

Program esrD.

The purpose of the program esrD is the treatment of experimental EPR spectra and preparation of spectra for simulation procedure. This program can be used for removal of the unnecessary spectra tails, subtraction of the base line or base spectrum, double integration, normalizing of area under the spectrum, for visual comparison of experimental and calculated spectra etc. The program is particularly useful when the spectra were recorded in different and possibly irregular grids of magnetic field. Program esrD enables to carry out necessary operations with the set of spectra at once.

The program is presented free for any use with the only conditions that the authors are not responsible for any consequences and insist on citation of source if results obtained using the program are published.

The program can be loaded from the site [http://www.chem.msu.ru/eng/lab/chemkin/esrD/Files of EPR spectra](http://www.chem.msu.ru/eng/lab/chemkin/esrD/Files%20of%20EPR%20spectra) that can be treated by esrD are ASCII files. By default these files have the extension '.esr'. They consist of two columns of real numbers. The first column presents the magnetic field strength, the right one - the spectrum amplitude.

For the correct opening of the spectrum file should contain:

- free number of lines with numeral or literal remarks,
- the line containing the single word: "Spectr:"

After this line the two columns of numbers follow.

The program enables to work with the files containing calculated EPR spectra that are produced by the program ODF3.

The program is intended for treatment of ESR spectra consisting of up to 15000 points with arbitrary (non-regular) values of magnetic field. The values of spectrum intensity at any field point when it is necessary are calculated by linear interpolation between existing points.

The program window consists of

- a working field for the spectra display;
- the upper menu, bearing the properties of standard Windows menus;
- the lower menu, controlled with hot keys or with the mouse;
- the bar for short messages and data input; this bar (of white colour) is situated between the lower menu and the working field.

To display a part of the spectrum in the desired scale, the user can choose the necessary fragment of the working screen by dragging the mouse to the right with the pressed left mouse button. To return for the default scale, use dragging the mouse to the left with pressed left mouse button, or press F4. These actions do not affect ESR spectra in the program memory or in the file.

Section 'View' of the upper menu allows the user to show or hide the grid on the working screen, to show or hide windows displaying the parameters of the spectrum, to enlarge or reduce the size of points, representing the spectra after subtraction.

Section 'Options' allows the user to change the size of the program window, of the working screen for the display of spectra, and of the lower menu. The chosen sizes can be saved in the file '*.opt' and read back when necessary. To return to default sizes, choose "default size".

The spectrum files can be opened, saved or deleted using the upper menu or hot keys F3, F2 and F8, correspondingly. 'Batch' opening, saving and deleting is allowed. The parameters of opened spectra are displayed in the three panels in the right part of the working screen. To show or hide these panels, use keys F5 and F4.

The names of opened files are displayed in the tabs in the upper left part of the working screen. The checkmarked spectra are considered selected. All user operations are processed only with

the selected spectra. The selection of the spectrum is performed by left mouse button click on the desired tab. Parameter panels display the parameters for the first of the selected spectra.

After opening, all spectra are displayed on the working screen. By left mouse button double click on the corresponding tab, the user can hide the corresponding spectrum. The hidden spectrum is nevertheless saved in the operating memory. The tab "All spectra" is used for simultaneous selection or hiding/showing of all spectra.

The program can also read files imported in ASCII format by the program by Bruker. Such files should have the extension '.txt'.

The program can read a file containing more than two columns, if it has the extension '.dat'. In this case the program will automatically choose the columns corresponding to magnetic field strength and will treat the rest of the columns as spectrum amplitudes.

During reading of all the files, the program automatically sorts the spectrum points from the lower magnetic field magnitudes to the higher. This order can be reversed using Alt+Q (see Move,Scale).

Some program functionality will not work correctly with the reverse points order.

Lower Menu

The sections of the lower menu are chosen by left mouse clicks or by pressing keys 3,4,5,6,8 on the keyboard. During the baseline subtraction, integration, search of standard signal etc., white vertical lines (markers) are used, which can be moved by keyboard arrows or by clicking left mouse button in the point, where the marker should be situated. After confirmation of the marker position ('Enter'), the next marker appears.

In the upper left part of the screen the number of the point of the first selected spectrum, corresponding to the position of each marker, and the magnetic field strength in these points are displayed.

BaseLine

This operation performs the subtraction of linear baseline. The linear baseline is calculated by averaging of points in the edges of the spectrum and drawing a line between the central points of the left and the right edges. The number of points for averaging is specified in the parameter file 'EsrD.opt' (integer number NumAver). It should be noted that the choice of the edge fragments, their averaging and linear baseline calculation are performed independently for each spectrum.

After subtraction of linear baseline the user is allowed to manually choose the length of the left and the right parts of the spectrum for the determination of the linear baseline. The white vertical marker displays the boundary of the left edge of the spectrum used for averaging. This marker can be moved by the user with left and right keyboard arrows. After choosing the necessary fragment, the user should press 'Enter'. Then the marker in the right side of the spectrum appears. Its desired position (the length of the right edge of the spectrum) is chosen in the same way as for the left edge.

After pressing 'Enter', the linear baseline is subtracted, which is calculated between the right and the left fragments of the spectrum. For all selected spectra these fragments have the same magnetic field boundaries.

On the working screen the result of subtraction is then represented with pink points. The user may make pink points bigger with the corresponding command in section 'View' of the upper menu.

The program 'EsrD' also allows subtracting the baseline from a separate file (a specially recorded baseline ESR spectrum). For that, the user should choose the baseline spectrum from the list of opened spectra (click Choice... in the lower menu or Alt C). The choice is made with the mouse (the click on the tab of the selected spectrum). The selected baseline spectrum will be marked by

letter 'B' in the list of tabs. After this the subtraction is done (click Numerical... in the lower menu or Alt B). In the short message bar the user should input the value of the coefficient for the subtrahend and press Enter. The result of subtraction is displayed with pink points. The size of these points can be changed (in section View of the upper menu). The user can try different values of the coefficient by inputting the new value and pressing Enter. After obtaining the desired result, press 'Y'.

Double Integration

It is invoked by key "4", when the program is in the main menu.

After pressing "4", the program performs double integration of the spectrum and calculates the area under the absorption curve. It should be noted that the subtraction of baseline should be done before the integration. For obtaining more reliable results, it is recommended to perform linear baseline subtraction right before integration.

The integration result does not depend on whether the spectrum is recorded on the regular net of magnetic field strengths or not. To minimize errors, the integration is performed separately for the right and the left parts of the spectrum. The central point, which separates these parts, should be situated near the spectrum components with the maximum amplitude. The program automatically chooses such central point and displays it on the screen. In some cases, however, this procedure can fail. Then it is seen on the screen that the automatically chosen central point is shifted to peripheral parts of the spectrum. In this case, the area of the spectrum, which should contain the central point should be specified manually. It may be done by pressing Alt C. The choice of the desired area is done by moving the appearing markers with keyboard arrows.

During the calculation of the area under the absorption curve, the program ignores the edges of the spectrum, where the changes in the amplitude are less than the experimental noise. The noise is estimated as the triple standard deviation of the amplitude on the edges of the spectrum. For the estimation of the standard deviation the number of points NumAver, specified in file EsrD.opt, is used. The fragments of the spectrum, which were not used for the integration, are displayed in the spectrum by purple colour. For each of the chosen spectra, the fragments of non-integrated edges are chosen separately. For manual choice of these fragments, the user should press "Y" and choose desired fragments by moving white markers, as described in the section 'Lower menu'. After this the non-integrated fragments are the same for all processed spectra.

After integration the obtained values are displayed in the panel of integration results. The user's attention should be paid to the values of the first integrals of the right and the left parts of the spectra. The physical meaning of these values is the amplitude of the absorption curve in the chosen central point. The results of the integration can be considered satisfactory, if the amplitude of the absorption curve in the central point, calculated from the right part of the spectrum, coincides with the amplitude calculated from the left part of the spectrum, within 10% error. In the upper right part of the working screen, the number of erroneous points Imist, is displayed. The number of Imist is calculated as described in section 'Treatment'

The area under the absorption curve is used for the determination of the absolute number of paramagnetic particles in the sample. In the program, the number of paramagnetic particles is calculated automatically, if the spectrum file contains the amplitude of the intermediate standard (the value St on the second panel of spectrum parameters). In this case, the calculation uses value KoeCu from the file EsrD.opt. To evaluate KoeCu, test recording of ESR spectrum of the sample with known content of paramagnetic particles NpartCu and perform its double integration.

$$KoeCu = NpartCu * ModCu * GainCu * StCu / DoubleIntCu$$

where ModCu, GainCu, StCu - are the modulation amplitude, gain and the amplitude of the intermediate standard during the test registration.

During the integration of the considered spectrum, the number of paramagnetic particles is calculated as

$$NpartX = KoeCu * DoubleIntX / ModX / GainX / StX$$

where ModX, GainX, StX - are modulation amplitude, gain and intermediate standard amplitude during the spectrum registration.

The calculation assumes that the signal of the intermediate standard and the considered spectrum were recorded with the same microwave power.

Comparison of spectra

Allows to load and display additional ESR spectra without affecting the spectra already loaded into program memory. Batch load is allowed.

Move,Scale

Is invoked by key "6", when the program is in the main menu. The operations in this section change the scale of the selected spectra, without affecting non-selected spectra. All operation are divided into two types:

Operations, which do not change the spectrum in program memory:

- PageUp and PageDown increase and decrease the displayed scale of the selected spectra.

The scales on both abscissa and ordinate axes are modified; non-selected spectra are not changed;

- Ctrl Page Up and Ctrl PageDown increase and decrease the displayed scale of the selected spectra on the ordinate axis only; non-selected spectra remain unchanged;

- Up, down, left, right arrows on the PC keyboard shift the selected spectra in corresponding directions; non-selected spectra remain unchanged;

- Keys '+' and '-' increase and decrease the magnitude of movements and scale change;

To save the scale and shift in the program memory, the user should click the label 'Save spectrum as in plot' or press Alt W.

Operations, which change the spectrum in the program memory.

Alt A - normalizes the spectrum on the amplitude of the component selected by the user; the amplitude of the component is defined as the difference between maximum and minimum ordinate within the area specified by white markers, as described in section 'Lower menu'

Alt B - shifts the selected spectrum along the magnetic field axis according to the position of a component specified by the user. The position of a component is defined as the arithmetic mean of fields, corresponding to maximum and minimum signal within the area specified by white markers; the markers can be moved by the user, as described in section 'Lower menu'

Alt H - shifts the selected spectra along the magnetic field axis so that the component with maximum amplitude is situated at the field 3300 Oe.

Alt M - normalizes the spectrum on the maximum amplitude of the spectrum;

Alt N - normalizes the spectrum on the area under absorption curve, if it has been previously calculated;

Alt Q - sorts the spectrum points in the file from the lowest fields to the highest and vice versa;

Alt R - removes the edges of the selected spectra;

Alt S - normalizes the spectrum on the amplitude of internal standard;

Some additional operations of spectra scaling can be performed with the menu Treatment.

Treatment

Is invoked by key "8", when the program is in the main menu.

Operations Alt M, Alt L, ALt K and Alt R are used for searching the components of magnetic field markers.

As an internal standard, the signals of Mn²⁺ in the lattice of MgO (Alt M, Alt L, Alt K), and the signal of ruby (Alt R) can be used.

The following values are used for these signals:

Operation	Standard	Components	Position of low-field component	Distance between components
Alt M	Mn ²⁺ in MgO	№3 -№4	3196.00	86.76
Alt L	Mn ²⁺ in MgO	№1 -№6	3029.05	433.91
Alt K	Mn ²⁺ in MgO	№2 -№5	3111.42	260.34
Alt R	ruby		2229.0	1810.0

After the user chooses one of these commands, the program suggests specifying the intervals of spectra for the first and the second components of the chosen magnetic field marker. For this, white vertical markers, described in section 'Lower menu', are used. The position of the component is calculated as the arithmetic mean of the fields corresponding to the maximum and the minimum signal in the specified interval. The interval should be specified so that the maximum and the minimum points in the chosen interval should correspond to the extrema of the necessary component.

After finishing the choice, the ESR spectrum is shifted and scaled on the field axis, in correspondence with the chosen field marker.

Alt S - performs subtraction of spectra.

Press Alt S or mouse click the Label 'Subtraction'. To choose the subtrahend spectrum from the list of loaded spectra, the user should mouse click the tag of the corresponding spectrum. The chosen subtrahend spectrum is then marked with letter 'B'. After this, press 'Subtraction' again and input the value of the coefficient before the subtrahend in the bar of short messages, then press Enter. The result of subtraction is shown with pink points; the size of the points can be changed by the user (section View of the upper menu). The user can try different values of the coefficient, by inputting the new value and pressing Enter. After obtaining the desired result, press 'Y'. The resulting spectra will be named in spectra tags as res1...res10. If the resulting number of spectra is more than 20, the resulting spectra will overwrite the original spectra without the change of names.

Alt G - smoothes the chosen spectra and decreases the number of points in them. In the short message bar, the user specifies the number of points to perform averaging. For example, if the user specifies number 10, then each point of the spectrum will be substituted by the average of 10 closest points (5 to the left and 5 to the right). In the short message bar, the user also specifies, if the spectrum should be rarefied. For example, if the number 5 is inputted, then during the smoothing only every 5th point will be saved in the resulting spectrum. The information about other points will be lost. The operations of smoothing and rarefication are performed simultaneously. The resulting spectrum is displayed on the screen by pink points. To save the obtained result, press 'Y'. The resulting spectra will be named res1...10 in the spectra list. If the resulting number of spectra is more than 20, the resulting spectra will overwrite the original spectra without the change of names.

Alt T - measurement tool. White vertical markers, described in section Lower menu, are used. To change between measurements of field difference to amplitude difference and vice versa, press 'F11'. Measurement results are displayed in upper left corner of the working screen.

Alt I - changes the phase of the selected spectra (the sign of the amplitude)

Alt E - find points in the spectra, for which the magnetic field strength is lower than of the preceding point. Such points are considered recording errors and are deleted. The number of error points is specified by the number Imist in the upper left part of the working screen.

Alt P - deletes points of the selected spectra in the field interval specified by the user. The interval is specified with the use of white vertical markers, described in section Lower menu.

After pressing 'Esc', the remaining points are connected with a line. The information about deleted points is lost.

Presented description is available in the program esrD as a HELP.