **Add** button;
- to remove an element from the display: select this element from the right-side list, and then click the **Remove** button;
- the order of the columns can be changed: click an element of the right-side list, then click the **Up** or **Down** arrow button;
- click **OK** to validate the changes, or on **Cancel** to discard them.

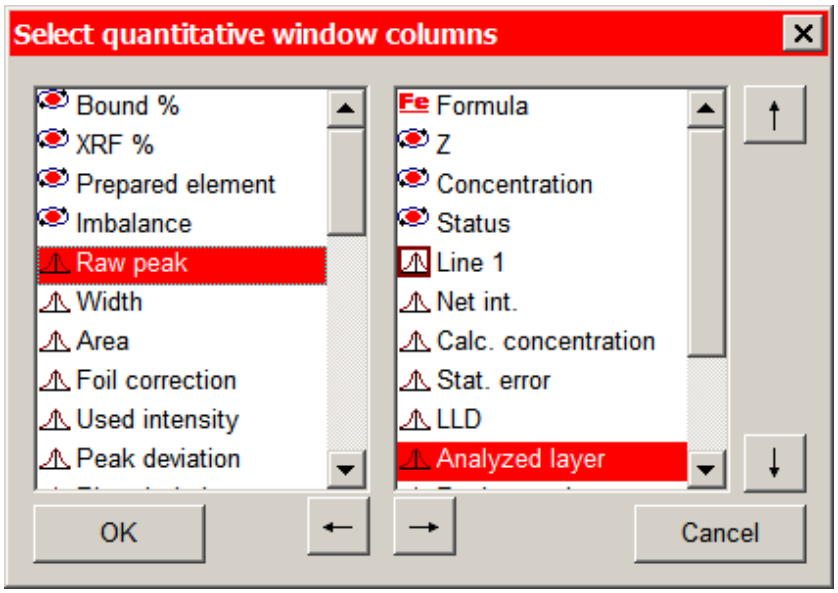


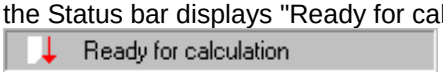
Fig. 4-11 Select Quantitative Window Columns dialog box

Launching the subsequent evaluations

Once the parameters have been modified, repeat the whole evaluation process, i.e.:

Initialize button

- initialize the calculation, with the **Initialize** command of the **Quanti** menu,
  — or —
  with the **Initialize** button;
  the Status bar displays "Ready for calculation";



Compute concentrations button

- launch the calculation with the **Compute** command of the **Quanti** menu
  — or —
  click the **Compute concentrations** button;

Stop calculation button

- if you want to interrupt the calculation (when it lasts e long time), press the **Stop calculation** button. As the calculation is not completed, it will not be possible to print or save it.

Note:	the calculation is launched directly after the initialization when the **Automatically run evaluation after successful initialization** option is checked (Qualitative Option dialog box, **Calculation** tab).

4.4. Saving and printing the quantitative results

If an error occurred during the computation, or if the computation was aborted, an error message is displayed in the Status bar and the **Save results** and **Print** commands are not available (the buttons are grayed).

Otherwise, once the result is calculated, the concentrations appear in black and the Status bar shows "ready".

Fig. 4-12 Status bar

Saving the results to the Results database

It is possible to save the result in the Results database (Measure.MDB); it can then be retrieved with the RESULTS MONITOR. For this:

Save results button

- choose the **Save results** command of the **Quanti** menu
  — or —
  click the **Save results** button.

When a batch (BAT file) or a script (VBS, JS… file) is defined in the application (EVM file), this batch or script is executed when saving the results in the database.

Copying the results to the clipboard

The results can be copied to the clipboard, as a table, and be pasted into another Windows®-based application (e.g. a spreadsheet).

To copy the results to the clipboard:

Copy button

- choose the **Copy to clipboard** command in the **Tool** menu
  — or —
  click the **Copy** button

Defining the printing style

The units and the number of decimal ciphers are defined by a WZM file. The other parameters of the WZM file (such as the character font and color) are not taken into account by EVAL2. To use all the features of the WZM, it is possible to print from the RESULTS MONITOR after the export of the results in the database (see above).

To declare a WZM file to the document:


Toggle method bar button

- when the Evaluation Methods dialog box is not on screen: choose the **Evaluation methods** command of the **View** menu
  — or —
  click the **Toggle method bar** button;


Browse button

- click the **Browse** button at the right of the **Format Method** text box to select a new WZM file;
  — or —
  to use the default formatting, clear the **Format Method** text box;


Close button

- if you want to remove the Evaluation Methods dialog box from the display, click the **Close** button,
- — or —
  click again on the **Evaluation Methods** button.

The general parameters, such as the page size and the layout (portrait or landscape) are defined in the Print Setup dialog box:

- choose the **Print Setup** command in the **File** menu.

Printing the results

To display a preview of the printout:

- choose the **Print Preview** command in the **File** menu.

To print the result:


Print button

- choose the **Print** command in the **File** menu
  — or —
  press the **CTRL+P** key combination
  — or —
  click the **Print** button.

The menu command and the key combination display the Print dialog box, where it is possible to choose the printer. The **Print** button directly starts the printing.

5. Graphical display and qualitative evaluation

The aim of the qualitative evaluation is to give the list of the detected elements (i.e. peaks above the detection limit), without any quantitative information (the concentration is not calculated).

The qualitative evaluation is performed in a Quali window (see section 2.3.2).

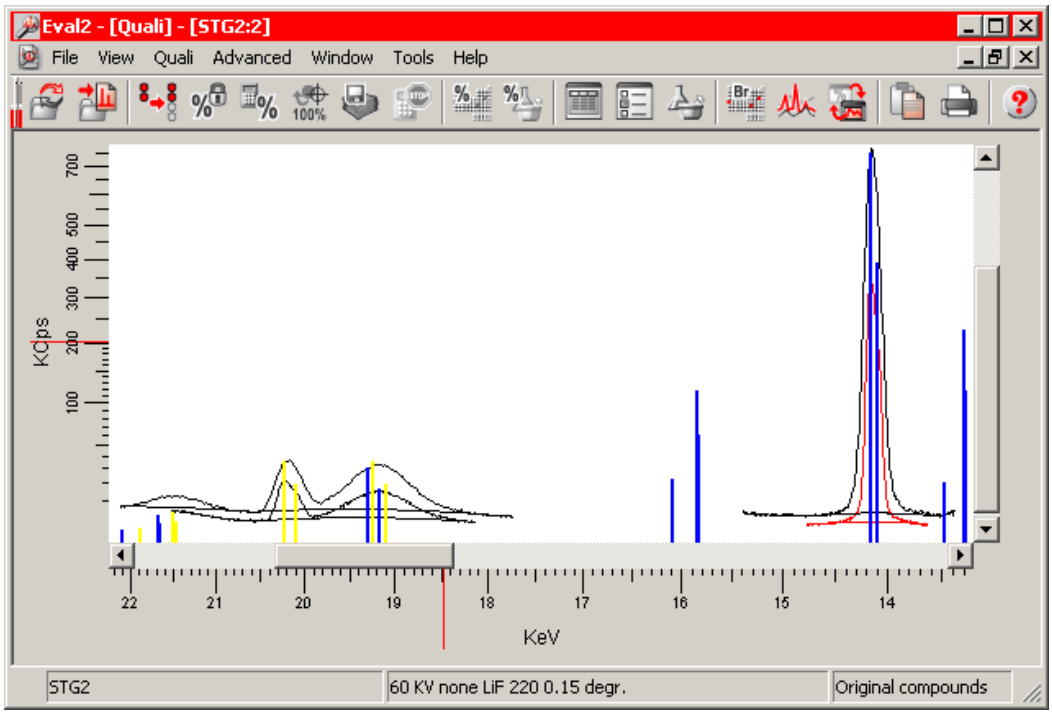


Fig. 5-1 Qualitative evaluation in a Quali window

5.1. Items of a Quali window

A Quali window is a composite document that can contain three types of objects: Ranges, Elements and Labels. As these words also have a general meaning, they are written with an upper case capital letter when they refer to the EVAL2 items.

Ranges

In a single run, a sample can be measured with different sets of parameters (tube high voltage, tube filter, detector parameters); in this case all the measurements are stored in a single SSD file.

When a single SSD file contains several measurements, each measurement is called a "Range". In the Quali window, each range is displayed as a separate curve.

To know more about Ranges, see:

- the section 5.5.3 "Color of a Range"

Elements

An Element is the set of spectral lines that are emitted by the chemical element. The spectral lines of the Element are displayed as sticks on the graphic.

The positions of the sticks correspond to the energy of the lines. The heights of the sticks are automatically adjusted to the graphical display of the Ranges. The height of the sticks can then be adjusted manually, but the relative height remains the same for the sticks of the same Element.

To know more about Elements, see:

- the section 5.4 "Qualitative evaluation"
- the section 5.5.5 "Display parameters of the spectral lines (Elements) "

Labels

A label is a text box that that is linked to a specific point of the graphic through a stroke. It can be used to point out a specific part of the graphic, and especially the spectral lines. It is just a graphical item for the convenience of the user.

To know more about Labels, see:

- the section 5.5.6 "Creation and handling of Labels"

5.2. Creation of a Quali window and import of a spectrum

The graphical window, or Quali window, is the window where the spectra are displayed. A graphical window can be created in two ways:

- in the **Window** menu, choose **New Quali window**;
  — or —
- in a Quant window, click the **Alternative Mode Window** button.

Alternative Mode Window button

When SSD files were already imported, the graphical window displays the related spectra. When the EVAL2 document was empty, the graphical window is also empty; the curves appear automatically when the SSD files are imported (see section 3 "Importing a sample"). There is one curve for each range, i.e. several curves can be displayed for a single file.

5.3. Graphical display after a quantitative evaluation

The Quali window can be used to display the spectra and the positions of the lines after a quantitative evaluation.

The Quali window automatically displays the spectra (ranges) of the SSD file used for the quantitative evaluation (i.e. processed in the Quant window). To add the sticks representing the line (Element):

- in the **Quali** menu, choose the **Show lines** command.

This command is only available after the quantitative evaluation.

To change the layout of the graphic, see section 5.5 "Display tools and options".

5.4. Qualitative evaluation

Automatic evaluation

To perform an automatic evaluation:

- select the **Evaluation** command in the **Quali** menu.

This is usually the first operation done after the import of the spectrum.

The qualitative evaluation algorithm performs a peak search on the spectra, using the curvature of the curves: a peak corresponds to a minimum of the second derivative. For this, the curves are smoothed with a Savitzky-Golay algorithm.

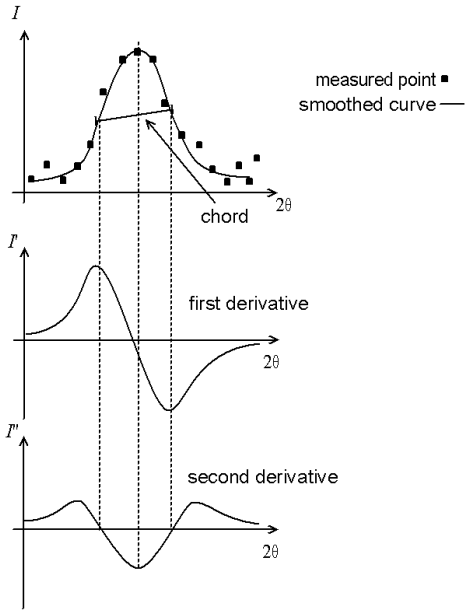


Fig. 5-2 Peak search algorithm using the Savitzky-Golay smoothing and the second derivative

An element is considered as present when the net height N_{net} of his peak (in cumulated counts) is above the level of the noise, determined by the level of the background N_{bkg} and the Poisson's law:

$$N_{net} > N_{bkg} + k \cdot \sqrt{N_{bkg}}$$

where k is a statistical coefficient related to the confidence level, usually set to 3. When more than one line is available for a single element, the algorithm considers several lines to avoid a "false detection" due to an overlap.

Parameters of the qualitative evaluation algorithm

Some parameters of the qualitative evaluation algorithm can be changed. They are in the **Auto Quali** and **Quali filter** tabs of the Qualitative Options dialog box.

To display the Qualitative Options dialog box:

- in the **Tools** menu, select the **Options** command.

Auto Quali tab

The peak search and peak filtering parameters are in the **Auto Quali** tab:

- **Peak search noise threshold**: the *k* statistical parameter in the Poisson's law; the higher the value, the more restrictive the filter (low concentration elements may not be detected);
- **Peak search energy window**: width of the sliding segment in the Savitzky-Golay algorithm;
- **WDX: 2-Theta search window**: when a peak is detected, it is attributed to the nearest element that is inside this search window (this is necessary due to possible shifts); the factor in this text box is multiplied by the collimator aperture;
- **Concentration limits for view line**: the lines of the elements which concentration is below this level are not displayed.

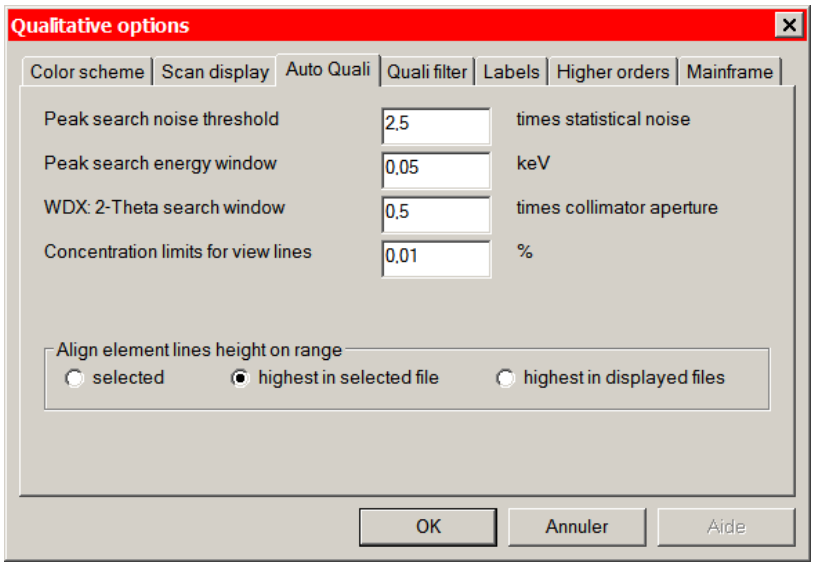


Fig. 5-3 ***Auto Quali*** *tab of the Qualitative Options dialog box*

Quali filter tab

This tab represents a periodic table of the elements. When an element is displayed in gray, it is never included in an automatic qualitative evaluation; when it is displayed in green, it is checked by the qualitative evaluation algorithm.

To activate or de-activate an element:

- Click the element box of interest
  — or —
  right-click the element and in the context-sensitive menu that appears, choose **Select** or **No check**.

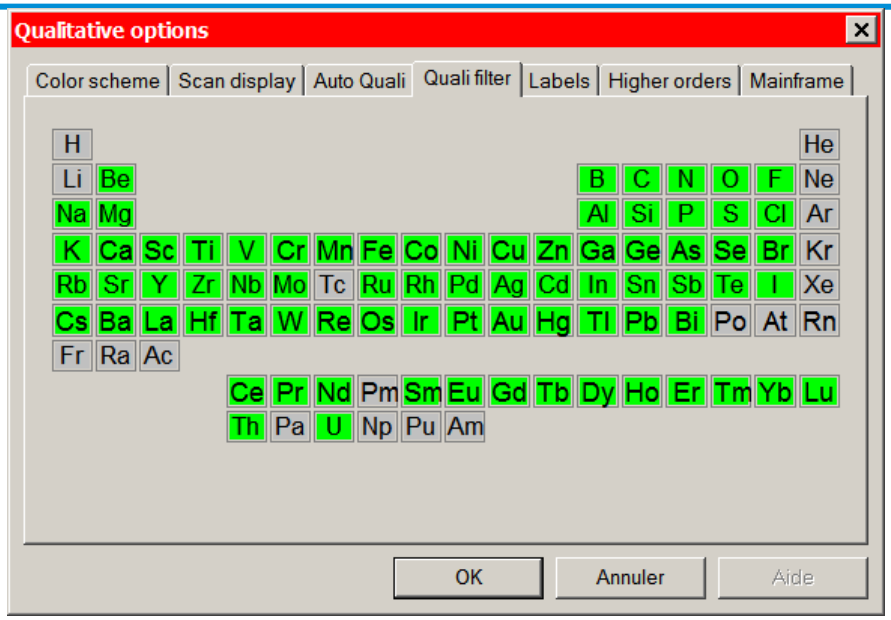


Fig. 5-4 **Quali filter** tab of the Qualitative options dialog box

Manual adjustment

To add or remove the sticks corresponding to an element:

Elements toolbar button

- if necessary, display the **XRF Lines** window: click the **Elements toolbar** button
  or
  select the **Elements toolbar** command in the **View** menu;
- Click the box of the element to display or hide.

The XRF Lines window represents a periodic table of the elements. When an element is displayed, its box is in light gray and its indicator is red. When an element is hidden, its box is in dark gray and the indicator is black.

Fig. 5-5 The iron lines are displayed and the cobalt ones are hidden

For more information on the **XRF Lines** window, see the section 2.3.3 "Organizing the windows".

Selection of a range or an element

Some tools only apply on one range (curve) or element (sticks). The selection determines the object that is affected by those tools. It is performed using the context-sensitive menu:

5. right-click the object of interest;
6. in the menu that appears, choose the **Select** option.

Identifying an element or a curve with the pop-up information

When the mouse cursor is let still on an object (a Range or a stick of an Element), a pop-up label (or tooltip) displays the name of the object.

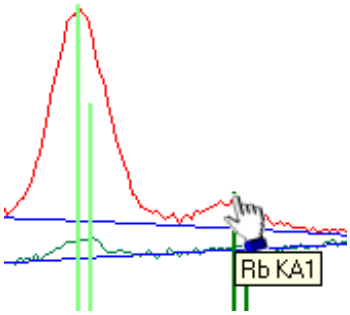


Fig. 5-6 Pop-up information window for the identification of a line

The information displayed in the pop-up window can be set up for the Ranges. The settings are defined in the **Scan display** tab of the Qualitative Options dialog box:

- in the **Tools** menu, choose the **Options…** command.

Option	Description
Show calculated background	In case of a scan measurement, it is possible to determine the background using the whole scan and not fixed positions; this option shows the background that is calculated in this case.
Show measurement parameters in tooltips	The measurement parameters for the range (i.e. tube high voltage and filter) are displayed along with the file name and the name of the measured lines.
Show integral rate in tooltips	The count rate **I. Rate** for the whole spectrum (i.e. the number of counts per second without consideration of the height of the count) is displayed
Hide non selected files by default	When several files are imported to EVAL2, the “selected file” is the file to which the selected range belongs. With this option checked, the non files are not displayed.
Auto select the active quantitative sample	When several files are imported to EVAL2, only one of them can be used for the quantitative evaluation. When this option checked, the selected file is automatically the sample that appears in the Quant window.
Intensity scale option	Select the unit of the Y-scale. The scale itself (linear or square root) is set by the context-sensitive menu (right-click the Y axis, see section 5.5.2 “X- and Y-scale setup”).

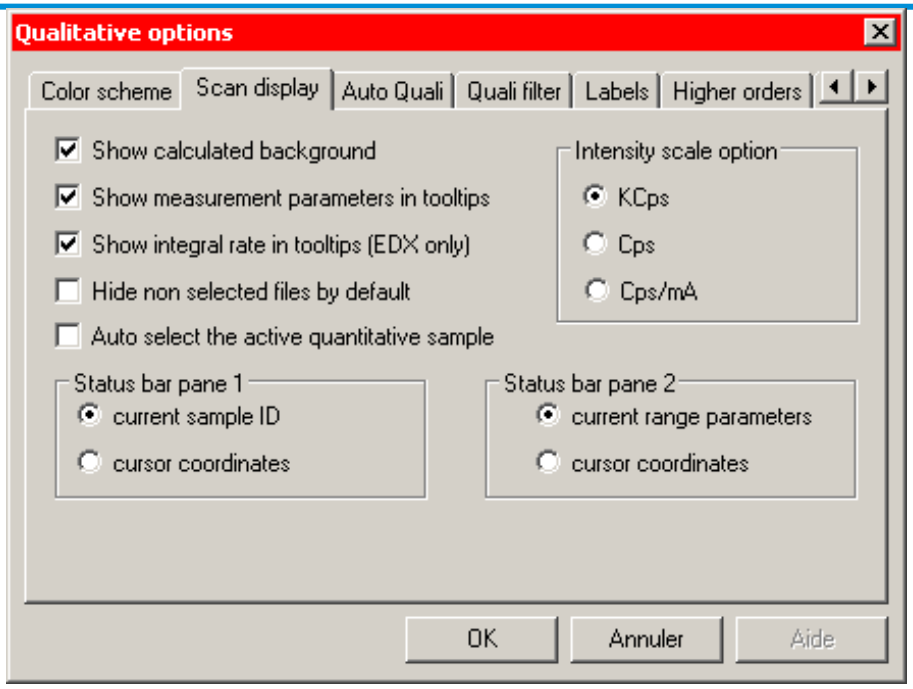


Fig. 5-7 **Scan display** tab of the Qualitative Options dialog box

5.5. Display tools and options

Zooming

The zoom can be performed in two ways:

- stretch a box around the area to be magnified: click the top left corner of the area of interest, and move the mouse pointer to the bottom right corner while holding the click; then release the click; during this operation, the mouse pointer looks like a magnifying glass;
  — or —
  right-click anywhere in the graphical window, and choose **Zoom+** in the context-sensitive menu that appears; the zoom is performed around the position of the click.

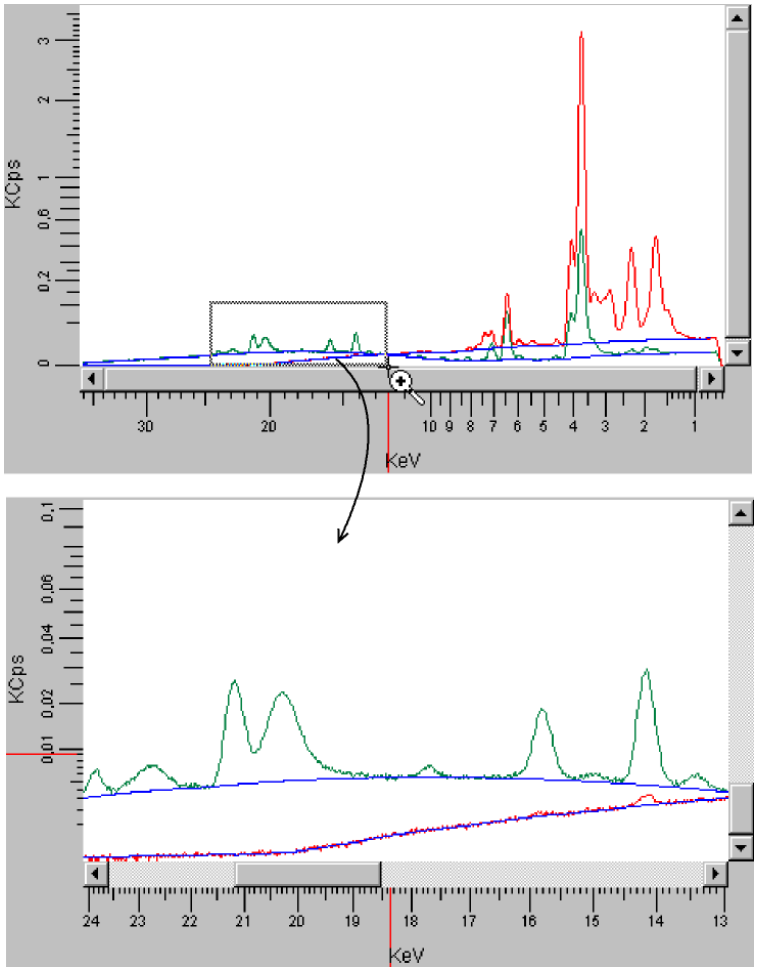


Fig. 5-8 Zooming the curves in a Quali window

There are three ways to zoom back (or unzoom):

- to double-click anywhere on the graphic;
- right-click anywhere in the graphic, and in the context-sensitive menu, choose **Zoom -** or **Zoom reset**;
- right-click the Y-axis and select **Reset y zoom**: this keeps the X range but displays the full data of this X range.

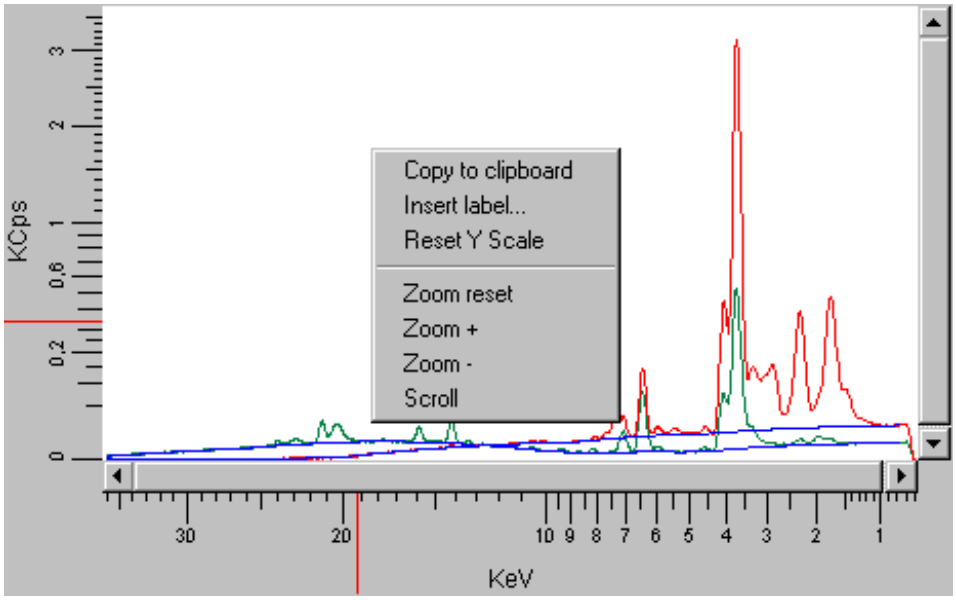


Fig. 5-9 Zooming with the context-sensitive menu

If the mouse has a wheel third button, it is also possible to use the wheel to zoom in and out.

X- and Y-scale setup

X-scale

The X-scale can be:

- proportional to the square root of the energy: according the Moseley's law, the lines of a given type (e.g. the Kα lines) are spaced evenly with this scale; in this case, the X-scale can be graduated in keV (energy of the photons) or in Å (wavelength of the radiation);
- proportional to the energy; in this case, the scale is graduated in keV.

It can also be:

- in increasing order of the energy: this is the "natural" order of an axis;
- in decreasing order of the energy: the lines are in the same order as the 2θ order in a wavelength dispersive spectrometer.

The X-scale is chosen with a right-click the X-axis; the options of the context-sensitive menu are:

- **Kev <-**: scale in square root of energy, in decreasing order, graduated in energy (keV); this is the default mode;
- **KeV ->**: scale in square root of energy, in decreasing order, graduated in energy (keV);
- **LKeV <-**: scale linear in energy, in decreasing order;
- **LKev ->**: scale linear in energy, in increasing order;
- **Ao**: scale similar to **Kev <-**, but the graduations are the wavelength of the radiations in Angström (Å);
- **° 2Theta *crystal*** (where *crystal* can be LiF200, PET…): scale linear in degrees; only the ranges measured on the same crystal are displayed

Y-scale

The Y-scale can be set with a right-click the Y-axis (context-sensitive menu):

- proportional to the count rate: select **Lin** in the context-sensitive menu;
- proportional to the square root of the count rate: select **Sqrt** in the context-sensitive menu.

Color of a Range

The colors of the Ranges (spectra) follow the rules set in the **Color scheme** tab of the Qualitative Options dialog box. To open this dialog box:

- click the **Options…** command of the **Tools** menu.

When several SSD files are imported, it is usually not possible to have individual colors for each Range (curve); a color is used to highlight the Ranges that have something in common, and thus point out the similarities and discrepancies between them. The options are:

- **Same color except selected range**: this highlights a single Range;
- **Same color for all except selected file**: this highlights the Ranges belonging to the same SSD file;
- **Same color for same parameters**: when only one SSD file is imported, this option allows a different color for each Range ; when several SSD files are imported, this allows to compare what can be compared;
- **Same color for same file order**: the color depends on the order of the Range in the SSD file.

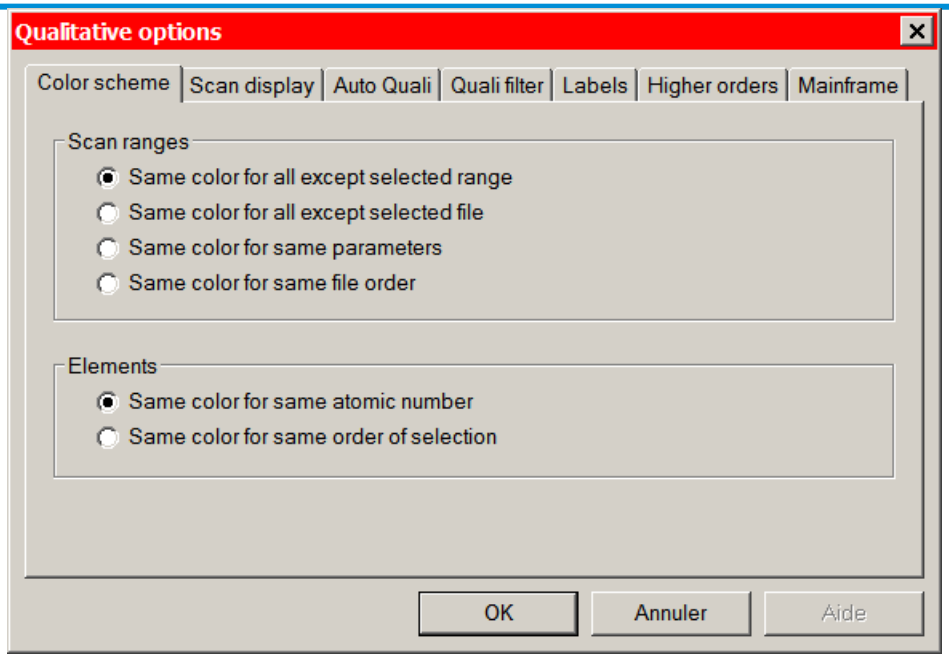


Fig. 5-10 ***Color scheme*** *tab of the Qualitative Options dialog box*

To select a Range:

- right-click the related curve, and in the context-sensitive menu, choose **Selection**.

When the **Same color except selected range** or the **Same color for all except selected file** option was set, this operation changes the colors of the curves.

To set the colors:

- right-click the related curve, and in the context-sensitive menu, choose **Color**;
- in the Color dialog box that appears, select the color and click **OK**.

Display of the background line

The background line is automatically displayed when the **Show calculated background** option is checked in the **Scan display** tab of the Qualitative Options dialog box (see figure 5-7).

To display the Qualitative Options dialog box:

- in the **Tools** menu, choose the **Options…** command.

The option must be checked *before* the import of the SSD file. The background line is computed with the same algorithm as the one used for the Lower Envelope method (see the subsection "Evaluation with the peak/background method" of the section 4.1.2).

The background line is always displayed in blue. A right-click the background line is considered as a right-click the related Range.

Display parameters of the spectral lines (Elements)

Height of the sticks

To adjust the height of the sticks:

- place the mouse pointer at the top of a stick; the shape of the pointer changes to a hand pointing the forefinger;
- press the mouse button and hold the click while moving the pointer up or down;
- release the button when the aimed height is reached.

This adjusts the height of all the sticks figuring the lines of the same element together.

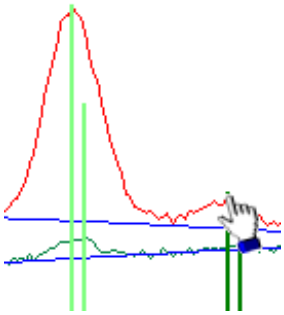


Fig. 5-11 Adjusting the height of the sticks figuring the lines for an element

Color of the sticks

The colors of the sticks figuring the spectral lines follow the rules set in the **Color scheme** tab of the Qualitative Options dialog box (see figure 5-10). To open this dialog box:

- Click the **Options…** command of the **Tools** menu.

The options are:

- **Same color for same atomic number**: all the sticks of a given Element have the same color;
- **Same color for same order of selection**: the color of each stick is defined independently; the colors are stored (in the Windows® registry), so for the next samples to be processed, the color of a stick can be set just by selecting it, following the same color pattern.

To change the color of an element (first option) or of a stick (second option):

- right-click one of the lines;
- in the context-sensitive menu, select **Color**;
- in the Color dialog box, select the color and click **OK**.

Removing the sticks of an element

To remove the sticks representing the lines of an element:

7. right-click one of the sticks;
8. in the context-sensitive menu, select **Delete element**.

where *element* is the chemical symbol of the element.

It is also possible to remove all the sticks on the display:

- in the **Quali** menu, choose the **Delete all elements** command.

Creation and handling of Labels

A label is a text box that that is linked to a specific point of the graphic through a line (see section 5.1.3 "Labels").

To add a label:

- right-click anywhere in the graphic (except on a curve or on an element stick)
- in the context-sensitive menu, choose **Label**.
- in the Insert Label dialog box that appears, type in the text of the label;
- choose the orientation of the text box: **Horizontal**, **45 Degrees** or **90 Degrees**;
- click **OK**.

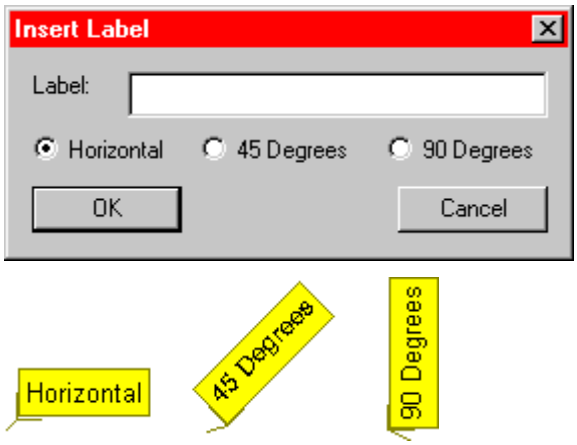


Fig. 5-12 Labels on the graphic

Once a label is created, you can:

- move the attachment point: click the attachment point, and move the cursor while clicking; the whole label (text box, line and attachment point) moves;
- move the text box, the attachment point remaining the same: click the text box and move the cursor while clicking;
- change the text or the orientation of the text box: right-click the label, and in the context-sensitive menu, choose **Edit**;
- remove the label: right-click the label, and in the context-sensitive menu, choose **Delete**;

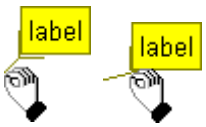


Fig. 5-13 Moving the attachment point (left) or just the text box (right)

Automatic creation of labels

To label the sticks corresponding to an element:

- right-click one of the sticks,
- in the context-sensitive menu that appears, choose **Label this element**.

This writes the name of the spectral lines on the top of the sticks.

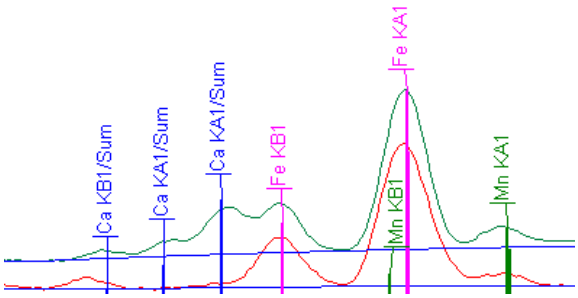


Fig. 5-14 Labels on the top of the Elements

To label a range:

- right-click the range of interest;
- in the context-sensitive menu that appears, choose **Label this range**.

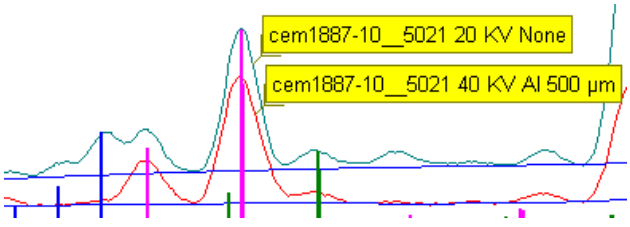


Fig. 5-15 Labeling the Ranges

5.6. Saving and printing the qualitative results

Copying the graphic to the clipboard

The graphic can be copied to the clipboard, as a picture, and be pasted into another Windows®-based application.

To copy the results to the clipboard:

Copy to clipboard button

- choose the **Copy to clipboard** command in the **Tool** menu
  — or —
  click the **Copy to clipboard** button

Printing the results

The results can be printed, provided a printer is installed.

To display a preview of the printout:

- choose the **Print Preview** command in the **File** menu.

The general parameters, such as the page size and the layout (portrait or landscape) are defined in the Print Setup dialog box:

- choose the **Print Setup** command in the **File** menu.

To print the result:

Print button

- choose the **Print** command in the **File** menu
  — or —
  press the **CTRL+P** key combination
  — or —
  click the **Print** button.

The menu command and the key combination display the Print dialog box, where it is possible to choose the printer. The **Print** button directly starts the printing.

6. Glossary

Analyzed thickness

The analyzed thickness describes the sample layer from which 90% of the intensity is generated. It is the thickness that corresponds to the depth from which the specific radiation can emerge and can be calculated depending on the matrix.When the sample is thinner than the analyzed thickness, the intensity of the line depends on the thickness of the sample. When the sample is thicker than the analyzed thickness, the intensity does not depend on the sample thickness; the sample has an "infinite thickness".

Compound

A chemical compound is a set of atoms linked by chemical bonds. In SPECTRA EDX, the compounds are used to determine the concentrations in light elements.

Light elements are difficult or impossible to measure in XRF (their fluorescence yield is poor, and their lines have a low energy and are easily absorbed). Thus, the line of the heaviest element (or key element) is measured, and the other elements of the compound are determined by stoechiometry. Typical compounds are oxides (e.g. CaO, Na2O, Fe2O3…) and single elements (mono-element compound, e.g. Ca, Na, Fe…).

Compton ratio

The purpose of X-ray fluorescence spectrometry is the qualitative and quantitative determination of the elements in a sample by measuring their characteristic radiation. As the sample is exposed to a beam of X-ray quanta from a tube, a proportion of these X-rays also reach the detector in the form of radiation background as a result of physical scattering processes. While the scattered Bremsstrahlung proportion generally produces a continuous background, the scattered characteristic radiation of the anode material contributes towards the line spectrum. Besides the lines of elements from the sample, the anode material's lines and the scattered Bremsspektrum usually appear as well as a background.

The intensity of the scattering depends on the composition of the sample: for samples that are mainly composed of light elements (light matrix), the proportion of scattered radiation is high. In samples composed mainly of heavy elements (heavy matrix), the scattered proportion is relatively low.

Background and characteristic scattering can be very effectively reduced by inserting a suitable absorption material between tube and sample.

The Rh quanta coming from the tube strike the sample elements' electrons. In this process, some of a quantum's energy is transferred to an electron. The X-ray quantum therefore loses energy. The intensity of the quanta scattered by the Compton effect depends, among other factors, on the tube radiation's angle of incidence to the sample and on the take-off angle of the radiation in the spectrometer. As these angle settings are fixed in a spectrometer, a somewhat wider peak appears on the low-energy side of the appropriate Rh peak. These peaks are called "Compton peaks."

In EVAL2, the Compton factor is defined as the calculated Compton divided by the measured factor; when the calculated concentrations are close to the real ones, the ratio is close to 1. If you get a Compton factor higher than 1, it means the matrix is too light and you can add oxygen or take away a light matrix.

If you do not know if your samples are oxides or elements you should use the Compton factor to optimize the matrix.

The Compton factor can be applied from a light to a moderate light matrix.

For heavier matrices you can use the Rayleigh factor (see further Rayleigh ratio).

Key element

In a compound, the key element is the element used for the evaluation. The other elements of the compound are determined by stoechiometry.

Lower limit of detection

The lower limit of detection, or LLD, is the minimum detectable concentration of an element or compound in a matrix. It is given by the following expression:

$$LLD = \frac{3}{m} \times \sqrt{\frac{I_{Bkg}}{t}}$$

in which

- m is the sensitivity;
- I_{Bkg} is the intensity of the background at the defined wavelength;
- t the counting time on the background.

A peak can be detected only when its net height is above the fluctuations of the signal, which can be determined by applying the Poisson's law on the background level; this net height is then converted into a concentration, with the calibration coefficient and the matrix corrections.

A LLD is always specific for an element in a given matrix and should be presented together with the counting time. The detection limit for the same element can vary because of the difference in matrix. For example, the detection limit for S in Oil is different from S in a metal sample.

Matrix

In general, the matrix is the part of the samples composed of the major compounds/elements. In most of the cases, the matrix is not measured, for example CH_2 in oils.

In SPECTRA EDX, a matrix is a compound whose concentration is evaluated from the other concentrations by balance to 100%. It appears in blue in the Concentration list. It is typically used to estimate the concentration of a compound that has no measurable element (e.g. oil, polymer, water), or when the concentration itself has no interest (e.g. iron in steel).

Moseley's law

The Moseley's law is an empirical law discovered by Henry Moseley in 1912: the square root of the frequency of the radiation follows an affin law in Z (atomic number):

$$\sqrt{\nu} = C \cdot (Z - \sigma)$$

where C and σ are constants for a given type of line (e.g. all the Kα have the same constants, all the Kβ lines have their own…). Therefore, the energy of the photon follows a similar law (this conclusion comes with the definition of the Planck's constant h):

$$\sqrt{E} = C \cdot \sqrt{h} \cdot (Z - \sigma)$$

thus, on a scale in square root of the energy, the lines of a given type are spaced evenly.

Planck's constant

The Planck's constant h links the energy E of the photons and the frequency ν of the radiation, or its wavelength λ:

$E = h \cdot \nu = h \cdot c/\lambda$

in which c is the speed of light in vacuum (2.997 924 58·10^8 m/s).

$h \approx 6.626\ 1 \cdot 10^{-34}$ J·s

When the wavelength is in Å and the energy is in keV, the formula becomes

$E \approx 12.4/\lambda$

Poisson's law

The Poisson's law is a statistical law followed by the XRF signal. When N counts are cumulated during a period t, then the standard deviation σ_N can be estimated by the square root of the number of counts

$$\sigma_N = \sqrt{N}$$

and the standard deviation σ_I on the intensity $I = N/t$ (count rate) is

$$\sigma_I = \frac{\sigma_N}{t} = \frac{\sqrt{N}}{t} = \sqrt{\frac{I}{t}}$$

This allows the calculation of the statistical error and of the lower limit of detection: the statistical error is taken as

$$\Delta N = k \cdot \sigma_N \quad ; \qquad \Delta I = k \cdot \sigma_I$$

where k is a constant related to the confidence level, usually taken as 3.

Rayleigh ratio

While some incident X photons are captured by the photoelectric effect (giving the fluorescence), some other are scattered by Rayleigh effect by the atoms of the sample. When the characteristic lines of the X-ray tube are not filtered, they give Rayleigh lines, i.e. lines with the same energy as the incident ones.

The height of the Rayleigh lines can be computed from the sample composition; the ratio between the height of the measured Rayleigh lines and the calculated Rayleigh line is called the Rayleigh ratio; when the calculated concentrations are close to the real ones, the ratio is close to 1.

The Rayleigh ratio can be used to optimized sample parameters (e.g. thickness, density, dilution…) of heavy matrix samples (the Rayleigh diffusion is more important on heavy elements), but only on amorphous, or best liquid sample (due to diffraction phenomena).

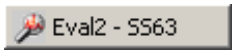
Statistical error

The statistical error is the error due to the fluctuation of the XRF signal. It can be evaluated with the Poisson's law (the statistical error is three times the standard deviation). It is a part of the error on the concentration, which also includes the error of preparation and the error of the calibration.

Appendix A Appendix

A Menus

Window Management menu

 **Window Management menu**		
Command	**Other access**	**Effect**
Restore		when the window is maximized or minimized, use this command to be able to adjust yourself the size of the window
Move		when this command is activated, the only possible action with the mouse is to move the window; this can be useful when, after having changed the resolution of the screen, the window spreads out of the screen and you are unable to reach the borders to resize it
Size		when this command is activated, the only possible action with the mouse is to resize the window
Minimize		for an Evaluation window: the window is reduced to a small toolbar, with only the name of the window and three buttons  for the EVAL2 window, the window disappears, only the button in the Taskbar remains 
Maximize		for an Evaluation window, it adjusts its size so it fits exactly the EVAL2 window; for the EVAL2 window, it adjusts its size so it fits the whole screen in both cases, the size cannot be changed
Close (Quali or Quant window)	CTRL+F4 	close the current Quant or Quali window
Close (EVAL2)	ALT+F4 	quit the program
Next	CTRL+F6	go to another Quali or Quant window

File menu

File menu		
Command	**Other access**	**Effect**
New	CTRL+N	create a new Quant window
Close	CTRL+F4 	close the current Quant or Quali window
Import raw data		open the Select Sample(s) for Evaluation dialog box; the selected SSD file is then imported in the document when the EVAL2 document already has an SSD file, then the new SSD file is added to the document; evaluation is no longer possible, but spectra can be compared
Next document		Remove the current SSD file and open the Select Sample(s) for Evaluation dialog box; the selected SSD file is then imported in the document
Print	CTRL+P	Quant window: print the concentrations; see section 4.4 "Saving and printing the quantitative results" Quali window: print the graphic; see section 5.6 "Saving and printing the qualitative results"
Print preview		display a preview of what will be printed
Print setup		open the Print Setup dialog box: choice of the printer, of the paper orientation…
Exit	ALT+F4 	quit the program

View menu

View menu		
Command	**Other access**	**Effect**
Toolbar		display or hide the Toolbar with the shortcut buttons
Status bar		display or hide the Status bar, at the bottom of the EVAL2 window
n^{th} Quant window — or — n^{th} Quali window		switch to the corresponding window
All elements		Display the elements that were found absent
Commands specific to the Quant windows		
Evaluation methods		display or hide the Evaluation Methods dialog box
Sample properties		display or hide the Sample Properties dialog box
Quant columns		display the Select Quantitative Window Columns dialog box
Commands specific to the Quali windows		
Elements toolbar		display or hide the Elements toolbar (periodic table of the elements)

Quanti menu

This menu is available only for the Quant windows.

Quanti menu		
Command	**Other access**	**Effect**
Initialize		set the concentration to their default values in order to start the calculation see section 4.2.3 "Launching the first evaluation"
Compute		start the calculation of the concentrations see section 4.2.3 "Launching the first evaluation"
Save results		store the results in the Results database (Measure.MDB) see section 4.4 "Saving and printing the quantitative results"

Stop calculation		stop the calculation that is running
Add compound		display the Insert Compound dialog box

Quali menu

This menu is available only for the Quali windows.

Quali menu		
Command	**Other access**	**Effect**
Evaluation		launch the qualitative evaluation, and display the elements sticks
Show lines		display the sticks representing the lines of the elements found in a quantitative evaluation;; only the elements which concentration is above a given threshold are displayed; this threshold is set at the **Auto Quali** tab of the Qualitative Options dialog box
Label lines		place a Label on the top of each line
Rearrange labels		move the labels according to the current zoom
Delete all elements		remove all the sticks figuring the elements from the display
Hide inactive files		when a curve is selected (right-click the curve, option **Select**), only the curves of the same SSD file are displayed
Display all files		display all curves, for the SSD files imported into the document

Advanced menu

Advanced menu	
Command	**Effect**
Specific to Quant windows	
Standard Material	Import a standard material and display its concentrations
Evaluate by GUID	Simulate the automatic evaluation by QUANTEVL2; type in the general unique identifier (e.g. read with DUMPSSD) to perform this evaluation
Specific to Quali Windows	
Sample absorption	Plot the sample absorption (calculated form the composition) in arbitrary Y-scale
Tube output	Plot the tube spectrum (theoretical model)

Window menu

Window menu	
Command	**Effect**
New Quali window	create a new Quali window
New Quant Window	create a new Quant window
Tile horizontally	all the windows are displayed, one above the other, without overlap
Tile vertically	all windows are displayed, besides each others, without overlap

Tools menu

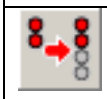
Tools menu	
Command	**Effect**
Options…	display the Quantitative Options or the Qualitative Options dialog box, according to the type of the current window
Copy to clipboard	copy the content of the current window, so it can be pasted into another document (e.g. text processor, spreadsheet or presentation) see section 4.4 "Saving and printing the quantitative results" and 5.6 "Saving and printing the qualitative results"

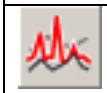
Help menu

Help menu		
Command	**Other access**	**Effect**
About Eval2…		display the About Eval2 dialog box, with the version number of the software

Appendix B Toolbar

File zone		
Command	**Other access**	**Effect**
	File | Next document	Remove the current SSD file and open the Select Sample(s) for Evaluation dialog box; the selected SSD file is then imported in the document
	File | Import raw data	open the Select Sample(s) for Evaluation dialog box; the selected SSD file is then imported in the document when the EVAL2 document already has an SSD file, then the new SSD file is added to the document; evaluation is no longer possible, but spectra can be compared

Evaluation zone		
Buttons common to both windows		
	View | All elements	display the elements that are absent
Buttons specific to Quant windows		
	Quanti | Initialize	set the concentration to their default values in order to start the calculation see section 4.2.3 "Launching the first evaluation"
	Quanti | Compute	start the calculation of the concentrations see section 4.2.3 "Launching the first evaluation"
		normalize: apply the **Sample smaller than mask** option (Sample Properties box, see section 4.3.3)
	Quanti | Save results	store the results in the Results database (Measure.MDB) see section 4.4 "Saving and printing the quantitative results"
	Quanti | Stop calculation	stop the calculation that is running
		display the concentration in compounds or in elements
		display the original concentration (i.e. in the material before the preparation) or the prepared concentration (i.e. in the sample that is measured, after preparation)
	View | Quant columns	display the Select Quantitative Window Columns dialog box
	View | Evaluation methods	display or hide the Evaluation Methods dialog box
	View | Sample properties	display or hide the Sample Properties dialog box

View/Quali zone		
	View | Elements toolbar	display or hide the Elements toolbar (periodic table of the elements)
	Quali | Hide inactive files Quali | Display all files	when a curve is selected (right-click the curve, **Select** option), this buttons allows to display or hide the curves that do not belong to the same SSD file as the active curve

Window zone	
 	Alternative mode window: in a Quant window, press the button to switch to the corresponding Quali window or to create it when it does not exist; in a Quali window, press the button to switch to the corresponding Quant window or to create it when it does not exist

Tools zone		
	Tools | Copy to clipboard	copy the content of the current window, so it can be pasted into another document (e.g. text processor, spreadsheet or presentation) see section 4.4 "Saving and printing the quantitative results" and 5.6 "Saving and printing the qualitative results"

Print zone		
		Quant window: print the concentrations (fast print)[1]; see section 4.4 "Saving and printing the quantitative results" and 5.6 "Saving and printing the qualitative results" Quali window: print the graphic (fast print); see section 5.6 "Saving and printing the qualitative results"

Help zone		
	Help | About Eval2…	display the About Eval2 dialog box, with the version number of the software

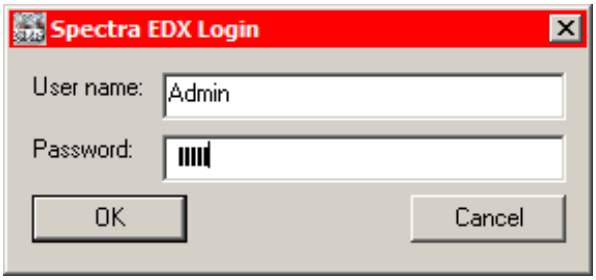
1 the printing is launched without opening the Print dialog box; it is thus different from and the **File | Print** menu command or the **CTRL+P** key combination

Appendix C Windows and dialog boxes

C.1 Importing a sample

SPECTRA EDX Login dialog box

This dialog box appears when the logon limit time is reached (see section 1.3 "Starting EVAL2"). This time is set in the SYSTEM CONFIGURATION. Most programs of the SPECTRA EDX package require to be logged.



To log on:

- Fill in the **User name** and the **Password** text fields;
- Click **OK**.

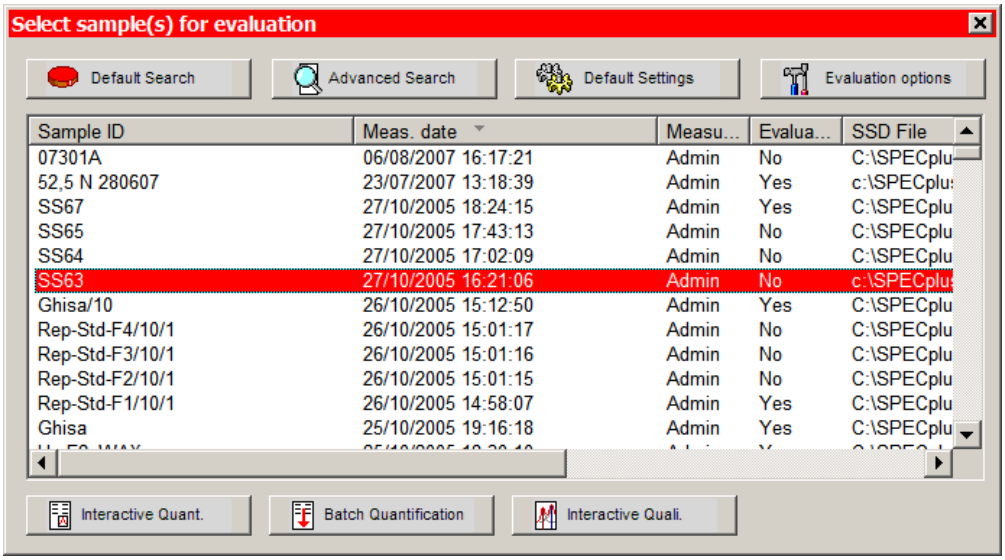
See also the section 1.3 "Starting EVAL2".

Select Sample(s) for Evaluation dialog box

This dialog box is used to choose the data that will be processed. It appears:

- when clicking the **Evaluation** button of the SPECTRA EDX Launcher
  — or —
- when importing a sample from EVAL2, with the **Import raw data/Next document** button or the related commands of the **File** menu.

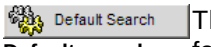
Import raw data/Next document buttons


Select sample(s) for evaluation
Default Search
Advanced Search
Default Settings
Evaluation options
Sample ID
Meas. date
Measu...
Evalua...
SSD File
07301A 06/08/2007 16:17:21 Admin No C:\SPECplu
52,5 N 280607 23/07/2007 13:18:39 Admin Yes c:\SPECplu
SS67 27/10/2005 18:24:15 Admin Yes C:\SPECplu
SS65 27/10/2005 17:43:13 Admin No C:\SPECplu
SS64 27/10/2005 17:02:09 Admin No C:\SPECplu
SS63 27/10/2005 16:21:06 Admin No c:\SPECplu
Ghisa/10 26/10/2005 15:12:50 Admin Yes C:\SPECplu
Rep-Std-F4/10/1 26/10/2005 15:01:17 Admin No C:\SPECplu
Rep-Std-F3/10/1 26/10/2005 15:01:16 Admin No C:\SPECplu
Rep-Std-F2/10/1 26/10/2005 15:01:15 Admin No C:\SPECplu
Rep-Std-F1/10/1 26/10/2005 14:58:07 Admin Yes C:\SPECplu
Ghisa 25/10/2005 19:16:18 Admin Yes C:\SPECplu
Interactive Quant.
Batch Quantification
Interactive Quali.

Control	Description
Search database	search in the Measure.MDB database and display the samples that correspond to the default criteria, or to the Advanced Search criteria is the related window is opened
Advanced search	open the Advanced Search dialog box, to define specific search criteria
Default search	open the Default Search Options dialog box
Evaluation option	display the Advanced Evaluation Options dialog box, to supersede the application
Controls available only from EVAL2	
OK	import the selected sample(s)
Cancel	go back to the main window without importing
Controls available only from SPECTRA EDX Launcher	
Interactive Quant.	open EVAL2 and import the sample into a Quant window
Interactive Quali.	open EVAL2 and import the sample into a Quali window
Batch Quantification	launch a batch quantification

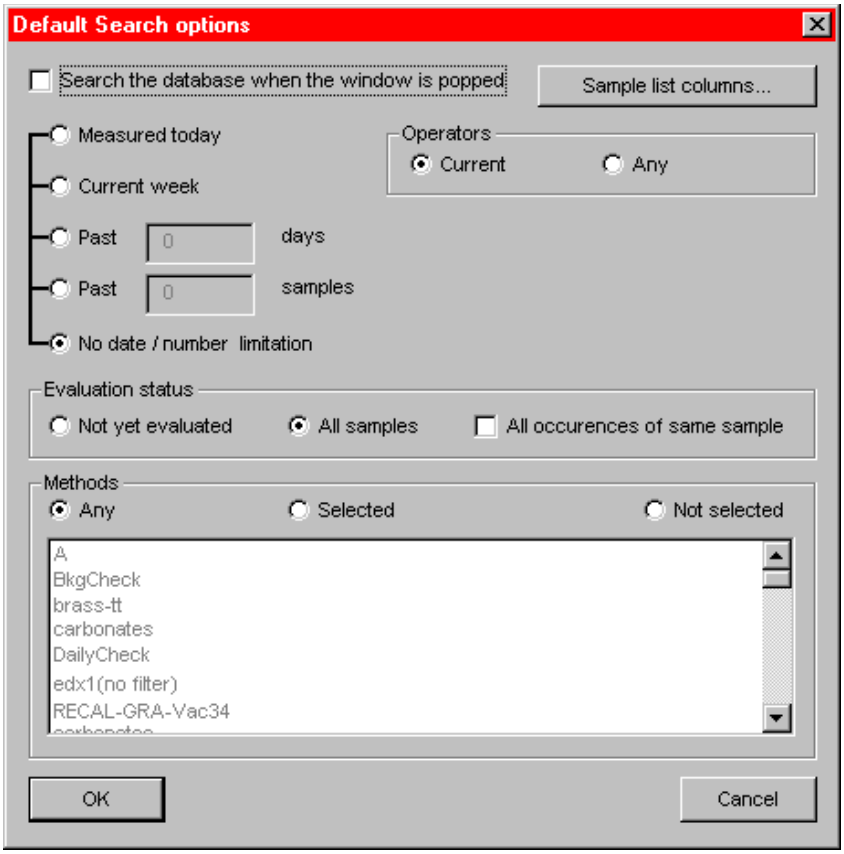
See also the chapter 3 "Importing a sample"

Default Search Options dialog box



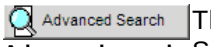
Default search button

This dialog box appears when clicking the **Default search** button in the Select Sample(s) for Evaluation dialog box. Here are defined the default criteria to select the samples in the Measure.MDB database.


Default Search options
Search the database when the window is popped
Sample list columns...
Measured today
Current week
Past
0
days
Past
0
samples
No date / number limitation
Operators
Current
Any
Evaluation status
Not yet evaluated
All samples
All occurences of same sample
Methods
Any
Selected
Not selected
A
BkgCheck
brass-tt
carbonates
DailyCheck
edx1(no filter)
RECAL-GRA-Vac34
OK
Cancel

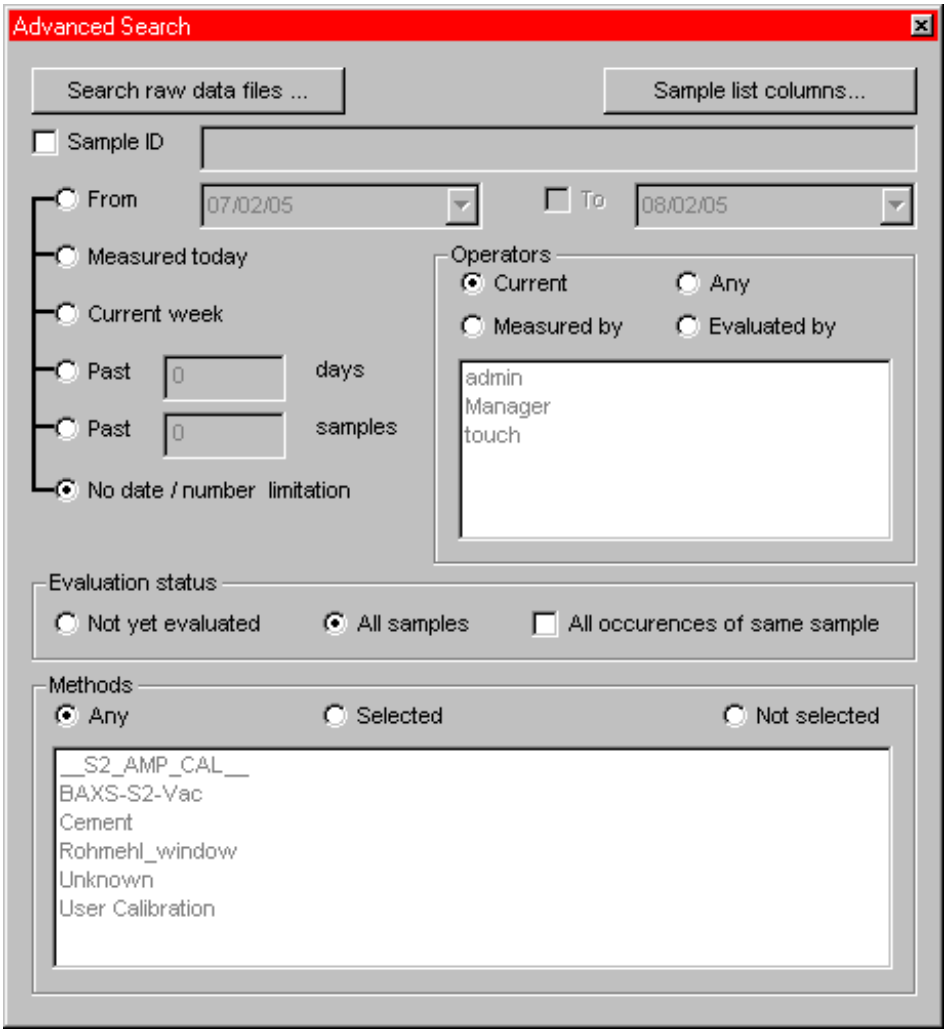
Control	Description
Search the database when the window is popped (check box)	when this option is checked, the search is automatically performed when the window is displayed, i.e. when clicking the **Import data file** button (EVAL2) or on the **Evaluation** button (SPECTRA EDX Launcher)
Sample list columns (button)	display the Select Samples List Columns dialog box, where it is possible to choose the columns of the table
Operators (radio buttons)	**Current**: only the samples measured by the operator that is logged; **Any**: no filter
Date and number options (radio buttons	**Measured today**: only the samples measured today **Current week**: only the samples measured this week **Past *n* days**: only the samples measured during the last *n* days **Past *n* samples**: last *n* measured samples **No date and number limitation**: no filter
Evaluation status	**Not yet evaluated** (radio buttons): only display the samples that are not evaluated **All samples** (radio buttons): also display the samples that are already evaluated **All occurrences of the same sample**:
Methods (radio buttons)	**Any**: no filter **Selected**: only the samples that were measured with the selected methods **Not selected**: only the samples that were not measured with the selected methods the two last options activate the list of measurement methods
OK (button)	Validate the parameters and close the window
Cancel (button)	discard the changes and close the window

Advanced Search dialog box



Advanced search button

This dialog box appears when clicking the **Advanced search** button in the Select Sample(s) for Evaluation dialog box. Here are defined the criteria to select the samples in the Measure.MDB database for one search.



Control	Description
Search raw data files (button)	click this button to retrieve an SSD file without searching the database
Sample list columns (button)	display the Select Samples List Columns dialog box, where it is possible to choose the columns of the table
Sample ID (check box and text field)	to retrieve a sample by its name (as entered in LOADER): check the box and type the name in the text field it is possible to use the wildcards "?" (any character) and "*" (any character string including the empty string), e.g. "alu" can be found with "a*" and "a?u"
Operators (radio buttons)	**Current**: only the samples measured by the operator that is logged; **Any**: no filter **Measured by**: only the samples measured by the operator(s) selected in the list **Evaluated by**: only the samples evaluated by the operator(s) selected in the list
Date and number options (radio buttons	**From — to**: only the samples measured between the two dates, or between the **From** date and today when the **To** box is cleared **Measured today**: only the samples measured today **Current week**: only the samples measured this week **Past *n* days**: only the samples measured during the last *n* days **Past *n* samples**: last *n* measured samples **No date and number limitation**: no filter
Evaluation status	**Not yet evaluated** (radio buttons): only display the samples that are not evaluated **All samples** (radio buttons): also display the samples that are already evaluated **All occurrences of the same sample**:
Methods (radio buttons)	**Any**: no filter **Selected**: only the samples that were measured with the selected methods **Not selected**: only the samples that were not measured with the selected methods the two last options activate the list of measurement methods

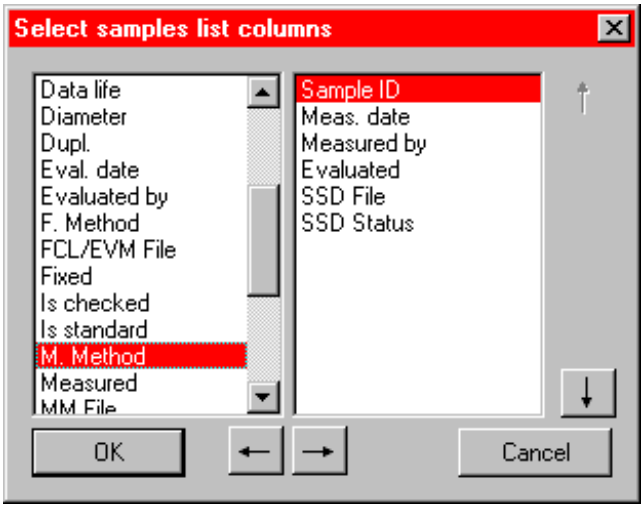
These options apply only as long as the Advanced Search dialog box is displayed.

Select Samples List Columns

This dialog box is used to set the columns that are displayed in the Select Sample(s) for Evaluation dialog box, i.e. the data that are shown for every sample.

To display it:

- in the Default Search Options dialog box or in the Advanced Search dialog box, click the **Sample list columns** button.



Control	Description
←	remove the selected column (in the right list) from the display
→	insert the selected column (in the left list) from the display
↑ ↓	move the selected column (in the right list) up or down in the list; the column will be displayed one position left or resp. to the right
OK	validate the changes and close the window
Cancel	discard the changes and close the window

Column	Description
Added compound	additive of the preparation
Additive/Original	mix ratio between the additive and the original material
All elements	WDX: in case of reference sample for drift correction: state of the MeasureAll field flag (set in the LOADER), 1 = force the measurement of the elements that belong to the measurement method but that do not belong to the drift correction method
C. Method	calibration method (name of the FCL file)
Color	color of the sample as defined in LOADER
Created by	name of the operator that was logged at the time of the creation of the data in LOADER (can be different from Measured by)
Creation date	date and time when the data were defined in LOADER (the measurement is performed after the creation)
Data life	For control samples and type standard samples: duration stored in the Specification database, typed in the **Validity (days) warning** field
Diameter	sample diameter as defined in the preparation
Dupl.	duplicated, means that the sample was evaluated several times
Eval. date	date of the evaluation
Evaluated	whether he sample was evaluated or not
Evaluated by	name of the operator that was logged at the evaluation time
F. Method	format method (name of the WZM file)
FCL/EVM file	path and name of the application (EVM file)
Is checked	whether the sample was validated in QUERYRES (Results Monitor), with the **Remove and validate** button (see the related manual, section 3.2.3 "Managing the Result List")
Is standard	whether the sample is the standard of a calibration
M. Method	measurement method (name of the MM file)
Meas. date	date and time when the measurement of the sample ended

Column	Description
Measured	whether the sample was measured or not; not measured means that the sample was created in LOADER, but the measurement is not finished yet
Measured by	operator that was logged when the measurement ended
MM File	path and name of the measurement method
Position	position of the sample on the sample loader when it was measured
Preparation	name of the preparation
Qual std invalid	When Quality Check is used: there was no valid
Run time	duration of the measurement
SSD File	path and name of the SSD file
SSD Status	exist or not; see the column "Measured"
UID	unique identifier of the sample in the database (16 bytes)
WZM File	path and name of the format method

The program reads the name of the fields in the Measure.MDB database. Additional fields created by the user may appear.

C.2 Columns of the Quant window

Select Quantitative Window Columns dialog box

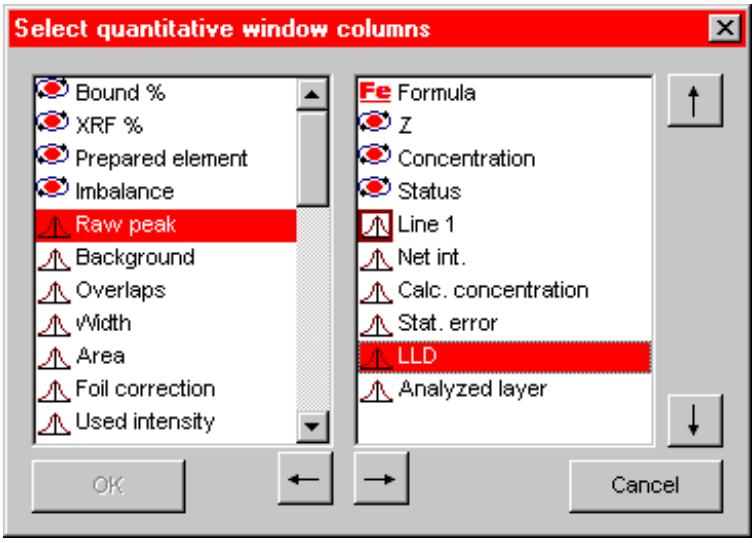
This dialog box is used to set the columns that are displayed in the Quant window, i.e. the data that are shown for every compound (see the sections 2.3.1 "The Quant window" and 4.3.5 "Adjustable display parameters").

Quant columns button

To display the Select Quantitative Window Columns dialog box:

- select the **Quant columns** command in the **View** menu,
  — or —
  click the **Quant columns** button.

Control	Description
	remove the selected column (in the right list) from the display
	insert the selected column (in the left list) from the display
	move the selected column (in the right list) up or down in the list; the column will be displayed one position left or resp. to the right
OK	validate the changes and close the window
Cancel	discard the changes and close the window



Description of the compound

Column	Description
Formula	Chemical formula of the compound
Z	atomic number of the key element of the compound (i.e. the heaviest element, the one which line is used to calculate the concentration)

Results

Column	Description
Concentration	concentration of the compound in the original material (before preparation); the unit is the one defined in the WZM file, otherwise the default unit is percent
Prepared element	concentration of the element in the measured sample; in case of a compound, only the concentration of the key element (i.e. the heaviest element of the compound) is displayed; the unit is the one defined in the WZM when the **Use format method to display prepared element concentration** box is checked (Evaluation Methods dialog box, **Display** tab), otherwise it is in percent
Bound%	concentration calculated by stoichiometry, when an element is linked to measured elements in a compound
XRF%	concentration calculated from the measured intensity
Imbalance	Bound% - XRF%, when an element is linked to measured elements in a compound
The columns below are displayed three times, corresponding to the three lines that can be defined for a compound	
Calc. concentration	when several lines are available for a compound, the different concentrations computed with each line are displayed in these columns
Stat. error	error on the concentration introduced by the fluctuation of the signal (Poisson's law); the error on the net intensity is calculated from the $3 \cdot \sigma$ of the gross intensity, background intensity and overlaid intensity
LLD	lower limit of detection
90% line absorption	thickness of the layer of the sample that absorbs 90% of the line, i.e. the layer that gives 90% of the signal for this line; when the sample is thinner, the "loss of intensity" is automatically corrected

Description of the line

Column	Description
Line *n*	name of the line
Line energy	energy of the photons of the radiation
Wavelength	wavelength of the radiation
Peak position	position of the peak
Bkg. position	position of the background in case of a peak/background method
Tube kV	high voltage of excitation of the X-ray tube
Tube mA	intensity of the current for the excitation of the X-ray tube
Filter	filter between the X-ray tube and the sample (material and thickness)
Mask	diameter of the mask
Collimator	aperture of the collimator, in °
Crystal	crystal used for the analysis: LiF 200, LiF 220, OVO-55…
Detector	detector used for the measurement: proportional counter or scintillation counter
PHA-UL — PHA-LL	upper limit (UL) and lower limit (LL) of the discrimination (pulse height analysis, PHA)

Description of the intensity

Column	Description
Mode and drift corr.	factor applied to the intensity to take the atmospheric mode and drift correction into account
Raw peak	raw intensity, corrected by the drift correction, the atmospheric mode, the absorption of the film (for liquids) and the overlaps
Background	background intensity, corrected by the drift correction, the atmospheric mode, the absorption of the film (for liquids) and the overlaps
Net int.	net intensity, corrected by the drift correction, the atmospheric mode, the absorption of the film (for liquids) and the overlaps
Actual int.	intensity written in the raw file, before any calculation or correction.
Overlaid int.	intensity from the neighboring peaks that contribute to the raw height
Foil correction	multiplication factor for the intensity to take the absorption by the film into account
Peak/Bkg/Ovl deviation	3σ error, i.e. three times the square root of the intensities expressed in counts

Raw int. = Actual int. × Mode and drift corr. × Foil correction

Net int. = Raw int. - Overlaid int. - Background

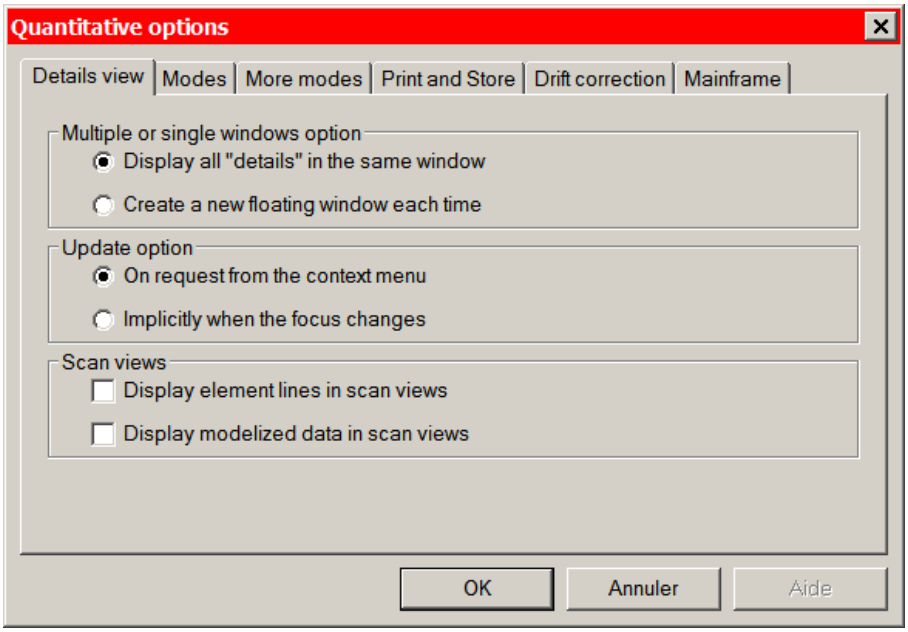
C.3 Dialog boxes and menus related to the Quant windows

Quantitative options

This dialog box is used to set the parameters of the Quant window (layout) and of the quantitative evaluation.

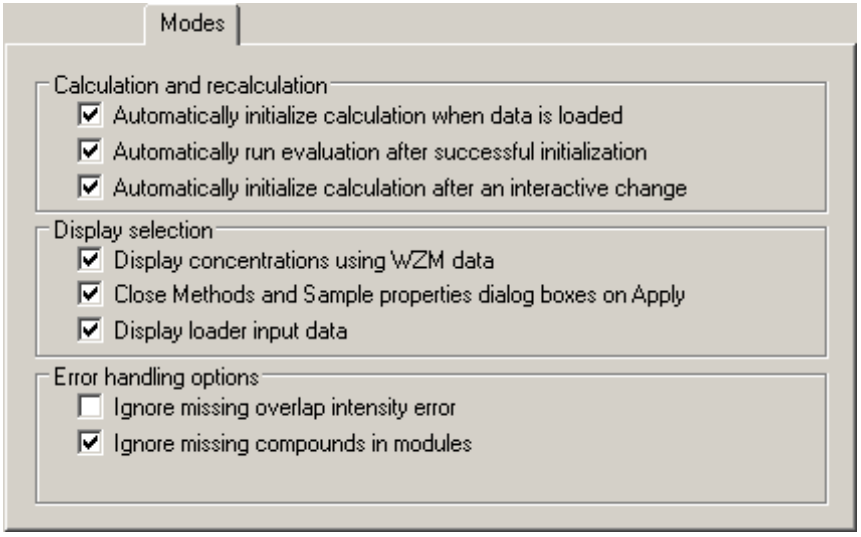
To display this dialog box:

- while the active window is a Quant window, select the **Options** command in the **View** menu.

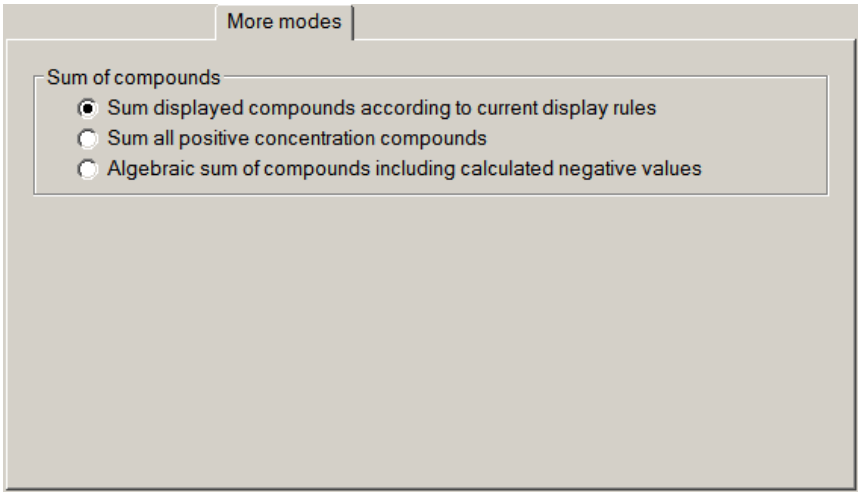


Details view tab	
Control	**Description**
Multiple or single window option	when displaying the Compound Details window (**View details** in the context-sensitive menu): • **Display all "details" in the same window**: there is only one Compound Details window; • **Create a new floating window each time**: there is one Compound Details window per compound;
Update option	This zone is active only when the **Display all "details" in the same window** option (see above) is checked • **On request from the context menu**: the content of the Compound Details window only changes when the **View details** command is chosen in the context-sensitive menu • **Implicitly when the focus changes**: the content of the Compound Details window changes every time another compound is selected (auto update)
Scan views	When displaying the spectrum in a Quali window: • **Display element lines in scan view**: the sticks of the lines

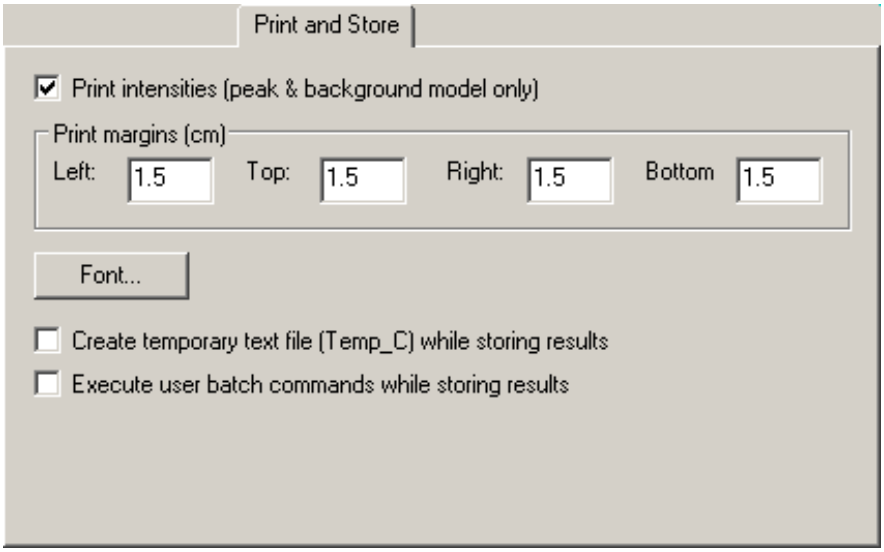
	for the detected elements (i.e. which concentration is above 0) are displayed



Modes tab	
Control	**Description**
Automatically initialize calculation when data is loaded (check box)	when this box is checked, there is no need to click the **Initialize** button (or to use the **Quanti | Initialize** menu option) after the importation of data
Automatically run evaluation after successful initialization	when this box is checked, there is no need to click the **Compute** button (or to use the **Quanti | Compute** menu option) after the initialization of the calculation
Automatically initialize calculation after an interactive change	Self-explanatory
Display concentrations using WZM data	When this box is checked, the unit (% or PPM) that is used is the one set in the WZM file
Close Methods and Sample properties dialog box on Apply	When this box is checked, the **Apply** button in these dialog boxes becomes **Apply and close**
Display loader input data	The LOADER input data are the data that are entered manually, depending on the definition file (e.g. LOI, mass before ignition etc.).
Error handling options	When these options are checked, the related errors are ignored



More modes tab	
Control	**Description**
Sum displayed compounds according to current display rules	When this option is selected, the concentrations are summed as they are displayed.
Sum all positive concentration compounds	When this option is selected, only the positive concentrations are summed.
Algebraic sum of compounds including calculated negative values	When this option is selected, all the concentrations, even the negative ones, are summed.



Printing tab	
Control	**Description**
Print intensities (check box)	in the peak/background method only: print the intensities next to the concentration
Print margin (text boxes)	type in the margins in centimeter
Font (button)	click this button to display the Font dialog box, where you can choose the font (e.g. Arial, Times New Roman etc.), the style (regular, italic, bold) and the size.
Create temporary file (Temp_C) while storing results	When a measurement is completed, the result of the automatic evaluation is stored in a temporary file, Temp_C.DAT. When this option is checked, this temp file is also created when the result of the evaluation is stored in the database Measure.MDB
Execute user batch command while storing results	The application (EVM file) can refer to a batch file, set in the **User calc.** field (usually a BAT file); this file is executed at the completion of the automatic evaluation after the measurement; When this option is checked, this file is also executed after an interactive evaluation, when storing the results in the database.

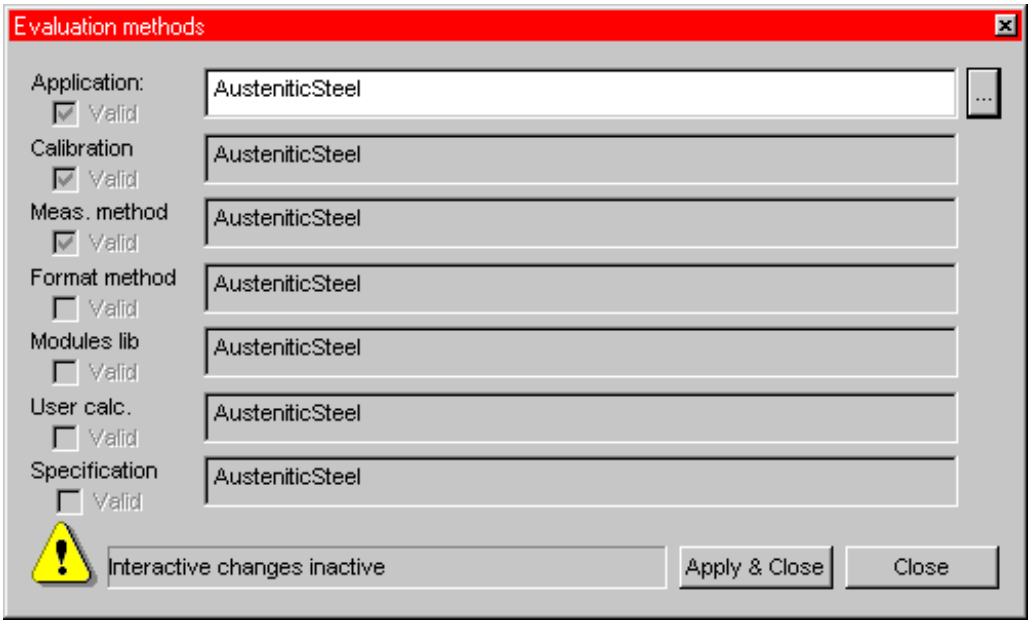
Evaluation Methods

This dialog box is used to choose the files used for the quantitative evaluation (especially the application and calibration files), i.e. the ones used for the initial evaluation parameters.

Toggle method bar button

To display the Evaluation Methods dialog box:

- click the **Toggle method bar** button
  — or —
  use the **View | Evaluation methods** menu option.



Methods tab	
Control	**Description**
Model	name of the application (EVM file), and possibly the path relative to the default directory
Calibration	name of the calibration (FCL file), and possibly the path relative to the default directory
Meas. Method	name of the measurement method (MM file), and possibly the path relative to the default directory
Format method	name of the format method (WZM file), and possibly the path relative to the default directory
Modules lib	name of the modules library (MLB file), and possibly the path relative to the default directory
User calc	name of the automatic script (BAT, VBS, JS… file) that must be run when saving to the database, and possibly the path relative to the default directory
… (Browse button)	click this button to retrieve the path and filename with the Open dialog box

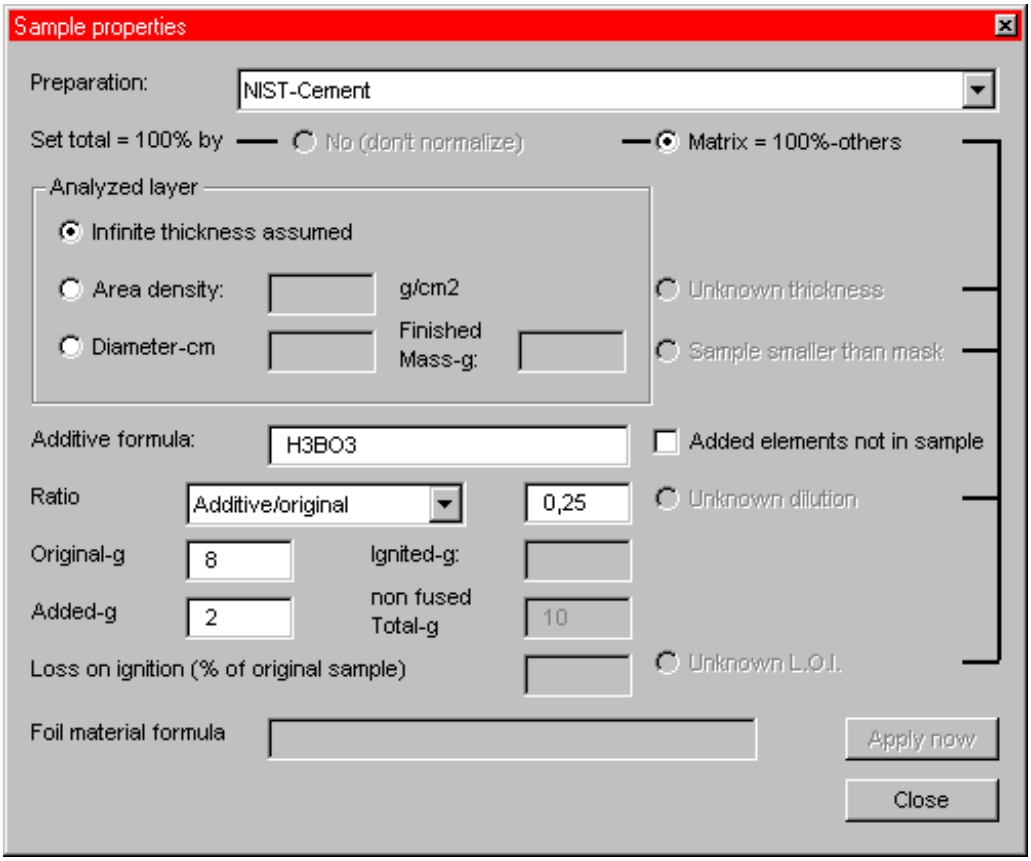
Sample Properties

This dialog box is used

Sample properties button

To display the Sample Properties dialog box:

- choose the **Sample properties** command in the **View** menu
  — or —
  click the **Sample properties** button.



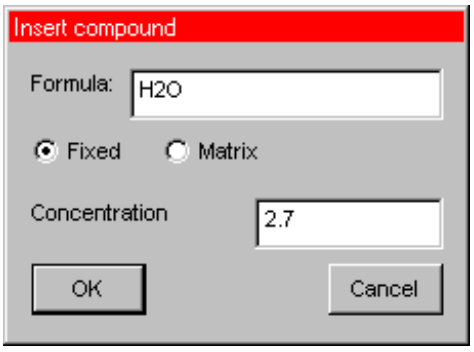
Parameter	Description and options
Analyzed layer	• Infinite thickness assumed: the sample thickness is greater then the analyzed thickness for every line; • Area density: the sample does not have an infinite thickness for every lines; the "thin sample" effect is determined with the area density, i.e. the mass of the sample divided by the analyzed area (in g/cm^2); • Diameter/Finished mass: the sample does not have an infinite thickness for every lines; the "thin sample" effect is determined with the diameter of the sample (in cm, assuming a cylinder) and its mass (in g).
Additive formula	chemical formula of the additive (see the section 4.1.3 Preparation: foil, dilution and loss on ignition). • **Added element not in sample**: when this box is checked, the elements contained in the additive are forced to 0

Parameter	Description and options
Ratio	dilution of the original material, expressed by the ratio between one of the following mass (see the section 4.1.3 Preparation: foil, dilution and loss on ignition): • **Additive**: mass of added material (Added-g); • **Original**: initial mass of sample, before preparation (Original-g); • **Total**: final mass of sample, i.e. Original + Additive (Finished Mass-g); Choose the ratio in the drop-down list and its value in the text box — or — type the initial mass of sample in the **Original-g** text box, ad the mass of additive in the **Added-g** text box.
Loss on ignition	for a Fused bead preparation only (see the section 4.1.3 Preparation: foil, dilution and loss on ignition): • **Ignited-g** is the mass of original sample, after calcination; • **Non-fused Total-g** is the mass of uncalcinated sample+flux before the fusion; • **Loss on ignition (% of original sample)** is the LOI

Insert compound

The Insert Compound dialog box is used to add a compound during an evaluation. As the compounds evaluated by measured elements are already in the material, the concentration of these compounds must be either fixed or calculated by balance to 100%.

This dialog box is displayed with the **Quanti | Add compound** menu option.

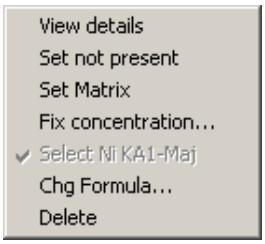


Control	Description
Formula (text field)	chemical formula of the compound
Fixed (radio button)	with this option, the concentration is fixed to a given value, typed in the **Concentration** text field
Matrix (radio button)	with this option, the concentration is calculated by balance to 100%
Concentration (text field)	active only when the **Fixed** option is checked; type the concentration in % in the text field
OK (button)	insert the compound and close the dialog box
Cancel (button)	close the dialog box without inserting the compound

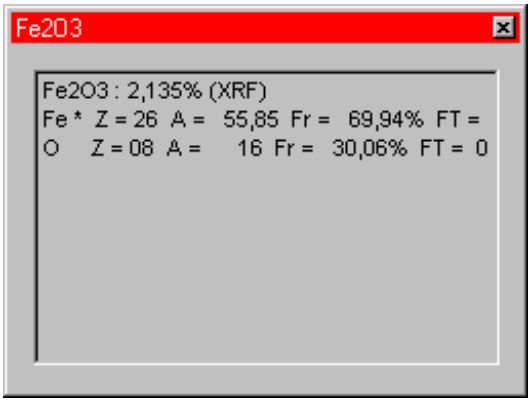
Context-sensitive menu

The **Context sensitive** menu provides tools that are specific to the environment or to a given object.

To display the **Context sensitive** menu: click with the right mouse button anywhere in the list of compounds.



Control	Description
View details	display the Compound Details window
Set not present	fix the concentration to 0
Set matrix	the concentration is computed by balance to100%
Fix concentration…	the concentration is fixed to a given value
Select *name of the line*	the concentration is computed from the measured XRF spectrum
Chg formula	change the chemical formula of the compound
Delete	the compound is removed; it does not appear even when the **Show all elements** option is set



Compound Details window	
Field	**Description**
First line	chemical formula of the compound, followed by the concentration and by the way the concentration is set : XRF (if it is computed), Fixed or Matrix)
Element	chemical symbol of the element; the key element (i.e. the line used to compute the concentration) is highlighted with a star
Z	atomic number of the element
A	atomic weight of the element, in $g \cdot mol^{-1}$
Fr	weight fraction of the element in the compound
FT	weight fraction of the element inside this compound in the whole sample (it is the weight fraction of the compound times the weight fraction of the element in the compound)

C.4 Quali window

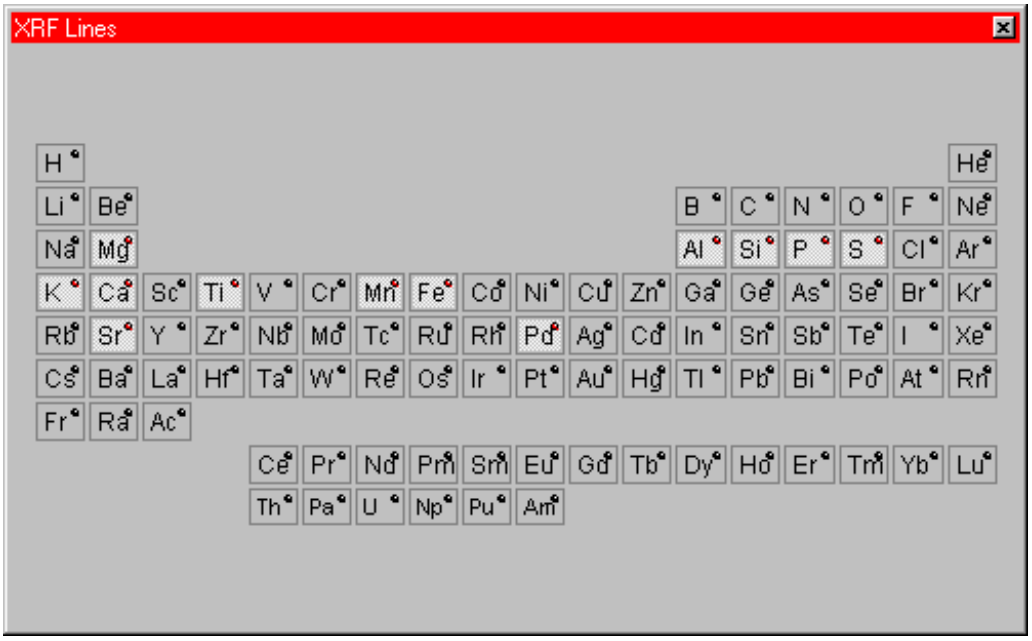
XRF Lines

Elements toolbar button

To display the XRF Lines window:

- click the **Elements toolbar** button
  or
  select the **Elements toolbar** command in the **View** menu;

The **XRF Lines** window represents a periodic table of the elements. When an element is displayed (i.e. the sticks figuring the lines of the element are superimposed to the spectrum), its box is in light gray and its indicator is red. When an element is hidden (the sticks are not displayed), its box is in dark gray and the indicator is black.

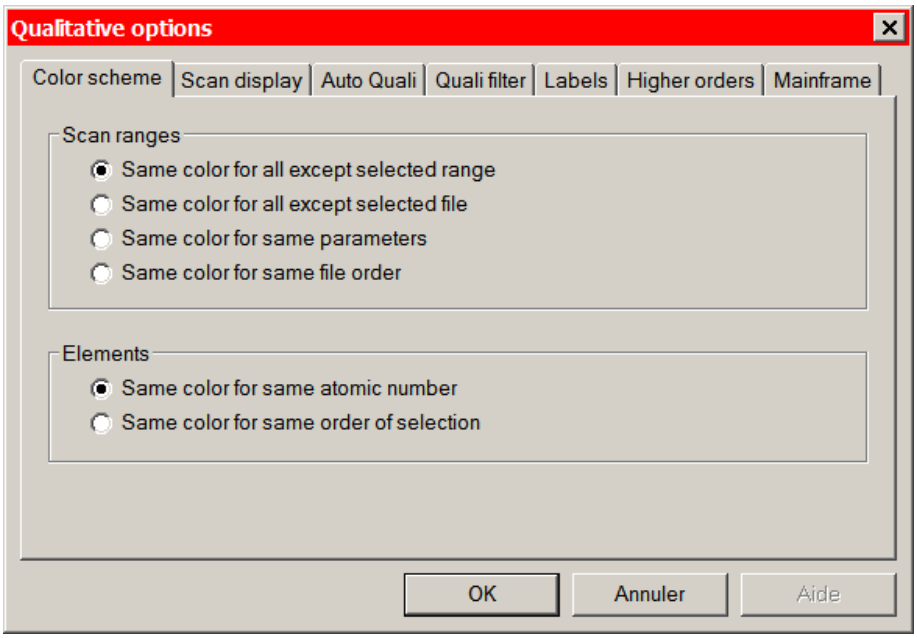


Control	Description
left (normal) click an element cell	display or hide the sticks figuring the lines of the element on the display
right click an element cell	display the context-sensitive menu, with only one option: **Check** (display) or **UnCkeck** (hide) the element

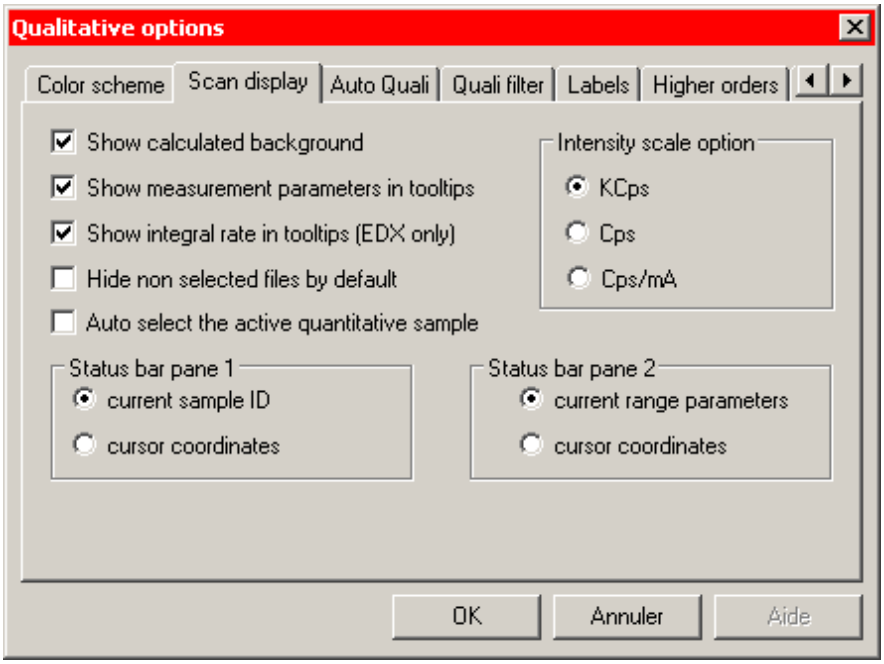
Qualitative Options

The Qualitative Options dialog box is used to set the default parameters of the qualitative evaluation and the display parameters.

To display this dialog box: while the active window is a Quali window, select the **Options** command in the **View** menu.

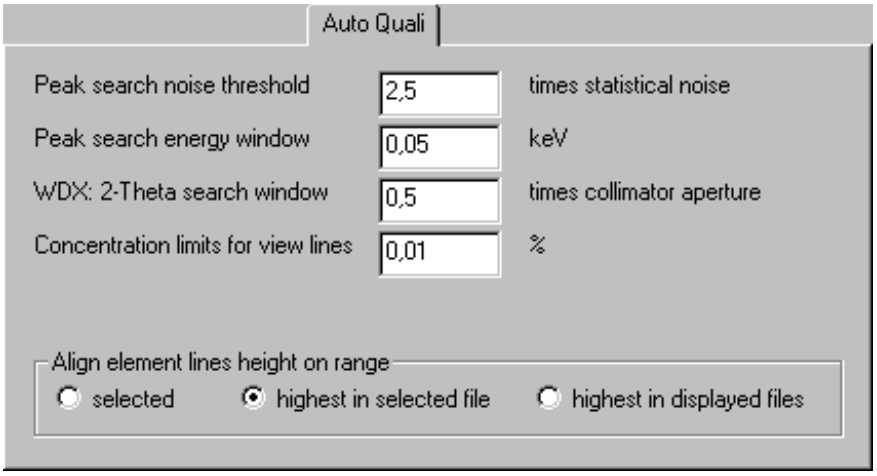


Color scheme tab	
Control	**Description**
Scan ranges	• **Same color for all except selected range**: this highlights a single Range; • **Same color for all except selected file**: this highlights the Ranges belonging to the same SSD file; • **Same color for same parameters**: when only one SSD file is imported, this option allows a different color for each Range ; when several SSD files are imported, this allows to compare what can be compared; • **Same color for same file order**: the color depends on the order of the Range in the SSD file.
Elements	• **Same color for same atomic number**: all the sticks of a given Element have the same color; • **Same color for same order of selection**: the color of each stick is defined independently; the colors are stored (in the Windows® registry), so for the next samples to be processed, the color of a stick can be set just by selecting it, following the same color pattern.

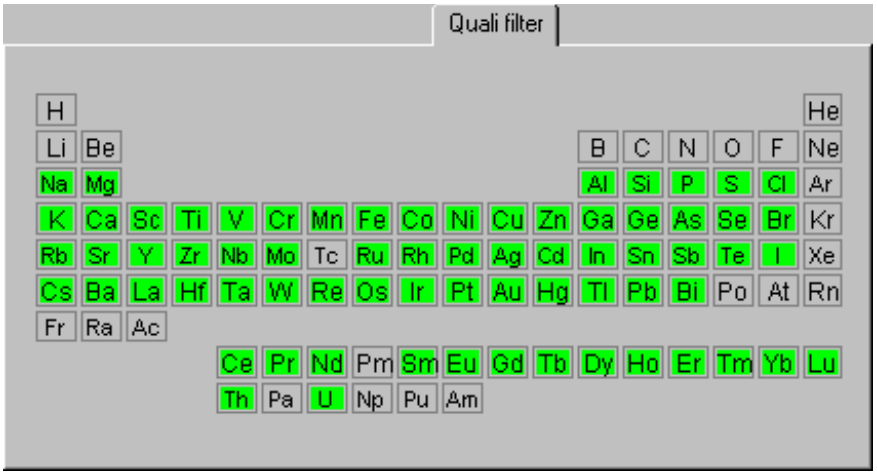


Scan display tab	
Control	**Description**
Show calculated background	display the background line
Show measurement parameters in tooltip	display the measurement parameters (tube high voltage, filter) used for the spectrum under the mouse pointer
Show integral rate in tooltip	display the total number of counts collected per second for the spectrum (it is he integral in energy of the spectrum)
Hide non selected files by default	when this box is checked, the **View selection only** button is pressed when creating the Quali window, the **Hide inactive file** option of the **Quali** menu is active; see the "View/Quali zone" table in the section B "Toolbar", and the "Quali menu" in the section A.
Auto select the active quantitative sample	when this box is checked, the sample being evaluated in a Quant window is set as selected.
Intensity scale option	Select the unit of the Y-scale. The scale itself (linear or square root) is set by the context-sensitive menu (right-click the Y axis, see section 5.5.2 topic “X- and Y-scale setup”).
Status bar pane 1 or 2	Sets what is written in the status bar (text box at the bottom of the window).

Note:	the "tooltip" is the popup window that appears when the mouse pointer is let still on a curve.

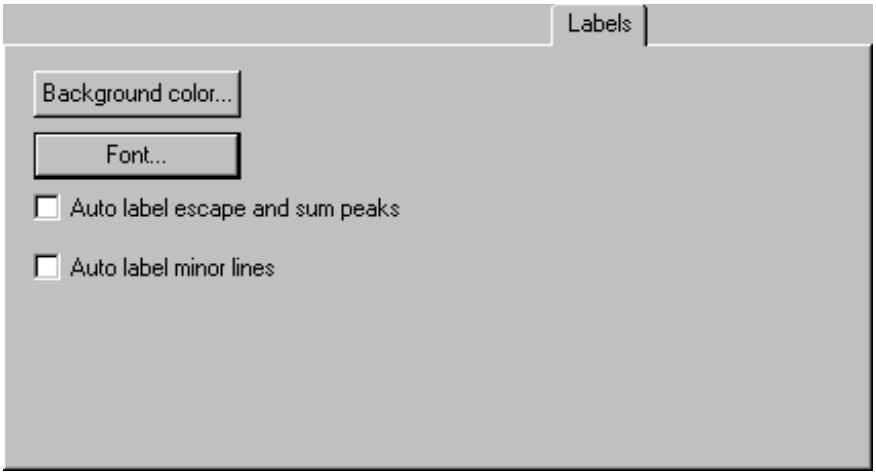


Auto quali tab	
Control	**Description**
Peak search noise threshold	the statistical noise is the square root of the number of counts of the background (Poisson's law); the peaks whose net height is less than *k* times this statistical noise are ignored; when the peak is higher, the element is considered as present (see the section 5.4.1 "Automatic evaluation"); *k* is the value in this text field
Peak search energy window	the peak search algorithm uses a Savitzky-Golay smoothing; this energy window is the width of the sliding interval used for the smoothing (see the section 5.4.1 "Automatic evaluation")
Concentration limits for view lines	when the concentration calculated in a Quant window is below this value, the line is not displayed when choosing the **Show lines** option of the **Quali** menu
Align element lines height on range	the height of the sticks figuring the lines are adjusted to the level of a spectrum (the spectrum can be different for each line), as defined by the option: • **selected**: the selected spectrum is used for all the lines • **highest in selected file**: for a given energy, the highest spectrum amongst the spectra which belong to the same SSD file as the selected spectrum • **highest in the displayed files**: for a given energy, the highest spectrum amongst the displayed spectra



The options defined here apply when selecting the **Evaluation command** of the **Quali** menu (see the section 5.4.1 "Automatic evaluation").

Quali filter tab	
Control	**Description**
Pd	**Select**: the element is part of the automatic qualitative search; it is displayed in the pop-up window (tooltip) when the mouse pointer is close to a position of one of its lines
Pd	**Discard**: the element is excluded from the automatic qualitative search; it is present in the tooltip and thus can be easily added interactively
Pd	**No check**: the element is excluded from the automatic qualitative search; it is not displayed in the tooltip

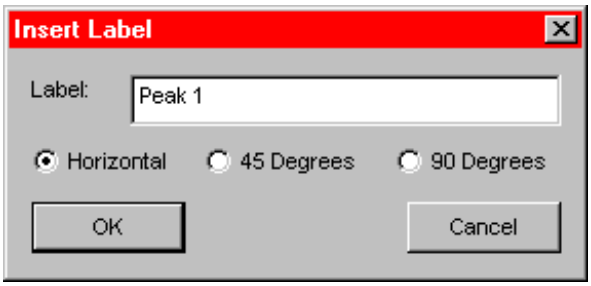


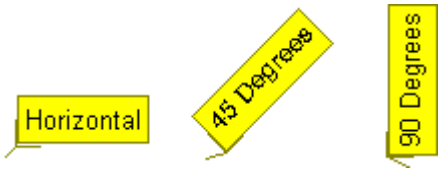
Labels tab	
Control	**Description**
Background color…	change the color of the background of the labels (yellow by default)
Font…	change the font of the labels
Auto label escape and sum peak	when this box is cleared (default), the escape peaks (loss of energy of the photon due to the ionization of the detector) and sum peaks (artifact of the detector, pile-up of pulses) are not labeled by the **Label lines** command of the **Quali** menu
Auto label minor lines	when this box is cleared (default), only the $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$ and $M\alpha$ lines are labeled by the **Label lines** command of the **Quali** menu

Label

The layout of a Label is defined in the Label dialog box. To display it:

- right click anywhere on the graphic, except on a curve or on an Element stick, and
- in the context-sensitive menu, select **Insert label**.





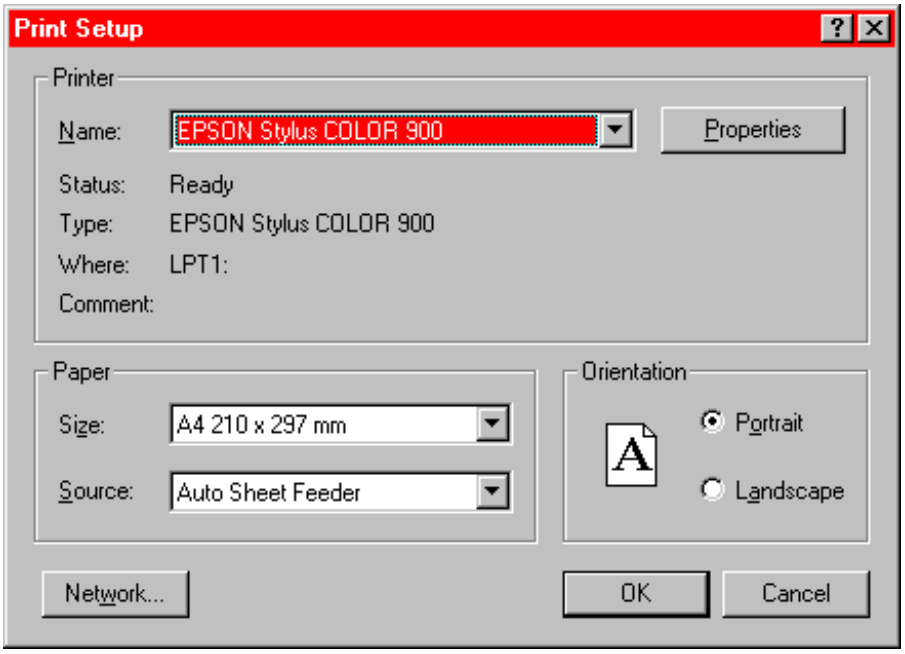
Control	Description
Label (text field)	type the text of the label in the text field
Horizontal, 45 Degrees, 90 Degrees	orientation of the label, see the picture above
OK	create the label and close the dialog box
Cancel	close the dialog box without creating the label

Print Setup

The aim of the Print Setup dialog box is to set the parameters of the printout.

To display it:

- in the **File** menu, choose the **Print Setup** command
  — or —
  in the Print Preview dialog box, click **Print**.

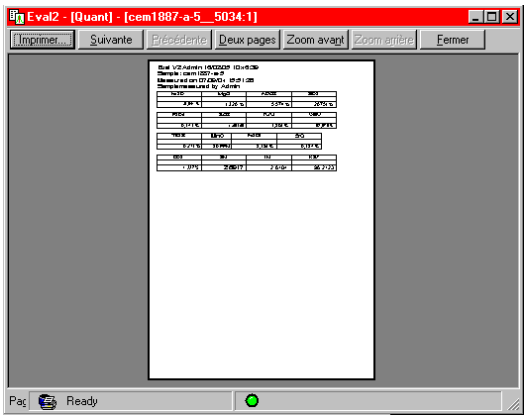


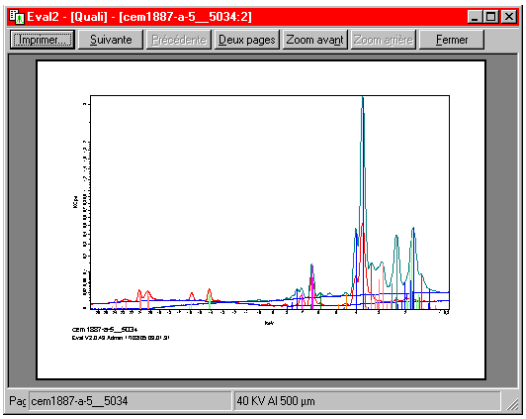
Control	Description
Name (drop-down list)	when several printer are available (i.e. connected, possibly through a network, and installed on the computer), choose the printer in the drop-down list
Properties (button)	set the parameters of the printer
Paper size and source (drop-down lists)	when several trays or sources are available, choose the one you want to use
Orientation	**Portrait** or **Landscape**, as shown on the picture
Network	browse through the network for a remote printer
OK	print the document and close the dialog box
Cancel	close the dialog box without printing

Print Preview

The Print Preview dialog box displays a preview of what will be printed. To display this dialog box:

- in the **File** menu, choose the **Print preview** command.



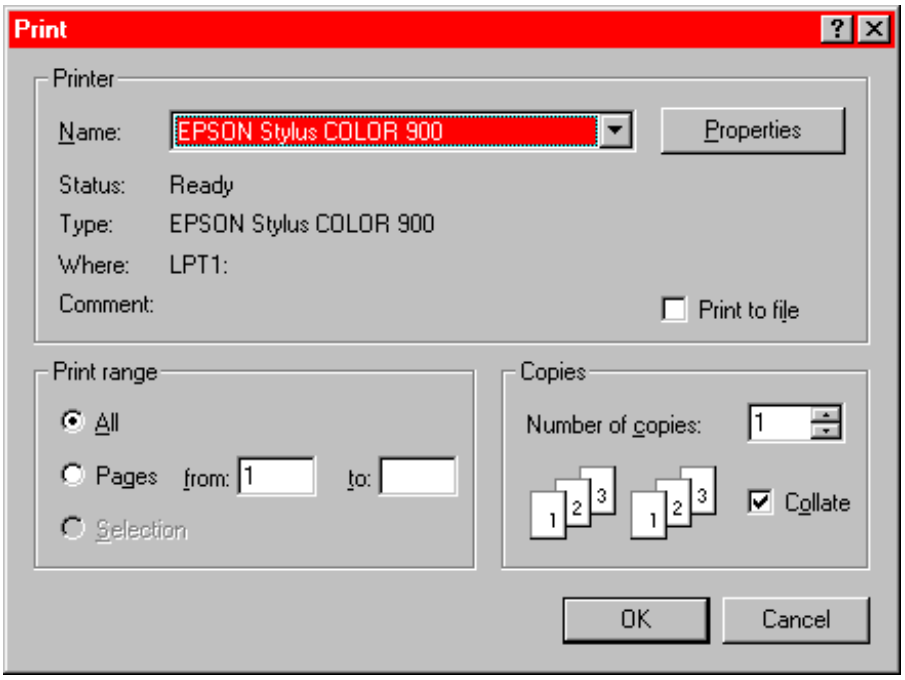


Control	Description
Print	print the document
Previous/Next (buttons)	when there are several pages: display the previous or the next page
Two pages/One page (buttons)	display two pages one beside the other, or one page on the screen
Zoom in/Zoom out (buttons)	magnify or reduce the picture
Close (button)	close the window

Print

The Print dialog box is used to print the current window. To display it:

- select the **Print** command in the **File** menu
  — or —
  use the **CTRL+P** key combination



Control	Description
Name (drop-down list)	when several printer are available (i.e. connected, possibly through a network, and installed on the computer), choose the printer in the drop-down list
Properties (button)	set the parameters of the printer
Print to file (check box)	instead of printing the document, the data a restored in a PRN file
Print range	• **All**: print the whole document • **Pages**: when the document is made of several pages, it is possible to print one or a set of pages
Copies	it is possible to print several copies of the same document • **Number of copies** (spin box): self explanatory; • **Collate** (checkbox): when it is cleared, all the pages #1 are printed together, then all the pages #2… when t is checked, the documents are printed as separate documents
OK (button)	print and lose the dialog box
Cancel (button)	close the dialog box without printing

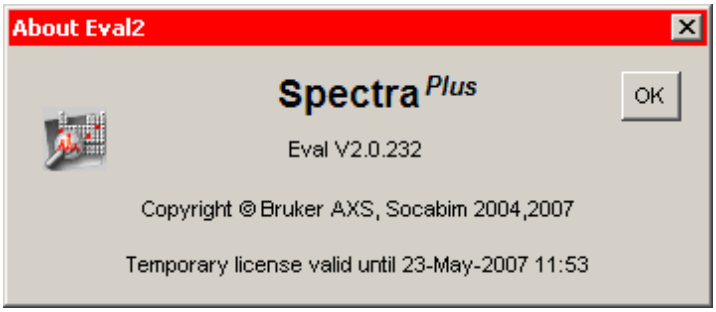
About Eval2

The About Eval2 dialog box gives information about the version of EVAL2, especially the version number.

To display it:

AboutEval2 button

- select the **About Eval2** command in the **Help** menu
  or
  use the **About Eval2** button.



Control	Description
OK (button)	close the window