

Quick Reference Guide

SESA

ecsoftware

Installation Instructions

This Title Page 1 will become the back side of the cover page.

You could use this page to describe the installation of the CD rom.

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1 Introduction

SESA

UNISOFT

Version 5.1

The Software for Emission Spectral Analyse (SESA) UNISOFT version is intended for spectral analyse as part of a measuring system SATE (Spectral Analyze Technical Equipment) . SESA provides operation of the board S527. The board S527 as part of system SATE controls spectrometers based on photomultipliers and provides the measuring spectra. SESA operates under FRAMEWORK.NET 2.0 or higher.

Some copies of SESA can be loaded simultaneously for comparison or copying.

The right button of mouse is used in two cases:

1) For exceptions of any measurements from the analysis
2) For contextual menu of the window "**Analytical conditions**"

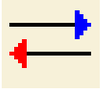
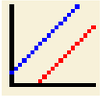
In other cases is used the left button.

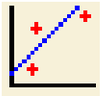
At the beginning of using SESA, it is necessary to adjust it to the spectrometer by filling the fields of the window **Settings**. The program imply following sequence of operations.

1. Creation of analytical program.
2. Analyzing of chemical composition of samples.
3. Output the data to screen, to printer or local network.

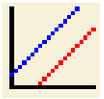
Sequence of operations

Creating a new analytical program

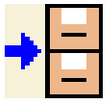
1.  Create the table of chemical composition of standards and set the conditions of spectra excitation source.
2.  Set the methods of mathematical treatment of measuring results.
3.  Save the incomplete analytical program.
4.  Connect the computer to spectrometer.
5.  Create the table of recalibration samples which is intended for correction of spectrometer parameters drift. Measure the spectra of recalibration samples.

6.  Measure spectra of standards.
7.  Mathematical treat of measuring results.
8.  Control and edit the analytical program by the graphs.
9.  Save the analytical program.

Spectral analysis of samples.

1.  Load the analytical program.
2.  Measure the spectra of recalibration samples.
3.  Measure spectra of samples.

Output the data

1.  Make the report of the current analysis.
2.  Print the report.
3.  Output the report to local network.

2 Output files

OUTPUT FILES

This program organizes files of following extensions:

.spi - parameters of spectrometer. Contains:

1) Spectral lines mounted in spectrometer
2) Parameters of electronic system
3) Parameters of com-ports
4) Parameters of local network and database
5) Parameters of autosave
6) Parameters of adaptation the SESA to source

.aps - analytical program. Contains:

1) Conditions, i.e. initial data for measuring:
   the times of flash, prespark and integration,
   the mode of source
   and concentration of chemical elements in standards.
2) Results of measuring of standards.
3) Methods of mathematical treatment of measured values.

.ars - archival file. Contains:

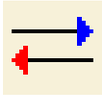
1) Results of measurements of samples.
2) The Analytical program, by which the measurements was done.

.rec – recalibration file for group of analytical files.

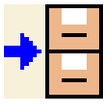
3 The Main menu and Toolbar

THE MAIN MENU AND TOOLBAR

The next buttons have no corresponding commands in the main menu:

 **Connect.** To connect computer with spectrometer.

 **Start**. To start the process of measurement.

 **Send to database**. To send results of samples analysis to database.

3.1 File

File. Contains the following commands:

1)  **New**. To create a new analytical program.
2)  **Open**. To load the previously saved analytical program or archival file.
3)  **Save**. To save the analytical program or archival file under the previously declared name
4) **Save As.** To save the analytical program or archival file under the name specified during dialogue.
5) **Autosave**. To set the automatic saving of the current work.

   If it is chosen "**Save the current file**", the file will be saved under the name "**tmp.ars**".

   If it is chosen "**Save all files**", files will be saved under names "**date_time.ars**".

   These files will be written in the folder **Autosave**, and their content will be rewritten after each measurement.

6) **Load recalibration**. To load the file ***.rec**

7)  **Print.** To print the previously made report. The format of document can be selected in the window "**Add-ins**". This window can be opened from the window "**Methods**".

8) **Exit.** To close the SESA.

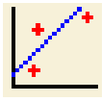
3.2 Analyse

Analysis. Contains the following commands:

1)  **Conditions**. To open the window of analytical program.

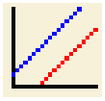
2)  **Methods**. To assign the methods of mathematical treatment and features of showing the graphic and tabular information.

3)  **Measure standards**. To measure spectra of standards.

4)  **Graph**. To show the graph of regression curve.

5)  **Analyze samples**. To measure spectra of samples and definition of their chemistry composition.

6)  **Report**. To make the report of the current analysis.

7)  **Recalibration**. To correct the changing of spectrometer parameters by measuring the control standards.

3.3 Settings

Settings. Contains the spectrometer adjustment commands:

1) **Spectrometer.** To adjust the program to the spectrometer. Has following installations:
    1) **Command register.** To set activities of bits of command register during flash, prespark and integration.
    2) **Modes of source**. To set activities of source mode bits of command register during flash, prespark and

integration.

3) **Settings of elements.** To assign the spectrometer channels to chemical elements.

2) **EEPROM**. To check and write FPGA configuration file cato.pcf to memory.

3) **Data base.** To assign a local network and a database parameters.

4) **Save settings**. To save the parameters fixed by commands of this section and the "**Autosave**".

4 Conditions

CONDITIONS OF ANALYSIS

This window appears automatically after loading the analytical program that was created earlier.

During creation an analytical program (by the command "**New**") you must choose times of flash, prespark, and integration, and mode of the source. Then fill the table of concentrations of standards.

After that keep conditions of analysis by the command

“**File/Save As**», choosing the name of the analytical program and extension "**.aps**".

4.1 The table of concentrations

The table of standards

There is possible to choose the “**table of concentrations**” or the **“table of weights”** by radio button**.** The statistical weights of standards may be entered by mouse wheel in window “**Graph”** or direct to table after measuring of spectra. In second case entering must be completed by button “**Apply**”**.** The button “**Clear**” will equate all weights with **1.**

The table of concentrations

The reference spectral line can be one for all elements or separate for each element, but in any case you must **choose the reference line at first**.

To create the column of element click the right button of the mouse on a blank place of window “Analytical conditions”

and choose "**Add elements**" of the contextual menu. Sequentially choose elements for inclusion to the analytical program from the appeared list of all elements.

If more than one line of the same element is used, these lines should be located side by side.

If the reference line is one for all elements, click on the row handle "**Ref. line**", and then on the **column handle** with the symbol of element. The row of reference line will be filled by symbols of the chosen element. If the reference line - separate for each element, sequentially click on the cell of row "**Ref. line**" and on column handle with the symbol of element.

If you need to remove last wrongly entered element, choose item of the menu "**Delete the last element**". The emerging list of all elements is closed by click on any cell of the table.

To create a row of standard, click on any cell of the empty row with sign " * " (asterisk) and enter the name of standard in the cell "**Standard N**". To remove the last entered row choose item of the contextual menu "**Delete the last standard**".

Fill the table of concentrations. If concentration of some

element of standard is unknown, do not fill the corresponding cell.

Press the button “**Apply**” after filling or correction the table. It is possible to change reference lines during work.

4.2 Copying of concentration tables

Copying of concentration tables

Twice load the SESA to copy the table into other analytical program. Open the table of concentrations in the first program and create or load the similar table in the second program. In the first program click on any cell of the chosen column and choose “**Copy the column**” of contextual menu. Insert the copied column into the table of the second program using item of the contextual menu " **Insert the column** ".

Distribution of spectral lines

The button "**Lines**" opens the window with table that distributes lines according to concentrations. If more than one spectral line of the same element is used, it is necessary to fill this table before using of "**Normalize to 100%**". When the tick **"Choose single analytical lines"** in window **"Criteria of Autosearch"** is set, if you use "**Autosearch**", not fill it. This table informs the program, what range of concentration must be used for every specified line.

Fill the cells of row "**Maximum**" only those elements, which have more than one spectral line. Enter there the concentrations, which are highest possible for correct using. One of such element lines must have the limit 100. If some line must not be used (for example, basis element line that not used as reference line), enter "101" or "-1" for this line. Press the button "**Apply**" in the window "**Lines distribution**". The row "**Minimum**" will be filled automatically. The general concentrations of all element lines must cover the range from 0 up

to 100 percent.

After measuring of samples the program calculates concentrations. Those values, which are within the limits, will go to the report and to the database. Other values will not be considered during Normalize to 100% and will be shown by grey color in the table of samples measurements.

4.4 File of recalibration

File of recalibration

If there is using single calibration for the matrix, not fill this window. For simultaneous calibration of some analytical programs with identical columns these programs must have common file of recalibration. The name of the file must be entered in window, where already placed on default (if push the black triangle) recommended name: "**element of matrix**" "**index**"**.rec.**

File of recalibration will be written as part of analytical program by button **Save** after recalibration if will be entered the

name of file. **File of recalibration** is loaded with file **.aps** automatically. To load this file for file **.ars** use the next command: **File/Load the recalibration**.

5 Measuring of specrums

MEASURING OF SPECTRA

Before measuring of spectra open com-port, through which spectrometer is connected to computer. The button "**Connect**" on toolbar is intended for that. The button is recessed if com-port is connected. It means that the system is ready to measure.

The toolbar button "**Start**" and the key "**Space**" of keyboard are intended for beginning of measure process. After a flash, prespark and integration are completed, the measured information goes to the table of standards measurements or samples measurements or recalibration, depending on what of them is active.

For an emergency stop of measuring press the key "**Esc**" of keyboard.

5.1 Measuring of standards spectrums

MEASURING SPECTRA OF STANDARDS

This window can be opened if analytical conditions are created. The table contains the average values of standards spectra (initially empty). If to click on a row of standard, it will be "opened", i.e. measured values (on which average value was calculated) will be shown under it. Second click on this row or on row of other standard "closes" a row, i.e. hides these values.

In many cases the intensity of basis element may define quality of analysis therefore in reference line columns are shown absolute linear values. In other columns - absolute or relative, linear or logarithmic, depending on instructions in window "**Methods**".

Before beginning of measuring (or remeasuring) it is necessary to mark a row, to which the measured values will go. After filling a row, the program organizes a new row automatically if it was last.

Clicking of the right mouse button on a cell causes its coloring in yellow-golden color and exception of corresponding value from the analysis. Second clicking returns normal color and its inclusion in the analysis. Clicking on the beginning of row causes similar action for all row.

Cells corresponding to unknown concentrations (blank cells in table of analytical conditions window) are painted in golden color.

The values with matrix correction are shown in the rows of average values, but in the measurement rows – without it.

If in window "**Methods**" the tick "**Show concentration in rows of standards**" is set, in the rows of average values will be shown the calculated concentrations of standards. These are the concentrations which the program will show if standards will be measured as unknown samples.

If in window "**Methods**" the tick "**Show errors for standards**" is set, in rows of average values will be shown the relative differences between veritable and calculated values of concentration.

If the key **F3** is pressed, the coefficients of variation for the average value will be shown in rows of average values;

second pressing of this key cancels this mode.

5.2 Analysis of samples

ANALYSIS OF SAMPLES

This table is similar to the table of standards measurements with the exception of:

1) After clicking on a cell of the column "**Sample**" it is possible to enter the name of sample. The name will be fixed if you click on other cell, and then close the row of sample.
2) In the rows of average values it is possible to show the average measured values or the calculated concentrations (if in the window "**Methods**" it is specified "**Show concentration in rows of samples**").
3) If it is used the method of two points, in rows of average values will be shown the next: for analyzing elements - corrected by recalibration values, for reference lines – not corrected values. But for calculations will be used the

corrected values in anyway.

6 Graph

GRAPH

Size of this window is changeable. This window is allowed if spectra of standards are measured. The element should be chosen in the window" **Methods**". The horizontal axis is for concentration, vertical axis is for intensity of spectral lines.

On datum lines are marked absolute or relative, linear or logarithmic values, depending on instructions in the window "**Methods**". Multiplier of scale is specified on the ends of lines. Points of standards are shown as circles.

Clicking of the mouse causes footnotes with exact coordinates of a point. Footnotes disappear if to click below and left than numerical datum lines.

If it is specified "**Always show concentration in the margin note**" of the window "**Methods**", on the footnote will be shown concentration even though the logarithmic scale will be

specified in that window.

If "**Normalize to 100%**" is chosen in the window "**Methods**", on the horizontal datum line will be marked concentrations, normalized to 100% and the sign "~" before concentration value will be on the footnote.

If the method **"One point**" is used, the control standard does not participate in designing of the graph, but the designed graph is parallel displaced on its point. This graph is represented by red color, and concentration of an element in sample will be defined by this line. The method "**One point**" is used with **logarithmic scale**.

Violet color represents points of standards, which concentration is not specified in the table of **Analytical conditions**. These points appear if the tick "**Calculate unnotified concentrations**" is set in the window **"Methods**".

If the tick "**Transparency of graph**" of the window "**Add-ins**" is set, the background of graph will be transparent, and this graph window will remains even if a new analytical program will be called. The cursor, located near, changes the transparency of the whole window. It may be useful for applying and comparing the graphs, designed under different conditions or

methods of analysis. For this purpose you can load some copies of SESA.

Any point may be marked by red color if enter number in window “**Mark the point number of standard**" of window "**Methods**”.

6.1 Exception of standards

Exception of standards

Clicking of the mouse right key on points of standards causes their exception from analysis, second click - inclusion in analysis. The excluded standards are represented by yellow color and lie on horizontal axis. Exceptions do not vary, if the tick “**Search**” of the window “**Methods**” is removed.

Similar actions can be made with group of standards if preliminary to outline their points with the pressed left button of mouse, and then to click the right button.

Changing of scale and weights

To approach a point of the standard to the curve, it is possible to increase the statistical weight of this point. If to click within the circle of standard, the name of this standard will be shown on the footnote. In this case a mouse wheel movement changes the weight of point of this standard.

If footnote with standard name is not shown, a mouse wheel movement changes the scope of initial part of the graph. To remove that footnote it is necessary to click on blank place of the graph.

In linear scale each movement of mouse wheel forward increases scope twice and movement back reduces it. Changing of weight will be fixed after pressing button **Refresh** of the window **Methods**.

METHODS OF ANALYSIS

The window "**Methods**" consists of three parts. In the top part are located the controls concerning of all elements: the choice of scale, the choice of relative or absolute values, and the choice of recalibration method. For logarithmic scale the method **"One point"** and for linear scale the method **"Two points"** must be used. The control standard for the method "One point" must be chosen in the window "**Standard**".

The analytical features for chosen in the window "**Element**" element are disposed in the middle. It is divided into the left, right and bottom parts. The left part is allocated for order and coefficients of polynomial, right - for matrix correction, bottom - the general.

The controls concerning of information displaying in tables and on the graph are disposed in the bottom part of the window "**Methods**".

If the tick "**Calculate unnotified concentrations**" is set,

the program considers the concentrations, which are not specified for standards (by the table of window "Analytical conditions"), but actually there are present. If to not consider them, the significant mistake falls into the analytical program when calculating the **Matrix correction** and **Normalize to 100%**. If full information about the chemical composition of standards is written in certificate, it does not matter, is that tick established or not. In that case the purple virtual points on graph not will considerably influence result of analysis.

The items "Calculate unnotified concentrations" and "Normalize to100%" for method "One point" and for logarithmic scale are not executed.

The tick "**Weigthed**" designates the "Weighted Method of the Least Squares". This method is used there only for linear scale. Thus the graph is drawn with the minimal relative error i.e. as possible close to points of standards with the minimal concentrations. However, if the spectral line is used only for greater concentration, this tick can be removed.

Coefficients of polynomial and coefficients of matrix correction can be entered manually or calculated by computer. In the first case it is necessary to set the tick "**Hand write**", and

remove “**Always search coefficients of polinom**” of the window “**Add-ins**”, and the entered values must be completed with the button “**Enter**” in this window. In the second case it is necessary to set the ticks in corresponding windows "**Search**" or to press the button “**Autosearch**”.

If you set the tick "**Search**" in panel “**Polynom**”, the program finds the coefficients A_k of polynomial, which describes the regression curve. If you set the ticks "**Search**" in panels “**Polynom**” **and** “**Matrix correction**”, the program finds the Additive or Multiplicative coefficients and coefficients A_k for minimal dispersion. The value, describing a dispersion of points around the regression curve, will be shown in the window "**Dispersion**".

If you set “**Weighted**”, you can compare dispersions of different elements; otherwise, it has comparative significance only for the chosen element.

If the analytical curve is described by a several polynomials (piecewise approximation), coefficients of polynomial must be entered into the table, which can be opened by the tick “**Piecewise**”. In this way the dispersion is not

defined.

Calculations of multiple regressions are made by the orthogonal polynomials of Chebyshev which are converted to algebraic polynomials at a final stage.

Coefficients A_k and order of polynomial are specified in corresponding windows.

Hereinafter:

C - absolute or relative concentration or logarithm of concentration,

I - absolute or relative intensity or logarithm of intensity of spectral line.

7.1 Definition of matrix correction

Definition of matrix correction

During the spectral analyze some elements can influence on others. It is conditionally supposed that points of standards does not lay on regression curve and are dispersed around it because of this influence, in other words, the matrix effect.

During definition of matrix correction you should search those influence coefficients, which will give the minimal dispersion at a minimum number of influencing elements. The number of standards in the analytical program should be as more as possible.

In some cases it is not possible to achieve sufficient dispersion due to an extreme deviation of some points, is not caused by matrix effect. In that case it is recommended to exclude these points or some measurements of these points from the analysis in order to not deform the regression curve.

There are used for linear scale additive correction by intensity or multiplicative correction by concentration; for logarithmic scale is used only additive correction by intensity.

Correction by intensity is expressed by a formula:

$$I = \sum_{k=0}^{3} A_k I_i^k + \sum_{j=1}^{10} B_j I_j$$

i - number of an analyzed element

j - number of a matrix element

I - intensity of a line

Bj – coefficients of additive correction (if B>0 –

overlapping)

Correction by concentration is expressed by a formula:

$$C_{mc} = C_{nc}\left(1 + \sum_{j=1}^{10} D_j C_j\right)$$

Cnc - uncorrected value of concentration

Cmc - concentration corrected by multiplicative effect

Cj - concentration of a matrix element

Dj – coefficient of multiplicative correction

It is possible to search the correction coefficients in automatic and manual modes. The program controls appropriateness of regression equation only in automatic mode. To set parameters of **"Autosearch"** it is necessary to open the window "**Criteria of Autosearch"** by specified button. After opening this window in the window "**Dispersion"** will be shown **SDCC** which characterizes error of spectral analyses of the element. **SDCC** (Standard Deviation of Calculated Concentrations) will be shown always if the window **"Measure**

standards” is opened, and the tick “**Show errors for standards**” is set

7.2 Criteria of Autosearch

Criteria of Autosearch

After opening this window computer open the window “**Measure standards**” in mode “**Show errors for standards**”. During searching process the program considers setting values of this window and window “**Methods**”**.** These values can be changed before the quest.

The first 3 windows for entering numbers influence elementwise. These windows: “**By Falling error in**”, “**While error more than**” and “**Criterion of inflection**”. To influence on all elements complete the entering by Ctrl/Enter. Other windows influence on all elements.

1. Quest of influencing elements. There are three radio buttons for three modes. The third mode is set on default.

1.1 By degree and number of elements. In this mode

the program is searching the influencing elements to element which chosen in window "**Element**" of window "**Methods**". The strict parameters "**degree of polynomial**" and "**number of influencing elements**" must be set in window "**Order**" and in window near the button "**Autosearch**".

1.2 All for chosen element. In this mode the program is searching influencing elements to element that chosen in window "**Element**" of window "**Methods**". The soft parameters "**degree of polynomial**" and "**number of influencing elements**" will be chosen by program, but maximal number of influencing elements will be limited by value that chosen in window near the button "**Autosearch**".

1.3 All for all elements. Similarly to point **1.2,** but the program searchs influencing elements for all elements. After searching the program choices the second mode on default.

2. Choice lines. Operates in mode **1.2 "All for chosen element".**

2.1 Choose reference lines. When this tick is set, the program chooses reference lines for all elements.

2.2. Choose single analytical lines. When this tick is

set, the program chooses the best analytical line for every element.

3. Criteria of adding element. Not operates in mode **1.1 "By degree and number of elements".**

3.1. By falling error. When this tick is set, the program add an influencing element while **SDCC** decrease N times. Where N is the number in appropriate window.

3.2. While error more than. When this tick is set, the program can not add an influencing element if **SDCC** became less than number in appropriate window.

4. Inflection of graph.

4.1. Criterion of inflection. For all modes 1.1, 1.2, 1.3, for third degree of polynomial. When this tick is set, there is allowing inflection (ogive) not more than number in appropriate window.

4.2. Maximal inflection. Only for mode **1.3.** When this tick is set, in special necessity there is allowing increasing inflection to number in appropriate window.

5. Exception of standards. Operates only in mode **1.3.**

5.1. Exception is allowed. When this tick is set, there is allowing exception of standards that falls out from graph and distorts the calibration equations. The criteria of Exception must be set in the lowest four windows of this window. If this tick is not set, then will be excepted only those standards which will bring to impossibility of analyze.

5.2. Allow to cut the tail. When this tick is set, there is allowing exception of standards if their points lie on the end of graph. The program uses it for curves of third degree when intensity of points is invariable.

If you want to monitor the changes of the curve during the search process, uncheck the "Not show graph during searching". Minimize the size of the graph to speed up the drawing

7.3 Sequence of operations

Advisable operations for mathematical treatment of spectra of standards

1. It is recommended to set the tick "**Calculate unnotified concentrations**" in the window **Methods**. Set the maximal number of influencing elements near the button Autosearch (it is recommended **3**). At the end of counting there will be shown number of found elements for every element.
2. Open the window "**Criteria of Autosearch**". It will open in mode **1.3.** Push button "**Autosearch**" of the window "**Methods**".
3. At the end of counting view the graphs and errors of all elements. If you will find bad results for any element, push button "**Autosearch**" once more in mode **1.2**. But before it choose other parameters (for example, more or less number of influencing elements) or except some standards or measurements from analyze.
4. In extreme case it is possible to search in mode **1.1** by automatic or manual method. If influencing elements for the element are known, factors for them can be found in mode **1.1** after end of "**Autosearch**" in mode **1.3**.
SESA controls appropriateness of regression equation only in automatic mode.

Recommended sequence of actions by automatic search in mode 1.1.:

1. After measuring spectrums of standards and control samples save the analytical program or the archival file.
2. In the window "Methods" set ticks: "Scale", "Value", "Method of recalibration", and if necessary "Calculate unnotified concentration".
3. Open the window "Graph" and sequentially set for every element in the window "Methods" :
   a) the tick "**Search**" of panel "**Polynom**" and if necessary, the tick "**Weighted**",
   b) an **Order** of approximation according to minimal dispersion,
   c) if necessary, the tick "**Normalize to 100%**".
4. Choose the first element. If there are more than one reference line, choose it in the table of window "**Analytical conditions**" according to minimal dispersion. Choose a number of influencing elements in the window that is right of the button "Autosearch" (begin it with "1" or"2"). Then press the button "**Autosearch**". Then computer finds the specified number of the most influencing to dispersion elements and

their influence coefficients. You can see these data if you choose the number in the window "[1] ". If the number zero is specified and pressed "**Autosearch**", all influences will be removed. If dispersion is too great, increase the number of influencing elements and press "Autosearch". If even so the dispersion is decreased slightly, there is no need to increase number of influencing elements, and it is better to return to an optimum variant. Try other reference lines for this element.

5. Repeat similar action for all elements.
6. Repeat similar action once again for all elements, consistently defining more exactly an order of approximation and number of influencing elements.
7. Changing parameters of some elements affects to parameters of others, therefore it is necessary to pass that action some times for all elements while the dispersion will be considerably changed. If the "**Calculate unnotified concentration**» is established, the **violet** points must be placed on the curve or on a vertical axis, otherwise it is necessary to reduce number of influencing elements.
8. If analysis results of the control samples in the window "Analyse samples" have coincided with their veritable values,

keep the found values. For this purpose press the button "**Enter**" in the window "**Methods**" sequentially for each element and check up that all ticks "**Search**" has disappeared. After that save the created analytical program.

In the manual mode the numbers and the symbols of influencing elements must be selected in the windows under the string «**Matrix element**». If to set the tick "Search" opposite to sign "**Additive**" or "**Multipl**", the program will search the corresponding coefficient. The found value will be shown in the corresponding window.

Recommended sequence of actions by manual search:

1. After measuring spectrums of standards and control samples save the analytical program or the archival file.
2. In the window "Methods" set ticks: "Scale", "Value", "Method of recalibration", and if necessary "Calculate unnotified concentration".
3. Open the window "**Graph**" and sequentially set for all elements in the window "**Methods**" **:**
   a) the tick "**Search**" of panel "**Polynom**" and if necessary,

the tick “Weighted”,
b) an **Order** of approximation according to minimal dispersion,
c) if necessary, the tick “Normalize to 100%”.

4. Choose the number **1** in the window “¹ ” and choose the first matrix element in the next window. If there are more than one reference line, choose it in the table of window “**Analytical conditions**” according to minimal dispersion.
5. Set the tick “**Search**” opposite to sign “**Additive**” or “**Multipl**”.
6. Look at the graph and dispersion. Try out variants with additive and multiplicative corrections, and then choose a variant, at which the dispersion will be considerably decreased. If such variant will not be found, choose other matrix element, and do the same actions.
7. Add a next matrix element (increasing “¹ ”), and do actions of items 5 and 6 for this element.
8. After the searching of elements is made, try to change the earlier entered elements. May be, their influence in a new combination will be weak. Try other reference lines for this element.

9 . Repeat similar action for all analyse elements.
10. Repeat similar action once again for all analyse elements, consistently defining more exactly an order of approximation and number of influencing elements.
11. If analysis results of the control samples in the window "Analyse samples" have coincided with their veritable values, keep the found values. Press the button "**Enter**" in the window "**Methods**" for keeping current element or **Ctrl/ Enter** for keeping all elements. Check up that all ticks "**Search**" has disappeared. After that save the created analytical program.

The found influencing elements and values are not the direct instruction for using, the final decision remains for an analyst.

7.4 Piecewise approximation

Piecewise approximation

The piecewise window will be opened if the tick "**Piecewise**" of the window "**Methods**"is checked.

If the method "One point" is used, the number of pieces of the graph can be only two, otherwise - no more than five. In the first case the cross point of pieces is defined automatically in the point of the control standard. In the second case - points are specified by click on the graph or are entered into the corresponding cells of the piecewise window manually. For manual writing of values it is necessary to set tick "**Hand write**" in the piecewise window.

If the linear scale is checked, in the column "**Limit**" must be entered the maximal concentration, up to which the polynomial of the piece curve is used. The same value is the minimal concentration for the polynomial of the next piece curve. The minimal concentration for the first curve is zero.

If the tick "**All fragments**" was checked, there will be shown all piece curves on the graph. Otherwise will be shown only those piece curves that participate in the analysis. The tick "Search" in the group box "Polynom" of the window "Methods" should be established if coefficients will be not entered manually.

Recommended sequence of actions for piecewise approximation:

1. Perform the matrix correction if necessary.
2. Mentally break the graph to pieces; notice, what orders of approximation corresponds to them, and where approximately will be points of their crossing. The cross point for the method "One point" always will be on the point of the control standard.
3. Set the tick "**Piecewise**" in the window "**Methods**". Then the program will open the piecewise window.
4. Exclude from the graph all points of standards which are not belong to the first piece from zero.
5. Choose an **order** of approximation for that piece in the window "**Methods**".
6. Click on any cell of the first row of the coefficients table.
7. Press the button "**Insert A**". Then the program will copy coefficients of the first polynomial from corresponding windows of the window "Methods" to the first row of table.
8. Repeat actions similar to actions of items 4, 5, 6, 7 for second piece (copy coefficients to second row).
9. If the method "**One point**" is chosen, press the button

"**Apply**" and then include all the excluded points in the analysis. On the graph will be shown the red curve, by which will be calculated concentration of the chosen element. **Save** the analytical program.

10. If the method "**Two points**" is chosen, repeat actions similar to actions of items 4, 5, 6, 7 for other pieces (copy coefficients to corresponding rows).
11. Set the tick **"All fragments**" and press the button "**Apply**". There will be shown all pieces on the graph. The tick "Search" of the window "Methods" will be removed.
12. Click on a point of the graph, where the first and second pieces are crossed. Click on any cell of the first row of the coefficients table. Press the button-cell "**Limit**" of the table. Concentration of the specified point will be brought to the table
13. Do the same for other pieces. For **last piece** it is not necessary to mark the cross point on the graph: if in that case press the button-cell "**Limi**t", number **100** will be entered in the corresponding cell.
14. Press the button "**Apply**", remove the tick **"All fragments**" and then include all the excluded points in the analysis.

15. On the graph will be shown the curve, by which will be calculated concentrations of the chosen element.
16. If any cross point was chosen wrongly, click more exact the cross point, click corresponding cell of the table, and press “Limit” and “Apply”.
17. **Save** the analytical program. Thus coefficients of piece polynomials will be kept.

7.5 Window "Add-ins"

Window "Add-ins"

This window contains the printing format and adjustments of the program for experienced users.

If set the tick “**Always absolute recalibrations**”, recalibration will be absolute regardless of choice in group box “**Value**” of window “**Methods**”.

If set the tick “**Edit the recalibration**”**,** all changes (**Low, High, reference lines** and other) will be reflected in window “**Recalibration**”.

If set the tick **“Read the reference recalibrations”**, there is allowed reading reference measuring from file of recalibrations.

If set the tick “**Safe calibration**”, there will be protected measuring (forbidden remeasuring) of standards (except for control standard for the method **“**One point”) and “**References**” for the method “Two points”**.**

8 Recalibration

RECALIBRATION

This function is allowed if spectrums of standards are measured, and operates if the method “One point” or the method “Two points” is used. The method **“One point”** is intended for use on logarithmic scale, **“Two points” -** on linear scale.

Method of recalibration “One point”

The logarithmic scale usually is used when intensity of spectral lines much more than intensity of background. In this case the changing of channel amplification causes parallel shift of

regression curve because the coefficient of reabsorption goes out of logarithm sign and logarithm of product is equal to sum of logarithms. Therefore it is enough one point for recalibration.

The control standard should conform to samples on physical and chemical properties; concentrations of its chemical elements should be approximately in the middle of concentration range of standards. This standard does not participate in designing of the graph, but the graph designed by other standards, is shifted on its point in parallel.

When recalibration is called, the program releases the rows of the control standard of the **Standards Measuring** table. Then you must measure its spectrums. After that the program will correct the graph, using new value of the control standard spectrum. The red line will be shifted in parallel, going through the new position of the control standard point.

Method of recalibration "Two points"

This method means use of two or more control standards with the minimal and maximal concentration of chemical elements. The program corrects the equation of regression comparing results of control standards measurements in a present situation

and at the time, when was created the analytical program.

If to press the button "**Recalibration**" of toolbar, the window with two tables will be opened. In the top table will be shown the "**Reference**" (the measurements that was made when was created the analytical program) and "**Previous**" (the measurements that was made last time) measurements. The bottom table is intended for "**New**" measurements (the measurements for recalibration).

After **new** measuring the program compares "Reference" and "New" measurements and calculates the **Shift** and **Factor**. These values are used by the program for correction of samples measuring results by the formula:

$$Y = aX + b,$$

where: Y- corrected value,

X - measured value,

a – factor,

b – shift

Concentration of chemical elements does not participate in these calculations. As control standards may be used any

standards or other samples.

If in the window "Methods" are chosen value **"Absolute",** the program uses recalibration with absolute values, if are chosen value **"Relative",** it uses relative values. However, if in the Add-ins window the tick "Always absolute recalibration" is set, recalibration will be made with absolute values in any case.

8.1 Sequence of operations

Sequence of operations

Recommended sequence of operations for method "Two points":

1. Set the tick "**Two points**" in the window "**Methods**"
2. Press the button "**Recalibration**" on the toolbar. ". Then the program will open the recalibration window.
3. Write the control standard name into the first row cell of column "**Standard**". Click on any sell of this row. The program will open a new row for next standard. Repeat these actions for all standards.
4. Measure spectrums of these standards.

5. Click the bold cell "**Low**" (row "Reference", column "Attribute"). The cell will be colored by blue color. Click the cells of bottom table that appropriate to minimal intensities. They will be colored by blue color.
5. Click the bold cell "**High**" (under the "Low").The cell will be colored by dark blue color. Click the cells of bottom table that appropriate to maximal intensities. They will be colored by dark blue color. Click the bold cell "**High**" once more. It will be discolored.
6. Press the cell-button "**Reference**" of top table (mode F3 "Coefficients of variation" must be off). Measured values from bottom table will be copied to top table. In cells of row «Shift" will be zero, in cells of row "Factor" will be one.
7. **Save** the analytical program.
8. During the periodic recalibration measure the spectrums of control standards. Then the program will calculate the current values of Shift and Factor.

9 Settings

SETTINGS

There is the file SESA.spi in the folder SESA. You will see almost empty fields when you open the windows **Settings**. You should change and save them by command “Save settings” and reload the SESA. But you can delete and recreate it.

9.1 Spectroometer

SPECTROMETER

Setting of the elements

Right-click an empty area of the window and select “Add the channel”. Fill in the appeared column. The column headers of the table “Settings of elements” contain channel numbers. You must enter the symbols of chemical elements corresponding to these channels in the first row “Element”. If spectrometer has more then one spectral line for an element, indexes of these lines

must be specified in the second row. The third row “Wave-length” may be filled optionally. Column 0 is the control channel. You do not need to fill it. In case of error you can delete the last channel by the choice “Delete the channel”.

Setting of the command register

The spectrometer is controlled by the measuring system via the parallel eight-bit port, whose operation is controlled by the table "**Setting of the command register**". The column header indicate the numbers of the bits. Digit 1 in the cell will cause the opening corresponding solid-state relay during the Flash, Prespark or Integration time respectively of the selected row. In the first row of the **Function**, write the assignment or conditional name of the bits, for example, Run, Gas, Integration.

Setting of modes

If the spectrometer is equipped with a source whose modes can be changed for Prespark and Integration, and you want to use them, follow these steps:

1) Write digit 1 in those cells of the row Modes that you choose to control the source modes. Name them in the row Function if you need it.

2) Select "Add the mode" from the right-click menu. The table will open, the rows of which will correspond to the named bits, and the columns - Prespark and Integration. Set the units to the cells whose corresponding bits should open at the right time for this mode.
3) Select "Mode Name" from the right-click menu. The window opens in which you want to enter the corresponding name.
4) If there are other modes, continue on items 2 and 3.

In case of an error, you can remove the mode by the right-click menu.

Other settings

Some manufacturers prefer that the ignition must be off during source mode switching. For this purpose an ignition control signal is outputted to the command register of source. Wire of this signal must be connected to bit 0 contact of S527 output register.

This signal may be either Run, which enables ignition, or Shut, which prohibits ignition. In the first case, the numbers 1

must be set in the cells **Preburn** and **Integration** of column 0. In the second case, column 0 should be clean. Bit 0 of S527 output register changes the logical level to the opposite during transition from Flash to Preburn and from Preburn to Integration. Thus, in the first case there are two voltage drops, and in the second case two positive pulses will be during the analysis process.

The check **Pause of source** enables the suspense of ignition. The suspension time in tenths of a second can be set in the window **Pause, deciseconds**. Before using the source pause, make sure that it does not reduce the accuracy of analysis.

The number and speed of the com-port must be set in the section **Parameters of port RS232**. Rate must be 9600.

The calibrated signal, designed to control of the system, is fed to the control channel 0 inside the measuring system. The value of this signal which accumulated during one second is indicated in the window **Count of the control channel**. The Check **Control a failure** sets or cancels the monitoring of the system failure on the control channel.

Profiling

You can profile spectrometer as follows. Open the window “Analyse samples” and via equal intervals of entrance slit

positions measure the spectra of some sample. Then set the slit to position of maximum intensity.

9.2 Database

DATABASE

This window is intended for reading and writing to database the concentrations of chemical elements in samples. The window with measured spectrums of samples must be opened before sending data to database.

If to press the toolbar button "**Send to database**", the program will record to database these values from the window "**Analyse samples**", which are not yet written there.

The window "Database" consists of three parts. In the top part is disposed the panel of connections, which can be opened and closed by the button "**Connections**". The central part is intended for work with the current table. In the bottom part is disposed the panel for creation a new table, which can be opened and closed by the button "**New table**".

Connections

The program can read records from tables of the databases SQL and Access but can make records only into tables of SQL. The tables created by WinOE in format DB-4, can be read by Access and are transformed to that format, and then can be read by the SESA.

The program can not create a new database but can create tables in existing database of SQL.

System administrator must fill out the connection string or replace the "***". You can fill out the right part of connection string (after sign +) during file dialog after pressing the button "Brows".

Connection with a database occurs when opening the window "Database" or when pressing the button "Tables" in this window or by pressing the button "Send to database" on the toolbar.

Reading and writing to database

If to press the button "**Tables**", the program will show the information about tables of the database. If to click on the

table name, the program will copy this name into the window "**Table name**". If to click on the button "**Read records**", the program will show all records of the specified table. The button "**Record strings**" is similar to the button on the toolbar "**Send to database**". The button "**Record string**" provokes record to database that row from the window **"Analyse samples**", which number is designated in the next digital window. To remove a record from database click the mouse right button on the chosen line. For correction of record it is necessary to correct the chosen string of the table and to press the button "**Correct the record**". Then the old record will be deleted, and corrected new record will be written.

New table

To open a new table enter its name into the window "**Table name**" and press the button "**Create the table**". To delete a table press the button "**Delete the table**".

The program can create tables with formats of ARL or SESA but only in 15-character string.

Format SESA

If to fill the windows under the digits 1, 2 and 3 on the panel "**First columns**", the columns under these names will be created, for example, Furnace, Workshop, Laboratorian, and so on. The mark of spectrometer must be entered into the column "**Spectrometer**".

Following columns: "Date", "Time", "Sample", and columns of elements will be created automatically.

If on the panel "**Elements**" is chosen the radio button "**Pattern**", the columns corresponding to loaded analytical program will be created. If it is chosen "**All elements**", the columns for all mounted elements will be created, but only analysed elements will be filled during record.

9.3 EEPROM

EEPROM

The spectrometer maintenance program and FPGA configuration data are written into the EEPROM. Another part of this program is written into the flash memory of the controller. An

electronic maintenance engineer can check and write the EEPROM in the event of failure. File for writing to EEPROM: cato.pcf is attached.

10 Report

REPORT

The window with measured spectra of samples must be opened before opening this window. On the form, prepared for printing, are shown the common text, which can be changed, and the concentration table of samples. It is possible to exclude unnecessary elements from the report by he right button of the mouse. To fix the changing press button "**Apply the correction of table**". The button "**Report**" on "**Toolbar**" renew the table and remove all changes.

If the first letter of sample name is "#", data of this sample not will be sending to print and database.

WINDOWS INTERACTION

It is possible to exclude standards from the analysis by the windows “Graph” and “Measure standards”. Changes will be shown in both windows.

It is possible to mark standards in the windows “Analytical conditions”, “Graph”, “Measure standards”, and “Methods”. The mark will be shown in all these windows.

If to click on a row of any standard in the window “Measure standards”, cursor of the window “Analytical conditions” will be set to corresponding row, the corresponding point of that standard will be marked in the window “Graph”, and number of that standard will be shown in the window “Mark the point number of standard” of the window “Methods”. Double click on row header of the window “Analytical conditions” causes similar actions in the specified windows. If to change the standard number in the window “Mark the point number of standard” or mark point of standard in the window “Graph”, will

be done the same actions.



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