PRESENTATION OF THE COLEGRAM SOFTWARE

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TITRE : Presentation of the COLEGRAM software

RESUME :

The purpose of COLEGRAM is the processing of complex experimental spectra to describe individual features and to derive individual area for each peak or shape of interest. The individual components are modeled using a mathematical function adapted to the spectrum nature. The fitting of the mathematical function to experimental data is achieved using the chi-squares method with the Marquardt-Levenberg algorithm.

The different capabilities of the sofware are presented.

Mots clés : fitting – spectrum processing – chi-squares -

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1. Introduction

The COLEGRAM software suite was originally designed for use in gamma-ray and X-ray spectrometry. The purpose of COLEGRAM was to accurately process experimental spectra to separate overlapping components and derive individual areas for each of them, especially in the 100 keV photon energy region including both X- and gamma-ray peaks [1,2]. Since this starting point, COLEGRAM has been upgraded and is now available with more options for processing different types of spectra. This is achieved by fitting mathematical functions to experimental data sets. Several types of functions can be used, depending on the kind of spectrum; most of them are specific to a particular peak shape: alpha, gamma, X, or beta. Functions for overall background shapes, such as exponential or polynomial, are also available. COLEGRAM uses the least squares fitting method with the Marquardt-Levenberg algorithm and is based on a visual management under the user control.

Thus, this approach makes the code fast running and induces an important visualization interface what makes it easy, at any time, to modify the spectrum region under study, to check the fitting procedure, to add or to delete any peak, to change its shape etc.

The present version of COLEGRAM requires a personal computer running Windows®. The code in written in Microsoft Visual C++ and is currently compiled with Version 6 of this language.

2. Principle of the fitting method

The purpose of COLEGRAM is to process complex spectra comprising several components, to describe overlapping features and to derive the area of each peak or shape of interest. The individual components are therefore modeled using mathematical functions, according to the user's theoretical knowledge of the spectrum constitution.

Fitting a mathematical function to n experimental data (x_i, y_i) consists in determining the optimum set of m parameters ($a = a_0, a_1, ..., a_m$), such that the computed values with function $f(x_i; a)$ will be as close as possible to the experimental values y_i. The different parameters of the fitting function are obtained by the non-linear least-squares method [3].

Generally, if Φ is the function to minimize:

$$\Phi = \sum_{i=0}^{n} \left(\frac{f(x_i; \mathbf{a}) - y_i}{\sigma_i} \right)^2$$

where σ_i represents the standard deviation of experimental value y_i.

The parameters values are obtained by minimization of Φ, *i.e.* by canceling out the values of its partial derivatives:

$$\frac{\partial \Phi}{\partial a_j} = 0$$

This minimization is performed using the Marquardt-Levenberg algorithm (Appendix 1) which uses two different approaches as fitting progresses: far from the minimum, the gradient method is first used, then, when near the minimum, it is replaced by the Hessian method. In both cases, solving the equation system requires computation of the first derivative for each of the m parameters. Uncertainties (variances) associated to each parameter are calculated during the fitting procedures, as well as covariances of the different parameters.

Two options are proposed for conducting the fitting. The first option corresponds to a simple minimization, without taking account of individual weighting of the experimental data ($\sigma_i = 1$): this is the "least squares" option. The second option uses the "chi-2" criterion, *i.e.* including the standard deviation of each experimental point ($\sigma_i^2 = y_i$).

3. Software presentation

3.1 General characteristics

COLEGRAM runs under Windows®. It can handle spectra from different origins. In the present version, spectra obtained by acquisition software such as Intergamma® (extension .spe), ACC (extension .dat), Maestro® (extension .chn or .spc) are directly identified by the file extension. ASCII files (extension .asc) can also be directly read: they must include two columns, the first with the channel number (or the energy) and the second containing the count number for the relevant channel. The entire spectrum loaded, including its energy calibration, is displayed in the main window (§3.1.1). Information useful for the user is presented in screens as described below. COLEGRAM generates its own spectrum file (extension .spm) including all the parameters obtained in the fitting procedure (§3.2.5).

3.1.1 Main window

All the windows used to display the data being processed (spectra or region of interest (ROI)) and fitting results are included in the main window shown in Figure 1. The menu bar is under the title bar: it changes according to the processing step. In the first screen, it includes three tabs:
- "File": used for file opening (see §3.2.1), and printing and saving results (see §3.2.5),
- "View": to display or mask the window elements,
- "Help": to provide help by indexed words and display the version number of the software.

Two other bars are also available: the upper one includes a set of buttons corresponding to menu item shortcuts; the second one, on the window bottom, displays information with a short help text about the item selected.
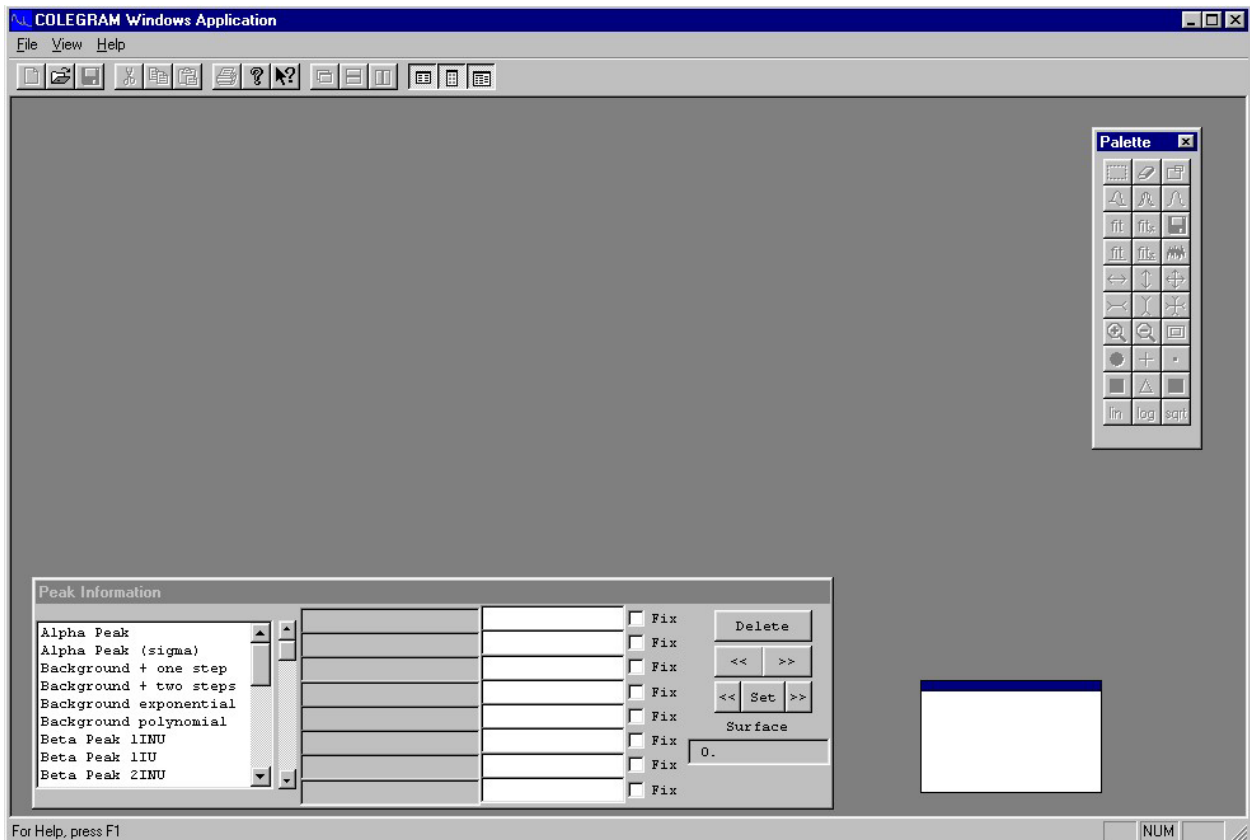
Figure 1 - COLEGRAM main window

3.1.2 Floating windows

The main window contains three floating windows allowing the user to control the application progress (Figure 1):

- the "Palette" window (upper right-hand side), which comprises a set of buttons corresponding to commands affecting spectra or ROIs: selection and modification of an ROI, opening of secondary window, processing of an ROI, peak fitting, zoom, spectrum display mode etc.,

- the "Cursor information" window, which appears underneath and shows information on the data (spectrum or ROI) being processed and the cursor position (channel number or energy - if the spectrum file includes the energy calibration - and content of the relevant channel),

- the "Peak information" window, which appears below the main window and is a dialog box displaying parameters of the peaks of any ROIs be processed.

3.2 COLEGRAM practical use

3.2.1 Opening a file

The user has several ways of opening a spectrum file:
- select "open" (shortcut: "Ctrl" + "O") from the "File" menu or use the equivalent button in the bar under the menu bar,
- click twice on the document (extension .spm) in Windows® Explorer,
- slide the document from the Windows® Explorer to the application window.

As soon as a document is open, the entire relevant spectrum is displayed in a secondary window (Figure 2). The menu bar includes two new tabs marked "Display" and "Window". The "Window" menu can be used to hide or show either floating window. With the "Display" menu, or with the "Palette" window tools, it is then possible to change the display mode (shape and color) of the experimental points, to zoom in and out, to slide the spectrum or to change the vertical scale (linear, logarithmic or root square) to better examine a region of interest.
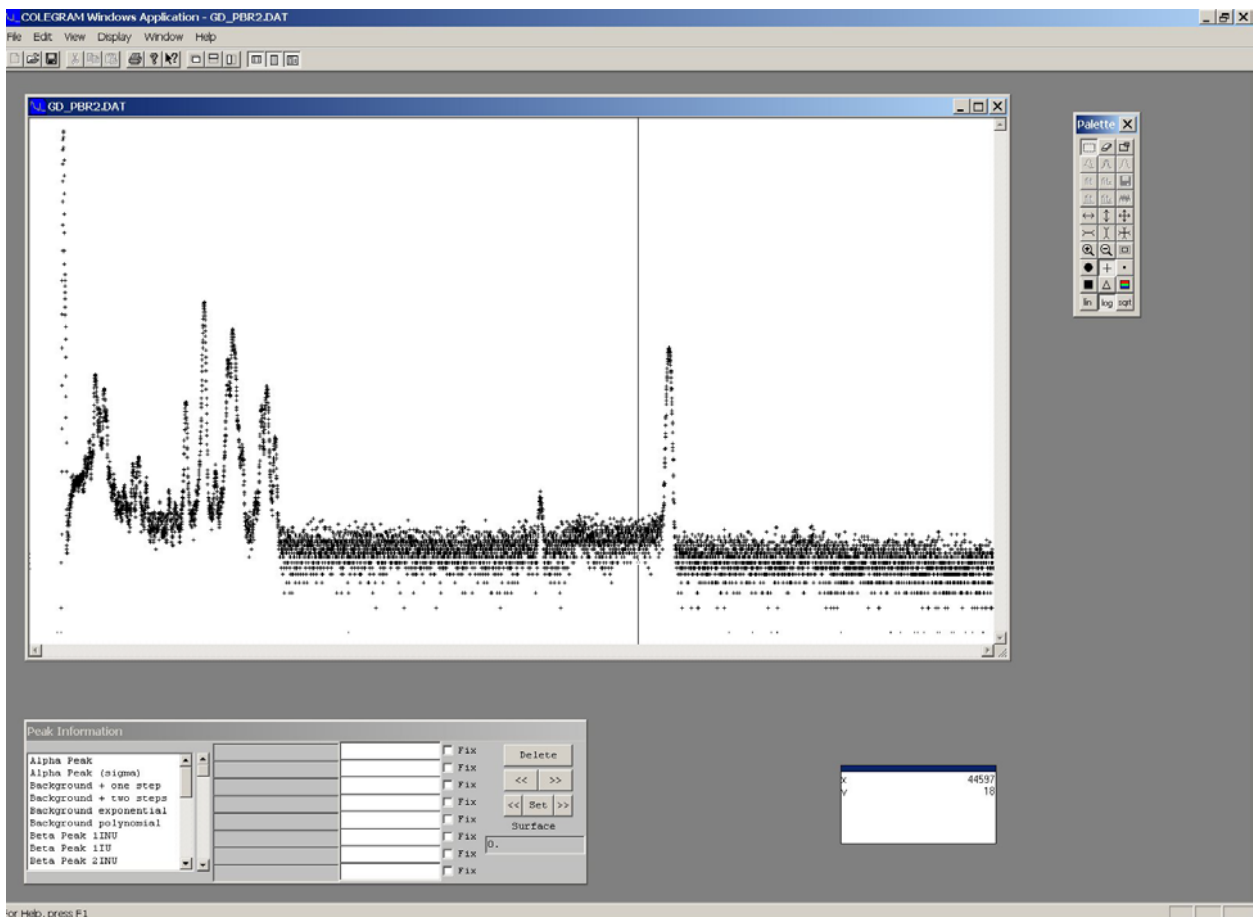
Figure 2 - Spectrum displayed in the secondary window (^{103}Pd).

3.2.2 Selecting a region of interest

The user can then select regions of interest with the first two upper left buttons (set and clear) of the "Palette" window and use the mouse to mark the selection. Experimental points of selected ROIs are shown in a different color and each ROI can hence be displayed it in its own window by clicking on the upper right button (Figure 3).
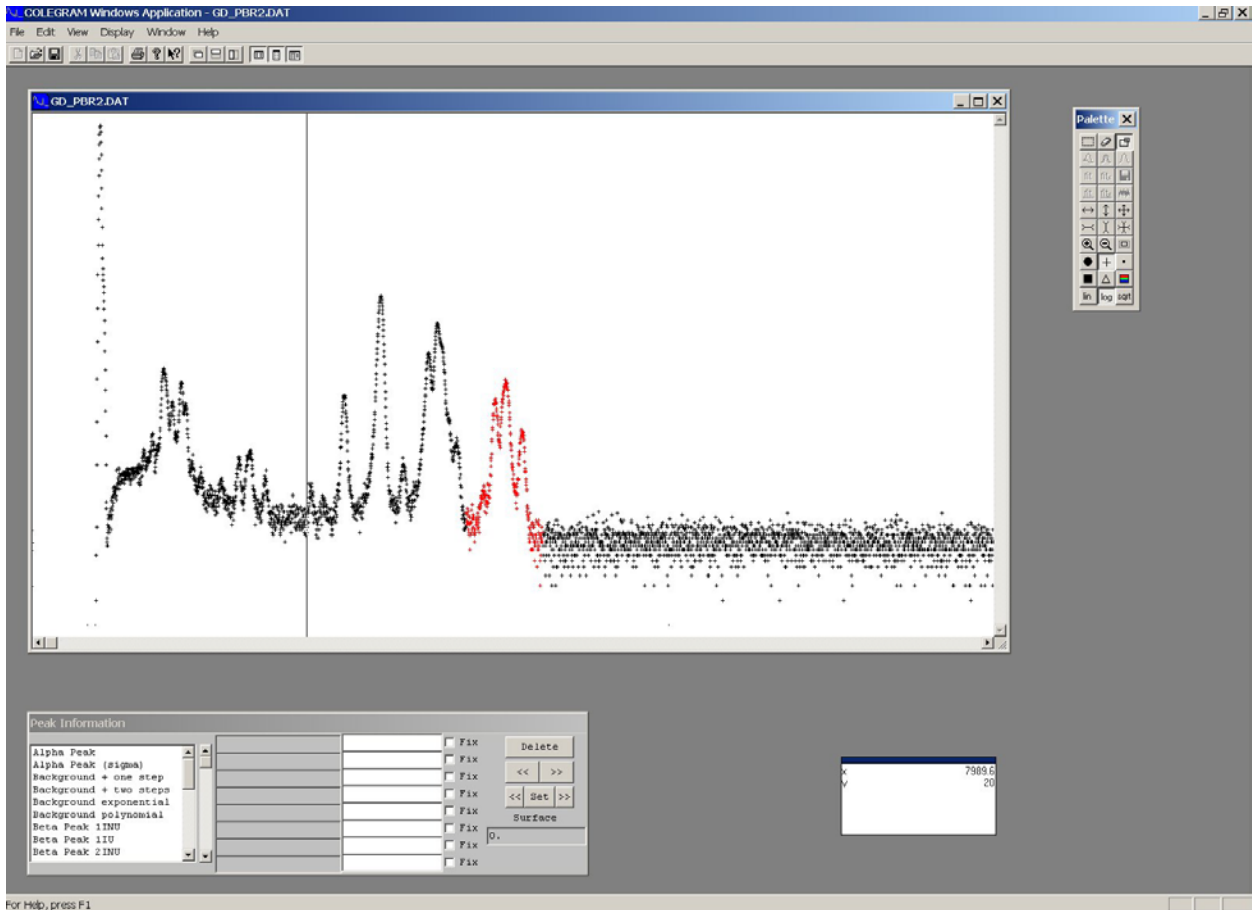
Figure 3 - Selection of a region of interest

3.2.3 Processing of a region of interest

The same display adjustments as for the whole spectrum are available for the region of interest ("Palette" tools). The button for subtracting the background from the selected ROI (left button on the second row) is a tool mainly used in gamma-ray spectrometry (Appendix 2). The user must then define the peaks included in each ROI. The default peak shape is selected either using the "Peak class preference" available in the "File" menu, or clicking on the middle button of second row in the "Palette" window. By default, the same shape is applied to each peak of the ROI.

A peak is input by setting the cursor at a defined position and clicking on the mouse left button. The defined peak is drawn as a continuous line in the graph of the experimental data (Figure 4).

Default parameters characterizing the peak shape are thus displayed in the "Peak information" window. Using this dialog box, the user can successively display parameters linked to each defined peak by clicking on one of the double arrows buttons (back or forward). For each one, he can change the peak shape, modify any parameter and fix or free it. Spurious peaks can also be deleted from this box. Any change must be validated by clicking on the "Set" button
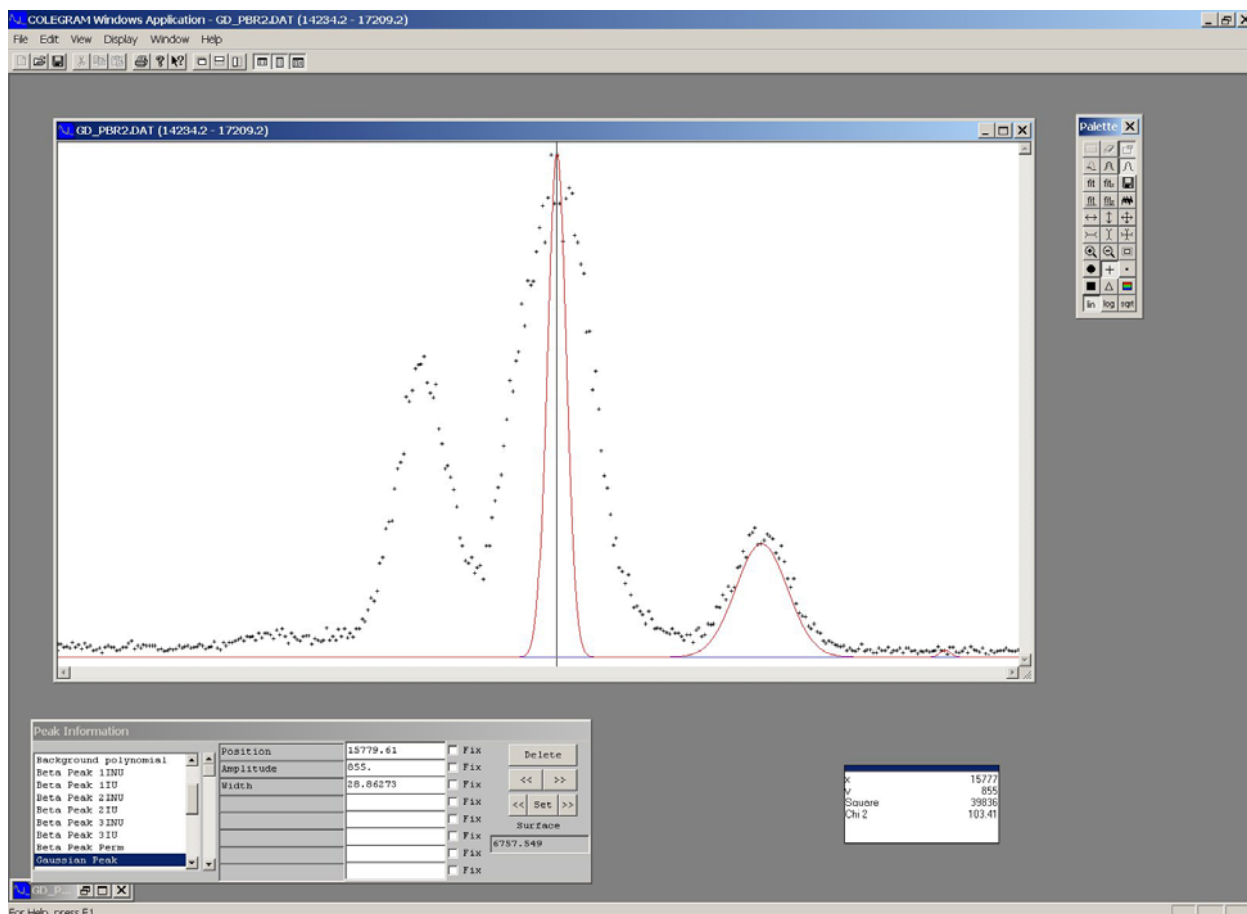
or on double arrows buttons on the last row of this window: using these last ones, at the same time, the parameters are validated and the cursor moves to the next (or previous) peak position.

Figure 4 - Initialization of the peaks of the selected ROI

3.2.4 Mathematical function fitting

At any stage of the processing, the user can run the fitting tool which searchs the best fit of a mathematical model to the experimental spectrum, thus improving the parameters. Two fitting methods are available: the "least squares" and the "chi-2" methods (§ 2). These methods are iterative and the user can run iterations either one by one or in series of ten. After each fitting, display is updated and the user can act upon the value of the different parameters (Figure 5). Both criteria (least squares and chi-2) are quoted below the cursor information, in the "Cursor information" window; this allows the user to judge the quality of the fit.
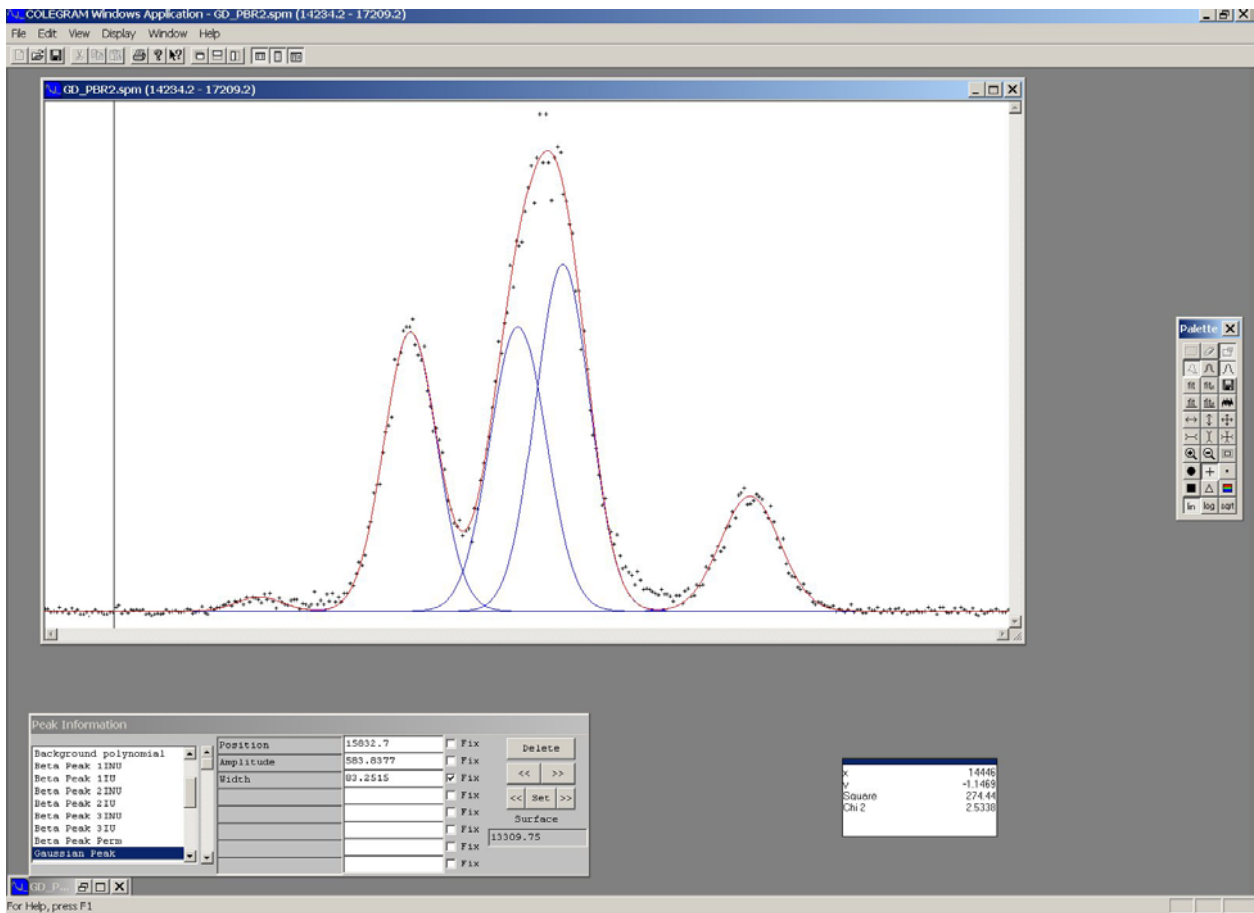
Figure 5 - Fitting peaks in selected ROI

There is another means of visual and quantitative control of the fitting results that is to display residuals in a different window (Figure 6). Two methods are available for computing residuals:

- the relative residuals are expressed as a percentage and computed as:

$$r_i = \frac{(y_i - f_i)}{\sigma_i^2} \cdot 100 = \frac{(y_i - f_i)}{y_i} \cdot 100$$

- the residuals relative to sigma are:

$$r_i = \frac{(y_i - f_i)}{\sigma_i}$$

The choice of the residuals computation mode is selected from the main window (command "Residuals preference" in the "File" menu).
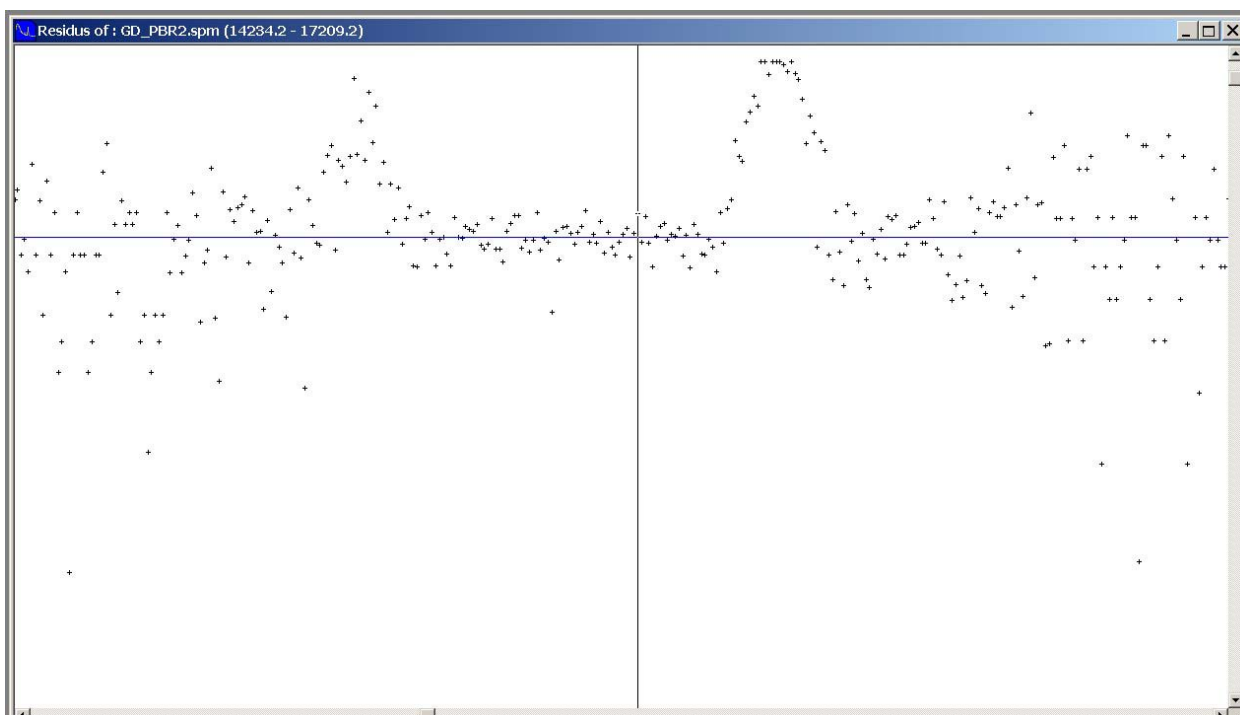
Figure 6 - Display of the fitting residuals

3.2.5 Saving results

At any time, the user can save the spectrum (item "Save as" on the "File" menu), including its ROI and the associated peaks, in a file with an "spm" extension: the file format is specific to COLEGRAM. Saves can be used as parameter starting points for processing similar spectra.

The user can also produce files including a list of all peaks of an ROI with their parameters and the associated areas, as well as uncertainties resulting from the fitting procedure (item "Save all ROIs" on the "File" menu). Peak areas are computed as theoretical values from the parameter values. Uncertainties are obtained by quadratic combination of variances and covariances of the parameters concerned. Result files are produced either in pure text format, or in format that can be imported by EXCEL® ("Save all ROIs EXCEL"). Appendix 3 gives, for each fitting function, a list of parameters as given in these result files, and the formula used for computing the associated area.

Last, it is possible to print (or to send to an external file in Windows® metafile format) a picture of the spectrum with its ROIs, or the ROI with its peak and the fitting function. Printing options are available on the "File" menu.

4. Functions used for the fitting process

In each region of interest, *n* individual peaks are defined, each one being characterized by its own shape and parameters such as position, amplitude, etc.. Depending on the nature of the spectrum under study, the user can choose between 25 different peak or background shapes. A peak is described by up to 9 parameters depending on the option selected. Each parameter is fixed or free, at the user's choice (§3.2.3); this can be changed at any stage in the fitting procedure.

4.1 Basic peak shapes

These shapes are traditionally associated with common kinds of spectra, gamma, alpha or X, and are based on a Gaussian function.

4.1.1 Gaussian: G(x)

Gamma-ray peaks can be simply fitted using a Gaussian profile:

$$G(x) = \frac{A}{\sigma \sqrt{2\pi}} \times \exp\left[\frac{-(x-x_0)^2}{2\sigma^2} \right]$$

The peak is entirely characterized by three parameters: position x_0, amplitude A, and standard deviation σ. Initial values for position and amplitude are taken from the experimental values at the cursor position; the standard deviation is evaluated from the peak full width at half maximum.

4.1.2 Tailed Gaussian: TG(x)

A left-hand tail can be added to the basic Gaussian. In gamma-ray spectrometry, this shape can be used to take into account events due to incomplete charge collection in the detector. The tail is modeled as an exponential function truncated at the peak position, convolved with a Gaussian representing instrumental broadening:

$$T(x) = \int_{-\infty}^{x_0} A \cdot T \cdot \exp(\tau \cdot x') \cdot \exp\left[\frac{-(x'-x_0)^2}{2\sigma^2} \right] \cdot dx'$$

what can also be expressed in a simpler way for computing:

$$T(x) = A \cdot \frac{T}{2} \cdot \exp\left[(x-x_0)\tau + \frac{\sigma^2 \tau^2}{2} \right] \cdot \text{erfc}\left[\frac{1}{\sqrt{2}} \cdot \left(\frac{(x-x_0)}{\sigma} + \sigma\tau \right) \right]$$

This shape includes two more parameters: tail relative amplitude T, and exponential slope τ. By default, the initial values are 0.1 and σ respectively.

Then:

$$TG(x) = G(x) + T(x)$$

erfc is the complementary error function:

$$erfc(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} \, dt$$

It is computed using an approximation [3] giving fractional error less than 1.2×10^{-7}.

4.1.3 Gaussian with two tails: DTG(x)

This function includes a tail on each side of the Gaussian: the high energy tail can be use to take into account event due to pile-up effects in the case of gamma-ray spectra recorded with a high count rate.

$$DTG(x) = G(x) + LT(x) + RT(x)$$

The left-hand tail function, $LT(x)$ is the same as the tail function described above, with parameters T_1 and τ_1; the right-hand tail function, $RT(x)$ is expressed as:

$$RT(x) = \int_{x_0}^{+\infty} A \cdot T_2 \cdot \exp(-\tau_2 \cdot x') \cdot \exp\left[\frac{-(x'-x_0)^2}{2\sigma^2}\right] \cdot dx'$$

or:

$$RT(x) = A \cdot \frac{T_2}{2} \cdot \exp\left[(x-x_0)\tau_2 + \frac{\sigma^2 \tau_2^2}{2}\right] \cdot erf\left[\frac{1}{\sqrt{2}} \cdot \left(\frac{(x-x_0)}{\sigma} + \sigma\tau_2\right)\right]$$

with right-hand tail relative amplitude T_2 and slope of the decreasing exponential τ_2. By default, their initial values are 0.1 and σ respectively.

erf is the error function:

$$erf(x) = \frac{2}{\sqrt{\pi}} \cdot \int_0^x \exp(-t^2) \cdot dt$$

4.1.4 Alpha: ALPHA(x)

This function in use in alpha spectrometry has been proposed by Bortels *et al.* [4]. It is another extension of the tailed Gaussian function, as it is sum of a Gaussian and of two left-sided tails:

$$ALPHA(x) = G(x) + T_1(x) + T_2(x)$$

Two additional parameters are required to entirely characterize this shape: T_2, the relative amplitude of the second left-side exponential and τ_2, its slope. These are initialized at 0.1 and $\sigma/2$ respectively.

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4.1.5 Voigt and Voigt'plus': V(x)

The Voigt function is adapted to the shape of X-ray peaks as it is the result of convolving a Lorentzian function (corresponding to the natural shape of X-ray line) with a Gaussian profile taking account of the instrumental broadening:

$$V(x) = \int_{-\infty}^{+\infty} L(x') \cdot G(x - x') \cdot dx'$$

Where: $\quad L(x) = \dfrac{\Gamma/2\pi}{(x-x_0)^2 + (\Gamma/2)^2}$

To entirely describe the Voigt function, it is necessary to include the Lorentzian width Γ in the parameters used for the Gaussian shape; by default, its initial value is $\sigma/5$.

The Voigt function is computed using approximations (see Appendix 4); in some cases (σ large compared to Γ), the simpler Voigt approximation fails and the more detailed "Voigt plus" approximation can then be used, but the computing time is longer.

4.1.6 Tailed Voigt: TV(x)

This function is similar to the tailed Gauss, with a Voigt function instead of the Gaussian:

$$TV(x) = V(x) + T(x)$$

This function is entirely defined using 6 parameters, as the parameters of the "Voigt" functions must be completed by the left-side tail parameters, T_1 and τ_1 (relative amplitude and slope) (§4.1.2).

4.1.7 Voigt with two tails: DTV(x)

Here, the Voigt shape is completed by a tail on each side:

$$DTV(x) = V(x) + LT(x) + RT(x)$$

As for the Gaussian with two tails (§ 4.1.3), the parameters of the "Tailed Voigt" functions must be completed by the right-side tail parameters T_2 and τ_2 (relative amplitude and slope). This function is thus entirely defined using 8 parameters.

4.2 Beta functions

These functions are dedicated to beta spectra processing: they include three options according to the transition type (allowed or forbidden). The function is described in [5]; it is a product of three factors:

$$\text{BETA}(E) = \text{STAT}(E) \cdot \text{COULOM}(E) \cdot \text{FORME}(E)$$

The statistical factor is:

$$\text{STAT}(E) = \sqrt{E^2 - 1} \cdot E\,(E_0 - E)^2$$

E is the electron total energy, expressed in $m_0 c^2$ units, and E_0 is the beta transition maximum energy. The electron momentum, p, is $\sqrt{E^2 - 1}$.

The Coulomb factor is the product of the Fermi function, $F(E)$, and the function $L(E)$:

$$F(E) = 2 \cdot \left(2 \cdot p \cdot R'\right)^{-2(1-\gamma_0)} \exp\left(-\,\text{sgn} \cdot \Pi \cdot \nu\right) \cdot \frac{\left|\Gamma(\gamma_0 + i\nu)\right|^2}{\left|\Gamma(2\gamma_0 + 1)\right|^2}$$

and:

$$L(E) = 1 + \left[\,1 - (\alpha Z)^2\,\right]^{1/2}$$

with $\gamma_0 = \left[\,1 - (\alpha Z)^2\,\right]^{1/2}$ and $\nu = \dfrac{\alpha \cdot Z \cdot E}{\sqrt{E^2 - 1}}$,

In these functions, Z is the atomic number of the nuclide daughter, and sgn, the sign of the emitted charge, α is the fine structure constant (1/137.036), and Γ is the complex or real gamma function.

$R' = R/h$, R is the radius for which the electron wave function is evaluated:
$R' = 0.002908\,A^{1/3} - 0.002437\,/\,A^{1/3}$, A is the mass number of the daughter nuclide.

If the electron screening effect is taken into account, the Fermi function becomes:

$$F'(Z, E') = F(\pm Z, E + V_0) \left[\frac{(E \mp V_0)^2 - 1}{E^2 - 1}\right]^{1/2} \cdot \left(\frac{E \mp V_0}{E}\right)$$

where V_0 is the Fermi-Thomas potential: $V_0 = 1.45\,\alpha^2\,Z^{4/3}$.

The form factor depends on the transition type:

- Allowed transition:

$$\text{FORME1}(E) = 1$$

or, to take into account an experimental shape factor:

$$\text{FORME1}(E) = 1 + aE + b/E + cE^2$$

- First forbidden non unique transition:

$$\text{FORME2}(E) = 1 + aE + b/E + cE^2 + d(q^2 + \lambda_1 p^2)$$

- First forbidden unique transition:

$$\text{FORME3}(E) = q^2 + \lambda_1 p^2$$

- Second forbidden non unique transition:

$$\text{FORME4}(E) = q^2 + B \lambda_1 p^2$$

- Second forbidden unique transition:

$$\text{FORME5}(E) = q^4 + 10/3\, \lambda_1\, q^2 p^2 + \lambda_2\, p^4$$

- Third forbidden non unique transition:

$$\text{FORME6}(E) = q^4 + A\, \lambda_1\, q^2 p^2 + B\, \lambda_2\, p^4$$

- Third forbidden unique transition:

$$\text{FORME7}(E) = q^6 + 7\, \lambda_1\, q^4 p^2 + 7\, \lambda_2\, q^2 p^4 + \lambda_3\, p^6$$

q is the neutrino momentum.

These functions respectively correspond to seven options proposed in the software: Perm, 1INU, 1IU, 2INU, 2IU, 3INU et 3IU.

Parameters of beta functions are:

- maximum energy, E_0, and amplitude; initial values are taken from the cursor position and the relevant channel content;

- atomic number, Z, mass number, A, and sign of the emitted charge: these three parameters depend on the considered radionuclide and are fixed; their default values are: 1, 3 and -1, respectively;

- shape parameters, according to the transition nature: a, b, c for the allowed transition, and for the forbidden ones: d, λ_2, λ_3 et λ_4. Each of them are initially set to 0.

4.3 Functions conditional upon standard deviation

Options have been included to take into account the variation of the instrumental width versus the energy. Then, the standard deviations of several peaks in the same ROIs can be linked as:

$$\sigma^2 = \sigma_0^2 + k \cdot x$$

x is the energy position, σ_0 is the width offset and k is the slope of the function; these Gaussian width parameters are common to all peaks characterized by the same "sigma" shape.

4.3.1 Gaussian (sigma): GS(x)

With this function, the Gaussian widths are linked according to the above relation, and then:

$$GS(x) = G(x, \sigma(x))$$

To describe each peak, four parameters are necessary: two parameters (amplitude and position) are characteristic of the individual peak, and two parameters are common to all linked peaks (σ_0 and k). By default, initial values of these are respectively 0.1 et 0.01.

4.3.2 Voigt (sigma): VS(x)

As for the Gaussian peak, here, the instrumental width broadens with the energy:

$$VS(x) = V(x, \sigma(x))$$

Each peak then includes three individual parameters (A, x_0 et Γ) and two common parameters for the Gaussian standard deviation (σ_0 and k), as above-described.

4.3.3 Alpha (sigma): AS(x)

In these case, there is no variation of the Gaussian standard deviation but the same constant width is affected to all peaks of the ROI. The tails parameters (relative amplitudes and slopes) are also parameters common to all these peaks. Description of this function thus requires 2 individual parameters for each peak (position and amplitude) and five parameters (standard deviation, relative amplitudes and slopes of the two tails), common to all peaks with the same shape.

4.4 Background functions

Four functions have been added to fit regions with smooth variations such as background, or discontinuities, such as Compton edge in gamma-ray spectrometry. They are defined only for channels included in the ROI (or just in part of the ROI for the last two functions), thus the quoted surface corresponds only to the relevant region.

4.4.1 Background with one step: STEP(x)

This function describes a step shape superimposed on a constant background: the discontinuity is the convolution of a step function, constant for $x \leq x_0$ and null for $x > x_0$, convolved with a Gaussian function representing the signal experimental broadening:

$$STEP(x) = B + \int_{-\infty}^{x_0} S \cdot \exp\left[\frac{-(x'-x_0)^2}{2\sigma^2}\right] \cdot dx' = B + S \cdot erf\left(\frac{x - x_0}{\sigma\sqrt{2}}\right)$$

Parameters useful to define the STEP function are: step position x_0 and amplitude S, Gaussian standard deviation σ and constant background amplitude B.

Initial values of the background amplitude correspond to the channel content of the first channel of the ROI; the initial position of the step is taken at the cursor position, and the initial step amplitude is the difference between contents of first and last channels of the ROI.

4.4.2 Background with two steps: DSTEP(x)

This function is the same as above but there are two steps to fit two successive discontinuities or a bump superimposed on a constant background:

$$DSTEP(x) = B + \int_{-\infty}^{x_1} S_1 \cdot \exp\left[\frac{-(x'-x_1)^2}{2\sigma^2}\right] \cdot dx' + \int_{x_2}^{\infty} S_2 \cdot \exp\left[\frac{-(x'-x_2)^2}{2\sigma^2}\right] \cdot dx'$$

That is:

$$DSTEP(x) = B + S_1 \cdot erf\frac{(x - x_1)}{\sigma\sqrt{2}} + S_2 \cdot erfc\frac{(x - x_2)}{\sigma\sqrt{2}}$$

The parameters are defined as for the STEP function, indexes 1 and 2 referring respectively to the first and the second step.

Initial values of the background amplitude correspond to the channel content of first channel of the ROI. The initial position of the first step is taken at the cursor position, and its initial amplitude is half of difference between the contents of the first and last channels of the ROI. The initial position of the second step is taken between the cursor position and the last channel of the ROI, and its initial amplitude is the same as the first step one.

4.4.3 Exponential background: EXPO(x)

This function is a simple exponential that can be defined for only part of the ROI:

$$EXPO(x) = A \cdot \exp\left[(x - x_0)\tau\right]$$

The function parameters are the exponential amplitude and slope, A and τ, and the starting and ending positions of the function, x_0 and E. By default these one are initialized with the

first and last channels of the ROI and fixed; the initial amplitude is the channel content of the first channel and initial slope is computed from channel contents of the ROI limits.

4.4.4 Polynomial background: POLY(x)

As in the previous case, this polynomial function of fourth order can be specified for only a part of the ROI:

$$POLY(x) = A_0 + A_1(x - x_0) + A_2(x - x_0)^2 + A_3(x - x_0)^3 + A_4(x - x_0)^4$$

Initial values of the function parameters x_0, E (end position of the defined function), A_0 and A_1 are respectively the first and last channel of the ROI, the channel content of the first channel, and the slope between channel contents of the ROI limits; x_0 and E are initially fixed. A_2, A_3, A_4, are initialized at zero and fixed.

4.5 More specialized functions

4.5.1 Hypermet: HYPER(x)

This fitting function was first introduced by Philips and Marlow [6]. It can be used for fitting gamma or X-ray peaks. It is the sum of a Gaussian, a low-energy tail and a discontinuity centered on the peak position:

$$HYPER (x) = G(x) + T(x) + S(x) = TG(x) + S(x)$$

The tail, $T(x)$, is modeled by an exponential function truncated at the peak position, convolved with a Gaussian representing the instrumental broadening.

The discontinuity, $S(x)$, results from the convolution of a step function, with a constant value for $x \leq x_0$ and zero value for $x > x_0$, by the Gaussian instrumental broadening.

$$S(x) = \int_{-\infty}^{x_0} A \cdot S \cdot \exp\left[\frac{-(x'-x_0)^2}{2\sigma^2}\right] \cdot dx' = A \cdot S \cdot [1 - erf\left(\frac{x - x_0}{\sigma\sqrt{2}}\right)]$$

This function is entirely characterized by 6 parameters; the fist five are the same as those of the Tailed Gaussian (§4.1.2), and the last one is the step function relative amplitude, S with an initial value of 0.01.

4.5.2 Hypermet Voigt: HYPERV(x)

This function is the adaptation of the above-mentioned HYPER function to X-ray peaks, replacing the Gaussian main peak by a Voigt function:

$$HYPERV\ (x) = V(x) + T(x) + S(x) = TV(x) + S(x)$$

It is described by 7 parameters: 6 correspond to the description of the tailed Voigt function (§4.1.6) and the last one is the step function relative amplitude, S with an initial value of 0.01.

4.5.3 Low Energy X Gauss: LOWE(x)

This function was introduced to handle the case of X-ray peaks in the vicinity of silicon K binding energy of silicon. This extension of the Hypermet function has been proposed by Scholze and Ulm [7]: it includes another discontinuity that is a double-step convolved with the basic Gaussian:

$$LOWE\ (x) = G(x) + T(x) + S(x) + ST(x) = HYPER(x) + ST(x)$$

with:

$$ST(x) = \int_{k\,x_0}^{x_0} A \cdot ST \cdot \exp\left(-\frac{(x'-x_0)^2}{2\sigma^2}\right) \cdot dx' = A \cdot ST \cdot \left[erf\left(\frac{x - k \cdot x_0}{\sigma\sqrt{2}}\right) - erf\left(\frac{x - x_0}{\sigma\sqrt{2}}\right) \right]$$

The supplementary parameters, ST (relative amplitude of the double step) and k (low-energy bound of the function) are initialized at 0.005 and 0.1 respectively.

4.5.3 Low Energy X Voigt: LOWEV(x)

This function is the adaptation of the above LOWE function to X-ray peaks, to take the natural width of the lines into account, thus replacing the Gaussian main peak by a Voigt function:

$$LOWEV\ (x) = V(x) + T(x) + S(x) + ST(x) = HYPERV(x) + ST(x)$$

This last function is the most complex one, as its definition requires 9 parameters: the seven first ones are the same as for the HYPERV function, and the last two ones, for ST, are defined and initialized as for the above-mentioned LOWE function.

5. Conclusion

The COLEGRAM software in use in LNHB since 1996 has enabled significant improvement in the processing of gamma- and X-ray spectra [2, 8-10]. In our laboratory, it has also been applied in alpha-particle spectrometry [11].

Now, this user-friendly tool can also be applied to other kinds of spectra. However, its right operation requires competence of an experienced user. Actually, the different fitting functions must be chosen according to the kind of spectra to be processed; moreover, some physical parameters can be efficiently imposed and fixed, for example, with the knowledge of the radionuclide decay scheme and acquisition conditions.

For efficient fitting and reliable results, the user must always keep in mind the physical meaning of the modeling and not only increase the number of adaptable parameters to make the fitting easier. Subject to this precaution, it will be possible to extend the application of COLEGRAM in to a number of cases, for example to beta or electron spectrometry or wavelength-dispersive X-ray spectroscopy.

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APPENDIX 1 - Approximation procedure with the Marquardt-Levenberg algorithm [3]

The fitting procedure using the Marquardt-Levenberg algorithm combines two methods, using respectively the Hessian and the gradient of the function to be fitted.

A1.1 Hessian method

The fitting procedure proceeds in the following steps: close to the minimum, function Φ can be developed as per the Taylor series:

$$\Phi(x;a_0 + \delta a) \approx \Phi(x;a_0) + \sum_j \frac{\partial \Phi}{\partial a_j}\delta a_j + \frac{1}{2}\sum_{j,k} \frac{\partial^2 \Phi}{\partial a_j \partial a_k}\delta a_j \delta a_k \qquad [A1]$$

If we set: $C = \Phi(x; a_0)$ $\qquad \mathbf{B} = -\nabla\Phi \big|_{x;\ \mathbf{a0}}$ $\qquad [H]_{j,k} = \frac{\partial^2 \Phi}{\partial a_j \partial a_k}\big|_{x;\ \mathbf{a0}}$

The development can be written in matrix form:

$$\Phi(x;\ \mathbf{a_0} + \delta\mathbf{a}) \approx C - \mathbf{B}\cdot\delta\mathbf{a} + \frac{1}{2}\delta\mathbf{a}\cdot\mathbf{H}\cdot\delta\mathbf{a} \qquad [A2]$$

The gradient of this expression is:

$$\nabla\Phi\big|_{x;\ \mathbf{a0}+\delta\mathbf{a}} \approx \mathbf{H}\cdot\delta\mathbf{a} - \mathbf{B} \qquad [A3]$$

Minimum value of Φ is obtained for values of the parameters a_{min}.

At $a_{min} = a_0 + \delta a$, $\nabla\Phi\big|_{x;\ \mathbf{a_{min}}} = 0$. Thus, we get:

$$\mathbf{a_{min}} = \mathbf{a_0} + \mathbf{H^{-1}}\cdot[-\nabla\Phi(x;\ \mathbf{a_0})] \qquad [A4]$$

This first process constitutes the so-called "Hessian" method.

A1.2 Gradient method

The Hessian method works when the Taylor series approximation is close enough to the function: this is the case near the minimum. Far from it, as the bias is wider, this method is less efficient. Thus, to come close to the minimum, the gradient method is used.

The parameters values are obtained by successive iterations according to the expression:

$$\mathbf{a'} = \mathbf{a} - \lambda \cdot [- \nabla \Phi (x; \mathbf{a})] \qquad [A5]$$

The λ constant must be small enough so that the procedure actually converges to a best fitting point.

A1.3 Computation of the Hessian

Both methods require computation of the components of the gradient of Φ:

$$b_j = -2 \sum_{i=1}^{n} \frac{[y_i - f(x_i; \mathbf{a})]}{\sigma_i^{2}} \cdot \frac{\partial f(x_i; \mathbf{a})}{\partial a_j} \qquad j = 1,2....,m \qquad [A6]$$

The complete Hessian determination requires computation of partial derivatives of the second order:

$$H_{j,k} = \frac{\partial^2 \Phi}{\partial a_j \partial a_k} = 2 \sum_{i=1}^{n} \frac{1}{\sigma_i^{2}} \left[\frac{\partial f(x_i; \mathbf{a})}{\partial a_j} \cdot \frac{\partial f(x_i; \mathbf{a})}{\partial a_k} - [y_i - f(x_i; \mathbf{a})] \cdot \frac{\partial^2 f(x_i; \mathbf{a})}{\partial a_j \partial a_k} \right] \qquad [A7]$$

For a correct model, term [yi - f(xi; **a**)] represents the random bias of each experimental point: it tends towards zero when summing over the i's and thus can be disregarded. This remark entitles simplifying the above expression:

$$\frac{\partial^2 \Phi}{\partial a_j \partial a_k} = 2 \sum_{i=1}^{n} \frac{1}{\sigma_i^{2}} \left[\frac{\partial f(x_i; \mathbf{a})}{\partial a_j} \cdot \frac{\partial f(x_i; \mathbf{a})}{\partial a_k} \right] \qquad [A8]$$

Thus, whatever the used method may be, only computation of first derivatives is required.

A1.4 Marquardt-Levenberg algorithm

In this process, the gradient method is used far from the minimum; it is then progressively replaced by the Hessian method.

From [A5], the gradient method can be written:

$$\delta a_j = \frac{b_j}{\lambda H_{jj}} \qquad [A9]$$

and the Hessian method is:

$$\sum_{j=1}^{n} H'_{kj} \cdot \delta a_j = b_k \qquad [A10]$$

A new matrix, **H'**, is defined by integrating both methods:

$$H'_{jj} = H_{jj} (1 + \lambda)$$

$$H'_{kj} = H_{kj} \qquad (k \neq j)$$

δa_j is then obtained when solving:

$$\sum_{j=1}^{n} H'_{kj} \cdot \delta a_j = b_k \qquad [A11]$$

When λ is large, H' diagonal terms are dominant and we are close to the gradient method; when λ decreases, the Hessian method is predominant.

In practical, the fitting procedure proceeds according to the following steps:

1. Definition of initial values for **a_0**;

2. Computation of $\Phi(\mathbf{a_0})$;

3. Choice of a value for λ (here, 10^{-2});

4. Resolution of the equation for $\delta \mathbf{a}$ and evaluation of $\Phi(\mathbf{a_0} + \delta \mathbf{a})$;

5. If $\Phi(\mathbf{a_0} + \delta \mathbf{a}) > \Phi(\mathbf{a_0})$: $\lambda \leftarrow \lambda \times 10$ and back to step 4;

6. If $\Phi(\mathbf{a_0} + \delta \mathbf{a}) < \Phi(\mathbf{a_0})$: $\lambda \leftarrow \lambda / 10$; $\mathbf{a_0} = \mathbf{a_0} + \delta \mathbf{a}$ and back to step 4.

APPENDIX 2 - Background subtraction in gamma-ray spectrometry

Two methods are mainly used to deal with spectrum background: modeling or subtraction. In the first case, the background shape is modeled using a simple function, polynomial or exponential, that is added to the functions used to fit the peaks. This induces supplementary parameters to be taken into account in the fitting procedure.

In the case of gamma-ray spectrometry, the background does not often provide any quantitative information useful in the spectrum processing. Thus, the second method has been implemented in COLEGRAM: it consists in subtracting the background from a (limited) region of interest of the raw spectrum.

Several models can be used to compute such a background: the simplest method fit a linear function to limiting channels of the ROI. More sophisticated models take into account the physical peak presence by an integration over the ROI channels [12,13]: this processing allows to include the discontinuity corresponding to the maximum energy of the full-absorption peak.

This technique is used in COLEGRAM, computing the background corresponding to channel i as:

$$F_k(i) = Y(m) + \left[Y(n) - Y(m)\right] \times \frac{S(i)}{S(n)}$$

where:

$$S(i) = \frac{Y(m) - F_{k-1}(m)}{2} + \sum_{j=m+1}^{i-1}\left[Y(j) - F_{k-1}(j)\right] + \frac{Y(i) - F_{k-1}(i)}{2}$$

k is the iteration number, m and n are the ROI start and end channels, respectively.

Several tests were conducted while repeating this processing and examining the iteration influence over the background shape. This study has shown that processing convergence is obtained after two iterations.

APPENDIX 3 - List of parameters in the results files

The following tables present for each function the parameters and the way of computing the peak area (Surface x calib) according to the order they are quoted in the results files. "calib" is the calibration factor (energy/channel)

In the results files, the parameters are named as follows:
"Param 1 = "Energy", Param 2 = "Amplitude", Param 3 = "Sigma", Param 4 = Gamma"
However, these labels are valid for the first two functions, for the following ones, there are no specific labels.

Table I-a - Basic peak shapes

Function	Gauss	Voigt	Tailed Gauss	Gauss with two tails
Param1	Position	Position	Position	Position
Param 2	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)
Param 3	Standard deviation (σ)	Standard deviation (σ)	Standard deviation (σ)	Standard deviation (σ)
Param 4		Lorentz width (Γ)	Tail relative amplitude (TA)	Left-hand tail relative amplitude (TA$_1$)
Surface x calib	$\sqrt{2\pi}\sigma A$	$\sqrt{2\pi}\sigma A$	$A\left(\sqrt{2\pi}\sigma + TA/\tau\right)$	$A\left(\sqrt{2\pi}\sigma + TA_1/\tau_1 - TA_2/\tau_2\right)$
Param 5	-	-	Tail slope (τ)	Left tail slope (τ$_1$)
Param 6				Right-hand tail relative amplitude (TA$_2$)
Param 7				Right-hand tail slope (τ$_2$)

Table I-b - Basic peak shapes

Function	Alpha	Tailed Voigt	Voigt with two tails
Param1	Position	Position	Position
Param 2	Amplitude (A)	Amplitude (A)	Amplitude (A)
Param 3	Standard deviation (σ)	Standard deviation (σ)	Standard deviation (σ)
Param 4	First tail relative amplitude (TA_1)	Lorentzian width (Γ)	Lorentzian width (Γ)
Surface x calib	$A\left(\sqrt{2\pi}\,\sigma + TA_1/\tau_1 + TA_2/\tau_2\right)$	$A\left(\sqrt{2\pi}\,\sigma + TA/\tau\right)$	$A\left(\sqrt{2\pi}\,\sigma + TA_1/\tau_1 - TA_2/\tau_2\right)$
Param 5	First tail slope (τ_1)	Left-hand tail relative amplitude (TA)	Left-hand tail relative amplitude (TA_1)
Param 6	Second tail relative amplitude (TA_1)	Left-hand tail slope (τ)	Left-hand tail slope (τ_1)
Param 7	Second tail slope (τ_1)	-	Right-hand tail relative amplitude (TA_2)
Param 8		-	Right-hand tail slope (τ_2)

Table II - Beta functions

Function	Beta 1INU	Beta 1IU	Beta 2INU	Beta 2IU	Beta 3INU	Beta 3IU	Beta Perm
Param1	Max energy	Max energy	Max energy	Max energy	Max energy	Max energy	Max energy
Param 2	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)
Param 3	Atomic number	Atomic number	Atomic number	Atomic number	Atomic number	Atomic number	Atomic number
Param 4	Atomic mass	Atomic mass	Atomic mass	Atomic mass	Atomic mass	Atomic mass	Atomic mass
Surface x calib							
Param 5	Electron charge	Electron charge	Electron charge	Electron charge	Electron charge	Electron charge	Electron charge
Param 6	Form coefficient a	Form coefficient λ_1	Form coefficient λ_1	Form coefficient λ_1	Form coefficient λ_1	Form coefficient λ_1	Form coefficient a
Param 7	Form coefficient b			Form coefficient λ_2	Form coefficient λ_2	Form coefficient λ_2	Form coefficient b
Param 8	Form coefficient c				-	Form coefficient λ_3	Form coefficient c
Param 9	Form coefficient λ_1						

Table III - Functions conditional upon standard deviation

Function	Gauss (sigma)	Voigt (sigma)	Alpha (sigma)
Param1	Position	Position	Position
Param 2	Amplitude (A)	Amplitude (A)	Amplitude (A)
Param 3	Standard deviation offset(σ_0)	Standard deviation offset (σ_0)	Standard deviation (σ)
Param 4	Standard deviation slope (k)	Lorentzian width (Γ)	First tail relative amplitude (TA_1)
Surface x calib	$\sqrt{2\pi}\cdot\sqrt{\sigma_0^2+kx\cdot A}$	$\sqrt{2\pi}\cdot\sqrt{\sigma_0^2+kx\cdot A}$	$A\left(\sqrt{2\pi}\,\sigma + TA_1/\tau_1 + TA_2/\tau_2\right)$
Param 5	-	Standard deviation slope (k)	First tail slope (τ_1)
Param 6	-	-	Second tail relative amplitude (TA_1)
Param 7	-	-	Second tail slope (τ_1)

Table IV - Background functions

Function	Background + 1 step	Background + 2 steps	Exponential	Polynomial
Param1	Step Energy (E)	Positive step Energy (E1)	Position (E)	Position (E)
Param 2	Step Amplitude (S)	Positive step Amplitude (S1)	Amplitude (A)	Amplitude (A_0)
Param 3	Standard deviation (σ)	Standard deviation (σ)	Exponential end	Linear slope (A_1)
Param 4	Background amplitude (B)	Negative step energy (E2)	Exponential slope (τ)	Quadratic term (A_2)
Surface x calib	$B * (LC-FC) + S*(LC-E)$	$B*(LC-FC) + S1*(LC-E1) + S2*(LC-E2)$	A/τ	$A_0*(LC-E) + A_1/2*(LC-E)^2 + A_2/3*(LC-E)^3 + A_3/4*(LC-E)^4 + A_4/5*(LC-E)^5$
Param 5	-	Negative step Amplitude (S2)	-	3rd order term (A_3)
Param 6	-	Background amplitude (B)	-	4th order term (A_4)

For the background functions, the area is computed between the ROI limits: from first channel (FC) to last channel (LC).

Table V - More specific functions

Function	Hypermet	Hypermet Voigt	Low energy X Gauss	Low energy X Voigt
Param1	Position (E)	Position (E)	Position (E)	Position (E)
Param2	Amplitude (A)	Amplitude (A)	Amplitude (A)	Amplitude (A)
Param3	Standard deviation (σ)	Standard deviation (σ)	Standard deviation (σ)	Standard deviation (σ)
Param4	Tail relative amplitude (TA)	Lorentzian width (Γ)	Tail relative amplitude (TA)	Lorentzian width (Γ)
Surface x calib	$A\left(\sqrt{2\pi}\,\sigma + TA/\tau + SA\cdot E\right)$	$A\left(\sqrt{2\pi}\,\sigma + TA/\tau + SA\cdot E\right)$	$A\left(\sqrt{2\pi}\sigma + TA/\tau + SA\cdot E + STA\cdot E\cdot(1-TE)\right)$	$A\left(\sqrt{2\pi}\sigma + TA/\tau + SA\cdot E + STA\cdot E\cdot(1-TE)\right)$
Param 5	Tail slope (τ)	Tail relative amplitude (TA)	Tail slope (τ)	Tail relative amplitude (TA)
Param 6	Step relative amplitude (SA)	Tail slope (τ)	Step relative amplitude (SA)	Tail slope (τ)
Param 7	-	Step relative amplitude (SA)	Truncated step relative amplitude (STA)	Step relative amplitude (SA)
Param 8	-	-	Truncation position (TE)	Truncated step relative amplitude (STA)
Param 9		-		Truncation position (TE)

APPENDIX 4 - Approximation of the Voigt function

A4.1 General approximation

The Voigt function can be written as the real part of the complex Voigt function, $V(z)$:

$$V(d,p) = \text{Re } V(\frac{x-x_0}{\sigma} + i\frac{\Gamma}{2\sigma})$$

With $d = \frac{\Gamma}{2\sigma}$ and $p = \frac{(x-x_0)}{\sigma}$

$$V(z) = \frac{2}{\sqrt{\pi}} \cdot e^{z^2} \cdot \text{erfc}(z)$$

and $\text{erfc}(z) = 1 - \text{erf}(z) = 1 - \frac{2}{\sqrt{\pi}} \cdot \int_0^z \exp(-t^2) \cdot dt$

$V(z)$ can be approximated by a sum of four Lorentz functions [14]:

$$V(z) \approx \sum_{j=1}^{4} (\frac{c_j}{z-a_j})$$

The real part is thus:

$$V(d,p) = \sum_{j=1}^{4} \frac{\gamma_j(p-\alpha_j) + \partial_j(d-\beta_j)}{(p-\alpha_j)^2 + (d-\beta_j)^2}$$

This approximation is used to compute the Voigt function and its derivatives required by the fitting procedure (see Appendix 1). This approach induces an easy computation, using simple arithmetical operations. In most cases, the accuracy is better than 10^{-4}, what is satisfactory when using this function in the fitting procedure.

A4.2 "Voigt plus" approximation

However, in some cases, if the ratio Γ/σ becomes lower than about 0.1, the previous approximation fails to represent the Voigt shape. It is then possible to use W. Gautschi's algorithm [15].